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MAXIMIZING THE LIFE CYCLE OF PLASTICS

Final Report

By
W. L. Hawkins

MASTER

February 1980

Work Performed Under Contract No. EC-77-S-03-1609

Plastics Institute of America, Inc.
Stevens Institute of Technology
Hoboken, New Jersey
- 050 6365

U. S. DEPARTMENT OF ENERGY

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MAXIMIZING THE LIFE CYCLE OF PLASTICS

FINAL REPORT UNDER CONTRACT No. EC-77-5-03-1609

WITH THE UNITED STATES DEPARTMENT OF ENERGY

IN CONJUNCTION WITH THE PLASTICS INSTITUTE OF AMERICA, INC.

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FEBRUARY, 1980

Plastics Institute of America, Inc.

A Non-Profit, Educational, and Research Organization

at Stevens Institute of Technology
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ABSTRACT

The Plastics Research Institute has conducted a coordinated research program designed to extend the useful life of plastics. Since feedstock for practically all synthetic plastics is derived from fossil fuel, every effort should be made to obtain the maximum useful life from these materials. Eventually, plastic scrap may be used as a fuel supplement, but this disposal route should be followed only after the scrap is no longer reuseable in its polymeric form. The extent to which plastic scrap will be recovered and reused will be affected by the economic situation as well as the available supply of fossil fuel.

The Institute's program was conducted at five major universities. Dedicated faculty, with an ongoing interest in some phase of the problem, were assembled into a research team. This team has met frequently with members of the Institute's Board of Trustees to review progress of the program. The research was conducted by graduate students in partial fulfillment of degree requirements.

The introductory section of this report summarizes the several, individual research projects; (1) Improved Stabilization, (2) Separation of Mixed Plastic Scrap, (3) Compatibilizing Agents for Mixed Plastic Scrap, (4) Controlled Degradation of Plastic Scrap, and (5) Determination of Compatibility. The addendum consists of five M.S. theses, one completed Ph.D. thesis, two preliminary drafts of Ph.D. theses and one publication. Several additional publications, which have resulted from this program, are based on theses in the report, and contain essentially the same information.

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The Plastics Institute of America is a non-profit professional organization, incorporated in the State of South Carolina, and with its headquarters at Stevens Institute, Hoboken, New Jersey. The Institute has two primary objectives. The first of these is in the area of education and is being fulfilled through a national fellowship program; by presentation of intensive short courses in plastics technology; and through cassette lectures. The second objective is to establish a cooperative research program in the plastics industry which would reflect broad needs of industry and the general public.

The synthetic plastic industry originated just over a hundred years ago, when the synthetic material, bakelite, was first commercialized. In the following century, production and use of synthetic plastics has experienced phenomenal growth, recording an accumulated annual growth rate of 10% between 1950 and 1979. Current domestic production now stands at 23 billion pounds, and this rapid growth is expected to continue. The plastics industry is also very diffuse, including large producers of synthetic plastics, innumerable fabricators and a highly diversified group of end users who employ plastics directly or incorporate these materials into a wide variety of products. Because of the intense competitive nature of this new and rapidly expanding industry and its diffuse nature, it has not been possible to acquire support for a research institute similar to those supported by and effectively serving the pulp and paper, textile, paint, and electric power industries. There is nonetheless an expressed need

within the plastics industry to establish broad-based research programs which are not likely to be conducted by individual companies. This background has led to development of the Coordinated Research Institute.

The Coordinated Research Institute has been established by the Plastics Institute of America through affiliation with several universities and engineering schools which have demonstrated an interest in applied research programs in areas of interest to the industry and to the public. The Plastics Institute, through its contacts with the industry, has used a systems approach in conjunction with these academic institutions to develop broad programs in which the various institutions have contributed in areas of their specialty. The Plastics Institute has been the coordinating body, sensing on the one hand those needs which are general in the industry and which would also be of concern to the public sector. Individual research programs, necessary to accomplish an overall solution, have been implemented at selected academic institutions, and coordinated into the systems effort. In this way, specialized knowledge and facilities at several institutions were focused on the research effort. The Institute has served as the reporting agency, continually moderating the programs and shifting emphasis as needed.

Continuity in the program was assured through the selection of faculty members at the appropriate institutions who served as collaborating investigators. Long - term, major programs could be completed since specific projects were of continuing interest to the collaborating investigators. The research was conducted under their

direction by candidates for the M.S. and Ph.D. degrees.

The initial program, *Maximizing the Life Cycle of Plastics*, was selected by the Institute's Research Committee, with input from the industry, academia, and our sister organizations: the Society of the Plastics Industry and The Society of Plastics Engineers. This program has now been concluded and is the subject of the following, final report. Subsequently, the Institute has initiated additional coordinated research programs on *Processing Phenomena* and on *Migration*. These are currently funded only by industry.

Maximizing the Life Cycle of Plastics has been the initial program of the Coordinated Research Institute. Synthetic plastics, almost without exception, are derived from petroleum or natural gas. Approximately, one and a half percent of these critical resources are consumed in direct conversion to synthetic plastics and another one to two percent used as energy sources in this conversion. Thus the synthetic plastics industry requires annually about three percent of natural resources already in critical supply for heating and transportation. Failure to obtain the maximum use from plastics materials results in an unnecessary waste of natural resources.

When properly stabilized, the useful life of plastics can be extended into several decades and this usually exceeds the period of initial use. Hence, large volumes of plastics appear as scrap when indeed, basic properties of the material have not been degraded to, a point which would preclude recycling into the original application or reuse in a lower priority product. For example, the variety of plastics now used in automobiles could have a useful life exceeding the

eight year life expectancy of the vehicle. When cars are "recycled" in modern automobile shredders, the resultant scrap is separated into ferrous and non-ferrous metal fractions and into a plastic fraction. Since it is estimated that plastics will eventually represent as much as one thousand pounds of the total weight of an average automobile, this plastic fraction may soon amount to several billion pounds annually. In a recent article,* General Motors President, E.M. Estes has stated that, "... recycling of plastic components (from scrapped automobiles) is among the most important developments still needed in the plastics field."

Separation of mixtures of plastic scrap, such as that originating in the shredding of junked automobiles, is an important aspect of extending the useful life of plastics. A considerable fraction of the plastic scrap generated each year can be isolated before entering the municipal waste stream. However, most of this scrap will be a mixture of two or more plastics. Collection of plastic bottles and other containers will lead to a mixed plastic scrap.

When mixtures of plastic scrap cannot be separated further, attention should be given to utilization of these mixtures. Unfortunately, most mixtures of plastics are incompatible and therefore exhibit poor mechanical properties. Upgrading of these mixtures through the use of compatibilizing agents deserves serious consideration. In conjunction with this approach, methods should be developed to measure the extent to which blends have been compatibilized.

Finally, when plastic scrap has lost all potential for reuse in its macromolecular form, attention should be directed to breaking down the material into useful organic fragments. Burning to recover fuel value should be the final step when the plastic scrap has no further application as a materials resource.

IMPROVED STABILIZATION

Objectives

Polymers are degraded by many components of the environment to which they are exposed. Oxygen, ozone, water, and many catalytic agents contribute to this degradation. Reactions of degradation are accelerated by heat, solar radiation and mechanical energy. Recent increases in the price of fossil fuels, the primary feedstock for synthetic polymers, has stimulated the search for polymeric materials which are more resistant to environmental degradation. For example, polymer films to be used as protective encapsulants for solar cells must retain a high level of stability since degradation, among other deleterious effects, reduces transmission of energy to the solar cells. Other polymers fail by loss of mechanical or dielectric strength.

This phase of the research program has been directed toward synthesis of plastic materials which contain a stabilizing moiety within their molecular structure. Several experimental polymers have been synthesized and their resistance to degradation determined. The report includes the experimental program of Ms. Annette Dudek, (11/77 - 8/78) who has been awarded a M.S. degree and Mr. Wayne Blabolil, (9/78 to 1/80) who is completing requirements for his Ph.D. degree.

SUMMARY OF RESEARCH

(A) November, 1977 to August, 1978

Academic Institution - Case Western Reserve University

Principle Investigator - Professor Charles E. Rogers

Student - Ms. Annette Dudek

Board Member Assigned - Mr. Charles Abramoff

Thesis - Addendum 1 (Blue)

The development of internally stabilized polymers has centered on copolymerization of selected monomer units having differing photostabilities into emulsion prepared polyisoprene. Polyisoprene was chosen as a model material since it has very poor thermal and photostability. Copolymers of isoprene with methyl acrylate (13%), methyl methacrylate (30, 47, and 63%), and ethyl methacrylate (25%) have been synthesized. The corresponding homopolymers also have been prepared by the same polymerization method. Their composition, structure, sequence distribution, and other characteristics have been determined by a variety of techniques including Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance, Differential Scanning Calorimetry, and Gel Permeation Chromatography. Certain data are given in Table 1.

Table 1

Characterization of IP/MMA Copolymers

<u>mole % of MMA</u>	<u>M_w</u>	<u>p (g/cc)</u>	<u>Tg (°C)</u>
0	252,000	0.908	-62
31	144,000	0.992	-23
47	104,000	1.049	12
63	66,000	1.088	34
100	166,000	1.176	117

The stability of these homopolymers and copolymers has been determined using pyrex glass-filtered UV radiation (QUV Accelerated Weathering Tester, Q-Panel Company) at 31-33°C and ambient RH. Samples were analyzed by Fourier Transform Infrared, and water vapor sorption methods (IP-MMA system). Initial studies used press-molded film samples of approximately one mil thickness. The results obtained by FTIR indicated that the thickness was too great for adequate quantitative analysis of carbonyl and hydroxyl formation in the copolymer samples.

Subsequent studies using very thin cast samples are continuing.

The results of the water sorption studies show that the copolymers of isoprene and methyl methacrylate apparently have improved stability over polyisoprene. This improvement is more than would have been anticipated from the mole fraction contribution of the inherently stable MMA units for the composition tested. The data in Figure 1 indicate that the 31% MMA content copolymer is much less affected by photooxidative exposure than is PIP and the 47% MMA content copolymer.

Figure 1

The greater sorptive capacities of the 63% and 100% MMA content materials, as indicated by the 4 hour exposure data in Figure 2, are due in part to the fact that those materials are below their respective T_g's at the temperature of the sorption experiment. The change in water sorption of the 100% MMA material with UV exposure is essentially nil over the exposure times used (120 hours).

Qualitative analysis of FTIR results indicate that the formation of excellent carbonyl groups, presumably due to oxidation, is in the order: MA > EMA >> MMA.

Figure 2

Comparable gross changes in the diffuse hydroxyl peak were also noted. It is to be emphasized that these FTIR results are considered only as preliminary, pending quantitative studies with suitable thin specimens and refinement of the data analysis (spectra subtraction with internal thickness compensation) method.

Ms. Dudek transferred to the Massachusetts Institute of Technology upon completion of the requirements for the M.S. degree, and this research program was then continued by Mr. Wayne Blabolil.

(B) September 1978 to January 1980

Academic Institution - Case Western Reserve University
Principle Investigator - Professor Charles E. Rogers
Student - Mr. Wayne Blabolil
Board Member Assigned - Mr. Charles Abramoff
Summary of Thesis - Addendum 2 (Buff)

Modification of the degradation behavior of polyisoprene was studied using a series of synthetic copolymers in which the comonomer had inherent stability to degradation. Copolymers of isoprene with varying amounts of methyl methacrylate were prepared by emulsion polymerization. Rates of thermal degradation at temperatures between 300 and 450°C were determined using a duPont 990 Thermoanalyzer fitted with a differential scanning calorimeter. Thermal crosslinking and cyclization were reduced by copolymerization, with the 31 per cent methyl methacrylate copolymer having the greatest thermal stability in air. In general, it was concluded that the copolymers have a level of oxidative stability intermediate between the corresponding homopolymers.

Sequence distribution of the monomer units would have an important effect on thermal stability. Block copolymers would be expected to behave much like a blend of the corresponding homopolymers. Random polymerization, on the other hand, should yield a product in which isolated monomer units might have a significant effect on the overall degradation mechanism. One continuing goal of this research is to more precisely determine the monomer sequence in these copolymers.

Because polyisoprene is so very unstable to oxidative degradation, the homopolymer and selected copolymers were hydrogenated. In this way, most isoprene units were converted to the more stable hydrocarbon analogues. As expected, isothermal oxidation showed the reduced polymers to be somewhat more stable. Again the hydrogenated copolymer with 31% methyl methacrylate was the most stable.

The thesis summary (Addendum 2) does not cover all of the work that will be required of the student. This research is continuing and conclusions at this point should be considered as tentative.

SEPARATION OF MIXED PLASTIC SCRAP

Objectives

Except for that material which is collected at a manufacturing site, either a resin producer or a fabricator, plastic scrap is usually generated as a mixture of several different materials. Mixtures may consist of representatives of one generic class, such as the polyolefins, or may consist of widely different plastics. In extreme cases, thermoplastic scrap may be mixed with intractable thermoset resins. Practicality of separation is directly related to the complexity of the mixture.

Many mixtures of plastic scrap can and some are being collected before reaching the municipal waste system. Returned plastic bottles, certain laminate structures and the plastic fraction separated by automobile shredders are typical. This phase of the report deals with development of a technology to separate source-separated scrap mixtures.

Two approaches to separation have been investigated. Solvent separation could be a practical technology for mixtures of similar plastics, as for example mixtures of varying density polyethylenes alone, or with polypropylene. The second approach has been directed toward delamination of composite structures through cryogenic grinding. Grinding would be a preliminary step to separation by mechanical or flotation techniques. In this approach, similarity of components in the mixture would be less important.

(A) By Solvent Separation

Academic Institution - Carnegie-Mellon University
Principle Investigator - Professor Stephen L. Rosen
Student - Mr. Mark Denis Karl
Board Member Assigned - Dr. Siegfried Altscher
Summary of Thesis - Addendum 3 (Green)

The polyolefins, poly(vinyl chloride) and polystyrene are major components in polymer scrap. Professor Rosen and his students, in previous studies, have separated these components at better than 99.5% purity. This separation was based on their thermodynamic incompatibility in a solvent mixture. It was not possible, however, to separate adequately the polyolefin fraction into polypropylene and the various density fractions of polyethylene. Fractional crystallization was investigated as a technique for resolving the polyolefin fraction, but this approach met with only limited success.

Differential extraction now appears to be an acceptable method for separating polypropylene from the polyethylenes. This technique requires selection of optimum solvents for the extraction. Results of extraction experiments are encouraging. Both bath and Soxhlet extraction are being studied. Though complete separation may not be achieved, controlled mixtures from this process could be upgraded rather easily by the use of compatibilizing agents.

This work is continuing with emphasis on bath extraction. An abstract of the thesis results to date appears as Addendum 3.

SEPARATION OF LAMINATES

(B) By Cryogenic Grinding (11/77 to 6/79)

Academic Institution - Case Western Reserve University
Principle Investigator - Professor Phillip H. Geil, Jr.
Student - Ms. Elizabeth Garcia
Board Member Assigned - Dr. Peter Hold
Thesis - Addendum 4 (Blue)

High-density polyethylene was used as the model to study effects of grinding temperature, particle size, annealing, swelling, orientation, and molecular weight. Films of Surlyn/polyethylene, and polyethylene/nylon were selected as representatives of the polymer laminates likely to be encountered as scrap. These materials were ground cryogenically, using liquid nitrogen, or at room temperature, using methanol/water mixtures.

Low-density polyethylene (LDPE) was expected to exhibit brittle fracture, but instead showed a high degree of plastic deformation. The energy required to grind LDPE is shown in Table I.

TABLE I

Energy Requirements (kj/g)

<u>Melt Index</u>	5000 μ to 500 μ		500 μ to 200 μ		500 μ to 80 μ
	Liq. N ₂	Annealed CH ₃ OH/H ₂ O	Liq. N ₂	MeOH/H ₂ O	Liq. N ₂
0.7	2.1	2.3			
1.2	1.1	2.9	5.2		8.3
3.5	2.2	3.0	9.3	7.9	

These data suggest that ultimate particle size, rather than melt index or grinding conditions, controls the energy required for the process.

High-density polyethylene, ground cryogenically, yields fluffy, fibrous powders -- apparently the result of plastic deformation. Heat generated in the grinding process may be responsible for the shift from brittle fracture to plastic deformation.

Cryogenic grinding of laminated films met with a reasonable level of success. Films in which the layers were sufficiently dissimilar to preclude fusion of the components during grinding could be separated by gravity differential in an aqueous column. A laminate of nylon and polyethylene was separated into components by this technique. However, a laminate of Surlyn and nylon showed no evidence of separation into components after cryogenic grinding. Apparently some fusion of the components of this laminated structure occurred during grinding.

COMPATIBILIZING AGENTS FOR MIXED PLASTIC SCRAP

Objectives

Except for the relatively small fraction generated at manufacturing sites, most plastic scrap occurs as mixtures of two or more components. Mixed plastic scrap is rarely reused, and unless burned as a fuel source this material is usually discarded as waste.

Mixed plastic scrap is rarely uniform in composition and in general, these mixtures have poor mechanical properties. Separation into pure components is not always economically feasible. Where complete separation is not practical, properties of some mixtures can be upgraded to a point where they could be employed to fabricate useful products. The use of compatibilizing agents, blended into these mixtures, is one practical approach to upgrading mixed plastics into useful products. Optimization of processing conditions may be another useful area for investigation.

Two approaches have been undertaken in studying the efficacy of compatibilizing agents in plastic mixtures. Professor Donald R. Paul has concentrated on commercial products which are copolymers. Three of Professor Paul's students have received the M.S. degree for work in this area. Professor Pearce has investigated the role of synthetic compatibilizing agents which make use of hydrogen bonding to break down domain barriers between components.

(A) COMPATIBILIZING WITH COMMERCIAL COPOLYMERS

Academic Institution - Polytechnic Institute of New York

Principle Investigator - Professor Donald R. Paul,
in collaboration with Professor J. W. Barlow

Students - Ms. E. Nolley, Mr. D. W. Bartlett, and
Mr. C. R. Lindsey

Board Members Assigned - Mr. Charles Abramoff and
Mr. Clyde S. Brenner

Theses - Ms. Nolley, Addendum 5 (Buff)
Mr. Bartlett, Addendum 6 (Green)
Mr. Lindsey, Addendum 7 (Blue)

Professors Paul and Barlow, in collaboration with their students, have explored the use of commercially - available copolymers in upgrading the properties of mixed plastic scrap. These compatibilizing agents were studied in model mixtures, selected as those likely to be encountered as mixed plastic scrap. Three theses and two publications have resulted from this phase of the program.

The first student on the project, Ms. Nolley, used blends of polypropylene (PP) and low-density polyethylene (LDPE) as a model mixture. The compatibilizing agents used were a variety of ethylene-propylene elastomers, and a block-like ethylene-propylene-diene* terpolymer. The basic concept of these copolymers is based on affinity of each of their segments for one component of the mixture. The terpolymer was found to be the most effective in improving mechanical properties of the selected model blend. For example, a thirty-five per cent increase in elongation resulted through use of the terpolymer. This improvement, however, was accompanied by a decrease in tensile strength.

Mixing conditions were shown to be important. Repeated blending improved both elongation and mechanical strength, up to the point where degradation became a factor. Screw design was shown to be important in intermixing dissimilar materials.

This work was continued with Mr. Bartlett who selected blends of high-density polyethylene (HDPE) with polypropylene and polystyrene (PS) with polypropylene. Whereas polypropylene and polyethylene are reasonably compatible and blends of these two have acceptable mechanical properties, polystyrene and polypropylene are completely immiscible. The terpolymer, used in the LDPE/PP blend, also improved compatibility in the HDPE/PP blend, but there was a reduction in modulus. Since the

terpolymer is elastomeric, its effect on the modulus of the blend is not surprising.

A new commercial compatibilizing agent, formed by random copolymerization of ethylene and butene -1 and end-capped with approximately 30% of styrene, was used to improve properties of PS/PP blends. Ductility and impact strength of the mixture improved dramatically.

The morphology of compatibilized PS/PP blends was examined. A lower degree of crystallinity resulted when these mixtures were processed at higher temperatures but crystallinity increased with increasing concentration of the compatibilizer. As a result, mold shrinkage is reduced in these blends. The mechanism by which the compatibilizing agent reduces the crystallinity of high-density polyethylene has not been established.

Blends of polystyrene with high-impact polystyrene (HIPS) were used as a model by Mr. Lindsey. The terpolymer of ethylene, butene-1 and styrene was also effective in improving mechanical properties of this blend. Elongation increased with increasing concentration of the compatibilizer, but modulus and yield strength decreased.

Laminated structures of the molding resin, ABS, with high-impact polystyrene appear frequently in molded items. Attempts to improve properties of this blend, however, were not successful.

Several important conclusions resulted from studies at the University of Texas. First, it was clearly demonstrated that commercially-available copolymers can be used to improve the mechanical properties of several blends of mixed plastics. The potential for upgrading available scrap mixtures to the point where they can be used for low-priority products has been clearly demonstrated.

Investigation of the effect of processing conditions on compatibility also produced interesting results. It was theorized that when one component is present as a minor constituent, processing at a temperature at which viscosity of the major component significantly exceeds that of the minor component, should result in high shear in the latter and a reduction in its domain size. The theory is being tested with the incompatible ABS/HIPS blends. Using a torque rheometer, it was found that above 230°C viscosity of the high-impact polystyrene is higher than that of the ABS resin. Thus when ABS is the minor component, improvement in compatibility should result when the blend is processed above 230°C. Work is underway to test this theory.

(B) COMPATIBILIZING WITH HYDROGEN-BONDING POLYMERS

Academic Institution - Polytechnic Institute of New York
Principle Investigator - Professor Eli M. Pearce
Student - Mr. Sai-Pei Ting
Board Member Assigned - Mr. Charles Abramoff
Thesis - Addendum 8 (Buff)

Hydrogen bonding is a strong, secondary chemical bond which contributes significantly as an intermolecular force between polymer molecules. For example, the abundance of hydrogen bonds in cellulose is generally believed responsible for the decomposition of this natural polymer, without melting. Likewise the strength of nylon is attributed to hydrogen bonding between molecules.

Professor Pearce and Mr. Ting have synthesized a variety of polymers with a high potential for hydrogen bonding. Commercial polystyrene was modified by a series of reactions which introduced hydroxyl-containing groups on a portion of the aromatic rings. Copolymers were synthesized from styrene and p-vinylphenol. Compatibility of these hydrogen-bonding polymers to poly(ethylene oxide) and other polymers was evaluated by dispersive infrared spectroscopy.

Hydrogen bonding was shown to occur in blends of the synthetic polymers with fifty per cent or less of poly(phenylene oxide). Compatibility was further confirmed by use of Fourier Transform Infrared Spectroscopy. The coupling of polystyrene with poly(phenylene oxide), using hydrogen-bonding polymers, was demonstrated.

Mechanical properties of the blends were shown to have improved by measurement of stress-strain relationships using an Instron Tensile Sensor.

In general, compatibility was found to improve with increasing hydroxyl(hydrogen-bonding potential) in the synthetic polymers. A single homogeneous phase is formed at high content of the hydrogen-bonding polymers, but phase separation takes place as the content of poly(phenylene oxide) in the blend increases. Hydrogen bonds in certain of the blends ruptured above 175°C but completely reformed on cooling to 25°C.

CONTROLLED DEGRADATION OF PLASTIC SCRAP

Academic Institution - Case Western Reserve University
Principle Investigator - Professor Alan G. Walton
Student - Mr. M. E. Soderquist (William B. Bradbury Fellow)
Board Member Assigned - Dr. Thomas W. Haas

The objective of this study, which terminated in the first quarter of 1979, was long range. Once a synthetic polymer has been used to the maximum extent, burning for fuel value or controlled degradation into useful fragments could be disposal routes for the scrap. Professor Walton has investigated the role of bacteria in the controlled degradation of polymers. Although support by the Coordinated Research Institute has terminated, Professor Walton's research is continuing with alternate sources of funding.

He has suggested that, faced with petroleum based polymers, nature would eventually respond by generating bacteria or molds containing enzymes which are capable of degrading such polymers. Two approaches were proposed to determine what types of enzymes or biological entities could effect biodegradation. The first approach is directed at the development of multicomponent copolypeptides as potential degradation catalysts. Appropriate mixtures of native amino acids in the L-configuration were polymerized in molten salt solutions as described previously. The product of the reaction was generally a mixture of low molecular weight product (cyclic di- and tripeptides) with material in the 15,000-20,000 molecular weight range. The latter was generally of narrow molecular weight distribution, with γ - carboxyl and ϵ amino linked residues.

The low molecular weight material contained compounds similar to bacterial antibiotics and antibacterial agents; consequently, mixtures are currently being tested for such activity by commercial microbiological laboratories.

Polymeric material (water soluble) contained approximately 150 residues, i.e. similar in size to several known enzymes (lysozyme, ribonuclease, etc.). All multicomponent samples tested possessed hydrolytic activity, and were most active in the pH 8 region. No activity has yet been determined against plastics, but work in that area is planned.

In the second part of the work they examined the interaction of several strains of bacteria with a number of different plastics. Particularly, they examined aerobic and anaerobic pseudomonas and their interaction with polyolefins, etc.

Two types of behavior were observed: i) in some cases the bacteria attached to a surface, adhered strongly, and appeared to etch the surface; ii) in the opposite extreme, clumping of pseudomonas was produced on the surface and the bacteria were inactive.

DETERMINATION OF COMPATIBILITY

Academic Institution - The State University of Pennsylvania
Principle Investigator - Professor Michael M. Coleman
Student - Mr. D.F. Varnell
Publication - Addendum 9 (Green)

Determination of the compatibility of polymer blends presents many difficulties. Fourier Transform Infrared (FTIR) spectroscopy, with its inherent sensitivity and computational facilities, offers considerable potential for studying this problem. Digital subtraction and addition techniques have been applied to the infrared spectra obtained from poly (vinylidene fluoride) (PVDF), poly (methyl methacrylate) (PMMA) and blend systems of these polymers. These studies revealed information that has been interpreted in terms of specific interactions between the individual polymer chains and changes in the conformation of the PVDF (1).

They have studied the polycaprolactone (PCL) - poly(vinyl chloride) (PVC) blend system. This system had been characterized by torsion pendulum studies (2) where a single T_g , changing with composition was reported. These results inferred a compatible system. Ong (3) Studied the morphology of these blends and showed that blends of up to about 50% PVC by weight consisted of spherulites composed of lamellae radiating from the spherulitic center and twisting regularly. In fact, the PCL crystal structure was unaffected by the presence of PVC. Stein and his coworkers (4) used small angle light and x-ray scattering and showed that the PCL lamellae are separated by amorphous regions of PCL and PVC. It was also concluded that this amorphous region was not homogeneous but partially miscible. Hence this was a very interesting system, leading to questions regarding the very basic nature of compatible blends.

Preliminary FTIR results on the PCL/PVC blend system were most interesting. They studied this system as a function of concentration both in the melt (75°C) and in the solid state at room temperature. In the melt, they obtained definite evidence for specific interactions involving the C=O group of PCL with PVC as shown in Figure 1. A progressive shift of the ν_s (C = O) to lower frequencies as a function of PVC concentration was observed. Additionally, the width at half height of the carbonyl band varied as shown in Figure 2. The S shaped curve indicated that maximum interaction of the carbonyl band of PCL with PVC occurred at concentrations of 60% PVC by weight (approximately 4:1 molar PVC). This may not have been fortuitous.

Fig. 1. FTIR spectra in the range 1675 - 1775 cm^{-1} ,
 A. PCL at 75°C (melt);
 B. 1:1 (PVC:PCL by mole) blend at 75°C;
 C. 3:1 (PVC:PCL by mole) blend at 75°C;
 D. 5:1 (PVC:PCL by mole) blend at 75°C.

Fig. 2. Band broadening of carbonyl groups as a function of wt. % PVC in the blends, all samples at 75°C.

Factors such as the relative size of the monomer repeat unit of the respective polymers may dictate a specific excess concentration of PVC relative to PCL in order to ensure a saturation effect (i.e. when all the C = O groups of the PCL are interacting with the PVC).

In the solid state there is a further complication of phase separation at the lower concentrations of PVC in the blend (<3:1 molar ratio PVC:PCL). As mentioned previously, spherulites were observed in the optical microscope. FTIR spectra in the range 1675 - 1775 cm^{-1} of blends of different composition at room temperature are shown in Figure 3. Spectrum A is of pure PCL in the solid state at room temperature. In the semi-crystalline solid state two bands are observed, one at 1724 cm^{-1} associated with the crystalline phase and the other centered at approximately 1737 cm^{-1} associated with the amorphous phase. At PVC concentrations in excess of 2:1 molar ratio PVC:PCL, the spectra (D, E and F) indicate that the blends are essentially amorphous. There is a slight shift towards a lower frequency as the PVC concentration is increased, similar to that observed for the molten state.

At PVC concentrations up to 3:1 molar ratio PVC:PCL the spectra indicated that the blends in the solid state consisted of a crystalline and amorphous phase. As the concentration of PVC increased there was a corresponding increase in the intensity of the amorphous band at about 1737 cm^{-1} compared with the crystalline band at 1724 cm^{-1} . In addition, the crystalline band shifted slightly to higher frequencies. These results were essentially in agreement with the conclusions of Stein and coworkers at the University of Massachusetts. Other more subtle changes in the spectra are presently being studied.

This project will continue beyond the term of the present contract. It is proposed to continue to examine the PCL/PVC blend system and to extend the studies to include the PCL/polyepichlorohydrin and poly (vinyl acetate)/poly (methyl acrylate) systems. Furthermore, they have recently acquired a Laser-Raman spectrometer and analogous studies using this equipment should be most rewarding. In summary, they believe that vibrational spectroscopic investigations of polymer blend systems will lead to a better understanding of the factors involved in compatible blend systems.

Fig. 3. FTIR spectra in the range 1675 - 1775 cm^{-1} .

- A. PCL, semicrystalline (aged at RT over a month);
- B. 1:1 (PVC:PCL by mole) blend at RT (aged at RT over a month);
- C. 2:1 (PVC:PCL by mole) blend at RT (aged at RT over a month);
- D. 3:1 (PVC:PCL by mole) blend at RT;
- E. 5:1 (PVC:PCL by mole) blend at RT;
- F. 10:1 (PVC:PCL by mole) blend at RT.

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SUMMARY

Of the nine, individual research projects, included in this report, six are completed and are represented by the corresponding theses. Three research projects at the Ph.D. level are continuing and thesis summaries or publications appear as addendum. To date, there has been a total of four publications based on these projects. These publications appear in leading scientific journals.

This coordinated research program has met its goal of developing a research background on which a practical technology can now be developed for the recovery and reuse of plastic scrap. A program has been developed to apply this information to resolution of the complex plastic mixture which is generated by automobile shredders. A modest beginning has been made on application of results presented in this report to practical problems encountered with plastic scrap. This work will be expanded and continued.

Plastic scrap as a fuel supplement is a viable route for utilizing this material -- but only after the maximum and economical use as a plastic material has been realized. At that point, fuel value should be recovered. It takes billions of years to convert the products of combustion back to the fossil fuel from which polymer feedstocks are derived.

Respectfully submitted,

W. Lincoln Hawkins
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EFFECTS OF PHOTO-OXIDATION ON THE SOLUBILITY AND
TRANSPORT PROPERTIES OF POLYMERS

by

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Submitted in partial fulfillment of the requirements
for the Degree of Master of Science

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May 1979

EFFECTS OF PHOTO-OXIDATION ON THE SOLUBILITY AND TRANSPORT PROPERTIES OF POLYMERS

Abstract

by

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A primary factor which must be considered for the use of any polymeric material as a protective coating is the probability and rate of deterioration of barrier properties as the result of environmental degradation. The most important degradative agents are undoubtedly heat, light and oxygen.

In this study, the effects of ultraviolet light and oxygen exposure were determined on:

- 1) the nitrogen and water vapor permeation characteristics of low density polyethylene film, and
- 2) the water vapor sorption and diffusion behavior of isoprene and methyl methacrylate homopolymers and three random copolymers of the two. One set used contained no further additives, while another set contained a chain-breaking antioxidant and was cross-linked with dicumyl peroxide.

Polyethylene permeation studies were performed at room temperature using a high vacuum gas transmission apparatus. When nitrogen gas was used as a penetrant, permeability and diffusion coefficients

in the polyethylene were found to decrease after photo-oxidation at 75°C, while solubility (S) increased. The decreases in diffusivity and permeability were attributed to cross-linking in amorphous regions, while the solubility increase was ascribed to the formation of polar oxidation products. The diffusion coefficient for water vapor in polyethylene also decreased, whereas both H₂O permeability and solubility coefficients increased substantially. Since hydroxyl and carbonyl concentrations have been found to increase linearly with time of UV irradiation, the apparent linear dependence of solubility on oxidation time supports the hypothesis that sorbed water molecules are localized on specific polar sites in photo-oxidized polyethylene.

Results from the water sorption studies on the isoprene/methyl methacrylate copolymers indicated that simple specific polar site sorption is not likely the major mode of sorption for these materials. For the unoxidized films, solubility coefficients, determined by gravimetric integral sorption at 100% relative humidity, deviated substantially from a rule of mixtures relationship.

Besides chemical composition, other polymer properties such as density and glass transition temperature varied with amount of methyl methacrylate in the sample; these properties were surmised to influence the equilibrium water uptake. The clustering of water molecules in pre-existing microcavities in the glassy samples was suggested to account for observed solubility and diffusion coefficient

behavior. A temperature study of one sample indicated that if rubbery behavior is extrapolated into the glassy regime, the resulting hypothetical value for S would be somewhat closer to the value expected from simple compositional considerations.

Behavior uncharacteristic of specific site localization of water molecules was also observed in the photo-oxidized isoprene-containing polymers. For polyisoprene itself, over the range of 2 to 120 hours of UV exposure at 45°C, the solubility coefficient was found to be largely independent of polar group content, which was measured by the carbonyl infrared absorption band. Solubilities for the three copolymers likewise levelled off following increases from short exposure times. Anomalous, non-Fickian sorption kinetics, including two-stage sorption, were observed in oxidized samples. These anomalies, plus the observed curling of film samples during water sorption, were postulated as due to swelling stress differentials caused by the presence of an oxidized surface layer bonded to the essentially unoxidized substrate.

Appreciable differences in solubility coefficient behavior were detected between samples containing no further additives and those containing 2% cross-linking agent plus 0.5% of 4,4'-methylene-bis(2,6-ditertbutyl phenol) stabilizer. Water solubility in samples containing additives was usually higher, often considerably so, than solubility in the corresponding samples without additives, both for oxidized and unoxidized films. This phenomenon was speculated to

have its origin in factors like water sorption on oxygenated groups of the additives and the harsher thermal history of the cross-linked materials.

The varied results of this initial investigation emphasize the complex effects that the photo-oxidation process can have on polymer films. All these chemical, physical and morphological effects may contribute in different degrees to determining solubility and transport behavior of photo-oxidized polymers.

ACKNOWLEDGMENTS

The author wishes to express her appreciation to Professor Charles E. Rogers for his valuable advice and guidance during the course of this study.

Special thanks are owed to Mr. Alexander Sfirakis, who not only performed much of the synthesis and characterization of the copolymers, but also provided extremely helpful suggestions and discussions, along with moral support.

The author also wishes to acknowledge the partial financial support for this research by the Jet Propulsion Laboratory (as part of the Low-Cost Silicon Solar Array Project sponsored by the U.S. Department of Energy), and the generous assistance of the Plastics Institute of America.

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CHAPTER I

INTRODUCTION

Ultraviolet light and atmospheric oxygen are two important environmental agents which lead to degradation in properties of polymers exposed to outdoor conditions. An understanding of the fundamental processes involved in the interaction of these agents with polymeric materials is desirable to aid in predicting property changes due to weathering. In the practical sense, knowledge of the effects of photo-oxidation would facilitate the design of polymer-containing systems whose desirable properties are maintained or enhanced through exposure to light and air.

Degradation processes resulting from the exposure of plastic films to light, air and heat have been investigated for various materials (1-6). Typically, these studies have focussed on the relationship between weathering and the changes in a specific property, with optical properties receiving considerable attention. However, relatively little information is available about changes due to ultraviolet oxidation in the transport properties of polymers (7), i.e., in the diffusion, permeation and solubility characteristics for low molecular weight penetrants in a polymer. For many outdoor applications, especially as protective coatings, photo-oxidative degradation of polymer barrier properties can lead to failure of the

system long before mechanical or optical properties have deteriorated to an unacceptable level.

The objectives of this study are:

- 1) to explore how ultraviolet oxidation affects the solubility and transport behavior of polymer films, and
- 2) to examine the effects of polymer composition on the photo-oxidative process, insofar as these are reflected in the transport properties.

A number of materials were chosen for study, in order to provide a spectrum of properties. Table 1 outlines the polymers and penetrants used, and lists various characteristics of these choices which make them of interest for a study relating ultraviolet oxidation to transport properties of polymers.

The permeation characteristics of polyethylene films before and after γ -irradiation have already been documented (8,9). Since the mechanisms of γ - and UV photo-oxidation are believed identical except for the quantum efficiency of the initiation process (10), a comparison of data trends should be possible between previous studies and this one.

The isoprene/methyl methacrylate series was chosen particularly for studying the effects of polymer composition on photo-oxidation and transport properties. Besides the homopolymers, three intermediate levels of methyl methacrylate concentration (31, 47 and 63 mole percent) were used in order to chart property changes as the amount of MMA was increased. Not only is poly(methyl methacrylate)

Table 1
Choice of Materials

Polymer	Features	Penetrant	Features
Low density polyethylene	semi-crystalline UV transparent if pure poor UV stability	N ₂ gas	inert useful in probes of physical changes
Polyisoprene	rubbery hydrophobic poor UV resistance		
Isoprene/Methyl Methacrylate Random Copolymers	↑ intermediate (?) properties ↓	H ₂ O vapor	small size hydrogen bonding outdoor environmental agent interacts with polar groups
Poly(methyl methacrylate)	glassy contains polar groups excellent UV resistance		

itself quite UV resistant (11), but Deanin and coworkers (12,13) have demonstrated that the color stability of butadiene graft copolymers are improved when methyl methacrylate is incorporated as a co-monomer. The authors concluded that methyl methacrylate retarded the ultraviolet-light-catalyzed atmospheric oxidation of C=C bonds in the polybutadiene backbone.

If such a stabilizing effect of the MMA units is also exerted on the isoprene double bonds in these random copolymers, then the stability characteristics of the copolymers would be better than those of the easily photo-oxidized polyisoprene. Furthermore, the rate of degradation would be less than the sum of the rates of PIP and PMMA, with each weighted according to its relative amount. This raises the possibility of using copolymerization of small amounts of a stabilizing monomer (e.g., MMA) into an otherwise easily degradable polymer (e.g., rubber), to produce a copolymer which is resistant to ultraviolet oxidation, yet leaves other properties (e.g., mechanical) of the material essentially unchanged. In this preliminary study, however, large amounts of MMA comonomer were used, and it was not desired to preserve the thermo-mechanical properties of polyisoprene.

Materials were chosen for this study on the basis of both their potential scientific relevance and their practical importance; these two considerations can also be applied to the objectives of this study. Particular attention will be paid to investigating the following questions:

- 1) What sort of changes are observed in the solubility and transport properties of polymer films which have been photo-oxidized?
- 2) How might these changes be related to known changes in other chemical or physical properties also caused by UV photo-oxidation?
- 3) Can water solubility be explained in terms of specific site sorption at polar groups?
- 4) How does the amount of methyl methacrylate present in copolymers with isoprene affect the UV degradation process and the water sorption process?
- 5) How do water solubility results from pure copolymers compare with those obtained for materials containing cross-linking and antioxidant, as many commercial materials do?

Answers to these questions, or even illumination of various aspects involved in determining their answers, would be of immense practical importance in the selection and modification of polymers for design purposes. Once the effects of photo-oxidation on polymer transport properties are understood, predictions of lifetime performance will be placed on a more firm scientific basis, and the development of UV-stable, high barrier polymeric materials may be aided. In addition, results from this study may help elucidate the mode of interaction which may occur between the components in polymer/environmental agent mixtures, including absorbed radiation.

CHAPTER II

TECHNICAL DISCUSSION

A. Purpose

It is the aim of this section to review those portions of scientific theory and experimental findings which provide background material for the interpretation of results from this study.

B. Photo-oxidation of Polymers

1) General Mechanism of Polymer Photo-oxidation. The photo-oxidation of polymers proceeds via a free radical mechanism largely similar to the mechanism of thermal oxidation. Hence, the series of reactions leading to degradation may be classified according to the typical free radical steps discussed below:

- a. initiation
- b. propagation
- c. termination

a) Initiation. In photo-oxidation, the formation of polymer radicals (P·)

is a consequence of bond scission due to absorption of photons of light. The energy of the visible and ultraviolet quanta involved in photodegradation is of the order of that which is absorbed by unsaturated structures as well as of the strengths of the bonds in the

polymer molecules (14). The photon absorption and subsequent bond scission need not occur exclusively via hydrogen abstraction as depicted in equation [1], although tertiary hydrogen bonds are especially susceptible to dissociation. Bond homolysis, with the formation of free radicals, can also occur along the polymer backbone, in side chains, at carbonyl groups, or selectively at end groups, especially unsaturated end groups.

b) Propagation and Chain Transfer. When chemical bonds are broken, and free radicals primarily formed, it is the way in which the radicals react that determines the nature of the overall reaction. The reactions which the radicals undergo depend upon the chemical nature, and often upon the physical state of the materials. However, some general features of free-radical reactions in oxidizing polymers can be described.

Since molecular oxygen has a biradical nature, it rapidly combines with other free radicals by addition to form peroxy radicals ($\text{POO}\cdot$):

The rate of reaction [2] depends on the structure of $\text{P}\cdot$ (15,16). The peroxy radical can abstract hydrogen from another polymer molecule to form polymer hydroperoxides (POOH):

Peroxy radicals are strongly resonance stabilized, and are relatively

selective electrophilic species abstracting tertiary bonded hydrogen in preference to secondary or primary.

Polymer hydroperoxides decompose under light irradiation or at elevated temperatures (17-24) according to the following equations:

Reaction [5] will predominate in photolysis with ultraviolet light.

Free radicals formed during reactions [4] and [5] can take part in radical-induced decomposition of hydroperoxides:

thus continuing the kinetic chain (25-29).

c) Termination. The termination of the radical chain is due to reactions of free radicals with each other by combination, in which inactive products are formed:

etc.

→ inactive products

When the reaction pressure is high, the termination reaction almost exclusively follows equation [8]. In the solid state when sufficient oxygen concentration cannot be maintained in the system, the termination reaction [9] becomes significant. Polymer radicals can couple mutually (Equation 10), and form crosslinks with peroxy radicals. Scission and cross-linking may occur simultaneously in the same polymer sample.

2) Formation of Oxygenated Products. In addition to the peroxide and ether linkages that can be formed respectively in the propagation and termination steps, the formation of other oxygenated products, particularly hydroxyl and various carbonyl moieties, commonly occurs in polymer photo-oxidation.

Hydroxyl groups (-OH) are formed in the reaction between alkoxy polymer radicals (PO·) and other polymer molecules:

Formation of carbonyl and aldehyde groups can occur in different ways:

a) β -scission of alkoxy radicals

This process plays an important part in backbone scission of chains (17, 30-32).

- b) Highly reactive hydroxyl radicals from the decomposition of hydroperoxide groups may, under cage effect conditions, abstract tertiary bonded hydrogens at the carbon atom

- c) Reactions between two polymer alkoxy radicals producing simultaneously a carbonyl and hydroxyl group by disproportionation:

3) Antioxidant Stabilization. Chain-breaking antioxidants (AH) act by retarding the propagation steps in oxidation, reactions [2] and [3]. Antioxidants react faster with peroxy radicals ($\text{ROO}\cdot$) than with $\text{R}\cdot$ radicals, so the main chain transfer reaction is:

which can be followed by the termination reaction

An outline of the proposed oxidation inhibition process of 4,4'-methylene bis (2,6-di-tert-butyl phenol) is given below (14,33).

The phenoxy radical may be stabilized by resonance

Instead of dimerizing, the $\text{AO}\cdot$ radical can function as a second free radical trap by $\text{ROO}\cdot$ abstraction of the methylene hydrogen, thus creating the quinone methide:

After formation of the quinone, the material is still capable of donating the other phenolic H to trap a third peroxy radical. The resulting radical has been observed by esr (34).

4) Photo-oxidation of Polyethylene

a) Chemistry. Before ultraviolet light can interact with a polymer molecule, the energy must be absorbed. A pure hydrocarbon molecule e.g., polyethylene - does not contain functional groups capable of absorbing energy in the near ultraviolet range. However, every polymer is oxidized to varying degrees during manufacture and processing, producing carbonyl, hydroxyl and ester functional groups. Burgess (35) has proposed that the observed polyethylene photodegradation products can be accounted for by Norrish Type I and Norrish Type II carbonyl photocleavage reactions:

Norrish Type I Norrish Type II

Since carbonyl groups acting as sensitizers for the photo-degradation of polyethylene are present in higher concentrations near the surface of a sample, it is likely that oxidation begins at the surface and gradually moves into the bulk of the polymer. This view is supported by the works of Hawkins and others (36,37), who have found that ageing effects were concentrated initially on the polymer surface.

b) Physical and Morphological Effects

i) Preferential surface oxidation. Photo-oxidation of polyolefin films has been found to be most intense at the surface of the polymer, then gradually levelling off with depth into the bulk of the material (37-39). Estimates of the thickness of this photo-oxidized surface layer have ranged from less than a micron (38) to several mils (39). Investigations have shown that the major factor influencing the formation of this layer on PE is the presence of oxidation-catalyzing carbonyl groups located preferentially on the surface. However, other factors, such as attenuation of UV radiation (especially for UV-absorbing polymers) or diminishing oxygen concentration would also tend to cause the level of degradation to be lower deeper inside the film.

ii) Microstructural changes. Increases (40,41), no change (41) and decreases (42) in the crystallinity of polyethylene film samples after UV photo-oxidation have been reported in the literature. Under fairly mild conditions, photo-oxidation is usually restricted to the amorphous regions of the polymer, where oxygen can

penetrate more easily. After long exposure times, the crystalline regions themselves become attacked, and crystallinity decreases. Increases in % crystallinity were ascribed to the reordering of oxidized amorphous regions into a more compact structure.

Cross-linking, which occurs primarily in the amorphous regions (43), is likely to prevail over chain scission, which occurs primarily in the crystalline regions (44); increased brittleness results (40,45).

5) Photo-oxidation of Poly(methyl methacrylate). The photolysis of PMMA results in a random scission of the polymer chain backbone by a radical process (46-52). Three major reactions are reported to occur at the same time:

- a) a random homolytic scission of main-chain carbon-carbon bonds
- b) photolysis of ester side groups
- c) photo-dissociation of methyl side groups

The main products of the photodegradation of PMMA in air are methyl formate, methanol, MMA, methane, hydrogen, carbon monoxide and carbon dioxide (50).

The infrared spectra of PMMA samples have been found to change very little on irradiation with light; only broadening of the carbonyl band at 1750 cm^{-1} and new bands at 1615 cm^{-1} and 1640 cm^{-1} attributed to olefinic unsaturation have been reported (50).

The strong attenuation of ultraviolet light in poly(methyl methacrylate) (53) indicates that the radiation cannot penetrate far

into the film, hence degradation must be concentrated near the surface. PMMA has shown no tendency to form crosslinks when irradiated as a film.

6) Photo-oxidation of Polyisoprene. Considerable research has been conducted into the photodegradation of 1,4 polyisoprene (54-58). The weakest link in the PIP chain is between the two methylene groups:

These allylic radicals (or their counterpart resonance structures) may then recombine, or add across double bonds, or react with oxygen according to the generalized scheme given previously. Cis-trans isomerization results from loss of sp^2 character, and oxygenated degradation products observed include: carbonyl groups, alkyl peroxides, epoxides, hydroxyl and trans methine groups.

C. Permeation, Solubility and Diffusion in Polymers

1) General. The transport phenomenon describing the movement of a penetrant molecule through a polymer film usually is described mechanistically as a three-step process. Penetrant molecules initially condense and dissolve at one surface of the film with the assumption that equilibrium is instantaneously established and maintained at the penetrant/polymer interface. For gases, the

concentration of penetrant, c , at the interface is usually low and can be related to the partial pressure, p , of the gas in contact with the film according to Henry's law :

$$c = Sp \quad [24]$$

where S is a solubility constant with units of volume penetrant at STP per volume polymer per cm Hg.

The second step involves passage of dissolved penetrant molecules through the film by a diffusion process. The driving force for this movement is the concentration gradient developed in the film.

If the penetrant concentration differs at the two film faces, the third step involves penetrant molecule evaporation from the low concentration side of the film. Equilibrium usually is established at this interface within some finite time interval and maintained.

The above mass transport process is known as permeation, and involves both solution, a thermodynamic process, and diffusion, a kinetic process.

2) Diffusion. When a penetrant molecule migrates by random motion through an isotropic material from regions of high concentration to regions of lower concentration, the rate of mass transfer is described by the diffusion coefficient, defined by

$$J = -D \frac{\partial c}{\partial x} \quad [25]$$

where: J = mass flux across a reference plane of unit area normal to the flow direction

D = diffusion coefficient

c = penetrant concentration

x = coordinate in the diffusion direction

Several diffusion coefficients may be defined, depending on the choice of reference plane, but in the limit of low concentration of one substance (i.e. a penetrant gas), the definitions converge to give the same value of D .

Equation [25] is frequently referred to as Fick's first law. Fick's second law describing the time dependence of the diffusive flux can be obtained by differentiation of equation [25] and written as:

$$\frac{\partial c}{\partial t} = \partial [D(\partial c / \partial x)] / \partial x \quad [26]$$

If D is constant, the more familiar form results:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad [27]$$

3) Experimental Methods for Determination of P , D and S .

Extensive reviews of various methods for measuring and calculating diffusion, solubility and permeability parameters for polymers have been published elsewhere (58,59). In this section, only those two experimental methods used in this study will be discussed: permeation time-lag and integral sorption.

a) Permeation Time-Lag. The case of interest is a sheet of polymer of thickness ℓ , initially free of penetrant. At time $t = 0$, a known pressure, P_1 , of penetrant is admitted to one side of the sheet ($c = c_1$ at $x = 0$), while essentially zero concentration is maintained at the other side (so $c = 0$ at $x = \ell$). The solution to equation [27] given these boundary conditions is:

$$c(x,t) = c_1 - \frac{c_1 x}{\ell} - \frac{2c_1}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{\ell}\right) \exp\left\{-\frac{Dn^2 \pi^2 t}{\ell^2}\right\} \quad [28]$$

The time dependent concentration gradient at the low pressure surface ($x = \ell$) can readily be found and used to determine the mass flux. Integrating J over time gives the quantity of penetrant (Q) evolved per unit area from the low-pressure surface as a function of time

$$\frac{Q(t)}{A} = \ell c_1 \left[\frac{Dt}{\ell^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left\{-\frac{Dn^2 \pi^2 t}{\ell^2}\right\} \right] \quad [29]$$

At long times this approaches the straight line:

$$\frac{Q(t)}{A} = \frac{Dc_1}{\ell} \left(t - \frac{\ell^2}{6D} \right) \quad [30]$$

The intercept of this straight line on the time axis is the time lag, L , and

$$L = \ell^2 / 6D \quad \text{or} \quad [31]$$

$$D = \ell^2 / 6L \quad [32]$$

Equation [32] can still yield a good approximation to D if the diffusion coefficient is concentration dependent. Pollak and Frisch (60) have shown that even if the exact functional dependence of $D(c)$ on c is not known, the following inequality holds for a very large class of functional dependence of $D(c)$ on c :

$$\frac{1}{6} \leq \frac{LD}{2} \leq \frac{1}{2} \quad [33]$$

Thus the estimate of D is, at worst, too small by a factor of three.

The slope of the straight line from equation [30] is the steady state mass flux:

$$J_{ss} = \frac{Dc_1}{\ell} \quad [34]$$

Since one can more readily measure the pressure of the penetrant in equilibrium with the dissolved penetrant than the concentration itself, it is convenient to employ the solubility coefficient, giving:

$$J_{ss} = DS \frac{(P_{\text{high}} - P_{\text{low}})}{\ell} \quad [35]$$

The product DS is frequently called the permeability coefficient:

$$\underline{P} \equiv DS \quad [36]$$

Thus from a record of $Q(t)$ from $t = 0$ to steady state, D , S and $\underline{P}$ may be determined from equations [32], [35] and [36].

b) Equilibrium Sorption. For the simplest case of vapor sorption, a sheet of polymer is preconditioned to a uniform penetrant concentration c_0 , often $c_0 = 0$. A convenient co-ordinate system is to take $x = 0$ at the center of the sheet, and the surfaces at $x = +1/2 \ell$ and $x = -1/2 \ell$. At time $t = 0$, the pressure of the penetrant vapor is instantaneously changed from P_0 to P_1 , corresponding to a new equilibrium concentration c_1 . If the diffusion coefficient is independent of concentration and if equilibrium is reached instantaneously at the surfaces of the sheet, the time dependent concentration profile is given by:

$$\frac{c - c_0}{c_1 - c_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left\{ \frac{-D(2n+1)^2 \pi^2 t}{\ell^2} \right\} \cos \frac{(2n+1)\pi x}{\ell} \quad [37]$$

If the quantity of penetrant which has entered the sheet at time t and at equilibrium ($t = \infty$) are denoted respectively as M_t and M_∞ , then:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{\pi^2 (2n+1)^2} \exp \left\{ \frac{-D(2n+1)^2 \pi^2 t}{\ell^2} \right\} \quad [38]$$

For small times the sheet may be regarded as of infinite thickness, and a more useful description is:

$$\frac{M_t}{M_\infty} = 4 \frac{\sqrt{Dt}}{\ell} \left[\frac{1}{\sqrt{\pi}} + \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{n\ell}{2\sqrt{Dt}} \right] \quad [39]$$

where $\operatorname{ierfc} z = \int_z^{\infty} \operatorname{erfc} y \, dy$

For values of t such that $\frac{\sqrt{Dt}}{\ell} < \sim \frac{1}{4}$, the entire summation is negligible, and M_t/M_∞ is linear with $\sqrt{t}$ up to values of $M_t/M_\infty \sim 0.6$ or higher. The diffusion coefficient may then be calculated from the initial slope of M_t/M_∞ vs. $\sqrt{t}/\ell$.

For the case where D is a function of concentration only, the initial part of the M_t/M_∞ curve is still linear with $\sqrt{t}/\ell$. The diffusion coefficient thus measured is some average value in the concentration range used (61).

4) Anomalous Diffusion Behavior. Polymers at temperatures below the glass transition temperature, polymers with long relaxation periods, and polymers with non-homogeneous structure often exhibit so-called "anomalous" or "non-Fickian" sorption and diffusion behavior, especially with penetrants that extensively swell or interact with the polymer. Diffusion and sorption in these systems cannot be adequately described by any generalized form of Fick's law with constant boundary conditions and the diffusion coefficient dependent only upon concentration.

A sorption process will be influenced by those segmental motions which occur at about the same rate or slower than the motivating diffusion process. Anomalous effects may be directly related to the

influence of changing polymer structure on solubility and diffusional mobility, or they may result from the internal stresses exerted by one part of the medium on another as diffusion proceeds.

Alfrey et al. (62) have proposed a useful classification according to the relative rates of diffusion and polymer relaxation. Three classes are distinguished:

- 1) Case I or Fickian diffusion in which the rate of diffusion is much less than that of relaxation;
- 2) Case II diffusion, the other extreme in which diffusion is very rapid compared with the relaxation process;
- 3) Non-Fickian or anomalous diffusion which occurs when the diffusion and relaxation rates are comparable.

Case I and Case II are both simple cases in the sense that the behavior of each can be described in terms of a single parameter. Case I systems are controlled by the diffusion coefficient. In Case II the parameter is the constant velocity of an advancing front which marks the innermost limit of penetration of the diffusant and is the boundary between swollen gel and glassy core. Anomalous systems lie between Case I and Case II in that two or more parameters are needed to describe the interacting diffusion and relaxation effects.

Extensive reviews are available of the experimentally observed diffusion anomalies in various polymer systems (58,59,62,63). In this chapter, attention will be confined to a qualitative description of the main characteristic features. The different types of behavior are summarized in Figure 1 from reference (59).

Figure 1. Characteristic Sorption Curves.

a) Fickian: Case I. The main feature of systems indicating Fickian behavior are: (1) the amount of sorbed penetrant is initially linear with the square root of time, up to $M_t/M_\infty > 0.5$; (2) above the linear portion the curve is concave towards the $\sqrt{t}$ axis and there are no inflections in the curve; (3) the sorption curves determined for the same concentration range in films of differing thickness, ℓ , are superimposed when the data is plotted

as $\frac{M_t}{M_\infty}$ vs. $\frac{\sqrt{t}}{\ell}$.

Characteristic features of the relative weight gain vs. $\sqrt{t}$ curves for other anomalous cases are as follows (64,65):

b) Pseudo-Fickian type: (1) the sorption curve resembles a true Fickian curve inasmuch as it does not exhibit any inflection in slope; (2) the initial portion of the curve is linear, but only over a small part (i.e., significantly less than 50%) of the total uptake.

c) Sigmoid type: (1) the sorption curve is non-linear in the region of small times; (2) the sorption curve is sigmoid-shaped; a single inflection of slope is present.

d) Two-stage type. Two inflections in slope. The first stage ($0 \rightarrow A \rightarrow B$) involves: (1) rapid sorption which apparently obeys Fick's Law; (2) establishment of a quasi-equilibrium at B. The second stage ($B \rightarrow C \rightarrow D$) involves: (3) a slow increase in the overall sorbed concentration without any significant concentration gradient;

(4) establishment of a true equilibrium at D after a long period of time.

A number of authors have proposed mathematical models of the anomalous penetrant-polymer diffusion phenomena (65-70). Essentially they are all concerned with the combination of penetrant diffusion and polymer relaxation proceeding at different relative rates according to the conditions of the experiment. However, no single one of these models can account satisfactorily for all the known aspects of anomalous diffusion. A synthesizing model is still needed to include the combined effects of history, orientation, and stress on the diffusion process within the polymer system and on the surface concentration.

5) Heterogeneous Media. Strictly speaking, the usual Fick's law diffusion equations are not applicable for systems of more than two components. Thus, in systems where polymer composition is a function of position, as in laminates or asymmetric membranes, the D and S values calculated via techniques described above and in Chapter IV cannot be considered as rigorous diffusion and solubility coefficients, but rather they represent some sort of average for the heterogeneous system.

6) Mode of Sorption (73). The term "mode of sorption" relates to the position, manner, and strength by which a sorbed molecule is held within a solid. The manner by which a penetrant is sorbed in a

polymer matrix depends on the physical and chemical nature of the two components. Penetrant molecule mobilities are very sensitive to the nature and magnitude of nearest neighbor interactions. In a given system the existence of preferred or inaccessible sorption regions, the presence of voids in the polymer structure, and the occurrence of specific interactions affect the distribution of sorbed molecules and cause deviations from randomness.

Various models have been proposed to account for the sorption characteristics of water in polymers. Localized sorption models postulate the existence of specific sites where water molecules may be strongly localized (71,72). Such models have been fairly successful in describing the sorption isotherms of the more hydrophilic polymers (74,75). For many polymers containing polar groups, a correlation between the concentration of polar groups and the amount of sorbed water can be made. (See Table 2.) However, other factors such as crystallinity and interchain hydrogen bonding may cause a lowering of the sorptive capacity so that the ratio of moles of water sorbed to polar groups in the polymer could be much less than unity.

For hydrophobic polymers, models assuming random distribution of water molecules are useful in describing sorption characteristics (76). However, when cohesive forces of polymer and penetrant are dissimilar, the penetrant tends to cluster in the medium (77,78). The formation of clusters gives rise to an important mode of sorption, since the

Table 2

Polar Group Content vs. Water Solubility (58)

<u>Polymer</u>	<u>Moles of polar groups</u>	<u>Moles H₂O sorbed</u>	<u>H₂O per polar group</u>
Polyvinylalcohol	2.27	2.11	.93
Polyglycine-DL-alanine	1.56	1.72	1.10
Polymethacrylic acid	1.16	0.91	.78
Polyacrylonitrile	1.89	0.42	.22
Polymethylvinylketone	1.43	0.29	.20
Polyvinylbutyral	1.4	0.18	.13
Polyvinylacetate	1.16	0.17	.15
Polyethylenevinylalcohol	0.86	0.15	.17
Polyvinylbenzoate	0.676	0.1	.15
Polyisobutylmethacrylate	0.705	0.08	.11

(per 100 g of polymer; $p/p_0 = 0.9$)

associated molecules are, to some degree, in a different phase from the polymer random solution phase. In these cases, such molecules are essentially immobilized and do not contribute to the overall flux.

CHAPTER III

EXPERIMENTAL

A. Preparation of Copolymers

Isoprene (IP) and methyl methacrylate (MMA) homopolymers, and three random copolymers of the two, were prepared by free radical initiated emulsion polymerization. The general recipe for the reaction is given in Table 3. The freshly distilled monomers were weighed into 12 oz. glass bottles containing the remaining ingredients. After the mixture was purged with nitrogen, the bottles were sealed with a bottle capper and placed in a 50°C water bath equipped with a rotating bottle holder.

Monomer feed ratios producing the desired copolymer compositions were calculated from reactivity ratios for isoprene and methyl methacrylate, as approximated from the Q-e scheme (79,80). Table 4 lists monomer feed and copolymer compositions, along with reaction times and conversion data for the various runs. The conversion levels for the copolymers were limited by the desire to maintain homogeneous compositions. An azeotropic composition exists at 30 mole percent methyl methacrylate (81); at this monomer ratio all polymer formed would have the same composition. Above this value the system is depleted of isoprene faster than methyl methacrylate, whereas below 30% MMA feed, methyl methacrylate is depleted faster than isoprene. Hence, for the non-azeotropic copolymer compositions, the conversion

Table 3

Isoprene/Methyl Methacrylate Polymerization Formulation

<u>Component</u>	<u>Weight (gms.)</u>
Monomers	75
Water	135
Sodium lauryl sulfate	3.75
Potassium persulfate	0.225
Dodecyl mercaptan	0.225

Table 4

Reaction Data for Isoprene/Methyl
Methacrylate Polymerizations

<u>% Methyl Methacrylate</u>		<u>Reaction time</u>	<u>% Conversion</u>
<u>Monomer feed</u>	<u>Copolymer</u>		
0	0	13 hr.	55
30	31	4 hr.	60
60	47	1 hr. 40 min.	35
85	63	1 hr.	15
100	100	1 hr. 15 min.	80

level must be kept low in order to produce uniform composition throughout the reaction. Further details of the synthesis procedure may be found elsewhere (81,82).

After the desired reaction time, the polymer emulsion was coagulated with acetone. The polymers were cleaned exhaustively using the procedure described below in order to remove residual soap and other impurities since water sorption studies are extremely sensitive even to minute quantities of ionic impurities (83,84).

After coagulation in acetone, the polymers were dried in air for one day. They were then cut into small pieces and washed three successive times in warm methanol for two hours each time. Next, the materials were dissolved in warm benzene and reprecipitated in methanol. After one day of air drying, the polymers were placed in a vacuum oven at room temperature for one week, then stored in vacuum dessicators in the dark. Methylene blue colorimetric analysis for residual soap content (85) showed the materials contained less than 0.0003% by weight of alkyl sulfates.

B. Characterization of Copolymers

1) Composition. The compositions of the isoprene/methyl methacrylate copolymers were determined by proton magnetic resonance spectroscopy, using a Varian-60 McNMR. The homo- and copolymers were dissolved in deuterated chloroform; the NMR spectra were taken at room temperature. Copolymer composition was determined from measurements of the area under the peaks of the olefinic protons ($\delta = 4.75, 5.20$ ppm), characteristic of the isoprene units, and the

area under the peak of the ester methyl protons ($\delta = 3.70$ ppm), characteristic of the methyl methacrylate units.

Spectra of the prepared isoprene/methyl methacrylate copolymers in chloroform (81) showed mainly 1,4-addition isoprene placements, evidenced by a large peak at 5.20 ppm and a very weak peak at about 4.75 ppm. The tacticity of the methyl methacrylate units could not be determined due to overlap of the isoprene protons in the distinctive areas. It would be expected that any methyl methacrylate triads would be syndiotactic due to the initiator system and temperature used (81).

2) Molecular Weight. The molecular weights of the polymers were determined by gel permeation chromatography (GPC). The instrument used was a GPC-200 (Waters Associates) with Styrogel columns having porosities of 10^6 , 10^5 , 10^3 , 500 and 60 Å. Analysis was performed at Glidden-Durkee Div. SCM, Inc. using tetrahydrofuran as solvent. Molecular weight and molecular weight distribution results are given in Table 5.

3) Glass Transition Temperatures. Glass transition temperatures of the polymers were determined from differential scanning calorimetry (DSC) and dielectric measurements (82). A DuPont R-900 DSC unit at Glidden-Durkee was used with a heating rate of 20°C per minute and sensitivity $\Delta T = 0.2^\circ\text{C/in}$ in static air. The thermograms for each of the homo- and copolymers showed only one well defined glass transition, implying the absence of sizeable block structure. The T_g 's thus determined are listed in Table 6.

Table 5

Molecular Weight Parameters

<u>Sample (% MMA)</u>	<u>$\overline{M}_n$</u>	<u>$\overline{M}_w$</u>	<u>$\overline{M}_w/\overline{M}_n$</u>
0	83,700	252,000	3.01
31	72,700	144,000	1.98
47	57,700	104,000	1.81
63	39,300	66,000	1.68
100	87,300	162,000	1.85

Table 6

Glass Transition Temperatures and Densities

<u>Sample (% MMA)</u>	<u>T_g(DSC, °C)</u>	<u>T_g(dielectric, 1 Hz, °C)</u>	<u>ρ(g/cm³)</u>
0	-62	-57	0.908
31	-22	-21	0.992
47	10	8	1.049
63	35	34	1.088
100	119	118	1.176

The dielectrometer used for the determination of T_g consisted of a sample cell (described in 86) coupled with an automatic bridge circuit. The sample conductance, proportional to the imaginary component ϵ'' of the complex dielectric constant, and the sample capacitance, proportional to the real component ϵ' , are plotted at four frequencies (50, 500, 5K and 50K Hz) as a function of temperature. The maximum of the $\tan \delta$ peak was taken as the glass transition temperature at each frequency. The values for T_g listed in Table 6 were obtained by extrapolation to 1 Hz of a plot of $\log$ frequency vs. $(T_g)^{-1}$.

4) Density. The room temperature densities of the polymers were measured at B.F. Goodrich using the hydrostatic weighing technique (87). Water was used as the immersion liquid and three measurements were taken for each sample. The densities calculated by this method, shown in Table 6, are accurate to $\pm 0.001 \text{ g/cm}^3$.

5) Microstructure. The structure of the copolymers was inferred to be random based upon: a) monomer reactivity ratios, b) glass transition temperatures, and c) electron microscopy evidence.

The reactivity ratios for both isoprene and methyl methacrylate are less than unity ($r_{IP} = 0.62$ $r_{MMA} = 0.12$) indicating that each propagating radical prefers to add to the other type of monomer. The product $r_1 r_2$ is an even better indication of the alternating tendency of a copolymer - if $r_1 r_2 = 0$, a perfectly alternating copolymer would

result. For the system of isoprene/methyl methacrylate, $r_1 r_2 = 0.074$, indicating that in this system the formation of appreciable-sized block segments is unlikely.

Additional evidence indicating that the copolymers prepared had essentially random sequence distribution is given by the composition dependence of the glass transition temperatures. The copolymers followed the Fox relation which is based on the assumption of random sequence distribution (88)

$$\frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} = \frac{1}{T_g} \quad [40]$$

where

W_1 = weight fraction of monomer 1

T_{g_1} = T_g of homopolymer 1

T_g = T_g of copolymer

The data and equation are plotted in Figure 2; the good agreement between theory and experiment suggests that the copolymers are random.

Electron microscopy also was employed to determine if any gross block structure existed in the copolymers. Samples were stained with osmium tetroxide, which is selective for the double bond in the isoprene units, and were examined under a transmission electron microscope (Jeol 100B). A uniform staining pattern for all samples

Figure 2. Composition Dependence of T_g .

indicated that the isoprene segments do not aggregate into distinct regions.

C. Introduction of Additives

Two sets of the copolymer samples were used in the sorption experiments, one set consisting of cross-linked polymer containing an antioxidant, while the other set had no additives. The antioxidant, 4,4'-methylene-bis(2,6-ditertbutyl phenol) (Eastman), was employed to retard degradation of the polymers during storage and cross-linking. Cross-linking agent, dicumyl peroxide (ICN Pharmaceuticals, Inc.) was used for the preparation of molded films which would maintain their shapes during photo-oxidation and subsequent transport property measurements.

The additives were introduced by swelling the isoprene-containing polymers with a benzene solution containing 0.5 weight percent (based on polymer) of the antioxidant and 2.0 weight percent of cross-linking agent. No additives were used with poly(methyl methacrylate). The formulated benzene mixture was allowed to equilibrate with occasional stirring in a dry box, under a nitrogen atmosphere, for five days. After vacuum oven removal of the benzene, the polymers were stored in a vacuum dessicator.

For the samples in which no antioxidant or cross-linking was desired (in order to assess the effect of additives on photo-oxidation and transport properties), the additives were removed from the polymer by repeated (at least three times) dissolution in chloroform and reprecipitation in methanol. These materials were

used as soon as possible (less than a week) after vacuum drying, since they were very susceptible to oxidation.

D. Film Pressing

Compression molded films of the copolymers were prepared using a Pasadena Press (Pasadena Hydraulics, Inc.). The appropriate amount of polymer was weighed and placed in a 10 mil thick (for PMMA) or 20 mil thick (for all other samples) picture frame mold between teflon-coated aluminum sheets. The polymer was placed in the pre-heated press, and the ram pressure was raised by 5000 lbf increments, held at each level for 10 seconds, then released and raised to the next level, in order to prevent trapped bubbles in the sample. This was repeated until the maximum force (40,000 lb, 3500 psi) of the press was reached. The sample was held at maximum pressure for the appropriate length of time, then cooled under pressure to room temperature. Details of the molding and subsequent treatment of the various films are given in Table 7. The longer times and higher temperatures were used as recommended cross-linking conditions (89), while the milder conditions were used with the unstabilized polymers in order to minimize degradation during molding.

E. Polyethylene Film

The polyethylene used was a commercial film (Ethyl Corporation) 5.6 mils thick. No attempt was made to remove additives (including any antioxidants), nor were special precautions taken to prevent air oxidation of the samples before they were exposed to the ultraviolet light.

Table 7

Molding and Treatment of Copolymer Films

<u>Film composition</u>	<u>Platen temperature</u>	<u>Press time</u>	<u>Film treatment</u>
Isoprene-containing polymers with additives	310°F	45 min.	55°C vacuum oven for 3 days then stored under vacuum at room temperature
Poly(methyl methacrylate)	410°F	45 min.	Same
Isoprene-containing polymers without additives	150°F	10 min.	Clamped between glass plates and stored at room temperature under vacuum

F. Photo-oxidation Procedure

The degradation apparatus used for the polyethylene studies consisted of an ultraviolet sunlamp (General Electric RSM) in a glass box which was open to the air. The film was placed ~12 cm from the lamp, and the temperature was maintained in the range 70-75°C by the sunlamp heat.

The copolymer and homopolymer samples were oxidized in a commercial weatherometer (Q-U-V, Q-Panel Co.). This apparatus, shown schematically in Figure 3, employed medium pressure mercury fluorescent UV lamps (FS-40, Westinghouse Electric Corp.), the spectral distribution of which is shown in Figure 4. Following the manufacturer's instructions, the lamps were rotated every 400-450 hours of operation and discarded after 1600-1800 hours of use, in order to keep exposure intensity uniform.

Films of the copolymers used in the sorption studies were taped along two edges to pieces of teflon, which were affixed to the specimen panels of the weatherometer. Upon completion of the UV exposure, which occurred at 45°C in the presence of air, films were kept in a vacuum oven at room temperature in the dark for at least 48 hours in order to remove any volatile oxidation products.

G. Measurement of Transport Properties

1) Permeation Apparatus. For the polyethylene films, an adaptation of the high vacuum gas transmission technique described by Barrer and Skirrow (90) was used to determine the diffusion, permeability and solubility coefficients of the unoxidized and photo-

Figure 3. Q-U-V Weatherometer Schematic

Figure 4. FS-40 Sunlamp Spectral Energy Distribution.

oxidized samples. The equipment and experimental procedure have been described in great detail elsewhere (81) and will only be briefly outlined here.

A 2-3/4 inch diameter film is clamped into a stainless steel permeation cell, exposing one face of the film to a high vacuum and the other side to a constant pressure of penetrant gas (nitrogen) or vapor (water). In the case of photo-oxidized films, the side which had been exposed to the UV source was used on the higher pressure side in the permeation apparatus. The permeability coefficient (P) is determined from the increase of penetrant pressure on the low pressure side of the film (this volume is automatically evacuated when the pressure rises to about 300 μ m of Hg), while the diffusion coefficient (D) is calculated from the time lag which occurs before the attainment of steady state. Solubility is calculated from the relation: $S = P/D$.

2) Equilibrium Sorption of Water. The sorption kinetics of water vapor in small samples (90 mg) of copolymer films were studied by an equilibrium sorption technique. The weight increase in a film sample suspended in air in a flask partially filled with distilled water (nominal 100% relative humidity) was measured as a function of time until an equilibrium weight was reached. A Perkin-Elmer Autobalance AD-2 with an accuracy of $\pm 1 \times 10^{-5}$ g (.01 mg) was used for the weighing.

The film thicknesses (~10 mil for PMMA, ~20 mil for all others) were measured with a micrometer, and the average value of 5 readings

on a single film was used as ℓ for the calculation of the diffusion coefficient. Each sample had to be removed from the 100% R.H. atmosphere for about 30 seconds in order for a weight measurement to be completed, but no detectable loss of weight occurred in this time. Measurements were made at 23°C in a temperature controlled room.

H. Preparation of Films for Infrared Spectroscopy

Thin films of the isoprene/methyl methacrylate copolymers were cast onto salt plates (NaCl or KBr) by placing 2 drops of the polymer solution (~.22 g/ml chloroform) on the plate, smearing it thin with a glass microscope slide, and allowing the solvent to evaporate. The infrared spectra of these samples were then taken with a Fourier transform infrared spectrometer (Digilab FTS-14), using the double beam mode vs. air with 200 sample and 100 reference scans, at a resolution of 2 cm^{-1} . The samples were then photo-oxidized using the weatherometer described previously for the prescribed lengths of time: 1,2,4,24,48 and 120 hours at 45°C. After volatile products were removed by room temperature vacuum oven treatment, the spectra of the oxidized samples were taken. Digital subtraction of the after-and-before UV-exposure spectra was performed by an on-line computer, thus permitting better visualization of the spectral changes induced in the polymers by UV photo-oxidation.

CHAPTER IV

RESULTS AND DISCUSSION

A. Polyethylene Studies

1) Transport and Solubility Data. Room temperature (~23°C) measurements of the nitrogen and water vapor permeabilities of low density polyethylene films exposed for 0, 24 and 72 hours to an ultraviolet sunlamp at 75°C were carried out. The transport properties calculated from these data are listed in Table 8.

2) Characterization.

a. General. Work by other researchers (detailed in Chapter II) indicates that, upon UV photo-oxidation, polyethylene can experience embrittlement, destruction of crystalline regions, and formation of cross links and various chemical oxidation products. An effort was made to investigate the possible occurrence of these phenomena in the PE films used in this study.

b. Brittleness. Although no mechanical tests were performed to quantify the observation, the photo-oxidized films were noticeably more brittle than the unexposed samples. The upper limit for oxidation time, three days, was necessary because films exposed for longer times cracked when clamped in the stainless steel permeation cell, rendering transport measurements impossible. In an attempt to circumvent this problem, the edge of the film (the part clamped with

Table 8
Permeability Properties of Degraded
Low Density Polyethylene Films

Penetrant = N₂

<u>UV exposure (@ 75°C)</u>	<u>P x 10⁹</u>	<u>D x 10⁷</u>	<u>S x 10³</u>	<u>T°C</u>
0	1.7	3.7	0.46	23°
24 hours	1.2	2.3	0.52	25°
72 hours	0.9	1.6	0.56	26°

Penetrant = H₂O vapor

<u>UV exposure (@ 75°C)</u>	<u>P x 10⁹</u>	<u>D x 10⁷</u>	<u>S x 10³</u>	<u>T°C</u>
0	16.5	2.2	7.5	24°
24 hours	22.5	1.7	13.2	24°
72 hours	38.0	1.4	27.1	23°

P given in cc gas (STP)/sec/cm Hg pressure/mm thickness/cm² area

D given in cm²/sec

S given in cc gas (STP)/cc polymer/cm Hg pressure

a rubber gasket) was shielded from the ultraviolet light. A doughnut-shaped collar covering about 1 cm of the film edge was cut from cardboard and laid on top of the circular polyethylene film before the sunlamp was turned on.

Figure 5 shows a comparison between an unoxidized PE sample (a), and one whose center was exposed in air to UV light for 150 hours, with the outer edge shielded from the rays (b). Both films are shown actual size. Evident is the film shrinkage upon oxidation and the extensive ruffling of the unexposed edges in the oxidized sample. Gross dimensional and weight changes were also determined for this ruffled sample, and are given in Table 9. This ruffling is also observed with UV exposure times of less than 24 hours, although the center remains wrinkle-free for up to 90 hours of UV at 75°C. Since it was impossible to clamp the ruffled films into the permeation apparatus with an air-tight seal, only 24 and 72 hour samples were studied; with these, the edge-shielding collar was not used.

c. Oxidation Sites. Crystallinity measurements and electron microprobe elemental analysis were employed to determine the location and distribution of sites of intense oxidation. X-ray diffractometry measurements of the crystallinity of the polyethylene films used in the nitrogen and water vapor permeability studies indicate that no appreciable change in percent crystallinity occurred after either 24 or 72 hours of UV exposure at 75°C. Table 10 lists the values calculated by measuring peak areas in the region $2\theta = 5^\circ$ to 30° . A sample exposed for 7 days gave only 30% crystallinity, but this film

(a)

(b)

(a) unoxidized sample

(b) sample photo-oxidized for 150 hours at 75°C

Figure 5. Polyethylene Film Ruffling.

Table 9

Dimensional Changes for Oxidized
Polyethylene Film

Initial Weight	0.5620 g	Initial Diameter	7.4 cm
Final Weight	0.5293 g	Final Diameter	6.6 to 6.9 cm
Change	-6%	Change	-11% to -7%
Average Thickness Changes:			
	Outer	-0.4%	
	Inner	-5%	

Table 10

Crystallinity of Photo-Oxidized
Polyethylene Films

<u>UV exposure time (hours)</u>	<u>% crystallinity</u>
0	40.4
24	40.8
72	40.3

was too brittle for use in the permeation apparatus. These results indicate that, for up to 72 hours of UV exposure in air at 75°C, oxidation takes place preferentially in the amorphous regions of polyethylene, leaving the crystalline segments unaffected.

Films of polyethylene exposed for 7 days to ultraviolet light were examined by electron microprobe elemental analysis to determine the distribution of sites of intense oxidation. The degraded films were exposed to SO₂ gas for 45 minutes, causing sulfate groups to be formed by selective reaction with the hydroperoxide groups in the oxidized polyethylene (91). The films were then scanned with an electron microprobe for sulfur content. Total area for each scan was $(450\mu)^2$. Scans are shown in Figures 6 and 7; a white spot indicates the presence of sulfur. In 6a) the sulfate groups seem to be randomly distributed for the scale of observation, while in 6b), another section of an identically treated sample, a clumping of sulfate groups in the center of the picture can be seen. For comparison, Figure 7 shows the sulfur distribution on an unoxidized polyethylene film also treated with SO₂.

d. Infrared Spectroscopy. Chemical changes due to photo-oxidation in the polyethylene films were studied using infrared spectroscopy. Transmission spectra of the actual permeation samples used were taken in the region $3800-600\text{ cm}^{-1}$ with a Perkin Elmer 621 diffraction spectrometer. Because the samples were so thick (5.6 mils), the polyethylene films showed almost total absorbance in the CH stretching region ($2600-3100\text{ cm}^{-1}$), the CH₂ deformation region

(a)

50 μ

(b)

Figure 6. Hydroperoxide Distribution in Photo-oxidized PE Film.

Figure 7. Hydroperoxide Distribution in Control PE Film.

(1430-1490 cm^{-1}), and the CH_2 rocking region (710-740 cm^{-1}). In addition, the carbonyl region (1675-1800) was found to over-absorb for the 72 hour sample. Figure 8 depicts the IR spectra for the unoxidized and the two photo-oxidized samples. A summary of the observed band changes appears in Table 11.

It is apparent that many of the new or greatly increased absorbances are due to the incorporation of oxygen into the polymer chain. The oxygen-containing groups (hydroxyl, hydroperoxide, aldehyde, ketone, carboxyl, ester and ether moieties) increase the polarity of the polyethylene. An increase in the degree of cross-linking, believed (92) to consist of -O- or -O-O- bridges, and an increase in the degree of unsaturation in the polymer are the other major chemical changes induced in polyethylene by ultraviolet photo-oxidation.

3) Discussion of Polyethylene Results. Results of the nitrogen and water vapor transport and solubility measurements, plotted as a function of UV exposure time in Figures 9 and 10, can be interpreted in light of the physical and chemical changes found to occur from the photo-oxidation process. (Units for the parameters are given after Table 8.)

Nitrogen was chosen as a penetrant gas since it is a rather inert probe, and would be relatively insensitive to chemical changes induced by UV oxidation, whereas physical or morphological changes would be reflected in the transport properties of N_2 in polyethylene. For the nitrogen penetrant, permeability and diffusion coefficients decrease

Figure 8. IR Spectra of Photo-oxidized Polyethylene

Table 11

IR Band Changes in Photo-oxidized PE (14,21,24,93)

Region (cm ⁻¹)	Assignment	Comments
3300-3500	O-H stretch	Broad OH peak increased in width and intensity upon oxidation
2600-3100	CH stretch	Peak greatly decreased in 72 hour samples
2400-1800	Combination modes of crystalline vibrations	No pronounced changes
1742	Aldehydic C=O stretch	Apparently little change - overlapped with ketonic stretch in oxidized samples
1716	Ketonic C=O stretch	Increased with oxidation
1260/1300	Amorphous phase CH ₂ wag	Increased and broadened
1150-1200	Ether	Increased with oxidation
1080	Composite of C-OH and C-O-C	Broadened
909	R-CH=CH ₂	Appeared and increased with oxidation

Figure 9. Nitrogen Transport in Photo-oxidized Polyethylene.

Figure 10. Water Vapor Transport in Photo-oxidized Polyethylene

upon photo-oxidation, and this decrease becomes less sharp at longer oxidation times. The solubility of the nitrogen gas is higher in the degraded polyethylene films, but S increases less between 24 and 72 oxidation hours than between 0 and 24 hours.

Since the amorphous regions have become more highly cross-linked, without measurable destruction of crystalline regions, the decrease in diffusion coefficient is expected. Studies on γ -irradiated polyethylene (9) confirm that decreases in D and P attributed to cross-linking was indeed observed.

Nitrogen solubility was observed to increase slightly in the photo-oxidized polyethylene films. A priori, one would expect either a) the solubility to be largely independent of exposure time for the extent of oxidation studied here, or else b) S might decrease slightly due to densification from cross-linking. Perhaps the observed solubility increase is due to the formation of polar oxidation products in the polymer; although nitrogen exhibits no specific interactions with the polar moieties, changes in the cohesive energy of the polyethylene, or increases in unsaturated structures in the polymer may increase the affinity of PE for N_2 .

The dependence of water vapor transport and solubility properties on the extent of photo-oxidation is somewhat different than the behavior of nitrogen. Once again, the diffusion coefficient decreases, this time rather uniformly, with exposure time. Again this is explained in terms of cross-linking, since the number and size of "holes" available to the diffusing molecule will decrease as the

extent of cross-linking increases and tends to immobilize the amorphous regions. The permeability and solubility coefficients, however, increase substantially and fairly uniformly with time of oxidation. These results parallel those of Russian workers (8) who used γ -irradiated samples.

The increase in the solubility of water vapor in polyethylene as the exposure time increases is evidently due to the appearance of polarity when PE is exposed to UV light in the presence of air. Unfortunately, the high absorption of the carbonyl peak, and the hydrogen bonding effects on the hydroxyl peak rendered a quantitative determination of polar group content impossible, since Beer's law is no longer valid under these conditions. However, investigations by Heacock et al. (93) on thin films of low density polyethylene photo-degraded with UV light in the presence of air at temperatures ranging from 50° to 90°C indicate that the concentrations of hydroxyl and carbonyl groups increase linearly with time of UV-irradiation. If it is assumed that the formation of these polar groups also proceeds linearly with time for the 5.6 mil samples studied here, then the apparent linear dependence of S on oxidation time is consistent with localized water sorption on specific polar sites. This hypothesis is also suggested by the fact that the increase of water content does not appear to cause any pronounced concentration dependence of diffusion within the extent of oxidation studied, i.e., the sorbed water has little effect on the mobility of surrounding polymer chain segments.

The increase in the permeability coefficient is connected with the increase in solubility, since $\underline{P} = DS$. Under conditions of steady diffusion, the photo-oxidized specimen sorbs water to a considerably greater extent than the unoxidized sample, hence the increase in permeability is also connected with the increase in the hydrophilic character of the polyethylene by the formation of polar groups.

B. Isoprene/Methyl Methacrylate Copolymer Studies

1) Transport and Solubility Data. Room temperatures (~23°C) measurements of the water vapor sorption kinetics of films of isoprene/methyl methacrylate copolymer samples exposed for 0,1,2,4, 24,48 and 120 hours in a QUV weatherometer at 45°C were carried out. Tables 12 and 13 list the solubility and diffusion coefficients (calculated as described in Chapter II) for the set of non-cross-linked, non-stabilized copolymers. Tables 14 and 15 give the parameters for the copolymer series in which the isoprene-containing samples have 0.5% 4,4'-methylene bis(2,6-ditertbutyl phenol) added as an antioxidant, and 2% dicumyl peroxide added as a cross-linking agent.

The numbers given in Tables 12-15 represent averages; in most cases 2 samples were run for each of the photo-oxidized films, while for the unoxidized polymers with additives the averages were calculated from 3-5 individual runs. The actual data used to produce Tables 12-15 can be found in the Appendix.

Table 12

H₂O Solubility in IP/MMA Copolymers without
Additives (moles H₂O per 100 g polymer)
Mole % MMA

<u>UV hours</u>	<u>0</u>	<u>31</u>	<u>47</u>	<u>63</u>	<u>100</u>
0	.028	.025	.020	.022	.095
1	.034	.030	.021	.028	.097
2	.051	.031	.025	.031	.100
4	.049	.033	.030	.036	.093
24	.050	.046	.039	.045	.094
48	.049	-	.040	.044	.093
120	.048	.045	.045	.051	.102

Table 13

Diffusion Coefficients for Water in IP/MMA
Copolymers without Additives ($D \times 10^8 \text{ cm}^2/\text{sec}$)

<u>UV exposure hours</u>	<u>Mole % MMA</u>				
	<u>0</u>	<u>31</u>	<u>47</u>	<u>63</u>	<u>100</u>
0	1.4	2.6	2.5	6.6	0.7
1	1.7	3.3	3.0	4.5	0.5
2	1.3	2.8	2.1	6.2	0.6
4	0.8	1.6	0.9	3.6	0.9
24	1.2	1.9	1.6	5.7	0.8
48	1.4	-	2.7	5.7	0.9
120	2.1	1.8	4.2	10.9	0.6

Table 14

H₂O Solubility in Copolymers with
Stabilizer and Cross-linking

UV hours	Mole % MMA				
	0	31	47	63	100
0	.043	.038	.035	.065	.095
1	.037	.028	.028	.060	.097
2	.031	.021	.027	.061	.100
4	.033	.021	.025	.055	.093
24	.050	.026	.028	.066	.094
48	.065	.034	.045	.068	.093
120	.093	.037	.048	.074	.102

Table 15

Diffusion Coefficients for Water in Copolymers
with Stabilizer and Cross-linking ($D \times 10^8 \text{ cm}^2/\text{sec}$)

UV hours	0	31	47	63	100
0	0.4	0.7	1.2	0.6	0.7
1	0.7	1.2	2.8	0.5	0.5
2	0.8	2.5	2.2	0.5	0.6
4	1.0	2.7	3.5	0.7	0.9
24	-	4.0	5.0	1.2	0.8
48	0.5	2.9	1.4	1.2	0.9
120	0.6	5.3	3.4	2.5	0.6

Sorption kinetics data were plotted by a programmable desk-top calculator, which also calculated solubility and diffusion coefficients. The plots shown in Figure 18 give some indication of the point scatter involved. The program also provided for computation of statistical parameters for testing the fit of the initial linear portion and the equilibrium uptake level, but the number of points used in the linear regression and the equilibrium average calculation was the choice of the experimenter. The slope-fit formula used for the initial region was that for a line known to pass through the origin:

$$\text{Slope} = \frac{\sum_{i=1}^N X_i Y_i}{\sum_{i=1}^N X_i^2} \quad [41]$$

where $X_i = \sqrt{t}/\ell$ for i^{th} point

$Y_i = \text{water uptake at } i^{\text{th}} \text{ point}$

It should be noted that the diffusion coefficients presented in Tables 13 and 15 were calculated under the assumption of uniform film composition. Since photo-oxidation is more extensive nearer the film surface exposed to the UV light, the case at hand is likely better described as laminate (oxidized top layer, unoxidized bottom layer) or an asymmetric membrane (composition gradient throughout film). However, our lack of knowledge about composition as a function of film depth in the photo-oxidized samples renders calculation of D for the

more complex non-homogeneous cases impossible. Hence, the diffusion coefficients discussed in this section should be thought of as apparent, rather than absolute values.

2) Infrared Spectral Characterization. As described in Chapter III, infrared spectra were taken of thin films of the IP/MMA copolymers (without additives). No attempt was made to provide uniform film thickness; films were roughly 1 to 2 μm thick. Spectra were taken before and after exposure in the weatherometer for 1,2,4, 24,48 and 120 hours. Different films were used for each exposure time. Figures 11 and 12 show spectra of polyisoprene and the 47% MMA copolymer, respectively, after 0,1,4,24 and 120 hours of exposure. Figure 13 shows the spectra of a PMMA sample before and after 120 hours of exposure, along with the difference spectrum. Band assignments for polyisoprene and PMMA are given in Tables 16 and 17 respectively. Copolymer bands can be attributed to those of the homopolymers, although peak broadening, frequency shifts, and relative intensity changes are evident.

As Figure 13 shows, the only change apparent in the PMMA spectrum, even after 120 hours of UV exposure, was a decrease in the 755 cm^{-1} C-C skeletal mode vibration. This is interpreted as indicating that main chain scission is the major mode of photo-oxidative degradation for PMMA, supporting molecular weight evidence of other authors (46,47,50,94). If chain scission occurred mainly at chain ends, i.e. if the "unzipping" mechanism characteristic of the thermal degradation of PMMA occurred, then the removal of volatile monomer during

Figure 11. IR Spectra of Photo-oxidized Polyisoprene.

Figure 12. IR Spectra of Photo-oxidized 47% MMA Copolymer

Figure 13. IR Spectra of Photo-oxidized PMMA

Table 16

PIP Band Assignments (33,57,103)

$\nu(\text{cm}^{-1})$	Assignment
3340*	O-H
2861	C-H stretch
2820	
2754	
2727	
1720*	C=O
1664	internal C=C stretch (1,4 addition)
1642	external C=C stretch (1,2 or 3,4 addition)
1450	C-H bend - CH_2 - and CH_3 -
1381	C-H bend, specifically CH_3 -
1332	- CH_2 - and C-C
1311	
1150	
1100	
1033	
1006	
1163*	C-O (ester)
1070*	
910	C-H bend - $\text{CH}=\text{CH}_2$
890	C-H bend $\text{C}=\text{CH}_2$
841	1,4 cis methylene deformation

*Appears upon photo-oxidation

Table 17

PMMA Band Assignments (102)

$\nu(\text{cm}^{-1})$	Assignment
2998	$\nu_a(\text{C-H})$ of O-CH_3 ; $\nu_a(\text{C-H})$ of $\alpha\text{-CH}_3$
2954	$\nu_s(\text{C-H})$ of O-CH_3 with $\nu_s(\text{C-H})$ of $\alpha\text{-CH}_3$ and $\nu_a(\text{CH}_2)$
2845	combination band involving O-CH_3
	$\nu(\text{C=O})$
1485	$\delta(\text{CH}_2)$
1450	$\delta_a(\text{C-H})$ of $\alpha\text{-CH}_3$
1436	$\delta_s(\text{C-H})$ of O-CH_3
1389	$\delta_s(\text{C-H})$ of $\alpha\text{-CH}_3$
1368	$\delta_s(\text{C-H})$ of $\alpha\text{-CH}_3$
1272	$(\nu_4)\text{C}$ or C-O stretch
1241	
1192	$\nu_a(\text{C-O-C-})$
1150	
1064	$\nu(\text{C-C})$ skeletal mode
989	O-CH_3 rock
969	$\alpha\text{-CH}_3$ rock
914	(?)
842	CH_2 rock
828	$\nu_s(\text{C-O-C})$
810	?
755	$\nu(\text{C-C})$ skeletal mode

vacuum treatment would have caused a decrease in intensity of other PMMA bands. However, this was not observed.

Polyisoprene different spectra reveal the formation of hydroxyl ($3600\text{--}3300\text{ cm}^{-1}$), carbonyl (peak at 1720 cm^{-1} , higher frequency shoulders), and C-O ($1100\text{--}1060\text{ cm}^{-1}$). The $1500\text{--}600\text{ cm}^{-1}$ region exhibits the "hammock effect" (95) where the broad absorbances result from the presence of many oxidation products. Decrease of the IR bands in the $3100\text{--}2800\text{ cm}^{-1}$ region represents loss of methylene.

As a means of following the progress of the photo-oxidation, the increase in the 1720 cm^{-1} carbonyl peak was followed in the oxidized polyisoprene samples. Since the various samples had different thicknesses, the carbonyl intensity was ratioed to the intensity of the unoxidized 2920 cm^{-1} C-H band to provide a relative measure of the extent of formation of oxidation products. A plot of this relative intensity vs. time of oxidation is shown in Figure 14. The carbonyl absorbance does not increase linearly with time for polyisoprene photo-oxidation as it did in the case of polyethylene (93). After about 4 hours, the increase in carbonyl concentration with time becomes progressively less steep; an inflection point occurs somewhere between 2 and 4 hours.

The extent of oxidation of the three copolymer samples could not be monitored by charting the change in the height of the carbonyl peak because pronounced broadening of this band actually resulted in a decrease in intensity at 1720 cm^{-1} upon oxidation for many samples. The extremely broad nature of the hydroxyl peak made its use similarly unsuitable.

Figure 14. Carbonyl Formation during Photo-oxidation.

3) Dependence of S on Extent of Oxidation. Figure 15 displays the calculated solubility coefficients plotted as a function of UV exposure hours for the two homopolymers, polyisoprene (without additives) and PMMA. Water solubility in PMMA shows little dependence on photo-oxidation time. This is not surprising in light of the IR evidence indicating that only chain scission occurs. Solubility in polymers is largely independent of molecular weight (96).

Water solubility in polyisoprene, however, first increases over the lower oxidation times (<2 hr.), but then levels out at longer times. Figure 17 shows a plot of S for the PIP samples vs. $\Delta I_{1720}/I_{2920}$ from the infrared spectroscopy results. Solubilities of the mildly oxidized films seem to be linearly dependent upon carbonyl concentration. As with the previously discussed polyethylene samples, this could be indicative of specific site (e.g., carbonyls, hydroxyls) water sorption.

It is apparent from both Figures 15 and 16 that water uptake in polyisoprene does not continuously increase with extent of oxidation, but appears to approach a plateau. This behavior is also observed for the three copolymers without additives. In Figure 17 are plotted the S coefficients vs. oxidation time for the 31,47 and 63% MMA samples.

If one assumes that polar product formation in the relatively thick ($\sim .05$ cm) samples used for sorption studies keeps occurring even up to 120 exposure hours, as it does in the thin ($\sim 10^{-4}$ cm) polyisoprene samples used for infrared studies, then one would

Figure 15. Water Solubility in Photo-oxidized PIP and PMMA.

Figure 16. Water Solubility vs. Carbonyl Concentration.

Figure 17. Water Solubility in Photo-oxidized IP/MMA Copolymers.

conclude that, after a certain level of oxidation, no additional water molecules can be sorbed, even though more polar sites are available. This could be due to photo-oxidation-induced physical constraints, such as extensive cross-linking or an extremely thin oxidized surface layer, which could spatially prohibit the accommodation of more penetrant molecules.

4) Anomalous Sorption Curves. Various types of anomalous sorption kinetics, as discussed in Chapter II, were exhibited by many of the oxidized polymer samples. Examples of these are shown in Figure 18. Figure 18a is the water sorption curve for poly(methyl methacrylate) oxidized 4 hours. It shows typical Fickian behavior (see Figure 1a) and Figure 18b for a 63% MMA sample oxidized for 120 hours may be termed pseudo-Fickian (see Figure 1b) since the initial linear region covers roughly only 30% of the total water uptake. Figure 18c (47% MMA sample oxidized 24 hours) and 18d (polyisoprene sample with additives oxidized for 120 hours) provide examples of two-stage sorption.

A possible explanation for these phenomena lies in the heterogeneous nature of the oxidized polymer film. As discussed in Chapter II, oxidation of polymer films occurs preferentially at the film surface. This effect would be magnified in photo-oxidation, since ultraviolet radiation cannot penetrate far into a sample containing UV-absorbing chromophores. In PMMA, only 1% of the incident intensity of 2537 Å light remains 5 μm into a film (53). Hence the oxidized film samples may be conceived of as having a

Figure 18. Experimental Sorption Curves.

laminate construction - a thin surface layer which has been extensively degraded, and a substrate layer which has been largely unaffected by the ultraviolet exposure. This is depicted schematically in Figure 19. Barrie and coworkers (97) have been able to fit diffusion data for rubber samples oxidized on both sides to a 3-layer composite film model.

Since the two layers (oxidized and unoxidized) will exhibit different affinities for the sorbed water, the extent of swelling will also likely be different in these two regions. Evidence of this is provided by the observation that polyisoprene and copolymer films became curled during the sorption experiments. This curvature was directed such that the film side which had been exposed to the UV light (the side of the oxidized surface layer) was always the outwardly bowed (convex) side.

Because the amount of water-induced swelling is different in the two layers, a swelling stress differential could exist across the boundary region. The substrate layer would then relax to relieve these stresses, i.e., it would swell further, thereby taking up more water. Such a substrate relaxation effect may be the cause of the second uptake region in the anomalous sorption curves. In Figure 20 is shown a schematic representation of an anomalous sorption kinetics curve (a) + (b) resulting from the additive superposition of a Fickian curve (a), and relaxation-induced penetrant uptake (b). This linear superposition approach has been used theoretically by Berens and Hopfenberg (70) to account for such non-Fickian anomalies

Figure 19. Schematic Diagram of Heterogeneous Photo-oxidized Film.

Figure 20. Superposition of Sorption Curves.

as a slow approach to equilibrium, and two-stage and sigmoidal sorption curves. The relative magnitudes and time dependency of the Fickian and relaxation contributions determine the precise shape of the composite curve.

Differences in the extent of swelling between adjacent regions in a polymer film, and the accompanying swelling stress differential, is also known to produce internal fissures or cavities during the sorption process (98,99). The differential stress developed locally within a non-uniformly swollen sample is thus adequate to literally tear the polymer structure apart (59), producing microcracks or microvoids. The microvoids thus formed may serve to accommodate more water molecules, perhaps clusters, which could account for the second stage in the anomalous sorption curves. This is another possible explanation for the observed anomalies in the sorption kinetics.

The first stage in the experimental sorption curves can likely be assigned to diffusional effects (the sum of diffusion through both sides of the film). The second stage may be the result of differential swelling stresses, producing relaxation-induced further substrate swelling, or producing microvoids allowing for additional penetrant accumulation. A combination of these latter modes is also possible.

5) Composition Effects on Solubility. Figure 21 shows the water solubility S for unoxidized polymer films without any additives plotted vs. mole % MMA of the sample. It is apparent that a simple rule of mixtures is not followed, even for these unoxidized materials, i.e. it cannot be said that each comonomer component sorbs water

Figure 21. Water Solubility vs. Mole % MMA; Unoxidized Polymers without Additives.

independently with the same solubility as the corresponding homopolymer. Figure 21 has two interesting features. First, S initially decreases with increasing MMA content up to the 63% sample, even though the polymer is becoming more polar and hydrophilic. Secondly, there is a sizeable jump in solubility between the 63% MMA and the PMMA sample.

These same features - a decrease followed by a sharp increase - can also be seen when water solubility is plotted vs. MMA content for the unoxidized samples containing antioxidant and cross linking, as seen in Figure 22. The solid line was calculated under the assumption of the rule of mixtures. For this set of polymers, however, the solubility jump occurs between 47 and 63% MMA. For these polymers with additives, the temperature at which the sorption studies were made falls between the glass transition temperatures of the 47% (10°C) and 63% (35°C) samples. Although determinations of T_g were not made for the materials without cross linking, it seems reasonable to expect that their T_g 's will be somewhat lower than for the cross linked samples. That is, at a given temperature (ambient), the transition rubber $\rightarrow$ glass ought to occur at a higher content of MMA.

The observed solubility jump may be caused by T_g factors. In the glassy polymers (63%, PMMA), it is possible that pre-existing, frozen-in holes are available for occupation by the penetrant molecules. Such a microporous structure has been reported in other glassy amorphous polymers (100,101) and influences their solubility and transport properties.

Figure 22. Water Solubility vs. Mole % MMA; Unoxidized Polymers with Additives.

If non-interconnected submicrovoids did exist in a glassy sample, the observed diffusion coefficient may be either higher or lower than expected. In the absence of penetrant clustering or other localization within voids, the overall rate of transport should be increased somewhat due to the smaller structural packing density afforded by the presence of the void regions. On the other hand, if penetrant molecules occupying void sites are essentially immobilized for any reason, as by clustering, the rate of flux will decrease. Water molecules, which in the liquid state are strongly associated through hydrogen bond formation, exhibit a pronounced tendency to cluster, especially in non-polar polymers.

A decrease in diffusivity for the copolymer series is indeed observed as the composition changes from that of a rubbery to a glassy polymer. Figure 23 shows the dependence of D on % MMA for polymers both with and without additives. A decrease in D is observed between the 47 and 63% samples for the cross-linked, stabilized films, whereas the drop occurs between the 63 and 100% MMA samples without additives. These drops in the magnitudes of the diffusion coefficient occur at the same composition as the increases in solubility. Thus, the clustering of water molecules in pre-existing microvoids in the glassy polymers might account for both the solubility and diffusivity dependence on composition.

6) Temperature Dependence. If solubility is affected by the presence of microvoids in glassy polymers, then the temperature dependence of S will exhibit deviations from that expected for a

Figure 23. Diffusion Coefficients vs. Mole % MMA.

purely activated process occurring within a homogeneous structural continuum. In order to investigate this possibility, the water solubility of a 63% MMA film containing additives was determined at different temperatures using a vacuum Cahn RG electrobalance and nominal 100% relative humidity.

In the absence of microvoid effects, the thermodynamic quantity S should be relatively unaffected by the glass transition. For the 17°C temperature range studied here (23-40°C), an Arrhenius plot should give very nearly a straight line, in the absence of complications. An Arrhenius plot of $\ln S$ vs. $1/T$ for the 63% sample is displayed in Figure 24. The points obviously cannot be fit to a straight line; it appears that S shows a discontinuous rise in the vicinity of T_g . If the points in the rubbery region are used to extrapolate (dashed line) into the glassy region, the hypothetical rubbery value for S can be found at 23°C - .0606 moles/100 g polymer. The observed value of S at 23°C is higher than this extrapolated value. This result indicates that there is likely some contribution to the solubility parameter from T_g effects, probably due to the clustering of water molecules in microvoids.

However, this T_g effect alone cannot account for the entirety of the increase in S occurring between the 47% and 63% polymers. The extrapolated value of $\sim .061$ moles/100 g still deviated significantly from the trends established by the other three rubbery polymers. Other workers have found that the fraction of sorbed water accommodated in PMMA is likewise small (102). Further investigations are necessary

Figure 24. Arrhenius Plot for Water Solubility.

to account completely for the dependence of S upon amount of methyl methacrylate.

It is in fact somewhat surprising that the water solubility in this series of copolymers should decrease at all as the MMA content is increased. Since MMA is more polar than isoprene, the rule of "like dissolves like" would imply that a more polar polymer, richer in methyl methacrylate, should sorb more water than a hydrophobic MMA-poor material. The cause of this observed decrease remains unclear. It is interesting to note that this phenomena, whereby the material with the lowest MMA content does not have the lowest water uptake, also occurs in the photo-oxidized samples, as can be seen in Figures 25 and 26. It is likely that the water solubility is a complex function of such factors as polarity, glass transition temperature, density, presence of microvoids, and others which change as a function of methyl methacrylate content in the polymer.

7) Effect of Cross-linking and Antioxidant Additives. When corresponding data in Table 12 (no additives) and Table 14 (polymers with 2% cross-linking agent and 0.5% antioxidant added) are compared, it is seen that large differences in solubility exist between the two sets of samples. Furthermore, the solubility dependence on time of UV exposure also differs.

Values of S for polyisoprene are plotted in Figure 27 as a function of oxidation time. Values for the samples with additives are higher than for the samples without. On the whole, this is true for most of the other isoprene-containing samples, although the 31%

Figure 25. Water Solubility vs. Mole % MMA; Oxidized Polymers without Additives.

Figure 26. Water Solubility vs. Mole % MMA; Oxidized Polymers with Additives.

Figure 27. Additive Effect on Solubility.

MMA films are a notable exception. Also, for the additive-containing samples, the solubility is actually lowered during the initial stages of photo-oxidation, then keeps on increasing, while for the other samples S first increases, then appears to level off. Again, competing effects - for example polarity changes, densification, and microvoid and surface layer formation - contribute to produce the decrease in solubility at low exposure times.

The origin of the difference in magnitude of solubility between the pure polymers and the cross-linked, stabilized polymers lies in the difference in composition (the extra compounds), physical properties (cross-linking), and history. The incorporation of dicumyl peroxide and 4,4'-methylene bis(2,6-ditertbutyl phenol) into the sample ought to cause some increase in the sample's affinity for water, since both compounds provide oxygen sites for H_2O molecules to sorb on. Even as the antioxidant is deactivated during the course of the photo-oxidation reaction, it is not consumed in the sense of removal from the polymer, so it is still available for water to associate with.

The cross-linking provided by the dicumyl peroxide would not be expected to raise the water solubility. This effect works against, or is at best indifferent to, the tendency toward increased S due to the presence of the extra oxygen-containing groups.

A third factor influencing behavior differences is the different thermal histories experienced by the two sets of samples. From Table 7, which gives the treatment conditions for the pressed films,

it can be seen that much milder conditions were experienced by the polymers without additives. Hence it is possible that the materials with stabilizer were actually further oxidized to begin with than the unstabilized materials, due to the difference in film molding conditions. Since the photodegradation reaction can be sensitized by the presence of carbonyl groups on the surface of the sample (38), a pre-degraded sample would be expected to show a faster rate of degradation than the unoxidized sample.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

Below are summarized observations made and inferences drawn from this study of the effects of photo-oxidation on the solubility and transport properties of selected polymers. Each conclusion corresponds to one of the questions for investigation listed in Chapter I.

1) No simple rule-of-thumb can be advanced about the effects of ultraviolet oxidation on the solubility and transport properties of polymer films. The solubility of water vapor usually increased in the polymers studied that had been photo-oxidized, although S actually decreased after short exposure times in some IP/MMA copolymers, and was unchanged in PMMA; nitrogen solubility in polyethylene also increased slightly. Apparent diffusion coefficients variously decreased and increased after photo-oxidation, but total change was well within an order of magnitude.

2) Both chemical and physical changes experienced by the polymer film during photo-oxidation influence penetrant diffusion and solubility. Formation of polar oxidation products in the material provides more hydrophilic sites for sorption of water. However, the extent to which these sites are available or utilized

determines how much water is localized there. Cross-linking and densification effects tend to lower D , and to lower S slightly.

A substantial effect on water solubility in photo-oxidized films is believed to be the development of heterogeneous film composition due to preferential surface oxidation. This composition gradient, which might be envisioned as a thin oxidized surface layer laminated to an unoxidized substrate, can cause swelling stress differentials. The response of the polymer to relieve this stress differential, either by substrate relaxation and additional swelling, or by the formation of microcavities along the two-layer interface, could account for anomalous sorption curves exhibiting increased water uptake after an initial Fickian region.

3) Water solubility data for photo-oxidized LDPE, within the limits of extent of oxidation studied, were consistent with the hypothesis of localized water sorption at polar sites. However, this was not the case for the IP/MMA copolymers (neither oxidized nor unoxidized).

4) Some MMA-containing copolymers exhibited lower water solubilities than the PIP homopolymer, although PIP is less hydrophilic. Along with composition, other properties, such as density and glass transition, also varied with amount of MMA; these are believed to contribute to the water sorption process. The chemical effect of MMA units on photo-oxidative reactions involving comonomer IP units could not be assessed from the infrared spectral data obtained.

B. Recommendations

This investigation has served to illustrate that many complex factors contribute to the determination of solubility and diffusivity parameters in photo-oxidized polymers. Among these factors are believed to be: polymer composition, morphology and microstructure; heterogeneity of oxidized film; densification and cross-linking effects; glass transition temperature; thermal history; presence of additives. It is recommended that, in subsequent studies, an attempt be made to isolate each contribution in order to determine its importance.

This might entail experimental conditions somewhat removed from conditions of potential use. For instance, studies of the mechanism of photo-oxidation are complicated in the solid state due to uncertainties of concentration. A detailed study of the possible chemical stabilizing effect of MMA ought to be undertaken on a system that can be homogeneously prepared and photo-oxidized.

In determining composition effects, both on solubility and photo-oxidation characteristics, copolymers which are homogeneous even at the microstructural level ought to be synthesized. Perhaps graft copolymerization would provide a suitable alternative to the batch emulsion copolymerization technique used in this study.

The influence of heterogeneous film composition should certainly be investigated. This study has demonstrated that preferential surface oxidation can result in geometric distortion of the sample and additional water uptake during exposure to a moist environment.

In practical applications, either of these swelling stress-induced phenomena could result in failure of the system. In order to predict the magnitude of the effect, a precise determination of the composition gradient in photo-oxidized films should be made. In addition, varying sample geometry and the temperature of sorption studies could aid in the resolution of sorption kinetics curves into separate diffusion and stress-induced components.

New or improved experimental techniques suggest themselves for future studies. In polymer systems where equilibrium water sorption is rather small, use of a sensitive recording microbalance would permit more accurate determination of sorption kinetics. Surface spectroscopy (ESCA,ATR) could aid in the elucidation of surface layer composition. Dielectric measurements, sensitive to dipoles in polymers, would be appropriate for the photo-oxidized materials, as these may give insight into segmental motions in the surface layer. Solid state NMR techniques might be used to probe polymer microstructure in unoxidized and photo-oxidized materials.

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APPENDIX

Individual S and D Values for 1P/MMA Copolymers

S units are moles H_2O per 100 g polymer

D units are $cm^2/sec \times 10^8$

PIP, additives

<u>UV hours</u>	<u>S</u>	<u>Avg.</u>	<u>D</u>	<u>Avg.</u>
0	.0462		.52	
0	.0401	.043	.39	0.4
0	.0440		.35	
1	.0364		.60	
1	.0370	.037	.71	0.7
2	.0305		.89	
2	.0305	.031	.80	0.8
4	.0333	.033	1.04	1.0
24	.0496	.050	-	-
48	.0654		.48	
48	.0646	.065	.60	0.5
120	.0927	.093	.63	0.6

31% MMA, additives

0	.0433		.36	
0	.0344	.038	.72	0.6
0	.0368		.66	
1	.0226		.72	
1	.0334	.028	1.41	1.2
2	.0189		2.30	
2	.0224	.021	2.77	2.5
4	.0210	.021	2.67	2.7
24	.0231		5.22	
24	.0257	.026	3.99	4.0
24	.0291		2.72	
48	.0344	.034	2.93	2.9
120	.0369		5.31	
120	.0373	.037	5.23	5.3

47% MMA, additives

<u>UV hours</u>	<u>S</u>	<u>Avg.</u>	<u>D</u>	<u>Avg.</u>
0	.0413		.85	
0	.0300		1.26	
0	.0358	.035	1.16	1.2
0	.0331		1.28	
0	.0346		1.27	
1	.0245		2.87	
1	.0313	.028	2.66	2.8
2	.0257		-	
2	.0290	.027	2.16	2.2
4	.0243		3.61	
4	.0256	.025	3.47	3.5
24	.0312		3.55	
24	.0249	.028	6.45	5.0
48	.0453	.045	1.39	1.4
120	.0475	.048	3.35	3.4

63% MMA, additives

0	.0654	.065	.56	0.6
1	.0603	.060	.49	0.5
2	.0670		.41	
2	.0547	.061	.52	0.5
4	.0555		.89	
4	.0551	.055	.41	0.7
24	.0723		1.07	
24	.0605	.066	1.23	1.2
48	.0624		1.17	
48	.0733	.068	1.17	1.2
120	.0743	.074	2.52	2.5

PMMA

<u>UV hours</u>	<u>S</u>	<u>Avg.</u>	<u>D</u>	<u>Avg.</u>
0	.0943		.63	
0	.0947	.095	.84	0.7
0	.0966		.52	
1	.0968	.097	.54	0.5
2	.1000	.100	.58	0.6
4	.0919		.83	
4	.0947	.093	.95	0.9
24	.0927	.094	.83	0.8
24	.0955		.76	
48	.0857		1.04	
48	.1004	.093	.82	0.9
120	.104		.54	
120	.100	.102	.57	0.6

PIP, no additives

0	.0287		1.14	
0	.0270	.028	1.58	1.4
1	.0223		1.57	
1	.0466	.034	1.80	1.7
2	.0511	.051	1.29	1.3
4	.0499		.90	
4	.0475	.049	.60	0.8
24	.0500	.050	1.22	1.2
48	.0486		1.54	
48	.0502	.049	1.24	1.4
120	.0476		1.87	
120	.0480	.048	2.29	2.1

31% MMA, no additives

<u>UV hours</u>	<u>S</u>	<u>Avg.</u>	<u>D</u>	<u>Avg.</u>
0	.0245	.025	2.91	2.6
0	.0258		2.28	
1	.0298	.030	3.31	3.3
2	.0290	.031	3.21	2.8
2	.0338		2.52	
4	.0330	.033	1.25	1.6
4	.0283		1.99	
4	.0390		1.63	
24	.0448	.046	1.10	1.9
24	.0468		2.70	
120	.0448	.045	1.82	1.8
120	.0460		1.70	

47% MMA, no additives

0	.0196	.020	2.33	2.5
0	.0194		2.62	
1	.0192	.021	3.17	3.0
1	.0235		2.78	
2	.0258	.025	3.12	2.1
2	.0248		1.13	
4	.0317	.030	.95	0.9
4	.0289		.75	
24	.0391	.039	1.61	1.6
48	.0416	.040	2.02	2.7
48	.0393		3.34	
120	.0449	.045	4.15	4.2

63% MMA, no additives

<u>UV hours</u>	<u>S</u>	<u>Avg.</u>	<u>D</u>	<u>Avg.</u>
0	.0209		6.60	
0	.0222	.022	6.68	6.6
1	.0280		4.53	
1	.0288	.028	4.49	4.5
2	.0311	.031	6.19	6.2
4	.0354		3.54	
4	.0360	.036	3.62	3.6
24	.0429		5.49	
24	.0470	.045	5.96	5.7
48	.0431		5.68	
48	.0449	.044	5.73	5.7
120	.0528		11.3	
120	.0494	.051	10.5	10.9

PRELIMINARY REPORT

THERMAL OXIDATIVE DEGRADATION OF
ISOPRENE-METHYLMETHACRYLATE
COPOLYMERS

by

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ABSTRACT

A series of random copolymers of isoprene and methyl methacrylate containing 0, 31, 47, 63, and 100 mole percent methyl methacrylate and their hydrogenated derivatives have been used to study the dependence of thermal oxidative degradation on copolymer composition, sequence distribution, and extent of residual unsaturation in the polymer chain. The samples were degraded in air and in nitrogen atmospheres at temperatures between 300 and 450°C using both isothermal and controlled heating rate methods. Rate constants, on-set temperature, and overall activation energies for the thermal oxidative and thermal degradations were determined.

The results to date indicate that the degradation behavior of the copolymers is generally intermediate between that of the corresponding homopolymers. Isothermal studies suggest that the hydrogenated copolymer samples are more stable than the corresponding unsaturated copolymers. The 31 mole percent hydrogenated copolymer is somewhat more stable than the hydrogenated polyisoprene homopolymer.

The investigation is being continued to include further experimental determinations to establish the dependence of degradation on copolymer sequence distribution and other variables. The stability of the systems to ultraviolet radiation exposure also is being determined.

INTRODUCTION

The degradation of polymers is of significant commercial interest, particularly for polymeric materials containing isoprene. Preventive stabilization of polymers by copolymerization has been successful in specific cases, but is not a general technique. For example, copolymerization of 1-3% ethylene or propylene with vinyl chloride yields a copolymer with improved thermal stability without any loss of the characteristic properties of poly(vinyl chloride) (1-3). Grassie (4) has shown that vinyl chloride and vinyl acetate copolymers and polyblends have decreased thermal stability compared to their component homopolymers. Butadiene-acrylonitrile copolymers have decomposition temperatures which are between those of the corresponding homopolymers (5).

Differences in the degradation behavior of copolymer systems have been attributed to neighboring group effects. In the absence of any specific interactions, block copolymers exhibit the same behavior as mixtures of homopolymers; i.e., the yields of the main degradation products are approximately the same because there is only one interface or boundary along the polymer backbone.

Random copolymers exhibit much different behavior. When the product of the reactivity ratios of the monomers is much less than unity, a copolymer is formed which has a greater tendency toward an alternating arrangement of the monomer units along the copolymer chain. The mean number of identical monomer sequence lengths is quite small. Therefore, it is expected that some monomer units

would become isolated, interfering with the degradation mechanisms operative in the corresponding homopolymers.

The degradative behavior of poly(isoprene) by crosslinking and of poly(methyl methacrylate) by depolymerization are well known. However, studies at high temperatures are scarce and reports on degradation of copolymers are very limited. The purpose of this work is to provide additional evidence for the modification of degradation behavior through copolymerization and to show the effect of copolymer composition on decomposition mechanisms.

EXPERIMENTAL

Materials

Polymers used in this study were synthesized by emulsion polymerization and purified by reprecipitation from benzene. Partially hydrogenated polymers were obtained by heating the dissolved polymer in refluxing para-xylene in the presence of para-toluene sulfonyl hydrazide (6). Excess reagent was removed by dissolving the polymer in chloroform, precipitating with methanol and vacuum drying. All polymers were stored in the dark in a vacuum desiccator until degradation experiments were run. Characterization of the materials was by IR and NMR.

Thermal Degradations

Thermograms were obtained using a DuPont 990 Thermoanalyzer fitted with a DSC module. The temperature scanning rate was 20°C/min.

TGA measurements were performed with a Perkin-Elmer TGS-1 Thermobalance equipped with a Cahn electrobalance. Carrier gas

of either air or nitrogen was passed through at a rate of 50 mL/min. About 5 mg of polymer was used in each run to avoid variations due to sample size. Heating was programmed at a rate of 20°C/min for the dynamic TGA studies.

RESULTS

The thermal degradation of poly(isoprene), poly(methyl methacrylate), copolymers containing 31, 47, and 63 mole percent methyl methacrylate, and partially hydrogenated copolymers was followed by DSC and TGA.

The effects of heating the polymers DSC studies are given in Table 1 for air atmosphere and in Table 2 for an inert (nitrogen) atmosphere. Poly(isoprene) has an exothermic response in either an air or nitrogen atmosphere. Three distinct peaks are noted at 192°, 337°, and 377°C. Poly(methyl methacrylate) has a single endothermic response at 377°C in nitrogen and at 360°C in air. The three copolymers exhibit the following effects:

- 1) in nitrogen, there is an exothermic peak at 190-192°C and an endothermic peak at ~ 370°C.
- 2) in air, three exothermic peaks occur within these temperature ranges at: 195-212°C, 332-355°C, and 377-395°C.

The effects of programmed thermal treatment by TGA are shown in Table 3 for air and in Table 4 for nitrogen. Data in Table 3 for PMMA, PIP, and the three unsaturated copolymers indicates a high dependence between copolymer composition and the temperature at which half of the original sample remains. Linear regression

Table 1. DSC Thermogram Data in Air (Flow Rate 100 mL/min)

Sample	Onset(°C)	Peak Max(°C)	Comment
PIP	163	230 >340	exo ignition
31% MMA	161	202 332 395	exo exo exo
47% MMA	155	195 335 391	exo exo exo
63% MMA	150	212 355 377	exo exo exo
PMMA	315	360	broad endo
Hy-PIP	155	387	exo
Hy-31% MMA	153	414	exo
Hy-47% MMA	157	397	exo

Table 2. DSC Thermogram Data in Nitrogen (Flow Rate 60 mL/min)

Sample	Onset (°C)	Peak Max (°C)	Comment
PIP	163	192	exo
		337	exo
		377	exo
31% MMA	345	383	endo
47% MMA	326	190	exo
		372	endo
63% MMA	308	192	exo
		360	endo
PMMA	344	377	endo

Table 3. Dynamic TGA in Air

Sample	Temp. @ 50% weight loss(°C)	Onset temp.(°C)
PIP	392	275
31% MMA	386	225
47% MMA	383	171
63% MMA	381	137
PMMA	373	319
Hy-PIP	411	272
Hy-31% MMA	396	229
Hy-47% MMA	396	235

Table 4. Dynamic TGA in Nitrogen

Sample	Temp. @ 50% weight loss(°C)	Onset temp.(°C)
PIP	393	324
31% MMA	383	325
47% MMA	371	201
63% MMA	363	174
PMMA	363	283

analysis shows a negative correlation coefficient (-0.998) and that about 0.2°C decrease in decomposition temperature occurs for one percent increase of methyl methacrylate content.

The loss of polymer through oxidative degradation has been determined from 300 to 450°C. The total decomposition rate was taken to be proportional to the weight loss of polymer in the isothermal TGA experiment. The apparent rate constants were obtained. From semi-log plots of the data (Figures 1-8). Arrhenius plots were used to determine the overall activation energies (Figures 9-16). The values of the rate constants and the activation energies are given in Table 5. Figure 17 illustrates the relationship between the activation energies and copolymer compositions.

DISCUSSION

The oxidative degradation behavior of polyisoprene has been the subject of much research. It is generally believed that the oxidative reaction can be explained on the basis of a free-radical mechanism involving hydroperoxides. However, the exact structure of the principal hydroperoxide is not clear. Bolland and Hughes (7), and Bevilacqua et al (8) have proposed that the reaction proceeds via a cyclic peroxide-hydroperoxide in which two adjacent isoprene monomer units become oxygenated before chain scission. More recently, Chien and Kiang (9) have accounted for oxidation products observed by GC pyrolysis and mass spectrometry from the homolysis of a hydroperoxide on the allylic carbon of an individual isoprene

Table 5. Degradation Kinetics in Air

Polymer	Temp. (°C)	Rate Constant (min ⁻¹)	Activation Energy (Kcal mol ⁻¹)
PIP	350	0.1	38
	375	0.7	
	400	2.0	
	425	4.1	
	450	7.2	
31% MMA	300	0.02	35
	350	0.1	
	375	0.7	
	400	2.0	
	425	3.6	
	450	7.2	
47% MMA	325	0.2	25
	350	0.6	
	375	1.6	
	400	2.7	
	425	4.6	
	450	6.4	
63% MMA	300	0.2	22
	325	0.3	
	350	0.9	
	375	1.4	
	400	3.4	
PMMA	350	1.0	17
	375	2.0	
	400	3.0	
	425	4.6	
Hy-PIP	350	0.1	30
	375	0.5	
	400	1.4	
	425	2.0	
	450	3.2	
Hy-31% MMA	350	0.07	35
	375	0.3	

Table 5 (Continued) Degradation Kinetics in Air

Polymer	Temp. (°C)	Rate Constant (min ⁻¹)	Activation Energy (Kcal mol ⁻¹)
Hy-31% MMA	400	1.1	
	425	2.1	
	450	3.4	
Hy-47% MMA	350	0.2	30
	375	0.5	
	400	1.0	
	425	2.7	
	450	5.1	

unit.

The mechanism of thermal oxidation of a hydrocarbon is often written simply as follows (10):

Initiation: Initiator $\rightarrow$ Free Radicals ($R\cdot$, $RO\cdot$, or $RO_2\cdot$)

Propagation: $R\cdot + O_2 \rightarrow RO_2\cdot$

$RO_2\cdot + RH \rightarrow ROOH + R\cdot$

Termination: $2R\cdot$

$R\cdot + RO_2\cdot \rightarrow$ inactive products

$2RO_2\cdot$

Hydroperoxides are formed at each step in the propagation chain. Hydrogen abstraction by hydroxy or alkoxy radicals can also occur. The termination reaction is by the bimolecular combination of radicals. In an oxygen starved environment, coupling of polymer radicals is favored and polymerization through the residual double bonds leading to crosslinking is possible.

Poly(methyl methacrylate) was observed to thermally degrade in a single endothermic step either in air or nitrogen. This suggests that depolymerization is the principal degradation pathway and that decomposition occurs at a lower temperature in air.

Poly(isoprene) was thermally decomposed in two exothermic steps in air. However, in nitrogen the decomposition reaction in the second step yields an endotherm. Brazier and Schwartz (11) have shown that for polybutadiene thermally decomposed in nitrogen the first stage of degradation is an exotherm, while the reactions

in the second stage give an endotherm. This result was explained from thermal crosslinking and cyclization occurring during the first stage and depolymerization due to chain scission occurring at the higher temperature of the second stage.

The copolymers of isoprene and methyl methacrylate in this study show a third intermediate exothermic peak only in air, which suggests that the exotherm is related to the initial absorption of oxygen.

In order to produce more thermally stable materials it is desirable to be able to relate stability and chemical structure. In this regard, isothermal TGA experiments were utilized to study systematically the relationship between copolymer composition and thermal decomposition characteristics.

TGA isothermal kinetic data are commonly treated mathematically with an Avrami-Erofeev mechanism. The decomposition rate of the polymer follows the general equation:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

where α is the decomposed fraction of polymer after time t ; n is the reaction order and k is the rate constant given by the equation:

$$k = A \exp(-E/RT) \quad (2)$$

where A and E are the Arrhenius preexponential factor and the activation energy, respectively. The temperature range of interest (300-450°C) is greater than 100°C above the highest melting compo-

nent (syndiotactic PMMA m.p. is 200°C (12)); and full liquefaction of the polymer had set in before decomposition. Therefore, a first order reaction might be expected ($n = 1$). Then, the integrated form of equation (1) becomes:

$$\ln(1 - \alpha) = -kt \quad (3)$$

From a plot of $\ln(1 - \alpha)$ against time, the gradient of the straight line gives the apparent rate constant. From the plot of $\ln k$ against $1/T$, the overall activation energy may be calculated from the gradient of the straight line.

Inspection of the data in Table 5 shows that there is a very marked difference in stability for the copolymers. The Hy-31% MMA copolymer has the greatest stability of the polymers investigated.

CONCLUSIONS

A copolymer containing 31 mole percent methyl methacrylate was found to have the greatest oxidative stability and thermal crosslinking or cyclization below decomposition temperatures was not as dominant as the other copolymers. Saturated polymers from hydrogenation exhibited a substantial decrease in degradation rate. The decomposition temperature and the overall activation energy show a high degree of correlation with the copolymer composition. Thermal decomposition increases with the content of methyl methacrylate.

Further analysis and interpretation of the present data, and additional studies now underway should lead to an elucidation of

the dependence of thermal oxidative degradation on copolymer composition, sequence distribution, and degree of residual unsaturation. The results to date indicate that the degradation behavior of the copolymers is generally intermediate between that of the corresponding homopolymers.

ACKNOWLEDGMENT

This work was supported in part by a grant from the Plastics Institute of America.

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FIG. 2 HY-PIP

FIG. 3 31 MMA

FIG. 4 HY-31 MMR

FIG. 5 47 MMA

FIG. 8 PMMA

FIG. 13 47 MMA

FIG. 14 HY-47 MMA

FIG. 17

SEPARATION OF POLYOLEFIN WASTES

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ABSTRACT

It has been demonstrated earlier that the major polymer constituents of a waste mix, polyolefins, polyvinyl chloride and polystyrene can be separated at better than 99.5% purity by a process based on their thermodynamic incompatibility in a common solvent. The polyolefins-polypropylene and the various densities of polyethylene are compatible in solution, however, and other methods have been investigated to effect their separation.

Various fractional crystallization processes, based on the differences in crystalline melting points of the polyolefins were investigated with little success. However, a process based on extraction of the mixed polyolefins shows great promise. Work is progressing to determine optimum solvents, temperatures and extraction times, and to investigate the mechanism of separation.

Introduction

The large scale recycling and reuse of polyolefin materials is presently hindered by thermodynamic considerations. The recovery of polyethylene and polypropylene in a substantially pure form is desirable to guarantee suitable mechanical properties. However, separation is hindered by the compatibility of these polyolefins in most solvent systems. Even so, a process capable of polyolefin recovery from waste streams would indeed constitute valuable technology. Several years ago, G. W. Miller discussed such a process which, because of its economic promise became the springboard for the present research effort (1). A simplified flow diagram has been reproduced in Figure 1. Miller showed, given a plastic waste feedstock representative of usage levels for Allegheny County, that polymer components could be recovered from solution in separate phases at an average cost of \$.102/lb. product. The separated polymers, polyvinyl chloride, polystyrene and polyolefins, possess a striking degree of purity. Sperber and Rosen (2) showed that the purity of each phase is greater than 99.5% in a typical separation.

Although the polyolefin phase excludes all but an 0.5% impurity, the separation problem here is not completely solved. This polyolefin phase incorporates both polypropylene and polyethylenes of varying densities in mutually compatible solution. Were it cooled and dried to recover the solvent, a physically incompatible mixture of the two polymers would remain. The mechanical properties of this mixture depend, to a great degree, on its composition, the properties being much poorer than those of pure polyethylene or polypropylene. A method is being sought to separate the polyethylenes and polypropylene from one another. Whereas Miller's process relied entirely on recrystallization in separating the polyolefins, the present research is comparative in nature. It develops from a consideration of Miller's process, but seeks further to find new processes to improve the shortcomings of the original method. Recrystallization was analyzed, and the results appeared less encouraging than expected. A separation was not obtained by that method. In order to find out why, a characterization of the polyethylene-polypropylene-xylene system was required. Specifically, the recrystallization and solubility temperatures of polyolefin solutions of varying composition were examined. Regions were found where the preferential solubility of PE over PP occurred. Thus Polyethylene might be removed from a solution of both polymers, but in a substantially purified form. On the other hand, the recrystallization data of polypropylene indicate much scattering. Consequently the research effort extended toward exploration of extractive or "solubilizing" separations, which are contrasted with several

recrystallization methods.

More recently, research has been directed toward the documentation of the separation by extraction, and toward answering some questions about its mechanism. A study of the effect of temperature on a fractional extraction process is underway, while questions of mass transfer or thermodynamic control have been considered.

In this report, the research is discussed in detail beginning with some recrystallization separation experiments. Then the characterization of the three component system is discussed. With this as background, several alternative separation processes are detailed. Two variations on the original crystallization experiment were analyzed, along with two new extractive separation processes. A discussion of sample preparation and analysis techniques is given in the Appendix.

Crystallization Separation Process

The separation process analyzed by G. W. Miller forms the basis to which alternative processes are compared. In this process, concentrated thermoplastics are combined with a hot solvent. Residual nonthermoplastic components can be removed by centrifugation or filtration. Next, low molecular weight organics are removed by precipitation of the polymers with a nonsolvent. The low molecular weight compounds are then recovered while the polymer precipitate is redissolved. It is allowed to equilibrate into the separate layers containing polyvinyl chloride, polystyrene and mixed polyolefins. These layers are separated from one another by centrifugation or decanting, and the polyvinyl chloride and polystyrene are recovered by steam stripping.

The separation of the polypropylene and polyethylenes contained in the final layer is not quite as easy. Experimental results have shown repeatedly that the polyolefins are sufficiently similar in solution so that they remain in the same layer. However, in the original analysis, it was assumed that one could take direct advantage of the different crystalline melting points of the three polyolefins.

Since the recrystallization temperatures of the various polyolefins are different, it was thought that the components should be separable simply through cooling. Thus the crystallization of first polypropylene, and then various densities of polyethylene would occur as the solution temperature was lowered slowly. The crystalline phases would be recovered using centrifuges, (Figures 1 and 2), and dried to yield pure polyolefins

The slow cooling process is the easiest to understand thermodynamically, but may be the most difficult to carry out in the laboratory. Hot polymer solution is cooled in stages, causing the crystallization of polymer fractions which are then removed from the liquid. In his industrial process, Miller proposes that heat exchangers cool the solution while steady flow centrifuges remove the liquid from the crystallized polymer between the cooling stages. Centrifugation is not practical in the lab. The high temperatures needed to hold the remaining polyolefins in solution cannot be maintained in a spinning test tube without expensive temperature control equipment. Decantation has its problems, too. Hot solutions cannot be poured without cooling a bit. The polymer crystals are also swollen and usually stay suspended in the liquid.

However, these technical difficulties can be avoided by using a filtering apparatus with a moderately inexpensive heating system added on. In each of several crystallization experiments, a 50% polypropylene-50% polyethylene mixture was dissolved in dilute xylene solutions at a temperature above 115°C.

The solution was cooled to 85°C to precipitate the first crystalline fraction. It was then poured through the filter to remove the crystals from the liquid. The crystals were recovered from the filter paper and dried. Meanwhile, the remaining polymer was recovered from the solution phase on further cooling.

Results show, in Table I, that little or no separation was obtained in either of two experiments. Comparing the average filtrate (A) and supernatant (B) composition readings, we see an overall separation of only 6.7% for experiment 2 and even less for experiment 1.

The single redeeming feature of this study is fraction (C) in the first experiment. Here, a very small amount of crystalline polymer was removed "by hand" on a screen before the batch was filtered. The polyethylene content of this small sample was a surprising 80.3%. In most cases, then, the recrystallization techniques failed to provide a good polymer separation, as hoped. The question remained, however. Why was there no appreciable separation? In order to answer this, additional information about the thermodynamic behavior of the polyethylene-polypropylene-xylene system was required. An attempt to characterize its thermodynamic behavior was initiated with further experimentation.

Characterization of the System

A series of experiments was conducted to measure the solubility temperatures of polyolefins as well as the recrystallization temperatures as functions of polymer concentration. In effect, these experiments are patterned after the work of R. B. Richards in 1945(4) which has received considerable notice over the years. Specifically, an attempt is made to expand the available data by

considering not only low density polyethylene, but also a higher density polyethylene and polypropylene in the experiments. The commercial characteristics of the polymers are described in Table II below:

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Table II. Polymers Supplied

<u>Polymer</u>	<u>Trade Name</u>	<u>Supplier</u>	<u>Properties</u>
PE	DYNF-1 E-1020	Union Carbide	$\rho=0.92$
PE	Hifax 2400	Hercules	$\rho=0.96$, M.I.=.65
PP	Profax 6823	Hercules	M.I.=.45

The recrystallization temperature of a polymer in solution is affected by many factors, including concentration, but also cooling rate and the apparatus (e.g. stirring equipment). Never the less, the melting or solubility temperature should be reasonable correlated with the concentration or weight fraction of polymer. The Flory-Huggins equation

$$0 = \frac{\Delta H_m (T_m - T)}{T_m} + RT \left[\ln x + \left(1 - \frac{V_2}{V_1}\right) (1-x) + \frac{V_2}{V_1} \chi_c (1-x)^2 + \frac{V_2}{V_1} \chi_l (1-x)^3 + \dots \right]$$

allowed the quantitative characterization of the results, providing a known relationship between T and x. By applying a least squares fit to our own data, reasonable estimates of the interaction parameter χ were obtained. But first a few words about experimental procedure will be helpful.

The polymers and solvent were weighed accurately to prepare samples whose polymer content spanned the entire range of weight fractions. The mixtures, dilute or concentrated, were sealed inside Carius combustion tubes to prevent solvent evaporation during heating. The tubes were chosen thin enough to insure good heat transfer to the polymer within. See Figure 3. Once enclosed, each sample was slowly tumbled in an oil bath for a number of days at a high temperature at least 20°C above the expected solubility temperature. Figure 4 diagrams the tumbling apparatus. The actual temperature readings were taken under more strictly controlled conditions in a smaller bath filled with clear silicone oil. Rapid stirring, with the tube and tube support acting as a baffle insured good heat transfer and temperature uniformity. See Figure 5.

As each sample was tested, the temperature was increased slowly until the translucent crystals became amorphous and transparent. The increase in solution clarity was noted, and the temperature recorded. Similarly, while cooling by natural heat conduction, the onset of turbidity was noted to determine the recrystallization temperature. The rate of cooling at that temperature, well defined by the characteristics of the bath, was also noted.

The resulting temperatures are shown in table III. The Flory-Huggins solubility equation was applied to the solubility temperature results to generate the solubility curves shown in Figures 6 and 7. In this analysis a typical average molecular weight of 100,000 was assumed for the polymer. This allowed fixing the volume ratio constant, so that the interaction parameter χ might reflect the correlation of T with weight percent. It can be shown that for high molecular weight polymers, the value of V_2/V_1 has little effect on the correlation (3).

The solubility curves increase monotonically with weight fraction, in agreement with Richards' results. The solubility parameter for high density polyethylene, $\chi = .137$ is a bit lower than most data from the literature, but is within the same range. In comparing osmometric measurements for solutions of various low density polyethylenes, ($0.91 < \rho < 0.94$), Muthana et. al. obtain values between 0.50 and 0.52 (5). Harris obtains interaction parameters between 0.33 and 0.43 for various commercially available polyethylenes (5). A. Y. Coran, et. al., however, using an analytical technique similar to ours and literature values for H_m and V_2/V_1 , calculated a value of 0.04 for high density Marlex 50 in xylene (7). Data for the tetralin solvent systems were not available. The solubility temperatures correlate well with the weight fraction of polyolefin according to the Flory-Huggins equation. However, the recrystallization temperatures do not follow the theoretical correlation. It was best to describe the recrystallization results with a simple linear least squares fit. There is appreciable supercooling as the recrystallization lines in Figures 8 through 10 lag below the solubility curves somewhat. The recrystallization temperature of polypropylene does not correlate well with concentration at all. In fact, the recrystallization temperature of polypropylene is not always greater than that of polyethylene. Rather, the polypropylene data scatter throughout the region defined by the polyethylene recrystallization lines. See Figure (11).

The uniqueness of the recrystallization temperature is necessary to guarantee a clean separation in the cooling process. The scattering of data indicates the presence of other effects on the recrystallization temperature and presents serious difficulties. In practice, medium density polyethylenes and polypropylene may co-crystallize making separation impossible. The failure of the separation experiment in the filtering apparatus can be explained in the same way. But, even more important is the interaction of the two polymers crystallizing in the same solution, at the same time, which is apt to be even stronger. Fortunately, the dissolution temperatures of the two polymers were

clearly different from one another and well correlated with composition. This information is indeed useful; along with crystallization methods, others which rely on the selective dissolution of one species of polymer rather than another are under analysis. 6

The fundamental problem might be stated as follows. The separation of plastic waste mixtures into pure components offers great recycling potential through retention of strength and utility. However, the separation is complicated by the thermodynamic compatibility of the polyolefins in solution, and further by the equivalent recrystallization temperatures of polypropylene and some medium-density polyethylenes. Therefore, an alternative separation technique must be sought which provides an improvement over simple recrystallization on cooling. Adaptations of Miller's process were investigated in the light of these improvements. Two new crystallization schemes, a rapid chilling process and a non-solvent washing scheme were evaluated in some detail. Finally recrystallization was set aside, as two extraction processes were evaluated: soxhlet extraction, a well known chemical analysis technique, and a constant temperature extraction technique the bath extraction process.

Alternative Crystallization Processes

To avoid directly removing newly formed crystals from a hot polymer solution, hopefully alleviating the effects of co-crystallization, the separation process was divided into two consecutive operations. In the first step, crystallization - whether it be co-crystallization or not was of little concern - was allowed to take place.

In both alternative separation methods, a hot solution containing both polypropylene and high-density polyethylene was cooled in such a way that crystals begin to precipitate within the liquid. The way that the crystallization was induced was varied, depending on the separation technique under consideration. In one group the solution was chilled rapidly with dry ice. In another, it was mixed with a room temperature non-solvent, causing it to cool more slowly. In either test, the entire batch of solution was allowed to cool in the first step. The actual separation was delayed until the second. Here, the polymer crystal slurry was mixed with a solution of water and methanol with a density between that of the polymers. Theoretically, since polyethylene is more dense than polypropylene, the former ought to sink while the latter ought to float. The results were not so encouraging, as will be discussed later.

Apparatus for the rapid chilling technique is shown in Figure 12. During a separation test, mixed polymer is dissolved in the reboiler, while dry ice is placed in the Dewar flask. The stopcock is opened slowly, allowing the solution

to drip into the chilling agent. Crystals form, which are subsequently filtered, ⁷ washed and separated according to density. The polymer crystals disperse, some sinking, and some floating. Several fractions are recovered. Since the type of washing agent used can affect the extent of separation, it becomes an important variable. Several washing solvents were used. The compositions of the fractions obtained were determined by infrared analysis and are shown in Table IVa.

The extent of separation shown in the last column is obtained by calculating the difference between the largest and smallest percentage of polypropylene among the various fractions. Thus the two fractions DIM-A and DIM-B are compared. The separation extent is only $0.649 - 0.632 = 1.7\%$, a poor result.

The second recrystallization technique substitutes room temperature methanol for the dry ice chilling agent. The apparatus is diagrammed in Figure 13. The non-solvent reservoir allows methanol to be introduced into the solution in the mixer, causing crystals to form. The mixer is water cooled, maintaining a reasonably low temperature during the process. From the mixing tank, the polymer crystals are filtered and dispersed in a solution of intermediate density. Here, separation is obtained, and the products are analyzed as in the chilling process. Table V indicates that the non-solvent process is little better than the dry ice separation.

Having explored these several varieties of crystallization processes, we now turn toward extractive separation processes.

Extractive Processes

Soxhlet extraction is a well known technique in chemical analysis. Its application to the separation of polyolefins is unique only because both components are soluble. Soxhlet extraction is commonly used to remove soluble material from insoluble. In the extractive separation, solvent is heated in a reboiler. Fresh, pure condensing solvent fills the extraction thimble, washing the polymer crystals. Solvent and dissolved polymer return to the reboiler periodically as the thimble empties by siphon action. The apparatus is diagrammed in Figure 14.

The control of the thimble temperature is critical, because the relative preference for the solubilization of the two polymers must remain constant. But, as the solvent is refluxed through the sample, heat losses and the dissolution process itself cool the liquid while the thimble fills. Nonetheless, good separations were obtained with Soxhlet extraction, as shown in Table VI. The mixed solvent, (b. p. = 120°C), gave a better separation than the cooler toluene, (b. p. = 110°C).

A complete characterization of the separation process is ultimately desired. We would like to measure the effect of temperature on the rate of extraction, and we want to explore the mechanism of the separation. For instance, is there a large mass-transfer resistance in the thimble, or is melting the rate determining step? In order to examine these effects, better control of the sample temperature is a must. This precision is available, but at some sacrifice. By placing the extraction thimble in a rapidly mixed solvent bath, temperature control is no longer a problem. However, the solvent no longer remains fresh, due to the dissolved polymer. By using a large bath with regular removal of the extracted polymer, this problem is minimized. Figure 15 shows a schematic diagram of the bath vessel, including the thermometer, temperature control probe and heater.

The results obtained from the bath extraction experiments, shown in Table VII, are by far the best. Fractions EX4B and EX4F at 7% and more than 90% polypropylene illustrate the effectiveness of the technique. By manipulating the bath temperature, it is possible to obtain a rapid separation into a few discrete fractions, or to slowly collect an entire distribution of samples of varying composition. In either case, the separation is effective. Polyethylene and polypropylene can be recovered from polyolefin mixtures.

By plotting the weight of polymer extracted vs. time, some insight is obtained into the mechanism of the fractional dissolution process. Two 2.5g polymer mixtures were prepared. One was thoroughly mixed with 25g of celite diatomaceous earth as well. In this sample, we hoped to speed dissolution by providing a larger surface area for polymer-chain diffusion. Our first results, Figure 16, indicate the celite sample extracted more quickly than the control sample. Possibly the diffusion of polymer from the crystal phase to the solution plays a more important part in the process than the thermodynamics of melting.

Examining a large number of extracted polymer fractions also allows us to make a better estimate of the separation efficiency. Saying that sample EX4 yields a 90%-7%±83% efficient separation is somewhat misleading. The experiment began with an initial weight of polymer $w_0 = 2.4901\text{g}$ at a composition of 49.9% polypropylene. What we would like to know is what useful amount of polymer was separated at the nearly pure composition of 7% PP. Even though the two extreme fractions (out of six) have a large difference in polypropylene content, what about the others with intermediate composition? To discover the total weight of polymer separated at useful compositions, the weight of polymer extracted is plotted against the average composition in each fraction. The efficiency of separation is enhanced when a large part of the area under the

curves is at the ends of the composition axis, signifying a large weight of polymer with a pure composition. The efficiency might arbitrarily be defined as the percent difference in the concentration-weighted average amounts extracted of the two polymers.

$$\bar{S} = \frac{2|\bar{w}_1 - \bar{w}_2|}{\bar{w}_1 + \bar{w}_2} \quad (2)$$

where

$$\bar{w}_1 = \frac{\int_0^\infty x_1(w) w dw}{\int_0^\infty x_1(w) dw} \quad (3)$$

is the concentration-weighted average mass of polyethylene extracted. Similarly, $\bar{w}_2$ refers to polypropylene. $\bar{S}$ is simply the percent difference between the two averages. Figures 17 and 18 show the extracted composition distributions for samples EX4 and EXC-1. The separation efficiency $\bar{S}$ shown for samples EX4 and EXC-1 demonstrate the success of the bath extraction separation process.

Summary

Polyolefins are not easily separated from one another by crystallization from solution. Polyethylene and polypropylene can crystallize together at the same temperature in some instances. Even when the separation process is subdivided into cooling and density classification steps, the extent of separation is small. Soxhlet extraction is a viable alternative to separation by crystal formation. Bath extraction also yields a good separation, and has the extra advantage that the temperature is well controlled. With this technique it has been possible to explore the effects of temperature on the rate of extraction and to investigate the rate limiting step in the mechanism. By nucleating polymer crystals on different substrates, (for example, diatomaceous earth), the effects of surface area on the rate of fractionation are also being measured. We may then be able to distinguish between mass transfer and thermodynamic limitations in the extraction processes.

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Figure 1. Flow Diagram for the Thermoplastic Separation Process Discussed by Sperber and Rosen

Figure 2. Polyolefin Separation Section

Figure 3. Typical Tube Dimensions

Figure 4. Constant Temperature Bath with Tumbling Apparatus

Figure 5. Insulated Bath Used for Temperature Measurement

Figure 6. Solubility Temperatures of Polyolefins in xylene Solvent

Solubility Temperatures of Various Polyolefins (In Tetralin Solvent)

Figure 7

Solubility and Recrystallization Temperature Curves (Xylene Solvent)

Figure 8

Solubility and Recrystallization Temperature Curves (Xylene Solvent)

Figure 9

Solubility and Recrystallization Temperature Curves (Xylene Solvent)

Figure 10

Recrystallization Temperatures of Various Polyolefins (In Xylene Solvent)

Figure 11

Figure 12. Polymer Separation by Quick Chilling

Figure 13. Non-Solvent Polymer Crystallization

Figure 14. Soxhlet Extraction Apparatus

Figure 15. Bath Extraction Apparatus

Figure 16. Effect of Diatomaceous Earth on the Extraction Process

Extracted Polymer Composition Distribution, x vs. W

Figure 17

Extractive Separation Results (Sample EXC-1)
Extracted Polymer Composition Distribution, x vs. W

Figure 18

Figure 19. Infrared Calibration Chart

TABLE I RESULTS OF SLOW COOLING RECRYSTALLIZATION SEPARATION

Sample No.	Temperature of Filter	Fraction No.	Weight Percent Polypropylene	Extent of Separation (%)
R x 1	78°	A Filtrate	59.2	6.7
R x 1		B	65.9	
R x 1		C	19.7	
R x 2	75° approx.	A Filtrate	61.7	1.4
R x 2		B	60.3	

TABLE IIIa SOLUBILITY AND RECRYSTALLIZATION TEMPERATURES
FOR THE POLYPROPYLENE-XYLENE SYSTEM

Sample No.	Weight Percent Polymer	Tumbling Temperature (°C)	Tumbling Duration (Days)	Solubility Temperature (°C)	Recrystallization Temperature (°C)	Cooling Rate (°C/min)
PPX1	01.00	140	2	103	79	.435
PPX2	04.29	140	2	106	85	.483
PPX3	10.09	140	2	107	70.5	.367
PPX4	15.12	125-144	3	109	68	.347
PPX5	20.06	170	2	110	79	.435
PPX6	29.81	125-144	3	115	74.5	.399
PPX7	39.47	125-144	3	116	109	.677
PPX8	51.26	170	5	129	90	.524
PPX9	58.37	170	5	135	107	.661
PPX10	69.43	170	5	142.2	104	.637
PPX11	75.60	170	3	147.5	107	.661
PPX12	85.35	170	5	158	120	.766

TABLE IIIb SOLUBILITY AND RECRYSTALLIZATION TEMPERATURES
FOR THE HIGH DENSITY POLYETHYLENE-XYLENE SYSTEM

Sample No.	Weight Percent Polymer	Tumbling Temperature (°C)	Tumbling Duration (Days)	Solubility Temperature (°C)	Recrystallization Temperature (°C)	Cooling Rate (°C/min)
HPX1	0.97	140	2	97	85	.484
HPX2	4.98	140	2	98	88	.508
HPX3	10.08	140	2	100	91	.532
HPX4	14.85	144	7	99.5	93	.548
HPX5	19.86	144	7	102.5	91	.532
HPX6	29.7	144	7	105	97	.581
HPX7	39.03	145	10	109	100	.605
HPX8	48.64	145	10	111	104	.637
HPX9	57.81	145	10	115	107	.661
HPX10	66.56	140	4	121.5	110	.685
HPX11	76.43	140	4	123	113	.710
HPX12	89.43	140	4	130	121	.774

TABLE IIIc SOLUBILITY AND RECRYSTALLIZATION TEMPERATURES
FOR THE LOW DENSITY POLYETHYLENE-XYLENE SYSTEM

Sample No.	Weight Percent Polymer	Tumbling Temperature (°C)	Tumbling Duration (Days)	Solubility Temperature (°C)	Recrystallization Temperature (°C)	Cooling Rate (°C/min)
LPX1	01.02	140	2	73	66	.331
LPX2	04.70	140	3	78	72.8	.385
LPX3	09.06	140	3	77	73	.387
LPX4	13.95	144	7	81	76	.411
LPX5	19.35	145	10	85	77.5	.423
LPX6	28.95	144	7	86.5	82	.460
LPX7	38.93	145	10	90	85	.484
LPX8	47.23	125	7	90. ^s	88	.508
LPX9	59.23	125	7	95.2	93	.548
LPX10	68.75	125	7	100.5	95	.564

TABLE III d SOLUBILITY TEMPERATURES FOR THE
POLYPROPYLENE-TETRALIN SYSTEM

Sample No.	Weight Percent Polymer	Tumbling Temperature (°C)	Tumbling Duration (days)	Solubility Temperature (°C)
PPT1	12.77	125-144	3	104
PPT2	19.67	170	2	114
PPT3	28.35	170	2	122
PPT4	40.29	170	2	128
PPT5	50.03	164	5	133.5
PPT6	59.13	185-200	3	138.5
PPT7	68.03	185-200	3	150
PPT8	71.60	185-200	7	145
PPT9	80.30	185-200	3	156

TABLE IIIe SOLUBILITY TEMPERATURES FOR THE
HIGH DENSITY POLYETHYLENE-TETRALIN SYSTEM

Sample No.	Weight Percent Polymer	Tumbling Temperature (°C)	Tumbling Duration (days)	Solubility Temperature (°C)
HPT1	19.50	185-200	3	107
HPT2	28.64	180 approx.	3	109
HPT3	39.91	180 approx.	3	111
HPT4	49.78	180 approx.	3	114
HPT5	59.77	125-200	7	116
HPT6	63.38	175-200	7	117
HPT7	69.22	175-200	7	120
HPT8	79.30	175-200	7	125

TABLE IV. QUICK CHILLING RECRYSTALLIZATION RESULTS

Sample No.	Washing Agent	Fraction Number	Weight Fraction Polypropylene	Extent of Separation (%)
DIA	Acetone	I Float	0.391	3.4
DIA		II Sink	0.425	
DIM	Methanol	I Float	0.632	1.7
DIM		II Sink	0.649	
DIX1	Xylene	I Float	0.573	7.0
DIX1		II Sink	0.503	
DIX2	Xylene	I Float	.582	12.4
DIX2		II	.605	
DIX2		III Sink	0.481	
DIX3	Xylene	I Float	0.504	3.7
DIX3		II	0.492	
DIX3		III Sink	0.467	
DIX4	Xylene	Ia Float	0.470	1.8
DIX4		Ib Float	0.475	
DIX4		IIa Sink	0.488	
DIX4		IIb Sink	0.482	

TABLE V. NON SOLVENT RECRYSTALLIZATION RESULTS

Sample No.	Non Solvent	Fraction Number	Weight Fraction Polypropylene	Extent of Separation (%)
NSM-1	Methanol	I Float	0.531	6.4
NSM-1		II Med.	0.483	
NSM-1		III Med.	0.547	
NSM-1		IV Sink	0.54	
NSM-2	Methanol	I Float	0.483	4.5
NSM-2		II	0.457	
NSM-2		III Med.	0.467	
NSM-2		IV	0.485	
NSM-2		V Sink	0.502	
NSM-3	Methanol	I Float	0.623	8.1
NSM-3		II Med.	0.585	
NSM-3		III Sink	0.542	

TABLE VI. SOXHLET EXTRACTION RESULTS

Sample No.	Solvent	Fraction Number	Weight Fraction Polypropylene	Extent of Separation (%)
ST-1	Toluene	A	0.667	21.7
ST-1		B	0.450	53.9
SBTX-1	Mixed	A	0.301	53.9
SBTX-1		B	0.840	
SBTX-2	Mixed	A	0.176	73.3
SBTX-2		B	0.326	
SBTX-2		C	0.909	
SBTX-2		D	0.726	

TABLE VII. BATH EXTRACTION RESULTS

Sample No.	Solvent	Fraction No.	Weight Fraction Polypropylene	Extent of Separation (%)
EX-3	Xylene	A	0.140	55.2
EX-3		B	0.272	
EX-3		C	0.692	
EX-3		D	0.540	
EX-4	Xylene	A	0.181	>80
EX-4		B	0.072	
EX-4		C	0.273	
EX-4		D	0.731	
EX-4		E	0.757	
EX-4		F	>.90	
EXC-1	Xylene	A	0.279	90.0
EXC-1		B	0.211	
EXC-1		D	0.143	
EXC-1		E	0.004	
EXC-1		F	0.156	
EXC-1		H	0.477	
EXC-1		I	0.444	
EXC-1		J	0.904	
EX6	Xylene	A	0.478	29.7
EX6		B	0.274	
EX6		C	0.377	
EX6		D	0.194	
EX6		E	0.181	

TABLE VIII. BATH EXTRACTION RESULTS FOR DISTRIBUTIONS

Sample and Fraction No.	Weight Polypropylene	Weight Extracted (g)	Time (hours)
EXC1A	0.279	.1948	3.05
EXC1B	0.211	.3990	6.07
EXC1C	---	.4301	9.32
EXC1D	0.143	.5202	12.42
EXC1E	0.004	.6103	15.82
EXC1F	0.156	.6796	19.02
EXC1G	---	.6871	23.52
EXC1H	0.477	.9078	33.92
EXC1I	0.444	.9906	39.08
EXC1J	0.904	1.533*	41.45
EX6 A	0.478	.0700	2.08
EX6 B	0.274	.2974	4.75
EX6 C	0.377	.3127	7.65
EX6 D	0.194	.3522	11.48
EX6 E	0.181	.4009	15.75
EX6 F	0.196	.4486	19.28
EX6G	---	.5678	26.58
EX6 H	---	.6747	32.67
EX6 I	---	.9418	39.95

* Fraction J: Overheating caused rapid extraction, temperature unknown.

TABLE IX INFRARED CALIBRATION DATA

Sample No.	Percent Polyethylene	Percent Polypropylene	Absorbance Ratio: A1377/A1462
I	20.3	79.7	1.159
II	40.3	59.7	0.849
III	50.1	39.9	0.523
IV	79.9	20.1	0.717
V	100.0	0	0.0317
VI	0	100	1.469
VII	90.0	10.0	0.145
VIII	69.9	30.1	0.355
IX	50.0	50.0	0.6831
X	30.0	70.0	1.0498
XI	10.3	89.7	1.2322
XII	69.8	30.2	0.5152
XIb	10.3	89.7	1.586
XIc	10.3	89.7	1.665
Ib	20.3	79.7	1.306

Appendix A Procedures of sample preparation and analysis

Certain standard procedures were adopted in sample preparation and analysis for all of the separation methods tested. All polyolefin mixtures were prepared by dissolving commercial molding powders in xylene well above 100°C. In the preparation, temperature control was not considered critical, but sufficient mixing was provided to quickly form a polymer solution.

For all of the extractive separations, a simple flask, hot plate and magnetic stirrer were used. Once each solution had formed, the flask was cooled to precipitate a crystal slurry. To ensure easy transfer of the entire batch of polymer mixture into the extraction thimble, an upper limit of 2% on the total polymer weight percent in the solution and slurry was observed. For the separations by recrystallization, the polymer mixture was dissolved right in the apparatus reboiler. There was no need to transfer it from one place to another, but simply to adjust the temperature to the correct starting point in the process.

For the primary experiments on slow cooling recrystallization, the polyolefin mixture was simply dissolved in a reaction kettle.

Each separation, whether by recrystallization or extraction, required that the product samples be prepared for composition analysis. This preparation was carried out in a number of sequential steps that varied little from process to process.

- 1) The polymer crystals were dried, first by filtration and then in a vacuum oven at about 70°C.
- 2) The crystals were weighed if necessary and removed from the filter paper.
- 3) Using a Wabash compression molding press, each sample was pressed into a thin film between two guide blocks covered with protective sheets of aluminum foil. In this way, the polymer was kept from sticking to the moldblocks.
- 4) Hydrochloric acid was used to remove the aluminum foil from the films which were then fastened on cardboard guides for infrared analysis.

The polymer film samples were scanned with a Beckman model 4250 infrared spectrophotometer. In the infrared analysis, the absorption intensities of polyethylene and polypropylene at several wavelengths were used to determine the composition of each film.

Theoretically, the infrared analysis proceeds from the Beer-Lambert law which states, for any absorbing component at a given wavelength:

$$\log \frac{I_0}{I} = A = \epsilon l C \quad (A1)$$

When a film of polymer mixture is analyzed, both components will absorb simultaneously. Two absorption bands at 1377cm^{-1} and 1482cm^{-1} , were carefully chosen to minimize interference effects. At 1377cm^{-1} , the $-\text{CH}_3$ group hanging onto the chain backbone of the polypropylene absorbs strongly. At 1482cm^{-1} , the absorption is due to the C-C bonds in the chain backbone and is common to both polymers. By taking the ratio of two absorbances, the thickness of the sample is eliminated from the equation. The effect of the simultaneous absorption by components PE and PP is still present, however.

$$R = \frac{A_{1377}}{A_{1482}} = \frac{\epsilon_{1377, \text{PE}}^C C_{\text{PE}} + \epsilon_{1377, \text{PP}}^C C_{\text{PP}}}{\epsilon_{1482, \text{PE}}^C C_{\text{PE}} + \epsilon_{1482, \text{PP}}^C C_{\text{PP}}} \quad (\text{A2})$$

Though complex, this equation yields a calibration between the absorbance ratio between the two wavelengths and the composition, since concentration is directly proportional to weight fractions. A mathematical substitution was employed to reduce the four ϵ constants in the equation for the absorptivity ratios $\frac{\epsilon_{1377A}}{\epsilon_{1482A}}$ and $\frac{\epsilon_{1377B}}{\epsilon_{1482B}}$. To complete the calibration, a number of samples having

known composition were prepared and analyzed. See Table IX. These included two pure polymer samples, one polyethylene and one polypropylene, which allowed immediate and precise calculation of the ratios $\frac{\epsilon_{1377, \text{PE}}}{\epsilon_{1482, \text{PE}}}$ and $\frac{\epsilon_{1377, \text{PP}}}{\epsilon_{1482, \text{PP}}}$ from

equation A2. With the concentration of polypropylene equal to zero, Eq. A2 reduces to:

$$R = \epsilon_{1377, \text{PE}} / \epsilon_{1482, \text{PE}} \quad (\text{A3})$$

and vice versa. The final equation,

$$R = \frac{\epsilon_{1377, \text{PE}}(1-x) + \epsilon_{1377, \text{PP}}x}{\epsilon_{1482, \text{PE}}(1-x) + \epsilon_{1482, \text{PP}}x}$$

represented by the calibration curve, Figure 19, is almost a straight line. The curvature at the end points is due to the simultaneous absorption at both wavelengths.

Using the calibration in Figure 19, the composition of each polyolefin fraction was determined from the infrared absorbance ratio.

CRYOGENIC GRINDING AND SEPARATION
OF MIXED PLASTICS

by

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Submitted in partial fulfillment of the requirements
for the Degree of Master of Science

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August 1979

CRYOGENIC GRINDING AND SEPARATION OF MIXED PLASTICS

Abstract

by

ELIZABETH G. GARCIA

An approach to the problem of separating mixtures of plastics for recycling is the use of cryogenic grinding. Homopolymers, especially high density polyethylene, were used in characterizing the cryogenic grinding process and its effect on resultant powders. Although brittle fracture was expected with the use of liquid nitrogen, cryogenic milling of high density polyethylene produced a fibrous type of powder. Reasons for this are discussed.

Cryogenic grinding of laminated film produced small particle sized powders of the mixed plastics. Apparent delamination of the layers could be accomplished by the process when there is no appreciable fusion of the layers. Thus for the particular film studied, a nylon-polyethylene-Surlyn tri-laminate, the nylon could be separated but the Surlyn and polyethylene layers remained intact.

The ground film powders were separated using a sink-float method. Maximum degrees of separation achieved

were 4% impurity for the bottom (nylon) layer while the top layer had 10% impurity.

Mechanical properties of films from the recovered powders were, as expected, poorer than the original film. The recovered powder samples were generally more brittle.

ACKNOWLEDGEMENTS

The author gratefully expresses her sincere appreciation to Professor Phillip H. Geil for his help, support, and guidance throughout the course of this work.

Special thanks are extended to Dr. A. F. Burmester of the Dow Chemical Company for providing the high density polyethylene resins and for the gel permeation chromatography analyses.

The author also extends her thanks to the members, past and present, of Professor Geil's group as well as the other members of the Department of Macromolecular Science for their many kindnesses.

The generous contribution of the Plastics Institute of America in support of this research is especially appreciated.

In addition, the author wishes to acknowledge the encouragement and help given by her parents and family throughout her years as a student.

Lastly, a special thank you to Michael Grabnic for his understanding and love.

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INTRODUCTION

Plastics have replaced and are still replacing other materials such as metal, glass, and wood as or in parts of pipes, cars, boats, appliances and other consumer or industrial goods (1). Two problems, however, assail the plastics industry. First there is the limited supply of petrochemicals, the feedstock of plastics, and second there is the disposal problem for these same plastics. Thus it is clear that ideally we must learn to recover and reuse plastic wastes.

Waste plastics can be a valuable resource. There are estimates that the value of plastic waste by the year 2000 in the U.S. alone could exceed two billion dollars (2). As primary raw materials become more scarce and expensive and as the alternative costs of waste disposal also increase, recycling of plastics becomes more economically worth pursuing.

Reuse of materials has always been and is being done. By using varying mixtures of reclaimed and virgin materials, fillers, binders, and other processing aids in hot pressing, injection molding, and extrusion such diverse products as traffic markers, tiles, lining for drainage ditches, and even a coating for barn siding which replaces

the need for galvanizing and painting steel have been produced (3,4). A simple reclaim operation often practiced is one where scrap during production is pre-sized and then regularly processed through with virgin material. In this case composition and behavior of the material is usually known. However, use of waste plastics as raw materials, although it would ease the demand on petrochemical resources and at the same time alleviate the disposal problem, is not quite so easily managed. Technological innovations are still needed in recovering and separating the different plastics from general waste and from each other.

In the U.S. in 1974, four billion pounds of waste plastics were reclaimed for reuse. Industrial waste, usually homogeneous in nature, made up nearly all of this reclaimed material. However, nearly two billion pounds of industrial waste still remained unrecovered. One of the major difficulties was the recycling of mixtures of plastics (5). For example, laminated films are just such mixtures. Recovery of the components from these composites, although already part of source - separated scrap before the material is caught up in the municipal waste stream, is difficult. It is toward the recovery and reuse of this type of material that this

research is directed.

The potential for the recycle of laminated films by cryogenic grinding has been demonstrated. Initial experiments have shown that films can be fractured and that delamination is possible (6). Here at Case projects involving polymer blends, with powdered polymers being needed to produce homogeneous mixing, led to the interest in cryogenic milling to obtain the fine powders for processing. Cryogenic powdering of a laminated polypropylene - polyacrylonitrile film produced apparent delamination of the particles (7). There has been previous work on the study of the separation of waste plastics, notably the efforts of some Japanese workers (1,8,9). Shimoizaka et al. have shown the feasibility of separation of plastics using a sink-float type process carried out in static conditions (8,9). Thus, with the possibility for reclaim of laminated films by powdering evident, this research investigates the cryogenic grinding process as a technique for obtaining uniform, small particle size powders of delaminated mixed plastics. Investigation of the separation of the resulting powders into components then follows. This is an attempt to solve the difficult problem of recycling mixtures of plastics -- laminated films.

Initially, the research examines homopolymers, in particular high density polyethylene, as an available representative polymer to study the various powder characteristics such as particle size and shape, and effects of annealing and molecular weight. This helped to characterize the milling process and its effects. Homopolymer work was followed by milling and separation of a laminated film to assess the feasibility of obtaining viable processing feedstocks from recovered components of co-extruded films.

PART I

HIGH DENSITY POLYETHYLENE

INTRODUCTION

One of the objectives of the research is to characterize the cryogenic milling process as a means of preparation of powders for eventual use in extrusion, powder coating and other processes using reclaimed plastics. Polystyrene and a plasticized PVC were initially used but the bulk of the study was conducted with high density polyethylene (HDPE). Dow HDPE samples were available in three different molecular weights:

Dow 07065 with melt index = 0.7

Dow 12065 with melt index = 1.2

Dow 35063 with melt index = 3.5

These samples were used to characterize the milling process in terms of effects evident on the resultant powders. Grinding temperature, particle size, annealing, swelling, and molecular weight were some of the effects evaluated.

EXPERIMENTAL

All samples were ground using a Retsch Ultra-Centrifugal-Mill type ZM 1 (Figure 1). The mill has a rotor which spins against a sieve ring, thus grinding the samples to various sized powders. The rotor speed used was 20,000 rpm. Sieve rings used were 500, 200, and 80 micron sizes.

For cryogenic grinding, samples were cooled with liquid nitrogen (LN_2) for 15 to 30 minutes before processing. Liquid nitrogen was also fed in directly into the mill during grinding. Other liquids such as methanol/water solution, were added to the mill in a similar fashion.

Energy measurements for grinding a given weight of sample were obtained using a chart recorder attached to an ammeter on the mill. A constant voltage was assumed. The energy requirements to run the mill alone was subtracted from the total energy required, to obtain the energy needed to grind a certain weight of sample. Feed rates were essentially always the fastest possible for each sample without overheating or clogging the mill.

Particle shapes and morphologies of the different powders were characterized by scanning electron microscopy using a Cambridge SEM (model S4-10). A small

amount of each powder was scattered over double-sided adhesive tape. This was then mounted on aluminum stubs and surface coated with a layer of Pd under vacuum. The samples were then examined in the scanning microscope, usually with a tilt angle of 30 degrees.

Molecular weight and molecular weight distribution analyses were done by the Dow Chemical Company using gel permeation chromatography methods.

Annealed samples were obtained by annealing for 1 hour at 125°C in a vacuum oven before grinding.

Compression molded samples were prepared by compression molding the pellets into 1/16 inch sheets and either quenching or slow-cooling. The sheets were then pre-cut to 1/4 inch squares before grinding.

The effects of swelling the polymer were also studied. Samples were immersed in xylene for a period of 9 days before grinding.

RESULTS AND DISCUSSION

The grinding of various high density polyethylene (HDPE) samples produced the values for energy requirements of the milling process that are presented in Table 1. Variation in experimental values for duplicate runs was roughly within plus/minus 0.1. Variation within a run was also within 10 percent.

Because higher molecular weight usually produces more tie molecules between crystals, which gives more flexibility and greater toughness, it was expected that rupture properties such as ultimate strength and elongation would be affected by molecular weight (10). However, there appears to be no essential difference in energy requirements for all three Dow HDPE samples of varying melt indices when ground from pellets to 500 microns using liquid nitrogen. For comparison, Marlex 6015 (HDPE from another manufacturer) also had similar energy requirements.

In comparing grinding to various sizes it is noted, as expected, that more energy is required to grind to smaller sizes. On the other hand the total energy in the two step process, pellets to 500 microns and 500 microns to 200 microns, is about the same as that for direct grinding to 200 microns.

In addition, grinding through 80 microns with liquid nitrogen produced no apparent difference in molecular weight and molecular weight distribution as determined by gel permeation chromatography (GPC) (Figures 2-4). Figures 2 and 3 are the GPC curves (Molecular weight/1000 vs. Fraction %) for the Dow 12065 pellets and cryogenically ground powder respectively. Figure 4 superimposes these two curves to show the differences. The lack of appreciable change is expected because a rough calculation assuming brittle fracture and an 80 micron cube as the resultant ground particle translates into only .01 percent of polymer molecules being cut by the grinding process. This value is within GPC instrument accuracy. In other words, there is no anticipated reduction in molecular weight because the particle size is not small enough to show the change.

Another reason for the lack of change in molecular weight is that plastic deformation instead of brittle fracture occurs during grinding. Although a brittle fracture similar to polystyrene and PVC ground samples (Figures 5-6) was expected, HDPE scanning electron microscopy photographs (Figures 7-9) show fibrous structures with a high degree of plastic deformation in all the samples.

It is noted there is no apparent difference between the fibrous nature of the samples even in the two having the highest and lowest melt indices when ground to 500 microns. Grinding through the smallest sieve ring, 80 microns, also produces a similar appearing powder for each sample as represented by the micrograph in Figure 10 for the 1.2 melt index resin.

Mechanical properties for semi-crystalline polymers are affected by the nature of the non-crystalline regions. The disordered molecular segments in these regions can be thought of as producing a plasticizing effect on the bulk polymer by decreasing the modulus and increasing the toughness of the polymer (11). Polyethylene is known to crystallize from the melt in the form of spherulites composed of radiating lamellae. The disordered or amorphous regions are interlamellar and consist of polymer chain ends and other impurities. Annealing of polyethylene samples results in reorganization and recrystallization (12). The annealing process is expected to result in decreases in the number of tie molecules along with an increase in lamellar thickness (13). The resultant density and crystallinity increase produces an increase in the modulus and stiffness of the polymer and thus a decrease in toughness (14). Therefore, it was

expected that if the samples were annealed for suitable periods of time and temperature, brittle fracture would occur. Samples of the pellets were annealed at 125°C for 60 minutes, these conditions being known to produce significant increases in lamellar thickness and crystallinity.

From Table 1 it can be seen that the increase in crystallinity produced no obvious difference in the energy required for grinding Dow 07065 and 12065 samples. For the sample with the highest melt index, Dow 35063, there is an appreciable increase in the energy requirements. However, this is due to the clogging of the mill by this sample. The resulting powder is still fibrous as seen in Figure 11. Micrographs for the other two samples are similar. Thus, although we have no explanation for the clogging and in addition, all of the samples have a higher crystallinity following annealing, they are as hard or harder to grind than the original as-received samples.

Comparison of different rates of crystallization on the grinding process also produces no apparent differences in energy requirements or particle shapes. A slow-cooled sample would be expected to have larger, more perfect crystals as well as an overall greater

crystallinity than a quenched sample. Thus the slow-cooled sample would be expected to fracture more readily. However, on compression molding Dow 07065 and quenching or slow-cooling before grinding, the energy requirements for grinding with liquid nitrogen were similar to each other and to that for the as received sample. Micrographs (Figures 12-13) show no appreciable differences between quenched and slow-cooled samples. The powders are still fibrous with no brittle fracture evident.

Neither polyethylene nor polystyrene, which is brittle at room temperature ($T_g \approx 80^\circ\text{C}$), could be ground at room temperature at reasonable feed rates. Upon addition of the polymer the grinder rapidly became overloaded; the ammeter reading rose excessively. When the mill was opened it was found that the polymers had melted and clogged the sieve ring and rotor. Fibers were formed as well as large balls of polymer which had stopped the rotor from rotating.

It is known that polyethylene can undergo apparent brittle fracture at room temperature and above if the polymer is exposed to mechanical stress in the presence of low surface tension liquids. This phenomenon is known as stress cracking (15,16). The effect of stress cracking agents on the grinding process at room tempera-

ture was examined using methanol and methanol/water ($\text{MeOH}/\text{H}_2\text{O}$) mixtures. It was found that the HDPE samples could then be ground at room temperature but the energy requirements for grinding to 500 microns were higher than when grinding with liquid nitrogen (Table 1). Micrographs for Dow 12065 and 35063 samples ground with $\text{MeOH}/\text{H}_2\text{O}$ are shown in Figures 14 and 15, which can be compared with Figure 8 and 9 for the same samples ground in liquid nitrogen. The resultant powders are still fibrous. Comparing liquid nitrogen grinding of Dow 12065 pellets down to 200 microns with $\text{MeOH}/\text{H}_2\text{O}$ grinding (Figures 16-17) shows plastic deformation rather than brittle fracture also, but particles are more rounded and appear to be less fibrous than those ground to 500 microns. Energy requirements are also less than for liquid nitrogen milling even though it is done at room temperature. It is believed that this ability to grind at room temperature is due to the efficient heat transfer resulting from the liquid medium.

To further attempt to increase the ease of grinding, the effect of swelling the Dow 12065 sample with xylene before milling with liquid nitrogen was examined. Absorption of solvent by polymers on swelling occurs primarily in the amorphous regions and as a result the tie

molecules are drawn out, become clustered and oriented, forming interlamellar links (17). It was thought that this would be conducive to embrittlement of the polymer and thus would make it easier to grind. Results, however, show no brittle fracture occurring. The SEM micrograph (Figure 18) shows familiar fibrous structures and plastic deformation. In addition the energy requirements appear comparable to the value obtained when grinding untreated samples. Subjecting Dow 35063 pellets to the same treatment produces a slight increase in energy required when compared to liquid nitrogen grinding. This again may be due to clogging of the rotor shaft by this particular resin.

CONCLUSION

Tensile tests of most plastics show yielding, plastic flow and cold drawing. However, when the temperature is greatly lowered, polymer chain segments presumably are not able to reorient in the time of the experiment. Therefore the stress developed by the experiment cannot be relieved by plastic flow and chain rupture and brittle fracture may result, especially at high strain rates (18). Thus, processing with liquid nitrogen was attempted. However, although a brittle fracture was expected, cryogenic milling of HDPE produced fluffy, plastically deformed, fibrous types of powders. Various pre-treatments and grinding conditions produced no appreciable differences in the types of powders obtained.

The lowest molecular weight sample was the hardest to grind; it needed more energy to grind per gram of a sample. This is believed to be due to the clogging of the rotor shaft by this particular resin. We have no explanation for this tendency of this polymer to clog the shaft since particle sizes and shapes were similar to those of the other resins.

A factor to be considered for the lack of brittle behavior on grinding is the state of stress to which the material is exposed. Stress conditions which are

conducive to plastic deformation and viscous flow, for example shear stresses which occur in our grinding experiments, may result in ductile failure whereas tensile stresses result in brittle failure. The latter can be attributed to the dilational component of the stress (19). In addition although the samples were originally cold enough for brittle fracture, they may have been much warmer during their actual deformation. It is believed that considerable heat is generated in the grinding process which may not be completely removed locally even though liquid nitrogen was being supplied to pre-cooled polymer.

Figure 1: Retsch Ultra-Centrifugal-Mill type ZM 1

Table 1:

Energy Requirements - (kj/g)

Polymer	<u>pellets to 500μ</u>				<u>pellets to 200μ</u>		<u>500μ to 200μ</u>	<u>500μ to 80μ</u>
	<u>1N₂</u>	<u>Annealed</u>	<u>MeOH/H₂O</u>	<u>Xylene</u>	<u>1N₂</u>	<u>MeOH/H₂O</u>	<u>1N₂</u>	<u>1N₂</u>
Dow 07065	0.5	0.5						
Dow 12065	0.6	0.4	1.0	0.4	2.3	1.2	1.9	4.9
Dow J5063	0.6	1.0	3.5	0.9				
Dow 07065 compression molded:								
quenched	0.3							
slow- cooled	0.4							
Marlex 6015	0.6							

Figure 2: GPC curve (Molecular weight/1000 vs. Fraction %) for Dow 12065 pellets

Figure 3: GPC curve (Molecular weight/1000 vs. Fraction %) for Dow 12065 resin ground through the 80 micron sieve ring with liquid nitrogen

Dow 12065 pellets ———
Dow 12065 ground to 80 μ - - - - -

Figure 4: GPC curves (Figures 2 and 3) for Dow 12065 pellets and ground powder superimposed to show differences

Figure 5: Polystyrene pellets ground to 500 microns, $1N_2$
70X

Figure 6: Plasticized PVC, 1/8" cubes ground to 500
microns, $1N_2$ 70X

Figure 7: Dow 07065 pellets ground to 500 microns, $1N_2$
70X

Figure 8: Dow 35063 pellets ground to 500 microns, $1N_2$
70X

Figure 9: Dow 12065 pellets ground to 500 microns, $1N_2$
70X

Figure 10: Dow 12065, 500 microns ground to 80 microns,
 $1N_2$ 70X

Figure 11: Dow 35063 pellets, annealed 1 hour, 125 °C,
ground to 500 microns, 1N₂ 70X

Figure 12: Dow 07065 compression molded, quenched,
ground to 500 microns, 1N₂ 70X

Figure 13: Dow 07065 compression molded, slow-cooled,
ground to 500 microns, 1N₂ 45X

Figure 14: Dow 12065 pellets ground to 500 microns, MeOH/
H₂O 70X

Figure 15: Dow 35063 pellets ground to 500 microns, MeOH/
H₂O 70X

Figure 16: Dow 12065 pellets ground to 200 microns, $1N_2$
120X

Figure 17: Dow 12065 pellets ground to 200 microns, MeOH/
 H_2O 120X

Figure 18: Dow 12065, Xylene treated, ground to 500
microns, 1N₂ 50X

PART II
LAMINATED FILM

INTRODUCTION

Research work on grinding and separation of a laminated film followed the high density polyethylene work. A trilaminate film from Filmco Corporation, Aurora, Ohio marketed as DURAVAC meat packaging was used as a typical polymer composite film. The film was composed of 1 1/2 mil Nylon 6, 1 mil low density polyethylene (LDPE), and 1 mil Surlyn 1652. By weight the film was analyzed to be 45% Nylon and 55% polyethylene/Surlyn.

This film was ground cryogenically and separated by flotation. The powders obtained were evaluated with respect to such characteristics as size, shape, degree of delamination, surface treatment and morphology. The degree of separation as a function of these factors was characterized, as well as the mechanical properties of films prepared from the separated powders.

EXPERIMENTAL

Laminated film sheets were pre-cut to about 1/4 inch squares and then ground using the various screen sizes as described in Part I. Characterization of the powders was again done using scanning electron microscopy (SEM) in a manner similar to that used for the HDPE samples.

A transverse fracture surface of the film was also analyzed by SEM. The sample was obtained by immersing a portion of a sheet in liquid nitrogen and free fracturing under liquid nitrogen after 15 minutes of cooling. X-ray Non-Dispersive Analysis patterns of this film were obtained while in the scanning microscope to identify the Surlyn layer.

Separation of the laminate film powders was achieved by a simple specific gravity method using distilled water and soap (sodium lauryl sulfate) as the separating medium. The specific gravity of the solution was measured as .985 using a hydrometer. This density was chosen because it was between the densities of nylon (1.13) and LDPE (.925). The density of the Surlyn component was .939 and was thus expected to float to the top layer with the LDPE component. The powders were conditioned by pre-stirring for 15 minutes in the liquid medium using a small magnetic

stirring bar and magnetic stirrer before the mixture (powder and liquid) was put in the separation vessel. The mixture was then allowed to stand for 15 minutes before the top layer was removed. Visually there was a clear separation into two layers.

Centrifugation as a means of separation was also attempted. After the usual pre-stirring of the samples, the mixtures were placed in a small clinical lab centrifuge for varying time intervals to accomplish the separation.

Evaluation of the degree of separation was done using Differential Scanning Calorimetry (DSC). An Infrared Spectroscopy method was also attempted but proved to be difficult due to the water absorption by the nylon. The Amide I band at 1632 wavenumbers was interfered with by the water absorption and hence did not give an accurate measure of the degree of separation. DSC curves were analyzed by measuring the areas under the melting peaks using a planimeter and comparing with standard samples. As a further check, mixtures of nylon 6 and LDPE samples of several known compositions were also analyzed by DSC measurements. Standard samples for these DSC measurements were prepared by dissolving the nylon in the film with formic acid and recovering both the nylon and poly-

ethylene/Surlyn fraction. Another set of standard DSC samples for comparison were prepared by physically pulling the nylon layer from the polyethylene/Surlyn layer under liquid nitrogen.

Surface treatment of the film was achieved by running a Tesla coil over a sheet before grinding. Surface contact angle measurements monitored the change in wettability before and after surface treatment.

Annealed film samples were either prepared in the DSC or in a drying tube using a constant boiling solution to better maintain the annealing temperature. In this case a solution of 30 mole percent ethylene diamine and 70 mole percent toluene boiling at 102-103°C was refluxed around the jacketed glass chamber which held the film sample. This temperature was chosen to be between the melting points of the polyethylene and Surlyn.

For physical properties comparisons, samples of films were obtained by physically separating the nylon and LDPE/Surlyn layers under liquid nitrogen and then grinding each individually to 200 microns. An Instron was used to measure the tensile properties of samples compression molded from these powders and from the separated powders.

RESULTS AND DISCUSSION

Non-dispersive X-ray analysis of liquid nitrogen fracture surfaces of the laminated film identified the Surlyn layer as the outer layer with the rough surface (one surface of the film is smooth while the other has a matte surface; see subsequent SEM micrographs). This was the only layer with a peak at ca. 8.63 keV - Zinc $K\alpha_1$ spectra line - (Figure 19) indicating the presence of zinc in the material. Zinc is the heavy metal used to make the ionomer Surlyn 1652. The outer smooth layer and the center layer (Figure 20 and 21 respectively) show no such peak.

Scanning electron micrographs of the fracture surface of the laminated film (Figure 22) shows a sharp nylon-polyethylene/Surlyn boundary. However, there is only a slight indication of the boundary between the polyethylene and Surlyn layers. The adhesion between these two layers appears to be excellent even when fracturing under liquid nitrogen.

Grinding the laminated film with liquid nitrogen from 1/4 inch squares through the various screen sizes produced powders which showed brittle fracture and apparent delamination (Figure 23-27). In the 500 micron sample (Figure 23) some particles have not split into

individual layers. The polyethylene/Surlyn layer has the one rough side while both nylon surfaces are smooth. Figure 24 shows 1/4 inch squares ground to the 200 micron size. The thicknesses of the particles at this size appear to be less than for those ground to 500 microns, i.e., there are no particles at this size which appear to have more than 2 layers. Thus delamination seems to have occurred more completely when grinding to this size. There are obvious fine particles in the sample ground to 80 microns (Figure 25). These fine particles are believed to influence the degree of separation and will be discussed below. Also, particles passing through the 80 micron sieve ring are larger than 80 microns. The holes in the sieve ring were really 80 by 250 microns. At this particle size no further decrease in thickness of the particles appears to occur. The particles are as thick as those at 200 microns but are certainly less than for those at 500 microns. This confirms the observation that the bulk of the delamination occurs by grinding through the 200 micron size.

Grinding successively to 500 and then 200 microns (Figure 26) and then from 200 to 80 microns (Figure 27) reduces the amount of fines produced when compared to samples ground in one step directly from 1/4 inch squares

to 80 microns (Figure 25).

Separation of laminate film powders using a simple specific gravity method produced degree of separation values shown in Table 2. These values were calculated from DSC curves. Typical DSC curves for the mix, top and bottom layers after separation are shown in Figure 28. Variation of degree of separation values were usually within $\pm 2-5$ percent for duplicate runs on similar material (runs for the same separation as well as runs for a different separation of the same powder and also for the separation of a different ground batch). From Table 2 it is apparent that increasing soap concentration improved separation.

Based on a surface area/soap molecule of $20 \text{ \AA}^2$, 5 mg. of soap/liter would be a factor of ca. 10 greater than that required to completely coat all of the particles in a 200 micron powder if they were of uniform size. However, the particles are seen to be somewhat irregular in shape and this, plus the large amount of fines present, suggests that the improvement in separation obtained using 200 mg. of soap/liter is due to more complete wetting of the particles.

It appears that the 200 micron particle size is better for separation than the 80 micron size. In fact,

the best separations were for the 500 to 200 grind. The smaller sized particles and the fines obtained by one step grinding directly to 80 micron may not be sufficiently wetted and therefore may adhere to other particles resulting in poorer separations.

Scanning electron micrographs of the separated layers are shown in Figures 29-32. The top layer particles (Figure 29) show there has been no splitting of the polyethylene/Surllyn layers. The particles are thick, with a rough surface evident on some particles. There appears to be 2 particles in the micrograph which are thinner than all the rest of the particles (toward the upper left corner). These particles are nylon which contaminate the top component. There appears to be only thin particles with smooth surfaces in the bottom layer (Figure 30). For the 80 micron size separations, a large amount of the fine particles are in the top layer (Figure 31) when compared to the top layer of the 200 micron ground powder. The bottom layer particles again appear thinner than those for the top component but some fines are seen to adhere to these particles.

There is an apparent optimum separation time. Table 3 shows the effect of standing time after the mixture (liquid and powder) is poured into the separation vessel.

Increasing the standing time to longer than 15 minutes (visually, the mixture was separated into two distinct layers only after the 15 minute standing time; at time intervals less than 15 minutes, the liquid medium is still cloudy with particles at the center of the separation vessel) the separation appears to deteriorate slightly. We have no explanation why this occurs.

Surface treatment prior to grinding affected the degree of separation. The change in wettability of the polymers was monitored by surface contact angle measurements. The nylon layer gave an advancing contact angle of 48 degrees before surface treatment and an angle of 40 degrees after being treated with the Tesla coil. The untreated Surllyn layer gave a contact angle of 70 degrees and 60 degrees after Tesla coil treatment. The degree of separation values for these samples are given and compared to untreated samples in Table 4. There is a marked improvement in separation for the 500 micron particles. However, there appears to be no improvement for the 200 micron size samples. Apparently, the increased wettability of the particles was only effective for improved separation when the lateral size of the particles was much larger than the thickness. Micrographs for the top and bottom layers for the 500 micron size particles which

were surface treated (Figures 33 and 34) show the thicker rough-surfaced particles only in the top layer.

An attempt was made to separate the polyethylene/Surlyn layer by annealing at a temperature between the polyethylene and Surlyn melting points. Powdered samples of the top layer annealed in the DSC show rounded edges and apparent contraction of the Surlyn, as well as no rough surfaces, when compared to unannealed samples (Figure 35 and 36). A sheet of film was annealed at the same temperature before grinding in an attempt to obtain delamination between the polyethylene and Surlyn. However, no apparent delamination has occurred (Figure 37 and 38). It can be seen from the micrographs that again the rough surface, characteristic of the Surlyn layer when received, has smoothed.

In addition to the sink-float method of separation under static conditions, a batch centrifugation of the pre-stirred powder and liquid medium was also attempted. This method of separation produced similar results as those produced by the sink-float method. However, these same degrees of separation were attained in separation times as low as 5 minutes. Thus, this method, although more complicated in equipment needs, shows some promise if separation times are deemed critical for a recycling

process. A continuous centrifugation process could be used.

To get a better separation, i.e., less polyethylene/Surlyn content in the bottom layer, the tendency of the polyethylene/Surlyn particles to float was increased. This was achieved by increasing the density of the separation medium. Since the polyethylene has a specific gravity of .925, the ionomer a specific gravity of .939, the combined polyethylene/Surlyn particle a calculated specific gravity of .932, and the undelaminated particle with all three layers a specific gravity of 1.017, the specific gravity of the medium was increased to 1.085. This would insure that only nylon particles with a specific gravity of 1.13 would be likely to sink to the bottom layer and thus increase the purity of the bottom component of the separation. The increase in density of the medium was accomplished by the addition of 264 grams per liter of sucrose to the distilled water. The effect of the change in density of the separation medium can be seen in Table 5. As expected, this system gives the best separation for the bottom layer (4% polyethylene/Surlyn) but had about 15% nylon in the top layer. Scanning electron micrographs (Figures 39 and 40) again show thin smooth-surfaced particles in the bottom layer while thicker,

rough-surfaced particles appear in the top layer.

As the sample separated with the sugar solution gave the best bottom layer, this sample was used for physical properties comparisons. The tensile specimens were prepared from the sugar separated powders after the powders were thoroughly washed and dried in a vacuum oven at 80 °C overnight. The powders were then immediately compression molded after removal from the oven. Stress-strain curves of the film samples compared to pure nylon samples obtained by physically pulling apart the nylon layer under liquid nitrogen and either grinding or cutting to 1/4 inch squares before compression molding are shown in Figure 41. All the samples are brittle. The effect of the grinding process is seen to be a decrease in the stress for elongations greater than 3%. The recovered nylon powder stress-strain curve shows an initial higher modulus than the pure nylon samples but it also appears to be more brittle. The difference between the 100% nylon ground powder and the recovered polymer is attributed to the 4% polyethylene/Surlyn impurity in the sample.

Scanning electron micrographs of the tensile (Instron) and liquid nitrogen free fracture surfaces of the recovered powder sample are shown in Figures 42 to 45. Neither failure surface shows the presence of the

polyethylene as readily identifiable inclusions. In contrast the polyethylene in blends of similar sized powders of polyethylene and polycarbonate was readily visible as ca. 5 micron diameter spheres (20).

The recovered powder from the top layer (approximately 85% polyethylene/Surlyn, 15% nylon) was also made into tensile bars and tested. Figure 46 shows the stress-strain curve for the recovered powder compared to samples prepared from polyethylene/Surlyn squares, polyethylene/Surlyn ground after physical separation from the nylon under liquid nitrogen, and to an 80% LDPE and 20% nylon 6 mixture prepared from available resins. The recovered powder shows a higher modulus than the other samples but is brittle when compared to pure polyethylene/Surlyn samples. Polyethylene/Surlyn samples, both unground and ground show very high elongations before fracture. The yield stress for the ground sample is slightly higher, possibly because of better mixing. The 80% polyethylene/20% nylon 6 sample has the lowest modulus and is very brittle. The incompatibility of the nylon and polyethylene/Surlyn can thus be seen as making the samples very brittle.

CONCLUSION

Results obtained indicate the feasibility of using cryogenic grinding with a simple separation method for the recovery of mixed industrial polymer scrap such as laminated films. This method is especially effective if laminated film layers are different enough, for example nylon and polyethylene, so that no appreciable fusion of layers occurs. When appreciable adhesion between layers occurs, as in the polyethylene and Surlyn layers, because the materials are so similar in nature, cryogenic milling is not able to produce a delamination of the layers. The recovered powders could, however, be reprocessed with some fillers to improve certain mechanical properties and can then be used in low stress, less demanding applications.

Figure 19: X-ray Non-Dispersive Analysis pattern for the rough outer layer (Surllyn)

Figure 20: X-ray Non-Dispersive Analysis pattern for the smooth outer layer (Nylon 6)

Figure 21: X-ray Non-Dispersive Analysis pattern for the center layer (LDPE)

Figure 22: Liquid nitrogen free fracture surface of the
tri-laminate film 600X

Figure 23: Laminated film, 1/4 inch squares ground to 500
microns, $1N_2$ 140X

Figure 24: Laminated film, 1/4 inch squares ground to 200
microns, $1N_2$ 140X

Figure 25: Laminated film, 1/4 inch squares ground to 80
microns, $1N_2$ 140X

Figure 26: Laminated film, 500 microns ground to 200
microns, $1N_2$ 140X

Figure 27: Laminated film, 200 microns ground to 80
microns, $1N_2$ 140X

Table 2: Effects of Different Grinding Processes, Particle Sizes, and Soap Concentration on the Degree of Separation

	Top (%PE/Surlyn)	Bottom (%PE/Surlyn)
<u>1/4" squares ground to 500μ</u>		
5 mg/l soap, 15 min separation	65	33
200 mg/l soap, 15 min separation	71	20
<u>1/4" squares ground to 200μ</u>		
200 mg/l soap, 15 min separation	86	12
<u>1/4" squares ground to 80μ</u>		
200 mg/l soap, 15 min separation	67	14
<u>500μ ground to 200μ</u>		
5 mg/l soap, 15 min separation	88	17
200 mg/l soap, 15 min separation	90	9
<u>200μ ground to 80μ</u>		
5 mg/l soap, 15 min separation	79	17
200 mg/l soap, 15 min separation	81	13

Figure 28: Typical DSC curves for the mix, top, and bottom layers of separated laminated film powders

Figure 29: Laminated film ground to 200 microns, $1N_2$, top layer 140X

Figure 30: Laminated film ground to 200 microns, $1N_2$, bottom layer 140X

Figure 31: Laminated film ground to 80 microns, $1N_2$, top layer
140X

Figure 32: Laminated film ground to 80 microns, $1N_2$, bottom layer
140X

Table 3: Effect of Separation Standing Time on the Degree of Separation

	Top (%PE/Surlyn)	Bottom (%PE/Surlyn)
<u>1/4" squares ground to 200μ</u>		
200 mg/l soap, 15 min separation	86	12
200 mg/l soap, 60 min separation	81	16
<u>1/4" squares ground to 80μ</u>		
200 mg/l soap, 15 min separation	67	14
200 mg/l soap, 60 min separation	57	17
<u>500μ ground to 200μ</u>		
200 mg/l soap, 15 min separation	90	9
200 mg/l soap, 30 min separation	86	14
200 mg/l soap, 60 min separation	79	13
<u>200μ ground to 80μ</u>		
200 mg/l soap, 15 min separation	81	13
200 mg/l soap, 60 min separation	80	19

Table 4: Effect of Surface Treatment on the Degree of Separation

<u>1/4" squares ground to 500μ</u>	Top (%PE/Surlyn)	Bottom (%PE/Surlyn)
no soap, surface treated, 15 min separation	76	20
200 mg/l soap, surface treated, 15 min separation	95	8
200 mg/l soap, untreated, 15 min separation	71	30
<u>500μ ground to 200μ</u>		
200 mg/l soap, untreated, 15 min separation	90	9
200 mg/l soap, surface treated, 15 min separation	85	14

Figure 33: Laminated film, surface treated, ground to 500 microns, $1N_2$, top layer 50X

Figure 34: Laminated film, surface treated, ground to 500 microns, $1N_2$, bottom layer 50X

Figure 35: Laminated film, ground to 200 microns, 1N_2 ,
top layer 140X

Figure 36: Laminated film, ground to 200 microns, 1N_2 ,
top layer, annealed at 377.6 °K 120X

Figure 37: Laminated film, annealed at 102-103 °C then
ground to 200 microns, 1N₂ 70X

Figure 38: Laminated film, annealed at 102-103 °C then
ground to 200 microns, 1N₂ 140X

Table 5: Effect of Increased Density of the Separation Medium
by the Addition of Sucrose on the Degree of Separation

<u>500μ ground to 200μ</u>	Top Layer (% PE/Surllyn)	Bottom Layer (% PE/Surllyn)
200 mg/l soap, 15 min separation, no sucrose	90	9
200 mg/l soap, 15 min separation, sucrose	85	4
0 mg/l soap, 15 min separation, sucrose	76	3

Figure 39: Laminated film, ground to 200 microns, $1N_2$,
separated with sucrose in the medium, top²
layer 100X

Figure 40: Laminated film, ground to 200 microns, $1N_2$,
separated with sucrose, bottom layer 100X²

Figure 41: Stress-strain curves for the nylon samples

Figure 42: Tensile (Instron) fracture surface of recovered
nylon sample 200X

Figure 43: Tensile (Instron) fracture surface of recovered
nylon sample 1000X

Figure 44: Liquid nitrogen free fracture surface of
recovered nylon sample 200X

Figure 45: Liquid nitrogen free fracture surface of
recovered nylon sample 1100X

Figure 46: Stress-strain curves for the polyethylene/Surlyn samples

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BLENDS OF POLYPROPYLENE AND LOW DENSITY
POLYETHYLENE WITH ETHYLENE-
PROPYLENE ADDITIVES

by

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THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF SCIENCE IN ENGINEERING

THE UNIVERSITY OF TEXAS AT AUSTIN

December, 1978

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Acknowledgements

I wish to express my appreciation to the people without whom this work could not have been accomplished. Thanks goes to the many companies which donated plastic materials for this research. I am especially indebted to Dr. D. R. Paul and Dr. J. W. Barlow for their patience, guidance and assistance. Special thanks go to the Plastics Institute of America which provided funds for both the research and for a fellowship.

Abstract

The rising production of plastics and the rising costs of plastic raw materials has prompted investigation into methods of recycling scrap plastic products. A possible method of recycling is the reprocessing of mixtures of polymers as blends. Polyolefins are the major constituent of scrap plastics, but they apparently are immiscible with each other. Immiscible blends usually have poor mechanical properties. Previous studies have indicated that the mechanical properties of immiscible blends can be improved when certain copolymers containing monomer units of the homopolymers are added to the blend. A study of the effects of four copolymers and of various processing methods upon blends of low density polyethylene and polypropylene was initiated. The copolymers were two ethylene-propylene rubbers blended with polypropylene, an ethylene-propylene rubber, and a block-like ethylene-propylene-diene terpolymer. Blends were compounded in a Brabender mixer and an extruder, and samples of the blends were compression molded and injection molded. It was concluded from the results that the ethylene-propylene-diene terpolymer was the most effective additive for improving the mechanical properties of low density polyethylene and polypropylene blends. It was

found that multigated samples of both modified and unmodified blends had very poor mechanical properties at the weld-line where polymer fronts met. Processing conditions were determined to have a significant effect upon the resultant mechanical properties. Blended scrap polyolefins can be recycled into useful products by careful choice of modifiers and processing conditions.

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I. Introduction

Plastics production has increased greatly in recent years, as was detailed by Vinson (1). The low cost of many plastics has also promoted their increased use in short lifetime products, causing an increase in the amount of plastics to be found in solid wastes. Incineration of polymer waste leads to added air pollution, and in some cases harmful substances, such as hydrochloric acid, which must be removed from the air. Most plastics are not biodegradable and create subsurface land pollution where sanitary land filling has been used. The plastics industry is under pressure to find and implement methods of extending the useful lifetime of plastics to reduce the quantity of plastic wastes produced annually.

Recycling plastic products could result in a reduction of the accumulated discarded plastics and in the use of raw materials for the manufacture of short lifetime products. The major drawback to recycling has been the high cost associated with separating the polymers into generic types. The cost is a function of the degree of segregation required. Therefore, it would be economically useful to determine feasible methods of recycling mixtures of two or more different polymers to avoid the necessity

of separation.

Reprocessing of mixtures of polymers as a blend is a possible method of recycling. The first polymer blend was documented in 1912, and the first commercial polyblend was introduced in 1948 (2). Blending has been used industrially to improve flow in extrusion and injection molding, to improve ductility and melt strength for such applications as blow molding and thermoforming and to improve impact strength (3,4). In order to tailor blends for specific end uses and to characterize the wide variety of combinations and variations possible, there has been a motivation to investigate the relationship between composite structures and block copolymers (5). The technology used in modifying and blending polymers for commercial products could be applied in creating useful products from polymer blends of recycled materials.

Polyolefins are the most abundant waste polymers and are, therefore, likely candidates for recycling. The purpose of the following study is to evaluate recycling possibilities of polyolefins, specifically low density polyethylene and polypropylene, as blends. Blending usually results in poor mechanical properties since polymers are usually immiscible with one another. Agents which may improve some of the mechanical properties of the blends will be chosen on the basis of literature and patent

information. These will be added under various processing conditions. Mechanical testing results will be used as the basis for evaluating the effectiveness of these additives and of the processing conditions.

Various additives, as well as processing methods, are used commercially to improve the properties of polyolefin polymers and blends. Polyolefins, particularly polypropylene, have long been blended with butyl rubber and ethylene-propylene rubber to improve the impact strength, low temperature brittleness and stress crack resistance. This blending has been accomplished without serious loss in rigidity strength, or heat deflection temperature (3). The effect of ethylene-propylene rubber on low density polyethylene-polypropylene blends was investigated by Robertson (6), and the effect of the rubber on high density polyethylene-polypropylene blends was investigated by Williams (4). The studies reported improvement in the elongation of the blends which was accompanied by a loss in tensile strength.

Two patents concerning blends of low density polyethylene and polypropylene are of particular interest because of reportedly improved properties. The first patent reported that blends of at least seventy-five percent polypropylene, five to fifteen percent polyethylene, and five to fifteen percent ethylene-propylene-nonconjugated diene

terpolymer showed improved mechanical properties as compared to the blends without the terpolymer (7). In the second patent, a polypropylene web of non-woven fabric was impregnated with polyethylene powder, then heat treated. The fabric showed increased tensile strength and chemical resistance (8).

These examples illustrate that improvement in mechanical properties of polyolefin blends can be achieved by careful choice of additives and processing techniques. By applying some of the available technology used in modifying and processing blends of virgin plastics, commercially useful methods of blending scrap polyolefins may be developed.

II. Polymer Blend Behavior

Polymer blends are defined as an intimate mixture of two or more polymers with no covalent bonds between them (9). The above definition excludes graft, block and random copolymers since in these systems the components are chemically bound to each other.

Miscibility of Polymers

The miscibility of polymers with each other is an important factor which affects the resultant mechanical properties of a blend. Miscible polyblends are systems in which the mixing of two or more polymers results in a negative free energy. This leads to single phase behavior, or, in the case of materials consisting of crystalline and amorphous phases, to a single amorphous phase.

The thermodynamic equation describing the free energy of mixing is ΔF , is:

$$\Delta F = \Delta H - T\Delta S$$

The entropy term, $T\Delta S$, is usually positive, but is very small in polymer systems due to the large size of the polymer molecules being mixed. The enthalpy term, ΔH , is usually positive and is the major contribution to the free energy of mixing in polyblends (2,3,6,9). As a result, most polymer blends exhibit little or no miscibility. Single

phase behavior usually results from specific molecular interactions of the two polymers, such as hydrogen bonding or polar attractions (3). Homogeneous blends have only one glass transition temperature, but heterogeneous blends exhibit glass transition temperatures for each component.

Agents for Improving Properties

Most polymer blends are composed of immiscible components, and the polymers separate into phases. Poor interfacial adhesion resulting from immiscibility has been cited as a major cause of the poor mechanical properties of these blends (3,10). Immiscible blends may appear crumbly, "cheezy," and brittle (2). Graft and block copolymers, composed of monomer units of the polymers in the immiscible blends or ones miscible with the polymers, could act as emulsifiers and reduce the heterogeneity of the blend (9). Block and graft copolymers with fairly long segments of each monomer are known to separate into very interspersed phases, a phenomena which has been called "microphase separation." The chemical bonds between the copolymer segments are responsible for the interspersed phase separation (5). Random copolymers usually have very short segment lengths of each particular monomer type and cannot phase separate as easily as graft and block copolymers which have longer segment lengths (11). Random copolymers with a

large percentage of one of the monomers develop "block-like" behavior. The segments of the major constituent become longer, as can be shown statistically (12).

Block, graft, and block-like copolymers tend to concentrate and phase separate at the interfacial boundaries of immiscible polyblends. The result is improved interfacial adhesion due to the chemical bonds between the monomer segments. The diagram below depicts the behavior of these copolymers.

The increased interfacial bonding can provide stress and energy transfer between the phases via the copolymer molecules. Mechanical properties of blends modified with appropriate copolymers should improve as a result of the interfacial bonding.

Methods of Blending

Blends can be made using either mechanical mixing or solvent blending. Mechanical melting and mixing of components can be achieved using such devices as two roll

mills, Banbury mixers, and extruders. In solvent blending, the components are dissolved in a common solvent or mixture, and after they are mixed, the solvent is removed.

There are some inherent problems in both mechanical and solution blending methods. Excessive mechanical mixing can result in degradation and chain scission during melt blending (2,9). In solution mixing, most polymer mixtures show some phase separation. These phases do not intermix well if the polymers are immiscible, especially when the solvent is removed (2). Mechanical melt blending is favored over solution blending because of the economics involved in solvent recovery which requires additional capital investment.

In a miscible blend the mechanical properties, such as tensile strength and modulus, might be expected to be an average function of the weight fraction of the components of the polyblend (3). Each polymer would be expected to contribute to the properties of the blend independent of the other component, as is the case with glass transition temperatures. However, the mechanical properties of many immiscible blends are lower than those of the individual components (4).

The method of mixing and processing can effect the morphology and resultant properties of the polyblend. Binary blends of immiscible components form a two phase mixture

in which the major component may form a continuous matrix with dispersed clusters or domains of the minor component (3,5,9). The domains can exist in the form of spherulites, cylinders, layers, or interconnecting matrices, depending upon the method of processing and the relative volume fractions of the constituents (3,5). The domain shapes and sizes appear to affect the resultant mechanical properties of a blend. Blends with large domains may appear more heterogeneous than the same blends with smaller domains. Theoretically, when the polymers form two continuous phases, mechanical energy and stress may be transferred through each phase independently. Thus, the blend would have relatively good mechanical properties. Domain size depends upon the mixing methods used in compounding a blend. Since polymer molecules are large and viscosities are high in the melt, the phases resist breakup into smaller domains during mechanical mixing. Eventually, the blend will reach equilibrium, and the heterogeneity, that is, domain size, cannot be reduced by further mixing (2).

Improving Mechanical Properties of Blends

The mechanical properties of blends are dependent upon the interfacial adhesion of the polymers, since mechanical energy and stress usually must be transferred across these boundaries. The poor interfacial adhesion

present in most immiscible polyblends appears to reduce significantly the transfer of energy and stress between the polymer phases. The mechanical properties of the blends are therefore reduced in comparison with the individual polymers.

Agents, sometimes known as compatibilizers, such as block and graft copolymers, can promote interfacial adhesion, and increase a blend's homogeneity. The improved interfacial bonding allows for improved stress and energy transfer between the phases, causing an improvement in some of the measured mechanical properties. It is well documented that rubbery additives can improve impact strength, elongation, toughness, and ductility of blends, but may lower the tensile strength or other properties (4,9).

The processing methods used in blending affect the size and shape of the polymer phase domains and, therefore, the surface area of the interfacial boundaries. The surface area of the interfacial boundaries is important since stress and energy are transferred across these boundaries. Since the mechanical properties of the blends are of interest in this study, blend usefulness is defined in terms of the resultant properties instead of evaluations of thermodynamic quantities and homogeneity. The extent of miscibility and homogeneity will most likely have an effect upon the resultant properties of the blend (9), but these

quantities need not be directly evaluated in order to determine blend utility. Methods of determining homogeneity and miscibility are described in the literature (2,6).

Weld-Line Behavior

Due to the flow patterns in the injection molding process, molded articles often have weld-lines where the molten fronts meet. Articles with weld-lines have lower tensile strength and percent elongation than articles without weld-lines (13,14). There appears to be poor adhesion at the polymer fronts, even when both fronts are of the same material, similar to the behavior at the interfaces of the components of immiscible polymer blends. While strengths at weld-lines for pure polymers are often somewhat lower than bulk strengths, weld-line strengths for immiscible polymer blends are usually much lower. Paul has proposed a correlation for predicting the tensile strength of polymer blends at the weld-line (15). Below is a diagram of the two polymer fronts. For the mathematical

model the adhesive strength of polymer i to polymer j is denoted by σ_{ij} , and the fraction of the surface area of polymer i at the left front is denoted by $f_i^{(L)}$ and at the

right front as $f_i^{(R)}$. The surface of the right and left fronts is random, so that the component distributions of each are not related to the other. The fraction of mutual surface of the left and right fronts which form i-i contacts is given by $f_i^{(L)} f_i^{(R)}$. The surface fractions should be equal to the volume fractions in the bulk, ϕ_i , as a first approximation. The adhesion resulting from an i-j contact would be given by $\sigma_{ij} f_i^{(L)} f_j^{(R)}$. The total adhesive strength would be given by

$$\begin{aligned} \sum_{i,j} \sigma_{ij} f_i^{(L)} f_j^{(R)} = & \sigma_{11} f_1^{(L)} f_1^{(R)} + \sigma_{12} f_1^{(L)} f_2^{(R)} \\ & + \sigma_{13} f_1^{(L)} f_3^{(R)} + \sigma_{21} f_2^{(L)} f_1^{(R)} \\ & + \sigma_{22} f_2^{(L)} f_2^{(R)} + \sigma_{23} f_2^{(L)} f_3^{(R)} \\ & + \sigma_{31} f_3^{(L)} f_1^{(R)} + \sigma_{32} f_3^{(L)} f_2^{(R)} \\ & + \sigma_{33} f_3^{(L)} f_3^{(R)} - A(f_i) \end{aligned} \quad (1)$$

for a three component system. For a two component system

$$\begin{aligned} f_i^{(L)} &= f_i^{(R)} = f \\ f_j^{(L)} &= f_j^{(R)} = 1-f. \end{aligned}$$

The limiting case of no adhesion between immiscible phases of a two component blend may be examined by setting $\sigma_{12} = \sigma_{21} = 0$ but $\sigma_{11} \neq 0$ and $\sigma_{22} \neq 0$. Equation (1) then becomes

$$\sum_{i,j} \sigma_{ij} f_i^{(L)} f_j^{(R)} = \sigma_{11} f^2 + \sigma_{22} (1-f)^2 = A(f). \quad (2)$$

Based on information to date, one would not believe that polypropylene and low density polyethylene are miscible. The limiting case described by equation (2) will be used to evaluate the correlation by comparison with data from low density polyethylene-polypropylene blends.

III. Materials and Experimental Procedures

Materials and Additives

Virgin materials were used to simulate scrap plastic material as was done in previous studies (1,6). The various polymers used are described in Table I. All the properties listed were supplied by the manufactures except for the melt index of the polypropylene which was determined in the laboratory using ASTM D1238 test "L" (16). The DFD, DYNH, and DYNH-1 low density polyethylenes have similar properties and were used interchangeably.

The melt index, MI, of a polymer is inversely related to its viscosity (17). The viscosities of the polymers in the melted blend affect the dispersion of the phases. The more similar the melt indices of the polymers are, the more the phases of the blend should intermix.

The additives used to modify the blends were selected on the basis of information in the literature. The literature stated that the Renflex materials consist of an amorphous rubber and crystalline polypropylene with a third polymer which "compatibilizes" the other two. The materials "reportedly combine high elongation, tensile and tear properties with low flexural modulus and good abrasion resistance" (18). It was speculated that the third polymer

Table I
Materials Used

<u>Generic Type</u>	<u>Designation</u>	<u>Source</u>	<u>Designation Used in Thesis</u>	<u>Description</u>
Low Density Polyethylene	DYNH	Union Carbide	DYNH, LDPE	$\rho=0.917$ g/cc MI=1.2
Low Density Polyethylene	DFD	Union Carbide	DFD, LDPE	$\rho=0.917$ g/cc MI=2.0
Low Density Polyethylene	DYNH-1	Union Carbide	DYNH-1, LDPE	$\rho=0.918$ g/cc MI=2.0
Polypropylene	Rexene	El Rexene	PP	MI=2.5
Ethylene- Propylene Rubber	EPCAR 306	Goodrich	EPCAR 306, EPR	Low Molecular Weight Polymer, Weight % Ethylene- 60%
Ethylene- Propylene- Nonconjugated Diene Copolymer	EPCAR 847	Goodrich	EPCAR 847, EPDM	High Molecular Weight Polymer, Block-Like Behavior, Weight % Ethylene- 71%, Weight % ENB - 4%, $\rho=0.880$ g/cc
PP/Rubber Blend	Renflex D140	Ren Plastics	Renflex D140	$\rho=0.87$ g/cc, MI=1.7
PP/Rubber Blend	Renflex D150	Ren Plastics	Renflex D150	$\rho=0.87$ g/cc, MI=3.0

mentioned in the material description might be used to "compatibilize" blends of low density polyethylene and polypropylene. Two Renflex materials, Renflex D140 and D150, with different viscosities were selected for study.

The EPCAR 306 is an ethylene-propylene copolymer and was selected for study since previous work had indicated that ethylene-propylene rubbers can improve the elongation in polyethylene-polypropylene blends (4,6). The EPCAR 847 material is an ethylene-propylene-ethylidene norbornene terpolymer. This copolymer exhibits block-like behavior because of the relatively large percentage of ethylene present. The ethylene blocks may be long enough to crystallize and, hence, increase the tensile strength of the copolymer. Some literature and a patent indicate that the crystallinity of such terpolymers can result in improved tensile and elongation properties in some blends (7,13).

Blend Preparation

A Brabender Plasticorder was used to melt and mix blends of 50/50 weight percent polypropylene/DYNH polyethylene with 0, 10, and 20 weight percent additive. The laboratory mixer simulated the mixing of a commercial Banbury mixer. The experimental procedures used were similar to those used by Robertson and Vinson (1,6). Forty to forty-five grams of polymer pellets, including additive,

were hand mixed and placed in the Brabender. The blends were mixed at a setting of 190°C for 10 minutes at a rotor speed of 20 rpm.

Blends were also prepared in a Killion extruder. The four barrel temperature controls were all set at 430°C (~ 220°C). Most blends were made using a plasticating screw. A diagram and the dimensions of the screw appear in Figure 1. The extruder motor had a five-amp limit, and all the blends were mixed at that limit. The screw speed ranged from 15 to 26 rpm, depending upon the materials being blended. The extrudate was cooled in an ice bath and then pelletized by a Killion pelletizer. The pelletizer was equipped with a variable speed intake.

Two blends were prepared using a two staged fluted screw to evaluate the effect of more intensive mixing. This screw increased the shearing force exerted upon the blends. A diagram and the dimensions of the two staged screw appear in Figure 1. These blends were prepared at the same temperature settings used in preparing the other extruded blends. The screw speed ranged from 10 to 18 rpm at the five-amp motor current limit. These blends were cooled and pelletized in the same manner as mentioned above.

Sample Preparation and Mechanical Testing

Samples for mechanical testing were prepared from

Plasticating Screw

Two-Stage Fluted Screw

Figure 1. Screws used in processing extruded blends.

the blends by compression molding and injection molding to evaluate different processing techniques. The blends made using the Brabender Plasticorder were compression molded. The blends made using the Killion extruder were injection molded.

A Carver hand press was used to compression mold the blends. The press was heated to approximately 205°C, the blend was melted and compressed into a sheet. The cooling time for each sheet was approximately 45 minutes. The 50/50 polypropylene/DYNH low density polyethylene blends and the blends with Renflex D140 and D150 additives were molded into sheets 1/8 inch thick. Three to four batches of each of these blends were made in order to produce the appropriate number of sheets. Four ASTM D-1708-66 "dog bone" specimens were cut from each sheet using a cutting die. It was determined that Renflex containing samples of approximately 0.015 inch thickness yielded results similar to those of the 1/8 inch samples; therefore, the blends with EPCAR 306 and 847 were molded into sheets of about 0.015 inch thickness. One batch of each of these blends was made in order to produce the appropriate number of sheets. Twelve to sixteen ASTM D-638-68 Type IV "dog bone" specimens were cut from each 0.015 thick sheet using a cutting die. All of the 1/8 inch thick "dog bone" specimens were tested on an Instron, model type TTC, at a

crosshead speed of 1 inch per minute. All of the 0.015 inch thick "dog bone" specimens were tested on an Instron, model type TM, at a crosshead speed of 1 inch per minute. The cross-sectional area of each sample was carefully determined before testing.

Blends made using the Killion extruder were placed into a Van Dorn ram type injection molding machine which was outfitted with a mold that produced a "dog bone" ASTM D638-68 Type I 1/8 inch thick sample and an impact testing sample. The mold was cooled with tap water. The injection molder was run with barrel set points of 400° F (~205°C). for most blends; however, 50/50 blends were also molded with set points of 450°F and 500°F to evaluate the effect of molding temperature. The control settings used to process the blends are presented in Table II. The temperature settings of the injection molder dictated the pressure settings for the blends in order to prevent under filling of the mold or flashing.

One- and two-gated samples were made for each blend at each set of processing conditions by opening or closing the runners into the mold. Both types of sample were made from a single batch of each blend. The two-gated samples had a weld-line, whereas the one gated-samples had no weld-line. Previous studies indicate that specimens with weld-lines have lower tensile strength and percent elongation

Table II

Control Settings Used in Processing Injection Molded Samples

<u>Rear Barrel</u> <u>Temperature, °F</u>	<u>Front Barrel</u> <u>Temperature, °F</u>	<u>Mold Filling</u> <u>Time, Seconds</u>	<u>Compression</u> <u>Cycle Time, Seconds</u>	<u>Cooling Cycle</u> <u>Time, Seconds</u>
400	400	10	2.7	30
400	450	10	2.7	35
420	500	10	2.7	40 to 45

than samples without weld-lines because of poor adhesion across the polymer fronts (13,14). The injection molded samples were tested on an Instron, model type TTC, at a crosshead speed of 1 inch per minute.

Data Reduction

The mechanical properties of blends were calculated from tensile load versus crosshead movement curves obtained from the Instrons during testing. A typical tensile load versus crosshead movement curve is diagramed below.

The tensile strength at yield was calculated by dividing the tensile load at the yield point by the original cross-sectional area of the sample. The percent elongation at break was calculated by dividing the crosshead movement until break by the original gauge length of the sample. The gauge length used for the compression molded 1/8 inch thick samples was 2.0 inches, and the gauge length used for the compression molded 0.015 inch thick samples was 0.69 inches. The gauge length used for the injection

molded samples was 2.625 inches. The initial modulus was calculated using a method outlined in the ASTM Handbook (19). The initial modulus is defined as the slope of a line tangent to the initial portion of the curve of tensile load versus crosshead movement multiplied by the original gauge length and divided by the original sample cross-sectional area. The resilience, also called the energy to yield, is a measure of the energy absorbed by the material prior to yield (20). The resilience is a measure of the ability of a material to absorb energy in the elastic range. The resilience may be equated to potential energy which can be recovered. The resilience was calculated using the formula

$$\text{Resilience} = \frac{\text{Area}}{(\text{Gauge Length})(\text{Cross-Sectional Area})}$$

"Area" refers to the area under the curve between the start point and yield point, as indicated by the cross-hatched area in the diagram on page 22. The area was determined by hand integration. The original gauge length and cross-sectional area of the sample were used in the calculations.

Sources of Error

One source of error was the uncertainty of the original gauge length of the samples. An extensimeter was not used in the tensile tests. When an extensimeter

is used, the gauge length is the section of the sample located between the extensometer blades. The gauge length is assumed to be the measured length of the narrow section of the "dog bone" specimen between the inner fillets when an extensometer is not used. However, the material forming the fillets of the sample do contribute to the observed behavior. The "effective" gauge length may not be the same as the measured gauge length used in making calculations.

The percent elongation, initial modulus and energy to yield are affected by this uncertainty of the gauge length. However, it is not inappropriate to ignore this here since the main objective was to determine trends in the mechanical properties.

Another source of error was the scattering observed in the mechanical properties. Bubbles and other small defects, which can affect the mechanical properties, such as tensile strength and percent elongation, contributed to this scattering. The defects are products of processing and sample preparation and cannot always be eliminated by altering processing techniques. Data from samples with observable defects were deleted from calculations since these samples represented atypical behavior. The scattering noted in the data was reduced after applying this bias.

Hand-drawn slopes were used to determine the modulus. The moduli values are not very reproducible since

this is a crude way of determining these values. Error of approximately 10% can be expected in these values and the method used to obtain the moduli accounts for the scattering found in this data.

IV. Results

Summary

Previous work has shown that polyolefins are the major constituent of waste plastic materials. Even though the various polyolefins have similar chemical structures, they are evidently immiscible with each other, and, as a result, their blends do not generally have attractive mechanical properties. However, a significant increase in elongation was noted in blends of low density polyethylene and polypropylene modified with ethylene-propylene rubber as compared to unmodified blends (6). From this work, it was concluded that block or block-like copolymers containing monomer units of the homopolymers to be blended showed the most promise of being good "compatibilizing" agents. The patent literature also supports this conclusion (1). A study of the effects of several copolymers upon low density polyethylene-polypropylene blends was initiated and the results of these studies are given here. Tables of the values of the measured physical properties and standard deviations of compression molded and one- and two-gated injection molded blends are listed in the Appendix.

Mechanical Properties of Compression Molded Blends

Three basic types of additives were studied: ethylene-propylene rubbers blended with polypropylene, ethylene-propylene rubber, and a block-like ethylene-propylene-diene terpolymer. The designations used to identify the materials are presented in Table I. The copolymers were blended in zero, ten or twenty weight percent amounts with 50/50 weight percent low density polyethylene (DFD)/polypropylene. Twelve to twenty-five samples were tested for each blend.

The tensile strength and percent elongation data are plotted against the weight percent additive of these blends in Figure 2. Renflex D140, Renflex D150, EPCAR 306, and EPCAR 847 were used to modify the blends.

The results from blends modified with Renflex D140 were ambiguous. Both tensile strength and elongation were improved when 10% Renflex D140 was added, but tensile strength generally declined below or to the values of unmodified blends when 20% was added.

The Renflex D150 additive causes the tensile strength and elongation to increase slightly. From the trends it can be concluded that this modifier does not significantly improve the interfacial adhesion between polypropylene and low density polyethylene.

The Renflex compounds contain an unknown amount of

Figure 2. Variation of tensile strength and percent elongation with weight percent additive in compression molded blends.

polypropylene blended with an ethylene-propylene rubber. Polypropylene has a higher tensile strength than low density polyethylene. Blends of higher polypropylene content have higher tensile strengths and elongations than blends of 50/50 low density polyethylene/polypropylene. The polypropylene from the Renflex additives increased the weight percent of polypropylene in the blend. The increase in tensile strength and percent elongation noted in blends modified with Renflex D140 and D150 may be partially attributed to the effect of the additional polypropylene present in the blends. The individual contributions of the ethylene-propylene rubber, the third "compatibilizing" polymer, and the polypropylene in these modifiers cannot be separated. However, the increase in tensile strength due to the presence of thirty-three weight percent polypropylene in the Renflex compounds was estimated from information in Figure 7. The tensile strength could increase approximately 45 psi in 10% additive blends and 94 psi in 20% additive blends.

The percent elongation of blends modified with EPCAR 306 increased with increasing modifier content. The tensile strength rose slightly at 10% EPCAR 306 and then declined at 20% additive to a value much below the tensile strength of the unmodified blend. The addition of rubbery compounds, such as the modifiers used here, would be

expected to lower tensile strength and might be expected to improve elongation as modifier content increases. The blend of 20% EPCAR 306 behaves in this manner. However, the behavior of the blend with 10% EPCAR 306 indicates that other mechanisms may have contributed to the increase in tensile strength.

The tensile strength decreased and percent elongation increased with increasing additive in blends modified with EPCAR 847. This behavior is due in part to the addition of a rubbery compound to the blend. The percent elongation increased by up to a factor of 35 times that of unmodified blends. This dramatic increase in elongation was speculated to result partially from improved interfacial adhesion between the polypropylene and low density polyethylene phases of the blend.

Due to the long cooling cycle, the compression molded blends were rather crystalline since annealing occurred during this elapsed time. The crystallinity affects the blend morphology and properties. Crystalline materials are more brittle and have higher tensile strength than more amorphous materials made of the same polymer. The trends observed in the compression molded blends may have been partly related to the crystallinity of these samples.

The compression molded data above showed quite a bit of scattering which was attributed to sample imperfections,

variation in the crystallinity of blends, and possibly to polymer chain orientation. In an attempt to obtain more consistent results and to test other processing methods, it was decided that injection molded samples of these blends should be examined.

Mechanical Properties of Two-Gated Injection Molded Blends

Two-gated injection molded samples have a weld-line and tend to fail at this weld-line. These samples were made to evaluate any increased adhesion across the weld-line due to the presence of the additives. Improved adhesion across the weld-line should cause an increase in both tensile strength and elongation. Seven to fifteen samples of each blend at each set of processing conditions were tested.

Some of the two-gated injection molded samples exhibited a "tab" formation at the weld-line. The "tab" was observed after break and was apparently due to one polymer front penetrating another during molding. A diagram of this phenomenon appears below. One polymer front appeared

"Tabbed" Sample After Break

to consistently penetrate the other. One explanation of this phenomenon is that one polymer front may have gained

more momentum while entering the mold. Another possible explanation is that one end of the "dog bone" mold may have been cooled more rapidly causing the other front to flow around the cooled material.

The samples with "tabs" had mechanical properties higher than those of samples which had no "tabs." This was due in part to the increased surface area at the break point. The surface area at the break point of a "tabbed" sample is greater than the cross-sectional area of the sample. The "tab" is subject to both tensile and shear forces. The "tab" also elongated slightly during testing, complicating any calculations of the area which was in tension or shear.

The gates of the runners leading into the mold were adjusted to constrict the polymer melt flow, to eliminate the "tab" formations. This was done by trial and error for each blend. Samples with noticeable "tabs" were not used in the analysis since the data could not be properly analyzed.

The two-gated blends were processed at three different temperature settings to evaluate the effect of this variable on the resultant properties. Higher temperatures may lead to decreased properties since polyolefins are subject to oxidative degradation. On the other hand, the higher processing temperatures might allow for more mixing

and diffusion at the weld-line. This could increase adhesion.

Renflex D140, Renflex D150, EPCAR 847, and EPCAR 306 were blended in zero, ten, or twenty weight percent amounts with 50/50 low density polyethylene (DFD)/polypropylene. Blends with EPCAR 306 processed at a temperature setting of 500°F developed bubbles and were not tested. The bubbles were apparently the result of decomposition or of the vaporization of some compound in the EPCAR modifiers. Bubbles did not appear in the Renflex modified blends processed at these temperature settings. All samples were processed in the same manner. The tensile strength, percent elongation and initial modulus are plotted against weight percent Renflex D140 and D150 in Figure 3 and against weight percent EPCAR 847 and 306 in Figure 4.

In general, the tensile strength and elongation increased with increasing modifier content in blends with Renflex D140, Renflex D150 and EPCAR 847 additives. In general, the tensile strength decreased and the percent elongation increased as EPCAR 306 was added to the blend. As processing temperature increased, the tensile strength, percent elongation, and initial moduli declined in almost all blends. The initial moduli of blends with Renflex D140 were higher at higher processing temperatures. The initial moduli declined with increasing modifier content, in general.

Figure 3. Variation of tensile strength, percent elongation, and initial modulus with weight percent Renflex DI40 and DI50 in two-gated injection molded blends processed at various temperatures.

Figure 4. Variation of tensile strength, percent elongation, and initial modulus with weight percent EPCAR 847 and 306 in two-gated injection molded blends processed at various temperatures.

These trends suggest that Renflex D140, Renflex D150 and EPCAR 847 do increase adhesion across the weld-line, resulting in improved tensile strength and elongation. The rubbery nature of these materials is in part responsible for the increase in elongation and decrease in initial moduli. The increase in elongation noted in blends modified with EPCAR 306 is probably due simply to the effect of adding a rubbery material since the tensile strength of these blends decline instead of improve. As processing temperatures were increased the mechanical properties of the blends were reduced. The higher temperatures apparently did not cause increased mixing or diffusion at the weld-line, but merely increased the amount of thermal degradation.

No blends other than those of 50/50 low density polyethylene/polypropylene were modified with Renflex D140 and D150. The resultant mechanical properties were comparable with blends modified with EPCAR 847 and EPCAR 306. Part of the improvement in properties of blends made with the Renflex compounds may be the result of the additional polypropylene in the blend. The third polymer, mentioned in the literature, present in these compounds does not aid in compatibilizing low density polyethylene and polypropylene blends significantly.

Two-gated blends of 75/25 polypropylene/DFD low

density polyethylene were modified with EPCAR 306 and EPCAR 847. The tensile strength, percent elongation, and initial moduli are plotted against weight percent additive in Figure 5. The tensile strength of blends modified with EPCAR 847 increased at 10% additive. The tensile strength then declined but remained above the value of the unmodified blend. This behavior is similar to a trend described in patent literature of a similar blend modified with an EPDM terpolymer (7). The tensile strength of blends modified with EPCAR 306 decreased with added "compatibilizer." The percent elongation increased with increased EPCAR 847 additive. The percent elongation remained essentially the same in blends modified with EPCAR 306. The initial moduli of blends modified with EPCAR 847 and with EPCAR 306 increased at 10% additive then decreased at 20% additive.

EPCAR 847 evidently increases the adhesion across the weld-line in blends of 75/25 polypropylene/low density polyethylene based on the rise in tensile strength and moduli in blends with 10% EPCAR 847. The EPCAR 306 does not appear to increase the interfacial adhesion in the blends or across the weld-line. From these results one would conclude the EPCAR 306 does not "compatibilize" blends with high polypropylene content.

Two-gated blends of 25/75 polypropylene/low density polyethylene were modified with EPCAR 847 and EPCAR 306.

Figure 5. Variation of tensile strength, percent elongation, and initial modulus with weight percent EPCAR 847 and 306 in two-gated injection molded blends.

Both DFD and DYNH-1 polyethylene were used to make blends. The tensile strength, percent elongation and initial modulus are plotted against the weight percent additive in Figure 6.

The increase in tensile strength and percent elongation in blends modified with EPCAR 847 indicate that the additive increased the adhesion across the weld-line. The percent elongation improved by up to a factor of 22 times in blends modified with EPCAR 847. The EPCAR 306 did not significantly affect the tensile properties but did improve the percent elongation. Since the tensile strength did not decline dramatically, as it did in other blends modified with EPCAR 306, it might be concluded that the adhesion was improved slightly at the weld-line. Since the tensile strengths of two-gated blends were roughly half the values of the one-gated blends, it appears that the bulk properties effect the tensile strength at the weld-line. Rubbery additives are known to lower the tensile strength of polyolefins and to improve their elongation. Rubbery additives would be expected to have the above mentioned effect on both bulk and weld-line properties except when the additive improves interfacial bonding across the weld-line. The EPCAR 306 may provide enough adhesion across the weld-line to counteract the lowering of the bulk tensile strength due to the rubbery nature of the additive. The

Figure 6. Variation of the tensile strength, percent elongation, and initial modulus with weight percent EPCAR 847 and 306 in two-gated injection molded blends.

initial moduli of blends made with DYNH-1 declined very little with increasing modifier content.

Blends made with DFD low density polyethylene paralleled the behavior of blends made with DYNH-1 low density polyethylene but had slightly higher tensile strengths and percent elongations. It is interesting to note that DFD polyethylene has lower tensile strength and percent elongation than does DYNH-1 polyethylene, but blends with DFD have higher tensile strength and percent elongation than blends with DYNH-1. This would indicate that blends of DFD low density polyethylene and polypropylene develop a morphology which allows for improved transfer of stress and energy as compared to the blends made with DYNH-1.

Paul's correlation for determining the tensile strength of samples with weld-lines was plotted with actual tensile strength data from polypropylene/DFD low density polyethylene blends in Figure 7. Since blends of 25/75 polypropylene/low density polyethylene with 20% EPCAR 847, 10% EPCAR 306, and 20% EPCAR 306 were made with DYNH-1 polyethylene, the tensile strength values were estimated for blends made with DFD polyethylene. These values were estimated by assuming that the parallel behavior of the DFD and DYNH-1 blends continued. Weight fractions of polypropylene and low density polyethylene were used in

Figure 7. Variation of tensile strength for various low density polyethylene/polypropylene blends modified with EPCAR 847 and 306 in two-gated injection molded blends.

the weld-line strength formulation since the volume fractions and weight fractions are essentially the same. The percent deviation of the calculated tensile strengths and the experimentally obtained tensile strengths ranged from 0.3% to 13.2%, with the largest discrepancies occurring in blends of 50% or more polypropylene. This correlation is in good agreement with the tensile strength data when the assumption is made that polypropylene and low density polyethylene are completely immiscible with no interfacial adhesion.

Mechanical Properties of One-Gated Injection Molded Blends

One-gated samples were made for the purpose of comparison with results from compression molded and two-gated injection molded blends. Four or five samples of each blend at each set of processing conditions were tested. Previous experimental work has shown that an interpenetrating or a cocontinuous network of polymers can possibly be formed when the polymer mixture is sheared and quickly cooled (21). Extruded and injection molded specimens have been known to develop this type of morphology. Interpenetrating and cocontinuous polymer networks of immiscible blends have separate phases which are in contiguous contact. The morphology provides for better energy and stress transfer through the blend, though not necessarily across

the phases.

Continuous morphology also allows for energy and stress transfer through each phase but not necessarily between phases. Two continuous dispersed phases characterize this morphology. The domains may be either a set of continuous layers or continuous rods dispersed throughout a continuous matrix phase.

A study of the morphology developed using different processing techniques was beyond the scope of this research; however, some observations were made which seem to suggest that continuous or interpenetrating networks may have developed in the one-gated specimens. When a section of cooled extrudate of 50/50 polypropylene/low density polyethylene was stretched until it broke, the broken end frayed into several very thin filaments, similar to cord or string. Another observation was made during the mechanical testing of samples. Some samples began showing signs of delamination as they were tested. A thin layer of polymer would occasionally begin to crack and peel at the sample surface. This layer could be peeled off and sometimes another layer below had begun to peel. These delamination examples indicate that the specimens were multiphased and that the phases appeared to be semicontinuous layers or filaments.

If a continuous or interpenetrating polymer

network were formed, the blends might have resultant mechanical properties which would be similar to those expected for a miscible blend. Each polymer might be expected to transfer stress and energy proportional to its volume fraction in the blend, independently of other phases.

The actual percent elongation at break of one-gated specimens were not determined since the specimens did not rupture before the Instron reached its maximum crosshead travel. The percent elongation achieved in these samples ranged from 346% to 433%. The variation of the percent elongation was due to the change in maximum possible crosshead travel when different grips were used.

Two basic types of tensile load versus crosshead movement curves were observed. Diagrams appear below. All the one-gated blends exhibited behavior typical of one of these curves. Low density polyethylene-like behavior was observed in 50/50 polypropylene/low density polyethylene blend with 20% EPCAR 306 additive processed at a setting of 400°F and all 25/75 polypropylene/low density polyethylene blends. The tensile strengths were determined for all blends at the point indicated in the diagrams below.

One-gated samples of 50/50 polypropylene/DFD low density polyethylene were modified with Renflex D140,

Polypropylene or Polypropylene-Like Behavior

Low Density Polyethylene-Like Behavior

Renflex D150, EPCAR 847, and EPCAR 306. The tensile strength and initial moduli are plotted against weight percent Renflex D140 and D150 in Figure 8, and against weight percent EPCAR 847 and 306 in Figure 9. The energy to yield for these blends are presented in Table III. Blends modified with 20% EPCAR 847 processed at the 500°F setting and modified with 10% EPCAR 306 processed at 500°F developed bubbles and were not tested.

The tensile strength and initial moduli usually decreased as the weight percent modifier increased. Blends modified with Renflex D150 and EPCAR 847 exhibited a slight improvement in initial modulus at 20% additive as

Figure 8. Variation of tensile strength and initial modulus with weight percent Renflex D140 and D150 in one-gated injection molded blends processed at various temperatures.

Figure 9. Variation of tensile strength and initial modulus with weight percent EPCAR 847 and 306 in one-gated injection molded blends processed at various temperatures.

Table III

Energy to Yield in PSI of 50/50 PP/LDPE Blends

<u>Blend</u>	<u>Processing Set Point</u>		
	<u>400° F</u>	<u>450° F</u>	<u>500° F</u>
50/50 PP/LDPE	282	264	230
50/50 PP/LDPE With 10% EPCAR 847	687	646	564
50/50 PP/LDPE With 20% EPCAR 847	660	622	-
50/50 PP/LDPE With 10% EPCAR 306	590	482	-
50/50 PP/LDPE With 20% EPCAR 306	50.2	708	598
50/50 PP/LDPE With 10% Renflex D140	662	532	498
50/50 PP/LDPE With 20% Renflex D140	598	616	520
50/50 PP/LDPE With 10% Renflex D150	594	720	552
50/50 PP/LDPE With 20% Renflex D150	633	982	816
100% PP	370	-	-
100% LDPE	25.4	-	-

compared to 10% additive amounts. The energy to yield increased except when low density polyethylene-like behavior was observed. The energy to yield declined slightly as the EPCAR 847 content was increased from 10% to 20%. Rubbery compounds in general lower the tensile strength and initial modulus of blends formed with materials which are less rubbery (9). They also can improve energy to yield and impact strength. Overall, the additives used had these effects upon blends of 50/50 polypropylene/low density polyethylene.

In general, tensile strength, initial moduli, and energy to yield decreased as the processing temperature increased. Blends modified with Renflex D150 showed a slightly inverted trend with blends processed at a setting of 450°F having the highest property values. In most blends, apparently thermal degradation increased at higher processing temperatures causing a decline in mechanical properties. Some mechanisms other than thermal degradation are affecting the properties of blends modified with Renflex D150.

Blends of 75/25 and 25/75 polypropylene/low density polyethylene were modified with EPCAR 847 and EPCAR 306. Blends with Renflex D140 and D150 were not made since these compounds were not thought to improve the blend properties sufficiently, as was explained previously. Tensile

strength and initial modulus are plotted against weight percent additive for both types of blends in Figure 10. The energy to yield of these blends are presented in Table IV. The tensile strength usually declined as EPCAR 847 or EPCAR 306 were added to both types of blends, as would be expected since the modifiers are rubbery materials. The tensile strengths of blends made with 75% DFD polyethylene and blends made with 75% DYNH-1 polyethylene which were modified with EPCAR 847 paralleled each other. The initial moduli of blends of 75/25 polypropylene/low density polyethylene generally declined as modifier was added. The trend is probably a result of adding a rubber to the blends. The trends of the initial moduli of 25/75 polypropylene/low density polyethylene were a bit ambiguous. The moduli increased as the EPCAR 847 and EPCAR 306 content increased in blends made with DYNH-1 polyethylene, and the moduli declined as the EPCAR 847 was added in blends made with DFD polyethylene. The polyethylenes are not exactly the same materials and the EPCAR 847 additive apparently does not interact with them in the same manner.

The energy to yield of 75/25 polypropylene/low density polyethylene blends modified with EPCAR 847 remained essentially unchanged as additive content increased. The energy to yield increased slightly when 10% EPCAR 306 was added to 75/25 polypropylene/low density polyethylene

Figure 10. Variation of tensile strength and initial modulus with weight percent EPCAR 847 and 306 in one-gated injection molded blends.

Table IV

Energy to Yield of 75/25 and 25/75 PP/LDPE Blends

<u>Blend</u>	<u>Energy to Yield</u> <u>(PSI)</u>
75/25 PP/LDPE (DFD)	504
75/25 PP/LDPE (DFD) With 10% EPCAR 847	496
75/25 PP/LDPE (DFD) With 20% EPCAR 847	504
75/25 PP/LDPE (DFD) With 10% EPCAR 306	558
75/25 PP/LDPE (DFD) With 20% EPCAR 306	542
25/75 PP/LDPE (DFD)	46.2
25/75 PP/LDPE (DYNH-1)	45.6
25/75 PP/LDPE (DFD) With 10% EPCAR 847	31.5
25/75 PP/LDPE (DYNH-1) With 10% EPCAR 847	27.4
25/75 PP/LDPE (DYNH-1) With 20% EPCAR 847	29.9
25/75 PP/LDPE (DYNH-1) With 10% EPCAR 306	23.8
25/75 PP/LDPE (DYNH-1) With 20% EPCAR 306	26.9

and leveled out at 20% additive. The blends of 25/75 polypropylene/low density polyethylene exhibited low density polyethylene-like behavior and had very low energy to yields. The energy to yield decreased when 10% EPCAR 874 or EPCAR 306 were added. Then the composition of EPCAR 847 or EPCAR 306 was increased to 20%, the energy to yield increased slightly over the 10% additive values.

The energies to yield of blends which exhibited polypropylene-like behavior were higher than would be expected. The values were above the energies to yield of both polypropylene and polyethylene and rose, in general, as the modifier content was increased. Blends which showed low density polyethylene-like behavior had comparatively low energy to yield values.

Plots of tensile strength data versus weight percent polypropylene of blends modified with EPCAR 847 and EPCAR 306 appear in Figure 11. The tensile strengths of the blends appear to be linearly located between the tensile strengths of the pure homopolymers. Polypropylene and low density polyethylene do not appear to be miscible based on previous information. Therefore, it can be concluded that the linear relationship is the result of some other phenomenon. The morphology of one-gated blends may be the cause of this behavior. Blends with a continuous or interpenetrating polymer network might behave in a

Figure 11. Variation of tensile strength for various low density polyethylene/polypropylene blends modified with EPCAR 837 and 306 in one-gated injection molded blends.

manner similar to the behavior shown in Figure 11. The decline in tensile strength of the blends modified with rubbery materials can be seen as a consistent trend in these plots. The rubbery additive is probably present in both phases as well as at the phase boundaries. Therefore, the bulk tensile properties of each phase are lowered. Any improvement in adhesion between the phases would not be discernable in one-gated samples because the apparently developed morphology allows for energy transfer along each phase in the direction of testing. This morphology would not necessitate energy transfer between phases which may be facilitated by improved adhesion.

Effect of Mixing

Since the mixing process in melt blending determines the size of the polymer domains, which in turn affects the mechanical properties of the blends, a brief study of the effect of mixing was initiated. A large batch of 50/50 polypropylene/low density polyethylene was melt blended in the extruder using the simple plasticating screw. Part of that batch was run through the extruder a second and third time. The tensile strengths and percent elongations are tabulated in Table V. A steady rise in both percent elongation and tensile strength was noted through the third melt blending, indicating that domains

Table V
Effect of Multiple Mixings*

<u>Times Through Extruder</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>
1	1144	2.8	84000
	74	0.4	3360
2	1282	3.3	77950
	75	0.4	4380
3	1373	3.6	83160
	51	0.5	970

*Key: Mechanical Property
Standard Deviation

were becoming progressively more intermixed. It is speculated that this trend will eventually either level out or begin to decrease as mixing is continued because equilibrium will be reached or the mixing will lead to degradation and a subsequent loss of mechanical strength.

There was little change in the initial moduli.

A screw which increases the shearing force on the melt was used to mix blends of 50/50 polypropylene/DYNH-1 low density polyethylene with 0 or 10% EPCAR 847. A tabulation of these results and the results of similar blends mixed with the simple plasticating screw are presented in Table VI. Mixing with the high shear screw resulted in a lowering of the mechanical properties of the pure polymers, apparently caused by increased degradation. The degradation could be the result of either chain scission or thermal oxidation. The 50/50 blend of DYNH-1 polyethylene/polypropylene made with the high shear screw had lower physical properties than the 50/50 DFD polyethylene/polypropylene blend made with the plasticating screw. Conversely, the 50/50 DYNH-1 polyethylene/polypropylene blend with 10% EPCAR 847 compatibilizer processed with the high shear screw had improved physical properties when compared to the same blend made with DFD polyethylene and processed with the plasticating screw. These results indicate that mixing with the high shear screw can cause degradation and

Table VI
Effect of Shear Force Upon Mixing*

<u>Blend</u>	<u>Number Of Gates</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>
100% PP	2	3858 18	+330	143400 7845
100% PP - High Shear	2	3268 116	18.4 5.0	135120 7930
100% DFD	2	1174 15	81.6 1.6	16375 655
100% DYNH-1 - High Shear	2	1020 77	77 23	20250 6650
100% DYNH-1	2	1555 71	194 15	30335 -
50/50 DFD/PP	2	1137 31	3.5 0.4	83920 5000
50/50 DYNH-1/PP - High Shear	2	1017 59	3.3 0.3	74510 4875
50/50 DFD/PP With 10% EPCAR 847	2	1123 25	5.2 0.9	54530 4560
50/50 DYNH-1/PP With 10% EPCAR 847 - High Shear	2	1404 122	14.4 4.7	62185 2870

*Key: Mechanical Property
Standard Deviation

and decline in physical properties except in blends with EPCAR 847 additive. It can be concluded that mixing with a high shear screw can result in improved blend properties or sometimes in physical degradation of the individual polymers.

V. Conclusions and Recommendations

Based on the data gathered from a variety of blends processed in three different manners, it appears that EPCAR 847, a block-like ethylene-propylene-diene terpolymer, "compatibilizes" blends of low density polyethylene and polypropylene. The EPCAR 847 blends did show improved adhesion at the weld-line, especially in blends with a high polyethylene content. It can be inferred that adhesion at the interfacial boundaries of the blend components was improved by the presence of the EPCAR 847.

The Renflex compounds and EPCAR 306 do not appear to be promising agents for use in blending scrap plastics since adhesion at the weld-line of two-gated samples did not improve significantly. The improvements in mechanical properties of blends modified with either Renflex compound were thought to be due in large part to the polypropylene in the modifiers. Little proof of increased interfacial adhesion between polypropylene and polyethylene was observed. The EPCAR 306, an ethylene-propylene rubber, apparently did not significantly effect the adhesion of blend phases, except possibly in compression molded samples. The effect of EPCAR 306, or a similar material, upon the morphology of well-annealed crystalline blends might be studied.

Several general trends in the data were consistently observed. The addition of rubbery compounds usually reduces the blend tensile strength and increases the blend percent elongation, except in samples which have weld-lines where polymer fronts meet. Samples of blends with weld-lines modified with rubbery compounds can have an increase in both tensile strength and elongation. This simultaneous improvement is the result of improved adhesion between polymer fronts at the weld-line, and may indicate that the additive is also improving adhesion between the phases of immiscible polymers.

In general, it was noted that the mechanical properties of blends declined as processing temperatures were increased. This is thought to be the result of thermal oxidation, which is known to be a problem in processing polyolefins. Also, high shear mixing may cause degradation and a subsequent loss in mechanical properties. A study of the use of antioxidants to reduce the thermal oxidation should be initiated.

Physical properties also varied depending upon the processing technique used. In general, the properties of one processing method compared to another were as follows:

One-Gated Injection Molded Blends	>	Compression Molded Blends	>	Two-Gated Injection Molded Blends
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Processing methods were found to have a noticeable effect

on the blend properties evidently stemming from their effect on the morphology of the blend. In any plan to recycle scrap plastics, the processing methods should be carefully evaluated. One would not want to use blends of low density polyethylene and polypropylene to produce items with weld-lines based on information obtained in this research. In general, blend properties are poor at the weld-line.

The correlation for predicting the tensile strength of blends with weld-lines appears to work well based on comparison of data from polypropylene/low density polyethylene blends. The correlation could be used to predict the tensile strength in other types of blends. It is recommended that further studies of reliability and applicability of this correlation be initiated.

It is also recommended that studies be carried out using actual waste plastics instead of virgin materials since many polyolefinic wastes are already modified. Also, results indicate that different low density polyethylenes behave differently when blended. In this way the effects of combining various modifiers, as well as the effects of mixing various grades of homopolymers, could be evaluated.

Appendix

Table VII
Properties of Compression Molded Blends*

<u>Blend</u>	<u>Tensile Strength</u>	<u>Percent Elongation</u>
50/50 PP/DYNH	2329	11.2
	145	2.4
50/50 PP/DYNH	2490	25.8
With 10% Renflex D140	90	12.4
50/50 PP/DYNH	1783	16.4
With 20% Renflex D140	152	4.7
50/50 PP/DYNH	2331	14.0
With 10% Renflex D150	314	4.5
50/50 PP/DYNH	2350	20.4
With 20% Renflex D150	112	5.4
50/50 PP/DYNH	2149	173
With 10% EPCAR 847	74	159
50/50 PP/DYNH	1600	340
With 20% EPCAR 847	167	156
50/50 PP/DYNH	2565	19.1
With 10% EPCAR 306	193	5.4
50/50 PP/DYNH	1153	38.0
With 20% EPCAR 306	210	12.8

*Key: Mechanical Property
Standard Deviation

Table VIII

Properties of Two-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>
100% Rexene Polypropylene (400°F)	3858 18	+330	143400 7845
100% DFD Polyethylene (400°F)	1174 15	81.6 1.6	16375 655
50/50 LDPE (DFD)/PP (400°F)	1137 31	3.5 0.4	83920 5000
50/50 LDPE (DFD)/PP (450°F)	1043 68	2.5 0.2	99120 6590
50/50 LDPE (DFD)/PP (500°F)	830 41	2.9 0.2	82740 3530
50/50 LDPE (DFD)/PP with 10% EPCAR 847 (400°F)	1123 25	5.2 0.9	54530 4560
50/50 LDPE (DFD)/PP with 10% EPCAR 847 (450°F)	1187 11	4.6 0.9	59640 4460
50/50 LDPE (DFD)/PP with 10% EPCAR 847 (500°F)	1103 50	3.4 0.5	62580 1645
50/50 LDPE (DFD)/PP with 20% EPCAR 847 (400°F)	1262 21	8.1 0.6	59160 2420
50/50 LDPE (DFD)/PP with 20% EPCAR 847 (450°F)	1236 31	7.9 0.5	57750 2510
50/50 LDPE (DFD)/PP with 20% EPCAR 847 (500°F)	994 72	5.1 0.7	52390 3900
50/50 LDPE (DFD)/PP with 10% Renflex D140 (400°F)	1243 56	5.4 1.6	59830 2110
50/50 LDPE (DFD)/PP with 10% Renflex D140 (450°F)	1261 61	4.1 0.5	65625 2395

*Key: Mechanical Property
Standard Deviation

Table VIII (Cont'd.)

Properties of Two-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>
50/50 LDPE (DFD)/PP with 10% Renflex D140 (500°F)	1077 83	2.9 0.6	75940 2190
50/50 LDPE (DFD)/PP with 20% Renflex D140 (400°F)	1372 115	5.8 1.8	66600 2865
50/50 LDPE (DFD)/PP with 20% Renflex D140 (450°F)	1232 103	5.4 0.9	60145 1935
50/50 LDPE (DFD)/PP with 20% Renflex D140 (500°F)	1125 38	4.9 0.6	60815 1635
50/50 LDPE (DFD)/PP with 10% EPCAR 306 (400°F)	1243 76	4.5 1.0	76480 5020
50/50 LDPE (DFD)/PP with 10% EPCAR 306 (450°F)	1020 54	4.1 0.4	70085 3970
50/50 LDPE (DFD)/PP with 10% EPCAR 306 (500°F)	(No Data Due to Bubbles in the Samples)		
50/50 LDPE (DFD)/PP with 20% EPCAR 306 (400°F)	1022 23	5.4 0.1	67560 450
50/50 LDPE (DFD)/PP with 20% EPCAR 306 (450°F)	984 34	5.1 0.3	68040 970
50/50 LDPE (DFD)/PP with 20% EPCAR 306 (500°F)	(No Data Due to Bubbles in the Samples)		
50/50 LDPE (DFD)/PP with 10% Renflex D150 (400°F)	1231 43	4.1 0.3	72600 5925
50/50 LDPE (DFD)/PP with 10% Renflex D150 (450°F)	1134 64	3.3 0.4	72300 2870
50/50 LDPE (DFD)/PP with 10% Renflex D150 (500°F)	1068 102	3.1 0.5	66570 2740

*Key: Mechanical Property
Standard Deviation

Table VIII (Cont'd.)

Properties of Two-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>
50/50 LDPE (DFD)/PP with 20% Renflex D150 (400°F)	1180 39	5.5 1.0	57155 3260
50/50 LDPE (DFD)/PP with 20% Renflex D150 (450°F)	1166 72	4.3 0.5	56775 2685
50/50 LDPE (DFD)/PP with 20% Renflex D150 (500°F)	1105 52	3.9 0.3	58815 2200
100% DYNH-1 Polyethylene (400°F)	1555 71	194 15	30335 -
75/25 PP/LDPE (DFD) (400°F)	1979 125	5.4 0.8	83300 2280
75/25 PP/LDPE (DFD) with 10% EPCAR 306 (400°F)	1687 195	5.3 1.7	112480 5975
75/25 PP/LDPE (DFD) with 20% EPCAR 306 (400°F)	1526 69	6.2 0.8	74525 6460
75/25 PP/LDPE (DFD) with 10% EPCAR 847 (400°F)	2212 194	9.4 3.2	99425 4910
75/25 PP/LDPE (DFD) with 20% EPCAR 847 (400°F)	2025 143	14.9 4.6	88340 2725
25/75 PP/LDPE (DFD) (400°F)	893 42	5.1 0.5	69030 1985
25/75 PP/LDPE (DFD) with 10% EPCAR 847 (400°F)	1171 40	35.1 10.5	28530 1440
25/75 PP/LDPE (DYNH-1) with 10% EPCAR 847 (400°F)	1108 27	24.1 5.0	36010 1090
25/75 PP/LDPE (DYNH-1) with 20% EPCAR 847 (400°F)	1099 48	110.9 41.1	32535 1885

*Key: Mechanical Property
Standard Deviation

Table VIII (Cont'd.)

Properties of Two-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>
25/75 PP/LDPE (DYNH-1) (400°F)	829	4.7	42980
	69	1.0	2750
25/75 PP/LDPE (DYNH-1) with 10% EPCAR 306 (400°F)	898	11.2	30375
	64	1.8	1950
25/75 PP/LDPE (DYNH-1) with 20% EPCAR 306 (400°F)	826	14.9	29760
	19	1.9	1685
100% LDPE (DYNH-1) - High Shear (400°F)	1020	77	20250
	77	23	6650
100% PP - High Shear (400°F)	3268	18.4	135120
	116	5.0	7930
50/50 PP/LDPE (DYNH-1) - High Shear (400°F)	1017	3.3	74510
	59	0.3	4875
50/50 PP/LDPE (DYNH-1) with 10% EPCAR 847 - High Shear (400°F)	1404	14.4	62185
	122	4.7	2870

*Key: Mechanical Property
Standard Deviation

Table IX

Properties on One-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>	<u>Energy To Yield (PSI)</u>
50/50 PP/LDPE (DFD) (400°F)	2621 62	+330	83530 7840	282 20
50/50 PP/LDPE (DFD) (450°F)	2566 40	+330	88875 4755	264 8
50/50 PP/LDPE (DFD) (500°F)	2439 91	+330	60110 -	230 10
50/50 PP/LDPE (DFD) with 10% Renflex D140 (400°F)	2185 13	+330	63000 -	662 -
50/50 PP/LDPE (DFD) with 10% Renflex D140 (450°F)	2092 64	+330	63190 -	532 -
50/50 PP/LDPE (DFD) with 10% Renflex D140 (500°F)	2211 -	+330	64120 -	498 30
50/50 PP/LDPE (DFD) with 20% Renflex D140 (400°F)	2316 55	+330	65490 -	598 10
50/50 PP/LDPE (DFD) with 20% Renflex D140 (450°F)	2032 78	+330	52200 -	616 28
50/50 PP/LDPE (DFD) with 20% Renflex D140 (500°F)	1918 45	+330	62080 -	520 36
50/50 PP/LDPE (DFD) with 10% EPCAR 847 (400°F)	2414 111	+433	50140 -	687 35

*Key: Mechanical Property
Standard Deviation

Table IX (Cont'd.)

Properties of One-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>	<u>Energy To Yield (PSI)</u>
50/50 PP/LDPE (DFD) with 10% EPCAR 847 (450°F)	1966 16	+433	56960 2735	646 50
50/50 PP/LDPE (DFD) with 10% EPCAR 847 (500°F)	2118 43	+433	66335 1005	564 23
50/50 PP/LDPE (DFD) with 20% EPCAR 847 (400°F)	2128 74	+330	65450 -	660 52
50/50 PP/LDPE (DFD) with 20% EPCAR 847 (450°F)	1811 25	+330	58150 -	622 -
50/50 PP/LDPE (DFD) with 20% EPCAR 847 (500°F)	(No Data Due to Bubbles in the Samples)			
50/50 LDPE (DFD)/PP with 10% Renflex D150 (400°F)	2343 42	+433	63655 -	594 54
50/50 LDPE (DFD)/PP with 10% Renflex D150 (450°F)	2468 48	+330	56880 715	720 36
50/50 LDPE (DFD)/PP with 10% Renflex D150 (500°F)	2471 47	+330	54010 1930	552 22
50/50 PP/LDPE (DFD) with 20% Renflex D150 (400°F)	2227 27	+433	62160 1565	633 52

*Key: Mechanical Property
Standard Deviation

Table IX (Cont'd.)

Properties of One-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>	<u>Energy To Yield (PSI)</u>
50/50 PP/LDPE (DFD) with 20% Renflex D150 (450°F)	2442 41	+433	66150 3440	982 48
50/50 PP/LDPE (DFD) with 20% Renflex D150 (500°F)	2318 58	+433	64680 1910	816 36
50/50 PP/LDPE (DFD) with 10% EPCAR 306 (400°F)	2265 51	+330	71890 -	590 12
50/50 PP/LDPE (DFD) with 10% EPCAR 306 (450°F)	2174 42	+330	72655 -	482 14
50/50 PP/LDPE (DFD) with 10% EPCAR 306 (500°F)	(No Data Due to Bubbles in the Samples)			
50/50 PP/LDPE (DFD) with 20% EPCAR 306 (400°F)	2116 102	+330	70880 2165	50.2 2.1
50/50 PP/LDPE (DFD) with 20% EPCAR 306 (450°F)	1977 78	+433	67070 2120	708 16
50/50 PP/LDPE (DFD) with 20% EPCAR 306 (500°F)	1762 46	+330	51450 -	598 24
75/25 PP/LDPE (DFD) (400°F)	3098 85	+326	101050 4660	504 20
75/25 PP/LDPE (DFD) with 10% EPCAR 306 (400°F)	2502 76	+326	112270 6645	558 14

*Key: Mechanical Property
Standard Deviation

Table IX (Cont'd.)

Properties of One-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>	<u>Energy To Yield (PSI)</u>
75/25 PP/LDPE (DFD) with 20% EPCAR 306 (400°F)	2296 30	+326	85500 9770	542 6
75/25 PP/LDPE (DFD) with 10% EPCAR 847 (400°F)	2665 33	+326	95400 2070	496 2
75/25 PP/LDPE (DFD) with 20% EPCAR 847 (400°F)	2379 47	+326	92800 2200	504 8
25/75 PP/LDPE (DFD) (400°F)	2000 41	+326	77280 -	46.2 -
25/75 PP/LDPE (DFD) with 10% EPCAR 847 (400°F)	1974 70	+326	41325 4155	31.5 1.1
25/75 PP/LDPE (DYNH-1) with 10% EPCAR 847 (400°F)	1748 43	+326	68130 5660	27.4 0.9
25/75 PP/LDPE (DYNH-1) with 20% EPCAR 847 (400°F)	1719 23	+326	88200 7455	29.9 2.8
25/75 PP/LDPE (DYNH-1) (400°F)	1812 186	+326	36225 5360	45.6 1.2
25/75 PP/LDPE (DYNH-1) with 10% EPCAR 306 (400°F)	1465 33	+326	38500 9870	23.8 0.7
25/75 PP/LDPE (DYNH-1) with 20% EPCAR 306 (400°F)	1678 71	+326	45570 5510	26.9 0.7

*Key: Mechanical Property
Standard Deviation

Table IX (Cont'd.)

Properties of One-Gated Injection Molded Samples*

<u>Blend</u>	<u>Tensile Strength (PSI)</u>	<u>Percent Elongation</u>	<u>Initial Modulus (PSI)</u>	<u>Energy To Yield (PSI)</u>
100% DYNH-1 LDPE -	1495	209	20800	38.0
High Shear (400°F)	73	31	-	-
100% PP - High Shear	4062	+330	153825	328
(400°F)	110		7930	10
50/50 PP/LDPE (DYNH-1)	2260	+330	93660	430
- High Shear	50		3725	24
(400°F)				
50/50 PP/LDPE (DYNH-1)	2022	+330	83790	542
with 10% EPCAR 847	41		6750	30
- High Shear				
(400°F)				
100% Rexene PP (400°F)	4082	+326	145320	370
	109		5040	12
100% LDPE (DFD)	1398	+326	17640	25.4
(400°F)	28		-	0.9

*Key: Mechanical Property
Standard Deviation

MECHANICAL PROPERTIES OF PS-PP AND HDPE-PP BLENDS

by

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THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE IN ENGINEERING

THE UNIVERSITY OF TEXAS AT AUSTIN

December, 1979

ACKNOWLEDGEMENTS

I wish to thank Dr. Donald Paul and Dr. Joel Barlow for their guidance and help in this work. I am grateful for the assistance offered by my laboratory associates, particularly Carlos Cruz, Alan Wonders, and Carl Lindsey.

Special thanks goes to the Plastics Institute of America which provided funds for my fellowship. Cosden Chemical Company, Union Carbide, Shell Chemical Company, and B. F. Goodrich kindly supplied polymers for the research.

D. W. B.

August, 1979

ABSTRACT

It seems reasonable to assume the attractiveness of recycling of plastics will continue to increase due to environmental concern over non-biodegradable plastics and due to greatly increased costs of monomer sources, i.e., petroleum. One of the most economically feasible methods of plastics recycling is the reprocessing of mixtures of polymers as blends. Polyolefins and polystyrene are the major constituents of scrap plastics; however, since they are immiscible, the resultant blends have rather poor mechanical properties.

Blends of polystyrene/polypropylene (PS/PP), possessing egregious mechanical properties when unaltered, may be improved by the addition of Kraton G, a triblock copolymer of PS/a rubbery polyolefinic segment/PS. The addition of relatively small amounts of Kraton to all injection-molded blend compositions results in tremendous improvements in the ductility and impact strengths of the modified blends. These improvements are, as would be expected, accompanied by modest decreases in yield strengths and moduli of the modified blends. All injection-molded blends of PS/PP, including those with Kraton added, with weld-lines are simply too fragile to be of practical use. Trends in mechanical

properties of compression-molded specimens generally parallel, but are often lower than, those of injection-molded specimens.

This research looks also at the influences of processing conditions on mechanical properties and on crystallinity of PS/PP blends. Properties of blends are strongly affected by molding conditions, especially temperature, but are only weakly affected by blending conditions. Higher molding temperatures produce more rubbery-like blends of PS/PP and of PS/PP/Kraton. Thermal analysis of blends molded at various temperatures shows crystallinity decreases with increasing temperature for a given composition. DTA work indicates that, for various blends of PS/PP and of PS/PP/Kraton molded at the same temperature, the amount of crystallinity is a linear function of the amount of PP present.

Blends of high density polyethylene/polypropylene (HDPE/PP) may be modified by the addition of a rubbery ethylene-propylene copolymer, Epcar, which improves the impact strength of the blends, while decreasing the yield strengths and moduli. All mechanical properties, especially ductility, of samples containing weld-lines are lower than those without weld-lines.

The roles of processing parameters and methods are investigated. Higher molding temperatures yield more ductile blends. The properties of blends of HDPE/PP and of HDPE/PP/Epcar are strong functions of molding conditions, but weak functions of blending conditions.

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CHAPTER I

INTRODUCTION

A rapidly decreasing supply of many raw materials and increasing environmental pollution from discarded products of these resources have resulted in pressure on both industry and the general public to recycle waste materials. The plastics industry, with its wide variety of short lifetime products, has received much criticism and pressure in this area.

As plastics production has increased greatly in recent years (1), so has the problem of plastic wastes increased. The low cost of many plastics has encouraged their use in short lifetime applications; as a result, the amount of plastics present in solid wastes is increasing rapidly. The two most common methods for the disposal of municipal solid wastes have been unsatisfactory for the disposal of plastic wastes. Sanitary landfilling with essentially non-biodegradable plastics has created subsurface land pollution. Incineration of many plastics is unacceptable owing to problems of air pollution (2).

Coupled with environmental problems associated with discarding plastics are both increasing costs of and shortages of

monomer supplies. The recent shortage of petroleum stocks in the U.S. has created a double problem for the plastics industry. The raw materials from which polymers are made have become both less plentiful and more expensive, while the costs of manufacturing plastics--highly energy-intensive processes--have risen sharply. Hence, the economic feasibility of plastics reuse--although formerly impractical for financial considerations--is growing ever more attractive.

Complicated problems are associated with attempting to recycle plastics from wastes (3). With present technology the possibilities for utilizing manufacturing wastes are much greater than for reclaiming plastics from municipal wastes. For example, trimmings from injection moldings are sometimes ground and returned to the molding machine; but at present only a small amount is being recycled. Recycling of plastics from municipal wastes poses special difficulties because of the wide variety of plastics present in solid wastes. One solution to the problem would involve separating each of the major generic types of plastics present (4); however, this step can be very difficult and expensive (5,6). An alternative solution proposed by Paul (7) involves the recycling of plastics as polymer blends of the various generic types, thus eliminating the separation problem.

The purpose of this work is to examine two immiscible binary blends, with the idea of improving their mechanical

properties either by the addition of a suitable additive or by the manipulation of the processing conditions. The blend system of PS/PP was investigated for two reasons. PS and PP are two major constituents of municipal wastes and are of practical importance if these wastes are to be utilized via recycling. Secondly, the commercially available triblock copolymer Kraton G seemed an ideal compatibilizing agent for the system.

Blends of HDPE/PP, often found in both municipal and industrial wastes, do not have extremely poor properties when unaltered; however, this system seemed to offer interesting prospects for improvement. Previous work by Lindsay (8) and Batiuk (9) suggests that certain mechanical properties of polyolefins may be enhanced by the addition of rubbery ethylene-propylene copolymers; such a rubbery copolymer, Epcar 847, was added to blends of HDPE/PP with hopes of improving the impact strength. In addition, influences of processing conditions on the mechanical properties of the resultant blends were studied.

CHAPTER II

CONCEPTS

Polymer Blend Behavior

A blend of polymers is miscible if the mixing of the two or more polymers results in a negative change in free energy, ΔF , according to the equation

$$\Delta F = \Delta H - T\Delta S.$$

The entropy term, $T\Delta S$, is usually negligible in polymer systems owing to the large size of the molecules being mixed. The enthalpy term, ΔH , is usually positive and is the major contribution to the free energy of mixing of polyblends (10, 11, 12, 13). Consequently, most polymer blends exhibit little or no miscibility.

The concept of polymer blend compatibility may mean different things to different researchers. To some workers, compatible polymers are polymer mixtures that have desirable physical or mechanical properties when blended. For example, one concept is that blends are incompatible if the ductility of the blend decreases such that it exhibits a minimum at some intermediate

composition; therefore, a compatible blend displays values of ductility somewhere between the values of ductility of pure polymers. To other workers, compatible polymers are polymer mixtures that do not exhibit gross symptoms of phase separation when blended. Perhaps the most fundamental concept of compatibility refers to miscibility on a molecular scale. In this work, the most readily verifiable concept--lack of a minimum in ductility curves--will be employed. The two systems investigated in this work--polystyrene/polypropylene (PS/PP) and high density polyethylene/polypropylene (HDPE/PP)--are incompatible blends which show minima in ductility.

In an attempt to modify the mechanical properties of immiscible blends, this research focuses on the influences of processing conditions and of the addition of a compatibilizing agent.

Researchers (14, 15, 16) have found that the properties of blends can be improved if the size of the domain of the minor phase can be reduced. This reduction can be achieved by using different processing techniques and by varying processing parameters. (The second section of this chapter is concerned with this issue.)

The addition to a blend of component 1 and component 2 of a block or graft copolymer of 1 and 2 often improves the ductility of the blend (17, 18, 19, 20). It is believed that the

copolymer may locate, during the blending operation, at the interfaces of components 1 and 2. Chain ends similar to 1 may be embedded in component 1 and chain ends similar to 2 may be embedded in component 2. Hence, such graft or block copolymers may act as emulsifiers, reducing the heterogeneity of the blend (12).

Block and graft copolymers with fairly long segments of each monomer separate into very much interspersed phases, a phenomenon which has been called "microphase separation" (21). Since random copolymers usually have short segment lengths of each monomer, they do not phase separate as readily as do graft or block copolymers which have longer segment lengths (22).

Block and graft copolymers probably tend to concentrate and phase separate at the interfacial boundaries of immiscible polyblends, resulting in improved interfacial adhesion due to chemical bonds between the monomer segments. The increased interfacial bonding can provide stress and energy transfer between the phases via the copolymer molecules. Mechanical properties, especially ductility, should improve as a result of the interfacial bonding (8, 9).

Selection of Blending Temperatures

In the blending of polymers, the processing parameters play an important role in determining the final properties of the blend (23). In a recent publication, Work (24) found for two-phase

systems that if the viscosities of the materials are similar during blending, then the component in higher concentration will become the continuous phase. Work also noted that for blends of equal composition the component that has the lower viscosity becomes the continuous phase. Poor properties in blends are often attributed to poor stress transfer across the interface between the components due to adhesion (25). As a load is applied to a test sample, the stress will concentrate at the interface. Because there is poor adhesion, the stress cannot be transferred, causing the test bar to fail. As the size of the domains of the minor phase increases, there are fewer interfaces to share the load; therefore, the ductility of the blend decreases as the continuous phase attempting to deform pulls away from the minor phase. Hence, one may wish to decrease the size of the domains of the minor phase, thereby increasing the area of interface to share the load.

A facile technique for decreasing the volume-to-area ratio of the minor phase in an extrusion process involves blending the materials at a temperature at which the viscosity of the major component is greater than that of the minor component (26). This imbalance will increase the shear stress on the minor phase, which will reduce the size of the domain of the minor phase, thereby increasing the interfacial area. Using blends of PS and PE, Starita (14) has shown that the volume-to-area ratio of the minor

phase is related to differences in the viscosities of the two components during blending. When the viscosity of the minor component is less than or greater than that of the major component, the minor component is, respectively, finely dispersed or coarsely dispersed throughout the major phase. Van Oene (27) has demonstrated that in blends of PS and HDPE, in which HDPE is the major phase, a reduction in the size of the domain of PS can be obtained if the extrusion temperature is well below the temperature at which the viscosities of the two polymers are equal. At this temperature the viscosity of HDPE is higher than that of PS. The elongation and impact strength of blends of PS and PP, according to recent work (15), can be improved by reducing the volume-to-area ratio of the minor phase of the blend.

To apply this concept to the systems studied in this thesis, torque-vs.-temperature data for the pure materials were obtained from a Brabender Rheometer. At a constant shear rate, the torque is proportional to the viscosity of the material. The viscosities of two materials should be similar when the torques are equal at the same shear rate. Approximately 45 grams of pure material was introduced into the Brabender mixing chamber, which is described in Appendix B. The initial temperature was set at 180°C, while the rpm's were 120. After the meter registered a constant torque at this temperature, the

torque and temperature were recorded. The temperature was increased 10°C , and, after sufficient time had elapsed, the new steady torque and temperature values were recorded. This procedure was continued until the temperature was about 300°C , where thermal degradation was severe.

Figures III-1 and IV-1 show torque vs. temperature for the PS/PP system and the HDPE/PP system, respectively. The cross-over point represents a temperature at which the viscosities of the materials are similar.

CHAPTER III

BLENDS OF PS/PP

Injection-Molded Blends of PS/PP Without Weld-Lines

Many mechanical properties of blends of PS/PP and blends of PS/PP/Kraton G-1652 are generally equal to or slightly below those that would be predicted by weight averaging the properties of the pure materials; however, for elongation-at-break the actual values are considerably below the values predicted by weight averaging.

Shell Chemical Co. manufactures a triblock copolymer, Kraton G, with polystyrene endblocks and a central rubbery portion, approximately 70% of the chain structure, composed of a random copolymer of ethylene and butene-1, which is formed by the partial hydrogenation of polybutadiene with both 1,4- and 1,2-diene structures. The endblocks of PS are thought to act as physical crosslinking agents dispersed throughout a continuous phase of rubbery ethylene-butylene copolymer. The 1652 grade used in this study has the lowest molecular weight PS endblocks made commercially by Shell that will form the PS domains [Ref. (36) of Lindsey (28)]. The Kraton may locate at the PP and PS

interfaces during blending. If the PS portion of the Kraton locates in the PS and the rubbery portion locates in the PP, then the Kraton may act as an adhesive, allowing stress transfer between the two phases.

As discussed in Chapter II, a plot of torque vs. temperature of pure components can be used to find the temperature at which the viscosities of PS and PP are similar. Figure III-1 is a torque-vs.-temperature diagram in which the torque readings of the three pure components, PS, PP, and Kraton G-1652, are plotted. For PS and PP the cross-over point is about 270°C (515°F); the cross-over point for PS and Kraton is about 238°C (460°F); and for PP and Kraton it is about 250°C (480°F). Hence, for most blends a temperature of about 270°C or 515°F should be used for processing. More is said later in this chapter on the influence of processing temperature on mechanical properties of this system.

Samples of PS/PP blends with and without Kraton G-1652 were extruded and injection molded according to the procedure outlined in Appendix D. The injection-molded dog-bone samples were then subjected to testing on the Instron, according to the techniques of Appendix D.

Figure III-2 is a graph of tensile strength vs. weight percent PS. The upper curve shows the ultimate strength for each material when no Kraton is present, while the lower curve

Figure III-1. Torque vs. temperature data for the PS/PP/Kraton system.

shows the yield strength of each material when 20% Kraton is present. In the latter case the values of the ultimate strengths are identical to the values of the yield strengths, except for the case of 0/80/20 PS/PP/Kraton, which has an elongation-at-break beyond the range of the Instron, and hence, may have an ultimate strength greater than the yield strength. In the 0%-Kraton curve, one sees a departure from strictly additive tensile strength values with increased proportions of PS. However, this decrease is not present in the data for the 20%-Kraton curve. Figure III-2 shows that the addition of Kraton decreases the yield strength of every composition--a finding which may be attributed to the low yield strength, approximately 250 psi, of Kraton.

In determining the effect of varying the amount of Kraton added to this system, additional blends of 5, 10, and 30% Kraton were prepared. Figure III-4 is a plot of tensile strength vs. weight % Kraton; in all blends the remaining weight was evenly distributed between PS and PP. Although the graph appears linear, the curve would approach the value for pure Kraton asymptotically as the amount of Kraton in the blend increases.

Figure III-3 is a graph of modulus vs. weight percent PS. The upper curve shows the essentially linear relationship between modulus and composition for pure binary blends of PS and PP. The curve depicting 20% Kraton shows a slight concavity

Figure III-2. Tensile strength of injection-molded single-gated specimens of PS/PP blends vs. blend composition.

Figure III-3. Modulus values of injection-molded single-gated specimens of PS/PP blends vs. blend composition.

Figure III-4. Tensile strength of injection-molded single-gated specimens of 50/50-PS/PP blends vs. weight % Kraton.

Figure III-5. Modulus values of injection-molded single-gated specimens of 50/50-PS/PP blends vs. weight % Kraton.

upwards, and, in general, the addition of Kraton, a rubber, lowers the modulus, as would be expected when adding a softer material.

Figure III-5 indicates that modulus vs. % Kraton shows, as does tensile strength vs. percent Kraton, a linear relationship in the region of fairly low amounts of Kraton; but both are predicted to asymptotically approach the values of pure Kraton as the amount of Kraton in the blends increases.

Figure III-6 is a graph of elongation-at-break vs. blend composition. Although the pure PP samples did not break within the full traverse of the Instron, the manufacturer's estimated elongation of 500% is used on the graph. Furthermore, the 0/80/20 PS/PP/Kraton material is estimated to have an elongation even greater than that of pure PP. The presence of PS in the blends drastically reduces the ductility of the blends. The minimum in the Kraton-free curve at 75/25 PS/PP indicates extreme incompatibility. A minimum in elongation-vs.-composition graphs for polyolefin/PS systems is not unusual (28). However, as the upper curve of Figure III-6 shows, the addition of 20% Kraton to PS/PP blends not only greatly increases the ductility, but causes the interior minimum to vanish. This observation strongly suggests that Kraton acts to compatibilize the immiscible PS/PP blends. As would be expected, blends with 10% Kraton showed mechanical properties intermediate between those of 0% and 20% Kraton.

Figure III-6. % Elongation of injection-molded single-gated PS/PP specimens vs. blend composition.

Figure III-7 shows the effect of Kraton in improving ductility of PS/PP blends. Elongation data for blends containing 0, 5, 10, 20, and 30% Kraton with the remaining weight being evenly distributed between PS and PP are shown in the graph. A brittle 50/50-PS/PP blend with about 3% elongation shows more than an order of magnitude improvement in ductility as 30% Kraton is added. Each consecutive point shows an approximate doubling of the previous value for elongation.

Izod Impact Tests on PS/PP Blends

Izod impact testing of PS/PP blends were conducted according to ASTM D-256. Tensile bars $1/8 \times 1/2 \times 5.45$ inches were injection molded. A notch was made on the narrow face of each bar with the aid of a TMI Notching Cutter, Model 43-15-1 (29). The 45° notch of radius 0.010 inch was centered on the specimen such that a $22\frac{1}{2}^\circ$ angle was formed on either side of the normal. The Izod testing apparatus was a TMI impact tester model 43-1 (29).

The Izod impact test indicates the energy required to break notched samples under standard conditions. It is calculated as ft-lb/in of notch. The Izod value is useful in comparing various grades of plastics within a given family (30). In comparing one plastic with another, however, the Izod impact test may not always be a reliable indicator of overall toughness or impact strength. Some materials are notch-sensitive and derive greater concentrations of stress from the notching operation.

Figure III-7. % Elongation of injection-molded single-gated 50/50-PS/PP blends vs. weight % Kraton.

Figure III-8 is a graph showing Izod impact strength vs. blend composition. The results for blends of PS and PP without Kraton are essentially those that would be computed by weight averaging of the pure materials. That the values for pure PP and for pure PS are somewhat higher than those in the literature (refer to Appendix A) may be attributed to difficulties of accurate notching, as mentioned previously. Nonetheless, the relative differences in impact strengths of the pure polymers are accurately reflected, and one may assume the blends follow similar patterns.

The most significant observation concerning Figure III-8 is that although addition of 20% Kraton more than doubles the impact strengths of blends containing less than 80% PP, 20% Kraton added to pure PP quadruples its impact strength. An enhancement of impact strength is to be expected with the addition of a rubbery material such as Kraton; however, the vast increase of impact strength in blends containing large proportions of PP is both significant and puzzling.

Injection-Molded Blends of PS/PP With Weld-Lines

Injection-molded blends of PS/PP, with and without Kraton, containing weld-lines were prepared by allowing material to enter the die simultaneously from both ends. An attempt was made to test the double-gated dog-bone specimens on the Instron. But due to the extreme brittleness of the material in the weld-lines,

Figure III-8. Izod impact strength of PS/PP blends, with and without Kraton. (1/2 x 1/8-in. notched bar, Izod test).

the experiments were futile. Specimens containing no Kraton often broke as they were removed from the mold. All samples failed prematurely when tested on the Instron. Even blends with 20% Kraton were so brittle and fragile in the weld-line that they failed at about 3% elongation. The results of these experiments are not included.

The Effect of Injection-Molding Temperature on Mechanical Properties of PS/PP Blends

Additional dog-bone specimens of 50/50-PS/PP specimens injection molded at 213°C (415°F) and 268°C (515°F) were prepared and tested according to the procedures contained in Appendix D. This section is an investigation of how molding temperature affects mechanical behavior of PS/PP blends with or without Kraton.

Figure III-9 is a graph showing how tensile strengths of 50/50-PS/PP blends vary with weight % Kraton, for specimens injection molded at 213°C and at 268°C. With no Kraton, the tensile strengths of the materials molded at 213°C and 268°C are about the same. As Kraton is added, the specimens molded at 213°C show consistently lower tensile strengths; however, the relative differences are fairly minor.

Figure III-10 shows the influence of injection-molding temperature on modulus values of single-gated 50/50-PS/PP blends vs. % Kraton. The modulus of 50/50 PS/PP with no Kraton is

Figure III-9. Influence of injection-molding temperature on tensile strengths of single-gated 50/50-PS/PP blends with and without Kraton.

Figure III-10. Influence of injection-molding temperature on modulus values of single-gated 50/50-PS/PP blends with and without Kraton.

higher for the material molded at the lower temperature. With 10% Kraton, the moduli are about equal, but with 20% Kraton, the modulus of the material molded at the higher temperature is greater. There seems no consistent trend in these data, but, as with tensile strength data, the differences between data for material molded at 213°C and data for material molded at 268°C are relatively small.

Figure III-11 shows the influence of injection-molding temperature on ductility of 50/50-PS/PP blends. When no Kraton is present the molding temperature seems not to affect ductility to any appreciable extent. As more Kraton is added the ductility of blends molded at 268°C increases far more than does the ductility of material molded at 213°C.

The trends in the ductility curve may be explained by noting that hotter injection-molding temperatures usually produce less crystalline material, as observed by Reinshagen and Dunlap (31) while using pure PP. Similar trends are reported for the HDPE/PP system in Chapter IV, and a subsequent section of this chapter focuses on differences in crystallinity, as detected by DTA, in the PS/PP system, as functions of both PP content and temperature of molding.

A rationalization of the behavior represented in Figures III-9 and III-10 is more difficult. Assuming amount of crystallinity is inversely proportional to molding temperature

Figure III-11. Influence of injection-molding temperature on elongation of single-gated 50/50-PS/PP blends with and without Kraton.

(refer to Table III-1 and the accompanying text in the following section), one would predict relative values of tensile strength just the opposite of those actually reported in Figure III-9, because more crystalline materials generally possess higher tensile strengths. More crystalline materials usually offer more resistance to deformation; therefore the moduli graph, Figure III-10, should show consistently higher values for the material processed at a lower temperature.

The real explanation may be found in the ability of Kraton to compatibilize blends of PS and PP. At higher temperatures, the polymers are less viscous and much more mobile, allowing the PS and PP to phase-separate better, with the PS migrating to the PS endblocks of the Kraton and the PP migrating away from the PS domains. More complete compatibilization may, as discussed in Chapter II, result in improved interfacial adhesion due to attractive forces between the pure polymers and the analogous segments of the Kraton. The increased interfacial bonding can provide stress and energy transfer between the phases via the Kraton molecules. Such adhesion should be accompanied by enhanced mechanical properties.

Crystallinity Studies in PS/PP Blends

In an effort to explain some of observations of the effects of molding temperature on mechanical properties of PS/PP blends, the previous section suggests that processing temperature

affects both crystallinity of blends and compatibility of Kraton-containing blends. This section is concerned with crystallinity in PS/PP/Kraton blends and with the effect of molding temperature on the amount of crystallinity in blends.

An issue which has merited the attention of several research groups is whether the crystallinity of polyolefin in a polyolefin plus a second polymer (where the second polymer is, for example, a random copolymer, a block polymer such as Kraton, or PS) blend is affected by the second polymer. Recent work by Lindsey (28) indicates that the presence of Kraton G-1652 in high density polyethylene (HDPE) seems to lower the crystallinity of HDPE, but that PS blended with HDPE does not lower the crystallinity of HDPE. However, DTA analysis by Locke and Paul (17) suggests the presence of PS in blends with low density polyethylene (LDPE) seems to retard crystallization of the LDPE.

The findings about to be presented herein are for the PS/PP system, and, as such, will do little to resolve the apparent discrepancies in previous work on amount of crystallinity in blends. The issue of effect on the crystallinity of PP by a second polymer in a blend is significant in that recent work (31) has shown that the degree of crystallinity in PP will affect the mechanical properties of PP blends.

Figure III-12 is a plot of crystallinity, as determined by DTA analysis (refer to Appendix C), of PS/PP/Kraton blends vs.

total weight % PP. Data for blends with and without 20% Kraton are shown. The line connects the point for 100% PS with 100% PP, and data points for 0% Kraton and 20% Kraton all fall on or very near to the line. From the graph, therefore, one may conclude that the amount of crystallinity in PS/PP/Kraton blends is strictly a linear function of the amount of PP present. That is, neither PS nor Kraton seems to depress the crystallinity of PP blends.

These observations parallel those of Krager (32), who, by using DTA as well as other methods, found that the amount of crystallinity in PP plus EPM (ethylene-propylene copolymer) systems is not affected by the EPM additive, but that the type of crystallinity probably does change.

Blends of 50/50 PS/PP were extruded at 265°C (510°F) according to the procedures of Appendix D. The extrudate was injection molded at 213°C (415°F), 241°C (465°F), and 268°C (515°F). The three different products were subjected to differential thermal analysis, and their thermograms were analyzed for crystallinity according to the method of Appendix C. The results of the analysis appear in Table III-1, from which one can see the amount of crystallinity in 50/50-PS/PP blends is exactly inversely proportional to molding temperature.

The issue of amount of crystallinity in polyblends of PP is readily determined via DTA. But the type of crystallinity

Figure III-12. Area of melting endotherm of thermographs of PS/PP/Kraton blends vs. total weight % PP.

Table III-1. DTA analysis of 50/50-PS/PP blends injection molded at various temperatures. All blends extruded at 265°C (510°F).

Injection-molding temperature (°C)	Area of melting endotherm* (arbitrary units)
213	100.0
241	90.5
268	81.3

*Area of melting endotherm, as discussed in Appendix C, is proportional to the crystallinity of the material.

present is obtained with more difficult experimental methods, such as x-ray diffraction, which are not available in this laboratory. Experiments investigating the influence of processing conditions, especially temperature, on the type of crystallinity present in PS/PP blends would be most interesting and enlightening.

Mold Shrinkage in PS/PP Blends

Crystalline plastics exhibit large shrinkage on molding because they contract in volume considerably with crystallization. Nonuniform shrinkage is connected with nonuniform cooling. Objects cool nonuniformly in injection molds due to the inherent nature of the heat conduction process (thick sections cool more slowly than thin ones), rather than due to defects in the cooling system. Hence, polymer density increases more rapidly in thin sections than in thick ones.

Furthermore, local differences in polymer density and, especially, back-flow of hot molten polymer as it enters a much cooler mold cause mold shrinkage of two types--decrease in volume (due principally to crystallization) and decrease in mass (due to back-flowing of hot polymer as it comes in contact with a cool mold).

Figure III-13 is a plot of cross-sectional area of the dog-bone specimens vs. total weight % PP. The upper curve of 0% Kraton (i.e., the blends are all PS and PP) shows a strictly

linear relationship with cross-sectional area steadily decreasing as the % weight of PP increases. The lower curve of 20% Kraton is also linear and is extrapolated to intersect at the 100%-PP point on the Kraton-free curve. That the 20%-Kraton line does intersect at the 100%-PP point of the Kraton-free line may be interpreted as an indication that volumetric shrinkage is a function only of PP, the only crystalline material present.

Figure III-14 is a graph of the weight of the dog-bone specimens vs. the total weight % PP. The injection-molding conditions for all samples were essentially identical. The lines shown on the graph are derived from least-squares treatment of the data. The addition of Kraton decreases the weight of the dog-bone samples, but not by the same amount for each corresponding blend. The extrapolation of the 20%-Kraton line does not intersect the 0%-Kraton line or the 100%-PP ordinate. Therefore, the factors which govern the amount of material in each injection-molded specimen may not be entirely due to the amount of PP in the blend.

Table III-2 presents the effects of temperature on mold shrinkage in 50/50-PS/PP blends with and without Kraton. For each blend the cross-sectional area of the specimen injection molded at the hotter temperature is smaller than the cross-sectional area of the specimen molded at the cooler temperature, and this difference becomes progressively larger as more Kraton

Figure III-13. Cross-sectional area of injection-molded dog-bone samples of PS/PP/Kraton vs. total weight % PP.

Figure III-14. Weight of injection-molded dog-bone samples of PS/PP/Kraton vs. total weight % PP. ,

is added. This is significant because Kraton, having no crystallinity, may be expected, a priori, to lower the mold shrinkage effects of PP by diluting it. A quick glance at the amount of mass in the samples molded at 268°C reveals that the mass remains nearly constant (a decrease of 1.1%) in going from 50/50 PS/PP to 40/40/20 PS/PP/Kraton, while samples molded at 213°C show essentially no change in mass. Kraton G-1652, at room temperature has about the same density as PP and is less dense than PS (refer to Appendix A). Hence, the differences in cross-sectional area seen in each composition appear to arise from a compacting effect which results from additional Kraton. This compacting of material may reflect Kraton's role as a compatibilizer; however, as noted previously, Kraton appears not to affect the amount of crystallinity in PS/PP blends.

In summary, Table III-2 shows two factors occurring at once. That shrinkage increases with increasing melt temperature is consistent with the data of Table III-1, i.e., crystallinity increases as the molding temperature decreases. That the mass is higher at lower molding temperature may be due simply to thermal expansion of the melt. Less mass is injected at higher temperature because the mold volume is fixed and the melt density drops as the temperature is raised.

Table III-2. Temperature effects on mold shrinkage in 50/50-PS/PP blends with and without Kraton. Injection molding conditions are essentially identical for all specimens.

PS/PP/Kraton G-1652 (injection-mold temp.)	Cross-sectional area of specimen, in ² x 10 ²	Mass of specimen, grams
<u>50/50/0</u>		
(268°C)	6.077	10.5561
(213°C)	6.161	10.7736
<u>45/45/10</u>		
(268°C)	6.084	10.5440
(213°C)	6.250	10.7589
<u>40/40/20</u>		
(268°C)	5.972	10.4352
(213°C)	6.263	10.7767

Compression-Molded Blends of PS/PP

Compression-molded blends of PS/PP were prepared according to the procedures outlined in Appendix B. For each blend composition two batches of material were prepared, namely, a batch blended at 190°C (375°F) and a batch blended at 265°C (510°F). One portion of each batch was compression molded at 190°C, while the other portion was compression molded at 268°C. All compression moldings were slowly cooled. The resultant molds were analyzed on the Instron according to the methods discussed in Appendix B. The results of these experiments appear in Figures III-15 through III-22.

Figure III-15 shows tensile strength of PS/PP blends compression molded at 268°C but blended at 190°C and at 265°C. Figure III-16 shows the same kind of information for blends compression molded at 190°C. If one would superimpose Figure III-16 on Figure III-15, he would see virtually overlapping curves, meaning that for the PS/PP/Kraton system, essentially no difference in tensile strength results from changing the compression molding temperature from 190°C to 268°C. This finding agrees rather well with the data presented in Figure III-9, in which tensile strengths of injection-molded specimens show very little influence by molding temperature.

For materials blended in the Brabender mixing chamber (refer to Appendix B), instead of in an extruder, the temperature

is quite important. Blends prepared at 190°C show far inferior tensile strengths compared to those blended at 265°C. Perhaps the molten polymer undergoes increased phase separation at the higher blending temperature.

As expected, tensile strength of PS/PP blends without Kraton is greater than that for Kraton-containing blends. This trend has been observed in Figure III-2.

Another important observation concerning Figures III-15 and III-16 is that while tensile strength data for material blended at 265°C show essentially linear trends when plotted versus blend composition, the tensile strength data for material blended at 190°C show distinct minima about the region of 50/50-PS/PP composition. The addition of 20% Kraton appears to mitigate the sharpness of each minimum, presumably because Kraton aids in the compatibilization of the immiscible blend system.

Figures III-17 and III-18 show the influence of blending temperature on modulus values of PS/PP blends compression molded at 268°C and 190°C, respectively. As with the previous pair of figures, these graphs indicate that modulus of compression-molded samples is but a weak function of molding temperature, yet is more strongly affected by blending temperature. Materials blended at the lower temperature show consistently lower modulus values.

Figure III-15. Influence of blending temperature on tensile strengths of PS/PP blends compression molded at 268°C (515°F).

Figure III-16. Influence of blending temperature on tensile strengths of PS/PP blends compression molded at 190°C (375°F).

TENSILE STRENGTH (psi)

SOLID SYMBOLS: BLEND TEMP. = 510°F
OPEN SYMBOLS: BLEND TEMP. = 375°F

TENSILE STRENGTH (psi)

In agreement with the trends reflected in Figure III-3, Figures III-17 and III-18 reveal the usual decline of modulus with addition of Kraton to PS/PP blends.

Showing the influence of blending temperature on tensile strengths of 50/50-PS/PP compression-molded blends, the graph of Figure III-19 reveals a fairly significant difference in tensile strengths in Kraton-free material, with the tensile strength of the hotter blend approximately 40% greater than that of the material blended at 190°C. Yet, as more Kraton is added to 50/50 blends of PS/PP, the differences in tensile strength gradually decrease so that with 30% Kraton present, the tensile strengths of the hotter and cooler blends are nearly equal. This observation suggests that Kraton's ability to compatibilize immiscible blends increases as its content increases.

Figure III-20 demonstrates the influence of blending temperature on modulus values of 50/50-PS/PP compression-molded specimens. The modulus values of material blended at 190°C are consistently lower than the moduli of material blended at 265°C and there appears no merging of the values, even at 30% Kraton.

Figure III-21 is a graph showing the influence of blending temperature on elongation of PS/PP blends compression molded at 268°C. Following the pattern indicative of the ductility of injection-molded specimens, illustrated in Figure III-6, the curves for 20% Kraton show vast enhancement of ductility and

Figure III-17. Influence of blending temperature on modulus values of PS/PP blends compression molded at 268°C (515°F).

Figure III-18. Influence of blending temperature on modulus values of PS/PP blends compression molded at 190°C (375°F).

Figure III-19. Influence of blending temperature on tensile strengths of 50/50-PS/PP compression-molded specimens.

Figure III-20. Influence of blending temperature on modulus values of 50/50-PS/PP compression-molded specimens.

COMPRESSION MOLDED AT 190°C

a trend towards compatibilization (as reflected by the more nearly linear data), when compared to 0%-Kraton curves.

In keeping with the trends observed in tensile strength and modulus, the ductility data reflect a decided increase in elongation of hotter blends when compared to the results from blends at 190°C.

Figure III-22 is a graph of the influence of blending temperature on elongation of 50/50-PS/PP specimens compression molded at 268°C. The upper curve, which represents data for material blended at 265°C, is consistently higher than the curve for blends of 190°C. Here again, the results suggest that higher blending temperatures, which supposedly promote more thorough mixing, improve ductility by improving the extent of compatibilization of the PS/PP blends by Kraton.

That such dramatic effects of blending temperature on mechanical properties are not seen in extruded blends but are seen in batch blending may be due to the inherently rather inferior mixing which occurs in Brabender batch mixing. In extrusion processing the mixing is fairly thorough, even if the temperature is relatively low. But batch mixing may very much exaggerate, via resultant mechanical properties, the poor mixing or poor interdispersion.

Figure III-21. Influence of blending temperature on elongation of PS/PP blends compression molded at 268°C.

Figure III-22. Influence of blending temperature on elongation of 50/50-PS/PP compression-molded specimens.

CHAPTER IV

BLENDS OF HDPE/PP

Injection-Molded Blends of HDPE/PP Without Weld-Lines

Blends of HDPE and PP generally have mechanical properties that would be computed by simply weight averaging the properties of the pure polymers. The most noteworthy exception is ductility of HDPE/PP blends, which invariably is below the value predicted by weight averaging.

The B. F. Goodrich Co. manufactures a series of crystalline ethylene-propylene-diene monomer rubbers called Epcar elastomers. Epcar 847, the physical properties of which are detailed in Appendix A, was selected for this research with the idea that its presence would enhance the ductility and impact strength of HDPE/PP blends.

In an effort to find the optimum mixing temperature for the HDPE/PP-blend system, torque-vs.-temperature experiments were performed according to the concepts discussed in Chapter II. Figure IV-1 is a plot of the results of these experiments. From the figure, one sees there is no cross-over of viscosities within the given temperature range of 180°C (356°F) to 300°C (572°F).

Figure IV-1. Torque versus temperature curves for pure HDPE and pure PP.

An extrapolation of the curves below 180°C indicates that at 165°C HDPE and PP would have similar viscosities. This, however, is an unreasonably low temperature not only because HDPE cannot be processed easily at 165°C, but more importantly, because PP melts at 166°C. Similarly, an extrapolation beyond 300°C indicates a cross-over in viscosities at about 330°C--a temperature at which thermal oxidation of both materials is severe.

An extrusion temperature of 232°C (450°F) and an injection-molding temperature of 240°C (465°F) were selected. (Later in this chapter the influences of extrusion temperature and molding temperature on the properties of the blends are discussed.) At these temperatures blends of HDPE/PP and blends of HDPE/PP/Epcar flow readily and mix rather well, without undergoing extensive thermal degradation.

Figure IV-2 is a graph of tensile yield strength vs. blend composition for single-gated specimens. With 0% Epcar present, the yield strengths of intermediate blends are those that would be expected by the weight averaging of the values for pure components. Similarly, for the 20%-Epcar curve, the yield strengths of all blends are essentially a linear function of blend composition. The values for yield strength when no Epcar is present are consistently about double those when 20% Epcar is present. A lowering of yield strength is expected when a rubbery polymer is blended with rather crystalline

polymers such as HDPE and PP. Values of yield strength with 10% Epcar present, although not shown, fall between their respective values on the 0%- and 20%-Epcar curves.

Figure IV-4 shows the effect of the amount of Epcar present on the yield strengths of specimens of 50/50 HDPE/PP. The rather steep linear decline of yield strength with increasing amounts of Epcar is somewhat surprising, for one ordinarily sees a more gradual decrease in yield strength with increasing amounts of ethylene-propylene-diene monomer rubbers. In fact, Lindsay (8), using Epcar 847 plus low density polyethylene blends, has even found cases in which there is tensile strength synergism. Nonetheless, in the system under investigation at present, as the amount of Epcar is increased, one would expect the yield strength of 50/50-HDPE/PP specimens to asymptotically approach the yield strength of pure Epcar 847.

Figure IV-3 shows the value of the modulus of HDPE/PP blends as a function of composition. The results with 0% Epcar are those that would be predicted by simply weight averaging the modulus values of the pure components. When 20% Epcar is present, the results fall on a straight line between the modulus of PP with 20% Epcar and the modulus of HDPE with 20% Epcar. That the moduli of blends with Epcar present are lower than the moduli of the corresponding blends without Epcar can be expected from the addition of the softer Epcar rubber.

Figure IV-2. Tensile yield strength versus blend composition of HDPE-PP at constant amounts of Epcar additive. Specimens are single gated; i.e., they do not have weld-lines.

Figure IV-3. Modulus versus blend composition of HDPE-PP at constant amounts of Epcar additive, single-gated specimens.

Figure IV-4. Tensile yield strengths of single-gated, 50/50-HDPE/PP blends versus amount of Epcar present.

Figure IV-5. Modulus values of single-gated, 50/50-HDPE/PP blends versus amount of Epcar present.

EXTRUDED AT 232°C
INJECTION MOLDED AT 240°C

Figure IV-5 is a graph of modulus vs. weight % Epcar for 50/50 blends of HDPE/PP. The decrease of modulus becomes more gradual with increasing amounts of Epcar. As the concentration of the soft Epcar rubber becomes greater, the modulus curve should become an essentially horizontal line, for such is the influence of the addition of a rubbery polymer to a polyblend of rather crystalline materials.

Figure IV-6 is a graph of % elongation-at-break vs. blend composition when no Epcar is present. Showing a minimum in ductility at about 25/75 HDPE/PP, this blend system displays incompatibility as discussed in Chapter II. The results of 10% Epcar added and of 20% Epcar added are not shown because the specimens did not break within the full traverse (about 205% elongation) of the Instron; therefore, by not breaking, the 10%-Epcar specimens show an enormous increase in ductility over the corresponding Epcar-free samples.

Impact Strength of HDPE/PP Blends

Figure IV-7 is a graph of Izod impact strength vs. blend composition. (Chapter III contains details on the experimental procedures for Izod impact testing.) The incompatibility of the blend system is substantiated by the fact that the impact strengths of the blends fall well below the line of values which would have been calculated from the simple weight averaging of the impact strengths of the pure materials. Blends with 10%

Figure IV-6. % Elongation versus blend composition for single-gated material.

Epcar present, when subjected to Izod testing, could not be broken; instead, they simply bent under the force of the striking hammer. The conclusion of this observation is that Epcar, even in small quantities, greatly enhances the impact strength of HDPE/PP blends. Even the 90/10-PP/Epcar specimen failed to snap in the Izod test.

Inasmuch as the impact strength of a material often parallels its ductility, the results of the impact tests are to be expected when one reflects upon the marked increase in ductility of blends containing as little as 10% Epcar.

Injection-Molded Blends of HDPE/PP With Weld-Lines

While the first section of this chapter is a treatment of injection-molded HDPE/PP blends without weld-lines, this section has a comparable discussion of the influence of weld-lines in HDPE/PP blends with and without Epcar.

Due to flow patterns in the injection-molding process, molded articles often have weld-lines where the molten polymer fronts meet. Articles with weld-lines generally have lower tensile strength and less ductility than articles without weld-lines (33, 34). Even when both fronts are of the same material there appears to be a kind of poor adhesion at the polymer fronts, an adhesion demonstrating behavior similar to that at the interfaces of components of immiscible polymer blends. While strengths at weld-lines for pure polymers are often lower than bulk

Figure IV-7. Izod impact strength of HDPE/PP blends. (1/2 x 1/8 inch notched bar, Izod test)

strengths, weld-line strengths for immiscible polymer blends are usually much lower. Paul (35) has proposed a correlation for predicting the tensile strength of polymer blends at the weld-line; the details of Paul's proposal are discussed in Appendix E of Lindsey's thesis (28).

Blends of HDPE/PP with and without Epcar were prepared under the same processing conditions as were the single-gated specimens previously described. However, to achieve a weld-line located approximately in the center of the injection-molded dog-bone specimen, the second runner in the mold was open, allowing the mold to fill simultaneously from both ends. The specimens were then subjected to the usual testing on the Instron for modulus, elongation, and tensile strength. In every case failure occurred at the weld-line during Instron testing.

Figure IV-8 is a graph of tensile strength vs. composition for double-gated specimens. The upper curve, which is for 0% Epcar, shows a minimum in tensile strength around 75/25 HDPE/PP. The presence of such a minimum is predicted by Paul's (28) proposal of weld-line behavior. On the other hand, the 20%-Epcar curve shows no minimum and is essentially the straight line which results from weight averaging the tensile strengths of the pure materials. This finding is certainly an encouraging prospect for the improvement of materials containing weld-lines.

Comparing Figure IV-8 with Figure IV-2, the corresponding data for specimens without weld-lines, one sees the double-gated

material has slightly lower yield strength for the pure polymers and considerably lower yield strength in blends of HDPE/PP. Owing to the inherent weakness at a weld-line, this is expected, assuming yielding occurs at the weak weld-lines first.

Figure IV-10 shows the gradual decrease of yield strength with the addition of Epcar in 50/50-HDPE/PP blends. Comparing this graph with Figure IV-4, one notices the yield strengths of weld-line-containing materials are lower than those of specimens without weld-lines. But the decrease in yield strength with increased Epcar is more gradual in materials with weld-lines than in materials without weld-lines.

Modulus vs. blend composition for double-gated injection-molded specimens can be found on Figure IV-9. Comparison of Figure IV-9 with the corresponding modulus graph for single-gated materials, Figure IV-3, shows that the two 0%-Epcar lines and the two 20%-Epcar lines have essentially identical slopes; however, the moduli of specimens with weld-lines are slightly lower. This may be attributed to the inherent weaknesses of weld-lines, which do not have quite as much resistance to initial elongation as do the corresponding single-gated materials.

The graph of Figure IV-11 shows the gradual decline of modulus of 50/50-HDPE/PP double-gated blends with increasing amounts of Epcar. It should be compared with Figure IV-5, the graph of modulus values of single-gated specimens vs. amount

Figure IV-8. Tensile strength vs. HDPE/PP blend composition for double-gated injection-molded specimens, at constant amounts of Epcar.

Figure IV-9. Modulus vs. HDPE/PP blend composition for double-gated injection-molded specimens, at constant amounts of Epcar.

Epcar. The values on the latter graph are slightly greater than the corresponding values for double-gated material. Also, the decline in modulus as depicted in Figure IV-11 is somewhat less gradual than that for the single-gated material; however, the difference is not statistically significant. Furthermore, one may be hard-pressed to find an underlying cause for this slight difference in the curvatures of the two plots.

Figure IV-12 is a graph of % elongation of double-gated blends of HDPE/PP vs. blend composition. Because the weakness of a weld-line greatly influences the ductility of a sample, the intermediate blends--namely, those with HDPE/PP ratios of 25/75, 50/50, and 75/25--show a tremendous decrease in elongation. However, the presence of Epcar in these intermediate blends meliorates their ductility. Presumably, Epcar aids in binding the two polymer fronts at the weld-line. This suggestion is supported by the data displayed in Figure IV-13, in which % elongation of 50/50-HDPE/PP double-gated blends is shown as a function of weight % Epcar. Since the specimens all broke at the weld-line, the data of Figure IV-13 show, directly, the improvement of the ductility of the polymer junction at the weld-line.

Figure IV-10. Tensile strength of 50/50-HDPE/PP double-gated specimens versus weight % Epcar.

Figure IV-11. Modulus of 50/50-HDPE/PP double-gated specimens versus weight % Epcar.

EXTRUDED AT 232°C
INJECTION MOLDED AT 240°C

Figure IV-12. % Elongation of double-gated blends of HDPE/PP vs. blend composition.

Figure IV-13. % Elongation of 50/50-HDPE/PP double-gated blends vs. weight % Epcar.

The Effects of Extrusion Temperature and Molding Temperature
on Mechanical Properties of HDPE/PP Blends

Blends of 50/50 HDPE/PP with and without Epcar were extruded in the usual procedure, but using extrusion temperatures of 191°C (375°F) and 274°C (525°F). The blends were then injection molded in the usual fashion, using molding temperatures of 191°C for each extruded blend and 274°C for each extruded blend. The single-gated injection-molded specimens were tested on the Instron for tensile strength, modulus, and elongation.

The results of these tests, shown in Figures IV-14 and IV-15, are fairly obvious: (1) molding temperature has a strong effect on yield strength and modulus, while extrusion temperature has but a mild influence, (2) specimens molded at the higher temperature have lower yield strength and lower modulus values, and (3) in comparison of materials molded at the same temperature, those specimens produced from the higher-temperature blends have slightly higher yield strengths and modulus values.

Figure IV-14 is a graph showing the influences of blending temperature and molding temperature on the yield strengths of injection-molded specimens of 50/50 HDPE/PP, plotted as functions of weight % Epcar. In addition to the general conclusions previously mentioned, one may notice that the decline

of yield strength with increasing amounts of Epcar is more pronounced for specimens molded at high temperatures than for those molded at low temperatures. In other words, the upper pair of curves in Figure IV-14 shows a more gradual decrease in yield strength with increased % Epcar; the lower pair of curves has a more precipitous decline.

The graph of Figure IV-15 shows the influences of blending temperature and molding temperature on the modulus values of injection-molded specimens of 50/50-HDPE/PP blends, plotted as functions of weight % Epcar. The data points are connected by practically straight lines, all of which are mutually parallel. Modulus values seem less affected by processing conditions than are yield strengths.

Table IV-1 summarizes data on the influence of processing conditions on the % elongation of blends of 50/50 HDPE/PP. The trends are: higher ductility accompanies both increasing extruding temperature and increasing injection-molding temperature, with injection-molding temperature exerting a stronger effect. Not shown are data for 50/50-HDPE/PP blends with 10% Epcar, all of which elongated to the full traverse of the Instron without failing.

A section of Chapter III reports the effects of extrusion temperature and injection-molding temperature on the mechanical properties of PS/PP blends. That section includes

Figure IV-14. The influences of blending temperature and molding temperature on the yield strengths of injection-molded specimens of 50/50-HDPE/PP blends.

Figure IV-15. The influences of blending temperature and molding temperature on the modulus values of injection-molded specimens of 50/50-HDPE/PP blends, plotted as functions of weight % Epcar.

Table IV-1. Influence of processing conditions on the % elongation of blends of 50/50 HDPE/PP.

Extrusion Temperature	Injection-Molding Temperature	
	191°C	274°C
	<u>% Elongation</u>	
191°C	81%	99%
274°C	88%	131%

a conclusion that the observed trends may be due, at least in part, to different amounts of crystallinity resulting from different molding temperatures.

Likewise, for the HDPE/PP system, one may invoke an explanation based on increased crystallinity concomitant with decreased molding temperature. That is, the more crystalline blends would be expected to show higher modulus values and higher tensile strengths, as have been observed for samples molded at lower temperatures. The findings of Reinshagen and Dunlap (31), as discussed in Chapter III of this thesis, seem in concert with the data on the present system.

As noted previously, the tensile strength and modulus data for samples molded at the same temperature but extruded at different temperatures reflect a modest improvement with higher blend temperature. While a definitive explanation of this trend is lacking, it may be due to one or two factors. Higher extrusion temperatures may effect improved mixing and interpenetration of HDPE and PP. Secondly, although one may reasonably suppose that a second melting-crystallization (such as that which occurs when an extruded blend is injection molded) would completely revamp the total crystalline microstructure which resulted from previous melting-crystallization, there may be some mechanism by which the original crystalline microstructure is not totally destroyed. Assuming the kinetics of a reorientation of the crystalline microstructure is slow in comparison to

the residence time of the material in the injection molder, then the second proposal may be valid. However, these suppositions are without both strong theoretical substantiation and supporting experimentation.

Compression-Molded Blends of HDPE/PP

Compression-molded blends of HDPE/PP with and without Epcar 847 were prepared according to the procedure outlined in Appendix B.

Figure IV-16 is a graph which shows tensile strength of slow-cooled compression-molded HDPE/PP blends vs. blend composition. The 0%-Epcar curve, by showing a rather marked minimum around 25/75 HDPE/PP, reflects the poor miscibility of the blend. Not surprisingly, the addition of 20% Epcar lowers the tensile strength of all compositions; however, the Epcar in the blends seems to promote a less drastic minimum in the data of intermediate blends.

Figure IV-18 shows tensile strengths of slow-cooled compression-molded 50/50-HDPE/PP blends as functions of weight % Epcar. The expected decline in tensile strength with increased Epcar is fairly gradual.

Figure IV-17 is a graph showing the values of moduli of HDPE/PP blends vs. blend composition. When 0% Epcar is present, the data form a straight line between the modulus values of the pure polymers. Reflecting the expected decline in modulus

with the addition of a rubbery material, the curve for 20% Epcar, with its upwards concavity, indicates that the moduli of HDPE/PP blends show a decrease, relative to the moduli of the pure polymers without Epcar.

The graph of Figure IV-19 shows modulus values vs. weight % Epcar. The gradual decrease in modulus can be attributed to the softening of the polyblend by the addition of a rubbery material.

Figure IV-20 shows the % elongation of compression-molded HDPE/PP blends vs. blend composition. The curve for 0% Epcar is rather unusual, for HDPE is generally more ductile than PP. Although 30% elongation for HDPE is low, it represents the result of two series of experiments, each with twelve samples which failed in a 15%-to-50% range. As mentioned in Appendix B, compression-molded samples, for a variety of reasons, are subject to flaws in composition or texture. Notwithstanding the questionable pure HDPE point, the 0%-Epcar curve shows a dramatic minimum which reflects the poor compatibility of the compression-molded system. The addition of 10% Epcar, while also greatly increasing the overall ductility of the blends, causes a significant improvement in blend compatibility, as evidenced by the lessening of the severity of the minimum. With 20% Epcar, the ductility is enhanced further and the minimum vanishes.

Figure IV-16. Tensile strength of compression-molded HDPE/PP blends vs. blend composition. Moldings were slowly cooled.

Figure IV-17. Modulus values of compression-molded HDPE/PP blends vs. blend composition. Moldings were slowly cooled.

BLENDED AT 190°C
COMPRESSION MOLDED AT 190°C

Figure IV-18. Tensile strength of compression-molded 50/50-HDPE/PP blends vs. weight % Epcar. Moldings were slowly cooled.

Figure IV-19. Modulus values of compression-molded 50/50-HDPE/PP blends vs. weight % Epcar. Moldings were slowly cooled.

BLENDED AT 190°C
COMPRESSION MOLDED AT 190°C

Figure IV-20. . % Elongation of compression-molded HDPE/PP blends vs. blend composition. Moldings were slowly cooled.

Showing % elongation of compression-molded 50/50-HDPE/PP blends vs. weight % Epcar, Figure IV-21 illustrates the tremendous enhancement of ductility resulting from the addition of Epcar. From 0% Epcar to 30% Epcar, the graph depicts a two-orders-of-magnitude improvement in elongation.

Slow-Cooled and Quenched Compression-Molded

Blends of HDPE/PP

Blends of HDPE/PP without Epcar were prepared in a Brabender at 190°C (375°F) according to the procedure outlined in Appendix B. A Greenerd Hydrolair press (36), 30-ton capacity, equipped with heaters and an internal network for cooling with water, was used to compression mold the type of 1/64-inch thick films mentioned in Appendix B. The Hydrolair press allows either slow-cooling of the mold--190°C to 30°C in about four hours, or quenching of the mold--190°C to 30°C in about five minutes. The thin films were later cut into dog-bone specimens and tested on the Instron in the usual fashion. The results of the experiments appear in Figures IV-22, IV-23, and IV-24.

Figure IV-22 is a graph which compares the tensile strengths of slow-cooled and quenched compression-molded blends of HDPE/PP without Epcar. Quenched specimens show a gradual decline in tensile strength from a maximum of about 4420 psi at 100% PP to a minimum of about 3550 psi at 100% HDPE. Slow-cooled samples, on the other hand, display a steady rise from about

Figure IV-21. % Elongation of compression-molded 50/50-HDPE/PP blends vs. weight % Epcar. Moldings were slowly cooled.

3100 psi at 100% PP to about 3930 psi at 100% HDPE. While the curve for quenched samples follows the pattern seen in previous experiments with both injection-molded and compression-molded samples, the curve for slow-cooled specimens shows a different direction of slope. The low values of tensile strength of the slow-cooled blends with less than 75% HDPE may be attributed to premature failure (as illustrated in Figure IV-24); that is, 0/100-, 25/75-, 50/50-, and 75/25-HDPE/PP specimens failed below 9% elongation, while quenched samples of these blends, showing considerably more ductility, did not fail prematurely.

Figure IV-23 is a comparison of the modulus values of slow-cooled and quenched compression-molded blends of HDPE/PP without Epcar as functions of blend compositions. Both curves depart from the patterns seen in previous graphs of moduli of compression-molded material and injection-molded samples. Figure IV-23 should be compared with Figure IV-17, which shows comparable data for slow-cooled samples. The discrepancy may be explained as arising from poor specimen preparation in connection with the results shown in Figure IV-23.

The tensile strengths of slow-cooled samples should (the unusual results in Figure IV-22 notwithstanding) be generally greater than those of quenched samples owing to increased amounts of crystallinity in the slow-cooled samples. Table IV-2 gives DTA area-of-the-thermogram data, which are proportional to

Figure IV-22. Comparison of the tensile strengths of slow-cooled and quenched compression-molded blends of HDPE/PP without Epcar as functions of blend composition.

Figure IV-23. Comparison of the modulus values of slow-cooled and quenched compression-molded blends of HDPE/PP without Epcar as functions of blend composition.

crystallinity (as discussed in Appendix C). Slow-cooled HDPE shows 14.2% more crystallinity than quenched HDPE, and slow-cooled PP shows 16.4% more crystallinity than quenched PP.

The results shown in Figure IV-24, which is a graph of % elongation of both slow-cooled and quenched compression-molded blends of HDPE/PP without Epcar, bolster the proposition that differences in crystallinity may be responsible for observed differences in the mechanical properties of quenched and slow-cooled blends. Differences in crystallinity of polymers often are most noticeable in differences in ductility. In Figure IV-24, the data for quenched blends, i.e., those which presumably contain less crystallinity, are consistently greater than the data for slow-cooled samples.

Using pure PP, Reinshagen and Dunlap (31) have found that stress-strain behavior is a strong function of the degree of undercooling of the samples, where undercooling is the difference in the constant temperature of melting and the observed temperature of crystallization. For small amounts of undercooling, a condition comparable to slow-cooling, Reinshagen and Dunlap found the PP specimens are brittle and tend to fail prematurely. For larger amounts of undercooling, conditions comparable to quenching, they obtained ductile materials. At low undercoolings, the brittle failure without yield occurs, presumably, as the result of a sparsity of intercrystalline

links under these conditions. Increased undercooling is accompanied by increased link density.

Table IV-2. DTA data on slow-cooled and quenched compression-molded samples of pure HDPE and pure PP. Samples molded at 190°C.

<u>Material</u>	<u>Quenched</u>	<u>Slow-Cooled</u>	<u>Increase^b</u>
	<div style="border: 1px solid black; padding: 5px; text-align: center;"> Area of thermogram^a (arbitrary units) </div>		
HDPE	9.38	10.71	14.2%
PP	8.72	10.15	16.4%

^aAppendix C contains a discussion of the analysis of the area of a thermogram.

^b"Increase" denotes increase in area of the thermogram area of the slow-cooled specimen over that of the quenched specimen.

Figure IV-24. Comparison of % elongation of slow-cooled and quenched compression-molded blends of HDPE/PP without Epcar as functions of blend composition.

CHAPTER V

SUMMARY AND RECOMMENDATIONS

Immiscible blends of PS and PP were prepared in an extruder and in a Brabender mixing chamber. Both injection-molded and compression-molded specimens display minima in ductility curves and, in general, possess egregious mechanical properties. The addition of Kraton G-1652 enhances the overall mechanical behavior of PS/PP blends, with ductility and impact strength showing dramatic improvement. The influence of processing temperature on blends of PS/PP with and without Kraton was investigated, with higher temperatures producing more ductile and less crystalline materials. Crystallinity and mold-shrinkage studies were also performed on the system.

Immiscible blends of HDPE and PP were investigated. Although unaltered blends of these polymers do not show particularly poor mechanical properties, the importance of processing temperature on mechanical properties of HDPE and PP was studied. The addition of Epcar 847 to blends of HDPE and PP resulted in substantial improvements in ductility and impact strength, accompanied by a decline in tensile strength and modulus. Some

interesting and perplexing results are observed in comparing quenched and slow-cooled compression-molded specimens; slow-cooled blends display more crystallinity and less ductility than quenched samples, but the role of rate-of-cooling on tensile strength and modulus is not easily apparent. Weld-line behavior of blends of HDPE/PP was investigated also.

For both blend systems, the influence of thoroughness of extrusion has yet to be determined. In order to apply better the findings in this research to waste plastics, one should employ at least some waste plastics into the blends or reprocess the original virgin plastics. Ways to improve the rather poor behavior characteristic of weld-lines in the blends presented herein ought to be initiated, as weld-lines in industrial products are very common.

APPENDICES

APPENDIX A

MATERIALS

The manufacturers' specifications of the polymers used in this research are listed in this appendix. Properties of Cosden's "crystal" PS, type 550, are listed in Table A-1. Shell's PP, 5520, is outlined in Table A-2. Properties of Shell's Kraton G-1652 are found in the middle column of Table A-3. The HDPE used was Union Carbide's grade DGDA 6084, found in Table A-4. Table A-5 contains information on Epcar 847.

Table A-1. Physical properties of PS from Cosden Chemical Company.

Cosden Polystyrene 550

PRODUCT DESCRIPTION

550 is designed for crystal applications requiring maximum heat distortion and increased strength characteristics. The product has good flow and excellent clarity even in heavy injection-molded sections. This resin is an excellent extrusion grade polystyrene.

TENSILE PROPERTIES

ASTM D 638-64T	typical value
Strength, psi	8000
Modulus of elasticity, psi (10 ³)	3.6

FLEXURAL PROPERTIES

ASTM D 790-66	
Strength, psi	13,200
Modulus of elasticity, psi (10 ³)	4.1

IMPACT PROPERTIES

ASTM D 256-56	
Gardner Impact	
Izod, ft/lbs/in. of notch	0.4
Falling dart, inch pounds	4.0

THERMAL PROPERTIES

ASTM D 648-56	
Heat distortion, °F	
unannealed	174
annealed	200
ASTM D 1525-65T	
Vicat softening point, °F	225

OTHER PROPERTIES

ASTM D 785-65	
Rockwell hardness	
L	92
M	62
ASTM D 1238-65T	
Flow, grams/10 minutes "G"	2.3
ASTM D 792-50	
Specific gravity	1.05

The data shown above were obtained using 1/4" injection molded specimens and appropriate ASTM test methods. Since the tests were run under laboratory conditions on natural virgin polystyrene, the data are intended as a general guide only and do not necessarily represent results that may be obtained elsewhere. Cosden Oil & Chemical Company disclaims any responsibility for use of the above data. The use of Cosden Polystyrenes must be guided by the user's own methods for selection of the proper formulation. Cosden Oil & Chemical Company disclaims any responsibility for misuse or misapplication of its products.

OIL & CHEMICAL COMPANY

A wholly owned subsidiary of American Petroleum, Incorporated

P.O. Box 2155 2550 North Central Expressway Dallas, Texas 75221 214-628-6700	3525 West Peterson Avenue Chicago, Illinois 60645 312-853-6080	550 Putnam Avenue Greenwich, Connecticut 06830 203-461-2292 212-460-1940
9288 North Freeway Highway L.B. Andersen, California 90028 213-482-6700	P.O. Box 1911 Bay Spring, Texas 75720 915-283-7651	

*Registered Cosden Oil & Chemical Company

Litho USA 1273/WC/2Mmp

Technical Bulletin

Shell Chemical Company

SC:27-77
(Supersedes SC:27-74)

Shell Polypropylene 5520

Nominal melt flow 5.0

Shell Polypropylene 5520 is a medium flow general purpose material exhibiting a desirable combination of properties and moldability which makes this grade suitable for a large number of injection molding applications. Parts produced from this material exhibit the high strength-to-weight ratio, excellent chemical and solvent resistance, exceptional stress crack resistance,

and excellent heat resistance properties inherent in polypropylene.

Shell Polypropylene 5520 meets the specifications and requirements set forth in the applicable sections of FDA Regulation 177.1520, and may be used in food handling and food packaging applications.

Typical properties

Property	Value	Unit	ASTM Test
Melt Flow	5.0	g/10 min	D 1238-70
Density at 73°F	0.905	g/cc	D 1505-68
Tensile yield strength (at 0.2 in/min)	4,400	psi	D 638-71 ¹
Yield elongation (at 0.2 in/min)	10	%	D 638-71 ¹
1% Secant modulus (at 0.2 in/min)	195,000	psi	D 638-71 ¹
Tensile yield strength (at 2.0 in/min)	4,700	psi	D 638-71 ¹
Izod impact strength at 73°F	0.6	ft-lb/in-notch	D 256-72 ²
Vicat softening temperature	305	°F	D 1525-70 ³
Heat deflection temperature at 66 psi fiber stress	235	°F	D 648-72 ³

¹ASTM Type 1 specimen 1/8 in. thick.

²1/8 x 1/2 in. specimen.

³Compression molded specimen

Table A-3. Physical properties of Kraton G-1652
at 25°C.

Material	KRATON G-1650 Rubber	KRATON G-1652 Rubber	KRATON 1101 Rubber
Specific Gravity	0.91	0.91	0.94
Solution Viscosity* cp			
15%w Solids	350	150	300
25%w Solids	8500	2500	4000
Films Cast from Toluene Solution			
Appearance	clear water-white	clear water-white	clear water-white
Tensile Properties:**			
Tensile at Break (T _B), psi	6000	6500	4600
Elongation at Break (E _B), %	500	500	880
100% Modules (M ₁₀₀), psi	950	730	400
Hardness, Shore A	75	75	71
Approx Styrene Rubber Ratio	30/70	30/70	30/70
*Brookfield, see also Fig. 6 **Measured on films cast from toluene. INSTRON jaw separation rate 10 inches per minute, temperature 23°C, dumbbell specimens cut with ASTM Die D.			

Table A-4. Physical properties of HDPE, grade
DGDA 6084.

BAKELITE® POLYETHYLENES FOR FILM EXTRUSION (Continued)

Typical Properties		
FDA STATUS (a)	ASTM Test Method	DDDA-6084 Natural 7
CHARACTERISTICS		
Description		General purpose
Applications		Merchandise bags
Density at 23°C., g./cm. ³	D 1505	0.960
Melt Index at 190°C., g./10 minutes	D 1238	0.3
Secant Modulus at 1% Elongation, plaque, psi.	D 638	135,000
FILM PROPERTIES (1.5-mil tubular)		(c)
Dart Impact, Fso, g./mil	D 1709, Method A	
Tensile Strength, psi.	D 882	
Machine Direction (MD)		8,300
Transverse Direction (TD)		4,500
Elongation, %	D 882	
Machine Direction (MD)		700
Transverse Direction (TD)		450
Coefficient of Friction (COF)		
Rating, measured		
24 hours after extrusion	D 2103	
Haze, %	D 1003	
Gloss, Gardner Glossmeter	D 523	
60° Polished Background		
45° Dull Background		
Product Modification (f)		UM
Stock Temperature, °F.		475

(a) FDA Status—"Natural 7" denotes that the product complies with the applicable Food Additive Regulation. These materials may be used in all food contact applications within the limitations of the regulation.

Table A-5. Physical properties and additional information on Epcar 847.

EPB-1.002-R

Epcar®
ELASTOMERS

SELECTOR CHART

Epcar Type	Class	Specific Gravity	M.V.*	Characteristics	Suggested Uses
306	EPM	.86	30	Low Mooney, Copolymer, will not sulfur cure	This elastomer requires a peroxide cure. It is recommended for injection molded and extruded products such as electrical components, wire insulation, O-rings, and brake components. It provides excellent heat resistance, and superior ozone and weather resistance.
346	EPDM	.86	30	Low Mooney, std. cure-rate	Injection molded and extruded products. The low Compound-Mooney ensures good processing when medium to high hardness is required in the finished product.
505	EPM	.86	50	Medium Mooney, Copolymer, will not sulfur cure	This elastomer requires a peroxide cure. It is recommended for wire insulation and jacket compounds, molded O-rings, and brake components. It provides excellent heat resistance, and superior ozone and weather resistance.
516	EPDM	.86	50	Medium Mooney, slow cure-rate	Used alone or in blends where severe ozone conditions are encountered.
545	EPDM	.86	50	Medium Mooney, std. cure-rate	A general-purpose EPDM rubber for compounds containing low levels of loading and oil.
585	EPDM	.86	50	Medium Mooney, fast cure-rate	Used in applications where a fast cure is desired. Blends well with other general-purpose rubbers.
587	EPDM	.86	50	Medium Mooney, high green strength, fast cure-rate	For wire and cable, sponge, and other molded or extruded products where good dimensional stability and a fast cure is needed. Blends well with other general-purpose rubbers.
845	EPDM	.86	80	High Mooney, std. cure-rate	A general-purpose EPDM rubber for compounds containing high levels of loading and oil.
847	EPDM	.86	80	High green strength, std. cure-rate	For wire and cable, sponge, and other molded or extruded products where good dimensional stability is needed.
5465	EPDM	.90	50**	100 phr. naph. oil, std. cure-rate	Develops good properties with relatively low rubber content. Tire flaps, hose tube and cover, matting, etc.
5875	EPDM	.90	50**	100 phr. naph. oil, fast cure-rate	Used in applications where a fast cure and good properties with relatively low rubber-content is desired. Sponge, hose, matting, etc. Excellent for blending with other diene elastomers.

*Mooney Viscosity — ML-4 at 212°F

**Mooney Viscosity — ML-4 at 125°C (257°F)

EPCAR RUBBERS ARE VERSATILE

Epcar ethylene-propylene rubbers have most of the desirable characteristics associated with other general-purpose rubbers along with greatly improved ozone and weather resistance, better performance over a wide temperature range, and the ability to accept higher "loadings." They have excellent mixing, extruding and molding characteristics.

There are eleven Epcar rubbers for a broad range of applications: from low-Mooney 346 which provides excellent mold-flow for injection molding to high Mooney 845 or 847 for high loadings of oil. There's cure versatility from slow-curing Epcar 516 to fast curing 585 or 587. Oil-extended Epcar 5465 and 5875 accept very high loadings of fillers

and oils to reduce compound costs without major loss of physical properties.

Variations in ethylene content are also available. Increased ethylene in the rubber increases the green strength of compounds. High-ethylene stocks are more thermoplastic and take higher loading of pigments. Processing characteristics of these stocks are very good, particularly extrusion. Vulcanizates of high-ethylene rubbers may have higher compression and permanent-set values. Lower-ethylene stocks have more pronounced "rubberlike characteristics."

These are but a few examples of the versatility inherent in the Epcar family of elastomers.

B.F. Goodrich Chemical Company / 6100 Oak Tree Blvd., Cleveland, Ohio 44131

These data are based on tests believed to be reliable. They are given only for your information and do not constitute a contract. No liability is assumed by B.F. Goodrich for any loss or damage resulting from the use of these data in any application. The user is advised to consult the product literature for the latest information.

APPENDIX B

COMPRESSION MOLDING

Compression-Molding Blend Preparation

A Brabender Plasticorder (37) was used to melt and mix all compression-molded blends. Melt blending is accomplished on a commercial scale with two roll mills, internal mixers such as the Banbury, or extruders. However, in the laboratory the Brabender Plasticorder simulates the mixing of a commercial Banbury mixer.

The experimental procedures used were similar to those used by Robertson and Vinson (38,1), with some modifications. All blends, as mentioned previously, were based on weight fractions of the components. Blends of the various plastics and additives were prepared by mechanically premixing the proper ratio of pelletized components before their introduction into the Brabender chamber. For optimal mixing and minimal oxidative degradation, the mixing chamber was filled as full as possible without being overfilled. To ensure the proper blend volume, the density of the final blend was estimated by assuming it to be the weighted average of all the various component densities, then the total weight required to make 41 cc, an empirically derived optimum blend volume, as well as the weights of each component were calculated.

Before the ingredients were charged into the Brabender cavity, the Brabender mixing head was heated to 190°C (374°F). After a few minutes of mixing at this constant temperature, the blends became homogeneous at approximately 180°C (365°F), as indicated by a thermal couple in direct contact with the melt.

To keep the torque from overloading the shear pin, the polymer ingredients were introduced slowly into the mixing head cavity with the impellers rotating. An arbitrary speed of 20 rpm was chosen as a reasonable mixing rate for charging and blending the components.

Blends were allowed to mix until homogeneous appearances were noted. In most cases this required eight to ten minutes of mixing. The torque response of the Plasticorder, which is directly proportional to the viscosity of the blend, was monitored at all times. After the torque response became constant at constant temperature over a period of a few minutes, the mixture was considered homogeneous, and the molten polymer was removed from the cavity and the mixing blades.

Mechanical Testing of Compression-Molded Specimens

The mechanical properties of the compression-molded blends were determined on an Instron Model Type TM Tensile Tester. In order to accurately test and compare the mechanical properties, the tests were performed, as closely as possible, on uniform specimens prepared in uniform procedures.

Preparation of Test Specimens

As the molten polymer was removed from the Brabender mixing chamber, it was pressed into a disk. The disk was transferred to a mold preheated to 190°C-196°C (375°F-385°F). The mold was in a Carver hydraulic press (39). After two to three minutes for thermal equilibration, pressure was gradually applied until 2500 pounds of force was exerted on the mold. Distributed over the material in the mold, this was about 1100 psi of pressure. The temperature was maintained at about 190°C until the excess molten polymer no longer oozed from between the mold plates. At this point the heat was turned off, and the polymer blend, still under full pressure, cooled to room temperature over a period of approximately two hours.

The mold consists of three parts. There are two outside metal plates, each six and one-half inches square and one-quarter inch thick. The inner stainless steel plate is like a picture frame with a square hole cut away on the inside; it is six inches outside and 4.75 inches on the inside and 0.015 inch thick.

Prior to their preheating, the pieces of the mold were sprayed with Teflon mold release agent, Acheson Release Coating #7 (40). In the molding step, the molten polymers were placed in the space of the picture frame and between the two outer plates. When the pressure was applied, the plastics squeezed into the form of the picture frame hole, resulting in sheets about 0.015 inch thick and 4.75 inches square.

From a single sheet a maximum of sixteen samples could be cut; however, due to irregularities close to the edges of the sheets, only twelve samples were usually obtained. Previous work (38) suggests that 0.015-inch thick specimens give results rather similar to the results of 0.125-inch thick specimens (1). As the thinner specimens require less material, give a greater number of more reproducible results, and are, in general, less troublesome than the thicker samples, the 0.015-inch thick sheets were employed in this investigation.

Twelve to sixteen ASTM D-638-68 Type IV "dog-bone" specimens were cut from each thin sheet using a cutting die. The thickness of the gage section of each specimen was carefully measured to the closest 0.001 inch, and those samples varying more than 0.002 inch from the thickest portion to the thinnest were discarded.

Instron Testing of Compression-Molded Materials

All of the 0.015-inch thick "dog-bone" specimens were tested on an Instron, Model Type TM, at room temperature, and at least one day after the sample was molded. An initial chart speed of 50 inches/minute, a constant crosshead speed of 1 inch/minute, and a full scale load of 10 pounds or 20 pounds were best suited for accurate measurement of the materials. (Increased strain rate is expected to increase the yield stress and the modulus while decreasing the elongation-at-break.)

Before testing was begun, the Instron was warmed up and calibrated according to operating procedures (41). Extreme care was taken to mount the "dog-bone" samples exactly vertically in the grips of the Instron, as it was discovered that even slight misalignment resulted in significant deviations of the data. The specimen was then subjected to a constant rate of strain. This stretching was allowed to continue until the breaking point of the specimen was reached. For highly elastic materials, the chart speed was switched from 50 inches/minute to 5 inches/minute after the yield point was encountered.

Data Reduction of Compression-Molded Materials

The tensile force-vs.-time records from Instron tests were used to determine the mechanical properties of compression-molded blends. This section describes calculations made from Instron tests and discusses some systematic errors incurred in the Instron testing and specimen preparation.

Figure B-1 depicts a typical tensile load-versus-crosshead movement curve for a brittle material such as 75/25 PS/PP.

Figure B-2 shows the same information for a ductile material such as 90/10 PP/Kraton G-1652. The tensile strength at either the yield point or break point is calculated by dividing the tensile load at that point by the original cross-sectional area of the sample. The tensile strength at yield is the

Figure B-1. Schematic stress-strain diagram for a typical brittle material.

Figure B-2. Schematic stress-strain diagram for a typical elastic material.

engineering stress calculated for the point where the specimen "yields;" i.e., the yield is the point where the stress first begins to decrease even though elongation increases. This phenomenon is usually explained by noting that the material becomes oriented along the axis of elongation. Calculated in the same manner as yield strength, the ultimate strength is the maximum stress exerted upon a specimen during an Instron test.

For many materials tested here, the yield tensile strength is identical to the ultimate strength. However, for some brittle materials such as pure PS, there is no yielding, and the ultimate strength is the tensile strength at break. For some materials such as pure PP, failure occurred at a higher stress than yielding. The latter exceptions were noted by giving the ultimate strength in parenthesis after the yield strength. Both the ultimate strength and tensile strength are in units of pounds per square inch (psi) when tensile force is in pounds and cross-sectional area is in inches.

The percent elongation-at-break is the increment in length at the point of break divided by the original specimen gauge length and multiplied by 100; it is a dimensionless quantity.

The modulus is the slope of the initial portion of the stress-versus-strain curve. It indicates the stiffness or resistance to elongation of a material. The initial modulus was

calculated using the method outlined in the ASTM Handbook (42). From the Instron recordings, modulus was determined by multiplying the initial linear slope of the force-versus-elongation curve by original specimen length and dividing by original cross-sectional area. For some of the softer materials which did not exhibit an initial linear region on the stress-strain curve, the modulus was approximated by constructing a tangent on the initial curve part of the Instron recordings and assuming the tangent to be analogous to the desired linear region. The modulus has units of psi.

Sources of Error of Compression-Mold Samples

The variances of data in compression-molded samples, in all cases, were larger than the variances in the data for injection-molded samples. Irregularities in the texture of thin films of compression molds probably accounted for the largest sources of scatter in the data. Nonetheless, use of very thin films, 1/64-inch thick, as compared to results using 1/4-inch films used in previous research (1), gave specimens with properties more nearly in agreement with those reported in the literature (43) for the pure materials; furthermore, data from the very thin films had markedly less scatter than did data from 1/4-inch films used in this laboratory (38,1).

Another source of error was the uncertainty of the original gauge length of the samples. An extensometer was

not used in the tensile tests. When an extensiometer is used, the gauge length is the section of the sample located between the extensiometer blades. The gauge length is assumed to be the measured length of the narrow section of the "dog-bone" specimen between the inner fillets when extensiometer is not used. However, the material forming the fillets of the sample does not contribute to the observed behavior. The effective gauge length may not be the same as the measured gauge length used in making calculations.

Data for modulus values may easily vary as much as 10%, owing to the inaccuracy of hand-drawn slopes.

Regardless of the magnitude of the scatter in the data or the deviations of results from reported data, the main objective of this research was to determine trends in mechanical properties. Hence, the goal is accomplished.

APPENDIX C

DTA PROCEDURE AND ANALYSIS

DTA characteristics were made using an R. L. Stone apparatus manufactured by Tracor, Inc. The instrument is provided with a JP-202 Furnace Platform which has a F-1DF furnace and a SH-11BR 2-A1 sample holder. An LB-202 recorder/controller is attached to this unit, as described by Locke (44). Locke's work contains an elaboration on the functioning, response, and calculations related to this instrument.

In this research aluminum pans were used to hold the reference material and the polymer sample. In all cases, 10.0 milligrams of Al_2O_3 plus Al pan comprised the reference, while 4.0 milligrams of polymer blend was used. Care was taken to ensure that the polymer sample was a single piece, having disc-shaped geometry so that it made excellent contact with the aluminum pan.

In keeping with established practice, the recorder is set up to give a V-shaped curve in response to the endothermic melting of a sample. The area in the valley is proportional to the enthalpy change associated with the transition. It is useful in determining heats of fusion of a partially crystalline polymer, which may then be used to calculate crystallinity of the polymer.

The temperature of the melting transition, T_m , is difficult to determine since the materials melt over temperature ranges which are dependent on thermal histories. In this work the melting point was taken as the nadir of each melting curve.

Although the area of the curve of the thermogram is proportional to the heat of transformation, the issue is complicated by inconsistent methods of evaluating the area. In particular, when the baselines before and after the transformation are not in direct line with each other, various workers have used different methods to analyze the area.

In a recent paper (45), Dumas proposes a reasonable method of circumventing uncertainties associated with transition-area determination: Figure C-1 is a schematic drawing of a typical melting endotherm on a ΔT vs. T coordinate system. With substantiation through theoretical reasoning, Dumas' method considers the total area under the curve as Areas I + II - III. Area I is simply the area within the curve under the line defined by the extension of the pre-melting base line. Area II is the area within the quadrangle defined by: the pre-melting base-line extension on the bottom; the post-melting base-line extension on the top; the nadir perpendicular line (defined as the line normal to the abscissa and passing through the nadir) on the right; and the normal to the pre-melting base-line extension at the intersection of the tangent line. (The tangent line intersects the nadir and is tangent to the declivity on the pre-melting side of

Figure C-1. Schematic drawing of a typical melting endotherm analyzed by the method of Dumas.

the T_m). Area III is enclosed by the final segment of the transition curve, the pre-melting base-line extension, and the normal to the pre-melting base-line extension which intersects the beginning of the post-melting base-line extension.

Figure C-2 is a reproduction of an actual thermogram of 20/60/20 PS/PP/Kraton G-1652 (refer to Chapter III). The method of Dumas is employed to compute the area of the thermogram. That is, a xerox copy of the original was made; then the appropriate lines were drawn on the copy; the areas were cut out and carefully weighed; and the results appear in Chapter III.

Figure C-3 is another reproduction of the 20/60/20 PS/PP/Kraton thermogram. However, it depicts an alternative, yet reasonable, method of analyzing the thermogram for melting transition area. In this method, one simply draws a pre-melting base-line extension, a post-melting base-line extension, and a nadir perpendicular line--all a la Dumas; but the area is that to the left of the nadir perpendicular line which is under the pre-melting base-line extension plus that to the right of the nadir perpendicular line which is under the post-melting base-line extension.

As one may suspect, the differences in the values of the amount of crystallinity, as reflected by the different methods of analysis of thermograms, are often fairly small. Moreover, one is usually interested in relative differences among a series of

thermograms of various samples. Figure III-12 of Chapter III shows the results of thermogram analysis via the method of Dumas. Figure C-4 shows the same information (solid symbols) plus the results of analysis of the thermograms by the procedure outlined in the previous paragraph (open symbols). Obviously, the differences in this case are negligible, yet there are cases in which the differences may be pronounced.

Figure C-2. An actual thermogram showing the Dumas method of area analysis.

Figure C-3. An actual thermogram showing an alternative method of area analysis.

Figure C-4. Area of endotherm vs. total weight % PP in blends with and without Kraton. Method A is that of Dumas. Method B is that outlined in Figure C-3.

APPENDIX D

PREPARATION AND TESTING OF INJECTION-MOLDED SPECIMENS

Blends of the desired weight composition were prepared by first premixing by hand weighed amounts of polymer pellets. The blend was then introduced into a Killion laboratory extruder with a one-inch screw diameter, an L/D ratio of 25, compression ratio of 3/1, and a circular die diameter of 1/8 inch. The extruder has three heating zones and a heated die. After the temperatures of each zone and the die were set, the screw speed was set at about 20 rpm. The initial extrudate was discarded until the pure desired extrudate appeared. The extrudate was passed through a cooling trough containing flowing water at about 20°C. As the material exited from the trough it was blown dry with high-pressure air. The dry strand was then introduced into a Killion chopper where it was pelletized and subsequently collected.

The blends were molded on a Van Dorn injection molding machine which is equipped with two molds--a dog-bone ASTM D-638-68 Type I and an Izod impact test mold. After the zones and die of the molder reached the desired temperatures, the barrel was purged of material from previous use. At least twelve specimens were made for each set of conditions. The ram pressure was used to control the fill and reduce flashing. The average cycle time was 40 seconds.

The injection-molded samples were tested on an Instron, model type TTC, using a crosshead speed of 2 in/min. The method of obtaining mechanical properties is identical with the method discussed in Appendix B.

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MECHANICAL PROPERTIES OF HDPE-POLYSTYRENE
AND ABS-HIPS BLENDS

by

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THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF SCIENCE IN ENGINEERING

THE UNIVERSITY OF TEXAS AT AUSTIN

August 1979

ACKNOWLEDGMENTS

I wish to express my deepest appreciation to Dr. Donald R. Paul for his assistance, insight, support and supervision in this endeavor.

I am also indebted to Dr. Joel W. Barlow for his friendship, interest, enthusiasm and the endless discussions that we have had during the course of this work.

I would also like to thank the Plastics Institute of America for their financial support and grant that made this research possible; and to Cosden Oil and Chemical Co., Shell Chemical Co., and Union Carbide Corp. for the materials donated for this study.

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April, 1979

ABSTRACT

Blends of High Density Polyethylene (HDPE) with Polystyrene (PS) and ABS with High Impact Polystyrene (HIPS) were prepared in an extruder. Dog bone samples of the pure materials and each blend were prepared by injection molding and tested for mechanical properties on an Instron Tensile Testing machine.

HDPE-PS blends produced brittle materials displaying a minimum in elongation of 5% in the blends containing 75% PS. The addition of Kraton G, an SEBS block copolymer, increased the elongation by two orders of magnitude while lowering the modulus and yield strength.

Although ABS-HIPS blends are immiscible, the expected decline in elongation displaying a minimum did not appear. Instead the blends have elongations which are intermediate to the elongations of the pure materials.

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CHAPTER I

INTRODUCTION

Modern life throughout the world is turning to polymeric materials to raise standards of living. This expansion has been encouraged by the abundant availability of petroleum as a source of raw materials for the production of resins. Since the oil embargo of 1973 the world, and the United States in particular, has been acutely aware that crude oil is a dwindling resource and must be conserved as a source of fuel. In the past, oil and petrochemicals have been an inexpensive source of raw materials for virgin resins, and the expenses involved in reclaiming and recycling materials has made recycling of plastic waste an unattractive prospect.

The demand for thermoplastics is increasing. Appendix D shows a breakdown by categories of the production of polymeric materials in the United States. In the ten year period from 1965 to 1975, the packaging industry alone increased its use of plastics by 82 percent. Because a majority of plastics used in packaging are disposed of after one use, it has been suggested (14) that

half of the increase, in landfill waste generated in 1973, was due to the increase in the production of plastic packaging and containers.

Complicated problems are associated with attempting to recycle plastics from waste (17). First the plastic must be sorted from other materials. The only successful endeavors to date have relied upon individuals separating the waste by hand; for example, in Mexico, one experiment has been operating since 1969, where people remove glass, metals, paper and plastics as the refuse moves along a conveyor belt (1). This process would not be successful in the U.S. due to high labor costs and the unattractiveness of the job, but automated processes are under development that will sort 100K tons of refuse per day (1). Even if plastics as a group could be sorted from other waste, other problems exist. Specific identification of different types of plastics is not always possible and because the materials have already been processed once, some thermal degradation has occurred. Technology for upgrading and purification is still in its infancy, and the possibilities of nonuniformity adds yet another dimension to the manufacturer's problem (17).

With present technology, the possibilities for utilizing manufacturing waste are much greater than reclaiming plastics from municipal waste. For example, the trimmings from injection molding are sometimes ground and returned to the molding machine. However, trimmings from vacuum forming and other similar processes are being discarded, burned (14), or used in the production of chemicals like HCl (2); presently only a small amount is being recycled. New designs for manufacturing facilities are attempting to address the need for collecting and recycling materials by reducing spillage and cutting process losses.

Today's demand for coextruded films adds another dimension to recycling problems. As the packaging industry turns to coextruded sheet and films to enhance a particular aspect of a container or wrapping, the amount of this kind of material is increasing in refuse. Attempts to recycle this material without separating layers, as a mixed scrap, usually generates immiscible blends that many times result in materials with poor ductility.

It is the purpose of this work to examine two immiscible blends and to attempt to improve, by using an additive, any poor properties that may be found. The

blend system of HDPE and PS was chosen for two reasons. First, HDPE and PS comprise a large portion of manufacturing and municipal waste and, therefore, the physical properties of the blends are of practical importance if these wastes are to be utilized for recycle feed streams. Secondly, it was believed that a commercially available block copolymer, Kraton G, might improve the ductility of the blend. ABS-HIPS blends were chosen for their industrial importance. Many applications of ABS are colaminated with HIPS; for example, refrigerator door liners are vacuum formed from sheets of ABS laminated HIPS. One estimate (40) is that 25% of a sheet can be lost to trimmings.

CHAPTER II

CONCEPTS

In general, thermodynamics teaches that for any process to occur spontaneously the change in the free energy for that process must be negative (21). If the free energy of mixing is negative a blend of polymeric materials will be miscible or in other words form a single phase system. In many cases blends of two polymers will form a two-phase system unless chemical forces are at work such as hydrogen bonding or ionic attraction that can overcome a positive free energy of mixing. Several tests have been suggested (20) and are used to determine if blends are immiscible.

Of greater significance is the characterization of polyblends as to their compatibility. Many different ideas and inferences have been tied by different groups of people to the word compatible. One concept is that blends are incompatible if the ductility of the blend decreases displaying a minimum at some intermediate composition and therefore a compatible blend will display only intermediate values for the ductility of the blend. Figure I

Figure 1. Compatibility Trends in % Elongation.

demonstrates this definition using elongation at break as a measure of ductility. For the purpose of this work, this is the definition that I will refer to in utilizing the terms compatible and incompatible.

It has been found (18, 22, 23) that the properties of blends can be improved, thereby giving a beneficial result if the size of the domain of minor phase can be reduced. This reduction can be achieved by using different processing techniques and varying processing parameters.

Another method for enhancing the properties of a polymeric blend in the addition of another material to act as a compatibilizer; that is a material which will improve the ductility of the blend. In general block copolymers of the two materials present in a blend have been found (24, 25, 27, 28) to improve the blends ductility. It is believed that the copolymer, during blending, may locate at the interfaces of component 1 and 2. Chain ends similar to component 1 would be embedded in component 1 and chain ends similar to component 2 would be embedded in component 2. If the poor ductility of the blend can be attributed to poor or no interfacial adhesion, then the location of a covalent bond in the chain backbone across the interface will act as an adhesive and will permit a

transfer of load across the interface, requiring more energy to break and improve the ductility of the blend.

In a multiphase system, the minor phase does not always form a dispersion. Although the morphology of a system can be a dispersion of spheres or cylindrical rods, the phases may be interlocked forming two or more continuous phases (19). Often the type of morphology found is a function not only of the materials involved but is also dependent upon processing condition. A recent work (18) found that, for the system studied, processing conditions during blending affected the mechanical properties of the blend by changing the morphology of the blend from dispersion to cocontinuous phases.

CHAPTER III

BLENDS OF ABS AND HIPS

Extrusion Blending

It is generally accepted that in blending of polymeric materials, processing parameters can play an important role in determining the final properties of the blend (5). It has been found (41) for two phase systems that if the viscosities of the materials are similar during blending then the component in higher concentration will become the continuous phase. It was also noted that for blends of equal composition the component that had the lower viscosity became the continuous phase. In blends the poor properties are often attributed to poor stress transfer across the interface between the components due to poor adhesion (4). As a load is applied to a test sample, the stress will concentrate at the interface. Because there is poor adhesion, the stress cannot be transferred causing the test bar to fail. As the size of the domains of minor phase increases, there are fewer interfaces to share the load and, therefore, the ductility

of the blend decreases as the continuous phase attempting to deform pulls away from the minor phase. If this is the case, one might desire to decrease the size of the domains of the minor phase which would increase the area of interface to share the load. This concept is supported by the work of researchers utilizing blends of PE and PS.

One technique (6), for decreasing the volume to area ratio of the minor phase in an extrusion process, is to blend at a temperature where the viscosity of the major component is greater than the viscosity of the minor component. This imbalance will increase the shear stress on the minor phase which will reduce the size of the domain of the minor phase and, therefore, increase the area of interface. Starita (23) demonstrated for both dispersions and cocontinuous morphologies utilizing light interference microscopy, SEM and solvent leaching of extrudate blends of PS and PE, that the volume to area ratios of the minor phase was related to differences in the viscosities of the two components during blending. When the viscosity of the minor component was less than or greater than that of the major component, the minor component was respectively finely dispersed or coarsely dispersed throughout the major phase. H. Van Oene (29)

also demonstrated in blends of PS and HDPE, where HDPE was the major phase, a reduction in the size of the domain of PS could be obtained if the temperature of the extruder was set at 170°C, or 55°C below the temperature where the viscosities of the two polymers were equal. At this temperature the viscosity of the HDPE was higher than that of PS. Patterson and Noah (23) have further shown that the ultimate elongation and impact strength for blends of PS and PE could be improved by reducing the volume to area ratio of the minor phase of the blend. In their experiment the size of the domain of the minor phase was reduced by processing at a temperature where the viscosity of the minor component was lower than that of the major component.

In order to apply this idea to the ABS-HIPS system, torque-temperature data for the pure materials were obtained. At a constant shear rate, the torque is proportional to the viscosity of the material. If at the same shear rate the torque of two different materials were equal then the viscosities should be similar. A 40 gram sample of ABS was placed in a Brabender mixing head at 20 RPM. The temperature was initially set at 200°C. After the meter registered a constant torque at this temperature, the torque

and temperature were recorded. The temperature was then increased 10°C and sufficient time elapsed to allow the indicator to register a new steady torque. After the temperature and torque were recorded, this procedure was repeated at 10°C increments, each time allowing the torque to stabilize before a reading was taken. During the experiment the mixing head was filled completely and capped to prevent thermal oxidation of the material. This procedure was repeated for HIPS and Kraton G. Each experiment was repeated to insure reproducibility of the data.

Figure II is a plot of torque vs. temperature for the ABS-HIPS system utilizing HIPS/825 from Cosden Oil and Chemical (see Appendix A). As can be seen from the figure the torques of these particular grades of HIPS and ABS do not intersect. Extrapolation of the data suggests a point of intersection at 295°C; above this temperature HIPS might have the higher viscosity and, according to the concepts already outlined, blends rich in HIPS should be processed above this temperature to enhance its mechanical properties. However, blending at temperatures above 295°C causes considerable thermal degradation of the ABS and, therefore, blends of these particular materials were not made.

Figure III. Torque-Temperature Diagram for HIPS/825E.

Figure II. Torque-Temperature Diagram for HIPS/825.

Another grade of HIPS, 825E, having a higher molecular weight was obtained from Cosden. Figure III is a plot of torque vs. temperature for this grade of HIPS, ABS and Kraton G 1652. Kraton data were obtained since it was originally thought that it might act as a compatibilizer for this system. It is observed that the viscosities of the two materials are approximately equal at 230°C (446°F). At higher temperatures HIPS has the higher viscosity, and at lower temperatures the viscosity of two materials are about the same.

Blends of the desired composition were prepared utilizing the Killion extruder. When at lower temperatures the Killion extruder could not obtain reasonable throughput rates, the Brabender extruder was used. Appropriate weights of materials were dry blended in a 4-liter beaker; the total weight of the dry blend was 2000 grams. After a uniform mixture was observed, 0.1 grams of red pigment was placed into the feed hopper to mark the beginning of a change in the extrudate composition, and the dry blend was added. The zone and die temperatures were preset at the appropriate temperature, and the screw speed for the Brabender and Killion extruders was set at 70 and 20 RPM, respectively. The initial extrudate containing the red

pigment was discarded because the actual composition of this material was unknown since residual material was being purged from the previous experiment. When the core of the extrudate, which has the longest residence time, turned clear or white the composition of the extrudate was considered to have stabilized. The extrudate was passed through a cooling trough at 32°F. After passing through a high pressure air ring which removed remaining surface water, the strand was pellitized by a chopper and collected. After each blend the chopper was cleared of residual material to insure that the next blend processed would not be contaminated.

Injection Molding

Common industrial practices attempt to optimize productivity by reducing the time required to manufacture a molded part. Although manufacturers will raise the temperature of the melt to decrease fill time, they will also attempt to keep the melt as cool as possible to reduce energy cost and decrease the cooling time. The pressure during injection will be kept as high as possible to reduce the injection time while insuring a complete fill of the mold without flashing.

In the molding of multiphase systems the temperature of the melt and the materials present will play an important role in determining the final properties of a molded part. Researchers such as Van Oene (7) and Han (33) have found that during the coextrusion of pure PS and PE, side by side, through a circular die, the material with the lower viscosity encapsulated the other. Therefore, there was a migration of the lower viscosity fluid around the other during flow. Lee and White (30) extruded a two phase polymer blend of HDPE and PS through a long circular die. During flow the material with the lower viscosity displayed a tendency to migrate outward. White, Oda, Clark and Yonezawa (8) injection molded PE and PS as two melts side by side. They also found that at temperatures where the viscosities were unequal, the component with the lower viscosity tended to encapsulate the other. All of the above experimentation was performed at high velocities to simulate the type of flow found in injection molding under isothermal conditions.

White (32) and Dee and White (31) have examined the rheology of flow during injection molding under nonisothermal conditions as would be found when filling a cold mold with a hot melt. Utilizing a heterogenous system of

HDPE and PS, they found that the melt in the center of the core had the highest velocity. A velocity gradient developed within the flow since the material closer to the walls was cooler and had a higher viscosity. There is therefore a shear stress gradient that develops during injection molding and the shear stress is higher closer to the walls.

In the preceding section the possible effects of uneven viscosities during extrusion on the mechanical properties of the blend was discussed. A necessary consideration, then, in light of the research outlined above, is the role that viscous effects may play during molding. A 50/50 blend of ABS-HIPS was utilized along with the pure materials to explore the effect of temperature during the injection molding of the ABS-HIPS system. The blend was prepared utilizing the Brabender extruder at 450°F. After blending in accordance with the procedure outlined in the section on extrusion blending, the blend and pure materials were dried in an air oven at 190°F for 24 hours prior to molding.

The blend and pure materials were molded on a Van Dorn injection molding machine with the initial molding temperature set at 405°F. After the barrel had been

purged of material from previous experimentation, seven samples were molded at the initial temperature. The temperature was increased 15°F and 30 minutes elapsed to allow the melt to become isothermal. Another seven parts were molded and the process was repeated until a ceiling temperature of 525°F was reached. Between each new temperature setting, melt was purged to lessen possible effects of thermal degradation. The ram pressure was used to control the fill and reduce flashing. Cooling time was set for 45 seconds and the average cycle time was 55 seconds.

An Instron floor model testing machine was used to obtain the mechanical properties of the molded parts. Testing procedures are outlined in Appendix C. Figure IV is a graph of yield strength vs. molding temperature. All three compositions exhibit a linear relationship between the yield strength and molding temperature with the higher strengths at the lower temperature. The strength of the blend at every temperature lies between the strengths of the pure materials. Declines in strengths can be contributed to increasing thermal degradation as the temperature is increased; therefore, the molding temperature does not appear to affect the yield strength.

Figure IV. Yield Strength of ABS-HIPS System as a Function of Molding Temperature.

A graph of modulus vs. molding temperature was prepared but is not presented. Although the modulus data was reproducible within $\pm 7\%$, no trends but only random scattering was observed.

The most dramatic effect is noted in the graph of elongation at break vs. molding temperature as shown in Figure V. ABS samples show a linear relationship with a noticeable but small decrease in the elongation at higher temperatures. HIPS samples display a definitive pattern passing through a maximum of 240°C . The elongation at break vs. molding temperature graph for another grade of HIPS with a lower molecular weight, not presented, also displayed the same configuration but the curve passed through a maximum at a lower temperature. The data for the blend exhibits a curve with the same configuration as the pure HIPS; however, the maximum has been displaced to a lower temperature of 235°C . A comparison of this temperature and the same temperature on the torque-temperature graph in Figure III, reveals that at this temperature the initial viscosities of the components in the melt are equal. The possibility does exist, therefore, that the temperature where the viscosities of the components of a blend are equal, may be the optimum temperature for molding.

Figure V. % Elongation of ABS-HIPS System as a Function of Molding Temperature.

If, initially, the viscosities of the melt components are equal, as they enter the mold and begin to cool, the viscosities of the two materials will become unequal. It has already been shown that in systems extruded or molded side by side there is a migration of the lower viscosity material to the surface. It is possible then that in multiphase melts, an imbalance in the viscosities of the components will cause uneven shear stress on the components, and the material with the lower viscosity will migrate toward the walls in the regions of higher shear stress. This idea is further supported by observations made of the samples during testing. The ABS resin used in this work was not as ductile as the HIPS resin. Test bars, molded at high temperatures where the ABS had a much lower viscosity than HIPS, failed at the skin first with the core undergoing additional elongation before its failure (see Figure VI). This could be considered as evidence that the core of the test bar was richer in HIPS and, therefore, the ABS migrated during the molding process toward the surface. The possibility exists in specimens that show a skin-core configuration might also exhibit the chemical resistance of ABS if the ABS is concentrated in the skin.

FIGURE VI. Photograph of a 50/50 ABS-HIPS Blend Exhibiting the Skin-Core Phenomenon

The residence time of the melt in the molding machine will also affect the mechanical properties of the material. A 50/50 ABS-HIPS blend was molded at 525°F to examine the effect of cycle times. The injection molding machine was purged of all melt until the material flowing from the nozzle exhibited obvious regions of highly viscous material. At this time the cycling of the machine was started. The cycle was 56.5 seconds in duration consisting of 3 seconds for injection, 3.5 seconds for recharging, 45 seconds for cooling and 5 seconds for ejection of the part. Each part was marked and tested for its mechanical properties.

Graphs of modulus, yield strength and elongation at break vs. the cycle number are plotted in Figure VII. The modulus and % elongation at break pass through a minimum while the yield strength decreases with time. After 5 cycles the modulus and elongation level out, and it appears that the process has reached thermal equilibrium. Based upon these observations the first five parts molded were always discarded; if any disruption occurred in the cycle the next five parts were also discarded.

Figure VII. Mechanical Properties as a Function of Cycle Time.

Binary Blends Without Weld Lines

The torque-temperature graph, Figure III, for this system shows an isoviscous operating temperature of approximately 460°F. Following the ideas outlined in the first section of this thesis regarding extrusion blending, temperatures for the extrusion were chosen in order to reduce the size of the domain of the minor phase. Considering Figure III, 500°F was chosen for the extrusion of the HIPS rich blend; and, since the viscosity of ABS never rises substantially above the viscosity of HIPS as the temperature is lower, the ABS rich and equal composition blends were extruded at 460°F. These temperatures are denoted above the graphs of the mechanical properties for each composition. The pure materials were not extruded. Dog bone test bars of each blend and the pure materials were molded at 460°F. Mechanical properties were tested in accordance with the procedures outlined in Appendix C.

In Figure VIII, the mechanical properties are plotted against the HIPS content in the blend. The modulus appear to be a linear function decreasing with increasing HIPS content. The yield strength decreases also as the concentration of HIPS increases and, as the concentration of HIPS increases, the elongation at break increases.

Figure VIII. Mechanical Properties of ABS-HIPS Blends.

For all of the properties tested there appears to be a linear relationship between the properties and the composition. This observation conflicts with the minimum that was expected in the elongation at break.

Blends With Kraton G 1652

Without Weld Lines

The effect of the addition of Kraton to this system was studied. It was thought that Kraton might increase the ductility of the blend based upon observations of the HDPE and PS system described in Chapter IV. A 50/50 ABS-HIPS blend was prepared containing 20% Kraton; the results of the mechanical tests for this blend are plotted as triangles on the graphs of the binary systems. The yield strength and elongation at break are reduced by 50%. The modulus increases by 16%. This is an unexplainable result since one would expect the modulus of the blend to decrease when a softer material is added. Because Kraton did not improve the ductility of the 50/50 blend, it did not meet the criteria outlined in Chapter II for compatibilizers and, hence, cannot be classified as a compatibilizer for this system. ABS-HIPS blends of other compositions containing Kraton were not prepared.

Thermal Analysis

Because of the unexpected result in the elongation at break, thermal analysis of the pure materials and the blends was conducted on the DTA. The ABS and HIPS were found to have glass transition temperatures, T_g , of 97 and 95.2°C respectively. Since the T_g 's of the pure materials were so close, thermal analysis of the blend was inconclusive. The function appeared to display more than one change in the heat capacity of the blends but the T_g 's could not be determined.

Blends With Weld Lines

Double gated dog bone samples were injection molded to obtain weld line strengths for blends of ABS and HIPS. Most of the samples molded failed at the weld line when ejected from the mold. Only when the mold was opened very slowly could the specimens be removed with the weld line intact. During testing all of the samples failed at the weld line; blends did not yield before failure and elongated less than one percent. Figure IX shows a graph of weld line strength vs. weight percent HIPS. The solid line is the weld line strength of the blends based upon

Figure IX. Weld Line Strengths of ABS-HIPS Blends.

the strengths of the pure materials predicted by the equation developed in Appendix E. The experimental error was ± 20 percent; this large range in the data coupled with obvious difference in the predicted and measured strengths suggests that, even with careful removal from the mold, the samples of the blends had already partially failed before testing.

CHAPTER IV

BLENDS OF HIGH DENSITY POLYETHYLENE WITH POLYSTYRENE

Background

Blends of HDPE with PS are classic examples of immiscible polymer systems and have been the subject of much research. The rheology of HDPE-PS blends during extrusion has been studied by Han and Kim (9). In blends that were 75 and 50% HDPE, the PS formed droplets that were dispersed throughout a continuous phase of HDPE. In the blend which was 75% PS, both phases were observed to be interlocked and no continuous phase was apparent. Van Oene (10) also found that, during extrusion of blends rich in PS, 90%, the PE formed a "ribbon-type dispersion" interlocked with PS and that this rheology was stable only during flow. When the blend was melted again the ribbon of PE relaxed into droplets which were dispersed in a continuous phase of PS. Using several different shear rates, Van Oene was unable to obtain the "ribbon-type" dispersion of PS and in every case the PS formed droplets dispersed

throughout a continuous phase of PE.

The mechanical properties of PE-PS blends have been studied by Still, Paul and Barlow (26). After extrusion through a slit die, the blends were oriented in the machine direction by hot stretching prior to quenching. In the axial direction, blends treated in this manner displayed better ductility and strength than the same blend that had been compression molded. However in the transverse direction, the hot stretched blend was significantly weaker. It could be concluded that orientation of the two phase blend overcomes some of the difficulties of poor interfacial adhesion and permits the load to be transferred more readily between the phases.

Processing

In order to apply the techniques outlined in Chapter III, the sections on extrusion blending and injection molding, torque-temperature data were obtained for HDPE, PS and Kraton G 1652. This graph is presented in Figure X. The torques for PS and HDPE are equal at 205°C (400°F); therefore, the viscosities of the two materials in the melt should be equal at that temperature. All of the

Figure X. Torque-Temperature Diagram for HDPE-PS System.

samples were injection molded at 400°F to reduce the effect of unequal viscosities during molding as described in Chapter III. In order to reduce the size of the domains of the minor component, the blends were prepared at temperatures where the viscosity of the major component was greater than the viscosity of the minor component. From the figure it can be seen that at temperatures below 400°F, the viscosity of the PS used in this study was higher than that of HDPE; hence, blends rich in PS were prepared at 375°F and blends rich in HDPE were prepared at 450°F in the Killion extruder. In the graphs of the mechanical properties of this system, the temperature of the extruder appears above each graph for each particular composition. The molded samples were tested for modulus, yield strength, and elongation at break according to the procedure outlined in Appendix C. The pure materials were not extruded but were molded and tested under the same conditions as the blends. Ranges in the measurements of modulus, yield strength and elongation at break are $\pm 10\%$, $\pm 5\%$ and $\pm 5\%$ respectively.

Binary Blends Without Weld Lines

The mechanical properties of the binary blends with the exception of elongation at break are those that would be predicted by weight averaging the properties of the pure materials. Figure XII is a graph of modulus vs. weight percent PS. The modulus of each composition is within experimental error of the modulus predicted by weight averaging. The yield strength for the blends is depicted in Figure XI. The curve is concave upward with yield strength increasing with increases in the PS content of the blend. Elongation at break is plotted vs. the blend composition in Figure XIII. The pure HDPE samples did not break within the full traverse of the Instron but the manufacturer estimates the elongation to be 700%. As the content of PS in the blend increases the ductility of the blend falls quickly to 34% elongation at 25% PS and continues to decline reaching a minimum of 5.2% elongation at 75% PS. The ductility then increases until the elongation of pure PS is obtained at 6.5%.

In appearance, the test bars of the blend exhibited mold shrinkage on one surface due to the partial crystallization of the HDPE. As the amount of HDPE in the blend

Figure XI. Yield Strength for HDPE-PS Blends.

FIGURE XII. Modulus of HDPE-PS Blends.

Figure XIII. % Elongation for HDPE-PS Blends.

increased the mold shrinkage increased. This transformation of the crosssectional geometry was considered in calculating the mechanical properties of blend in accordance with the procedure outlined in Appendix C.

Blends With Kraton G 1652

Without Weld Lines

The yield strength and ductility of HDPE-PS blends have been improved by the addition of a compatibilizer to the system. Locke and Paul found (25) that the addition of a graft copolymer of styrene onto the backbone of polyethylene (24) improved the yield strength of a 50/50 blend as much as 50% and the elongation at break as much as 100%. It was postulated at the end of one paper (25), that the addition of a diblock copolymer of styrene-ethylene would also enhance the ductility of the blends. Currently Shell Chemical Co. manufactures a triblock copolymer with styrene endblocks, Kraton G. The central portion, approximately 70% of the chain structure, is in effect a rubber composed of a random copolymer of ethylene and butene-1 which is formed by hydrogenation of polybutadiene with both 1,4 and 1,2 structures (see Figure XIV). Forming distinct spherical domain, Figure XV, the endblocks of PS

Figure XIV. Structural Configuration of Kraton G.

Figure XV. Physical Morphology of Kraton G.

act as physical crosslinking agents dispersed throughout a continuous phase of rubber. The 1652 grade utilized in this study has the lowest molecular weight styrene end-blocks made commercially by Shell that will form the PS domains (36). It was postulated that during blending the Kraton might locate at the HDPE and PS interfaces. If the styrene portion of the Kraton located in the PS and the rubber portion in the HDPE, then the Kraton would act as an adhesive allowing stress transfer between the two phases.

Blends of the same composition as the binary blends already discussed were prepared containing 20% Kraton in the Killion extruder. Dog bone samples were prepared at 400°F and tested in the same manner as the binaries.

In general the addition of Kraton, a rubber, lowered the modulus as would be expected when adding a softer material. The yield strength also declined but the elongation at break increased dramatically. As shown in Figure XII, the modulus of the HDPE-PS blends and HDPE and PS are reduced by approximately 20% in each case. Figure XI shows that the yield strength of every composition is decreased by adding Kraton. This result is in contrast with the improvement in yield strength found by Locke and Paul (25)

and may be attributed to the low yield strength, approximately 250 psi, of Kraton itself. The improvement in the ductility of the blends can be seen in Figure XIII. In the 50/50 blend the elongation at break has increased more than two orders of magnitude above that measured for the binary system. A minimum in the curve has disappeared. The addition of Kraton to the pure PS created a material whose mechanical properties are more representative of HIPS than crystal PS.

In determining the effect of varying the amount of Kraton added to this system, additional blends of 5, 10 and 30% Kraton were prepared. In each blend the remaining weight was evenly distributed between PS and HDPE. Figure XVI is a plot of the elongation at break vs. weight percent Kraton in the blend; for each 10% increase of Kraton the elongation increases 50%. The yield strength and modulus are plotted vs. weight percent Kraton in Figure XVII. In both cases increasing the amount of Kraton decreases the yield strength and modulus. Although these relationships appear to be linear, they most likely are approaching the values for pure Kraton asymptotically as the percent of Kraton in the blend increases.

Figure XVI. % Elongation of HDPE-PS Varying the Concentration of Kraton G.

Figure XVII. Yield Strength and Modulus of 50/50 Blends of HDPE-PS Varying the Concentration of Kraton.

Adhesion Tests

During mechanical testing of two phase systems, stresses will be concentrated at the interfaces, and the lack of adhesion or any other method to transfer stress from one phase to the other could explain the poor properties observed in the binary system (4). If Kraton is locating at the interface of the two components and, therefore, improving the ductility of the blends acting as an adhesive, the Kraton would necessarily adhere to both PS and HDPE. To test the adhesion that might exist between pure HDPE, PS and Kraton, a double peel test was performed.

Sheets having dimensions of 6 x 6 x 0.125 inches, of HDPE and PS were formed by compression molding of the pellets. Sheets of a 50/50 blend were prepared from pellets of an extrusion blend. Molding was performed at 400°F and 3000 psi. After 5 minutes the mold was rapidly cooled by running water through the press. All of the sheets were washed with soap and water to remove surface oils after molding. Care was taken to avoid handling or otherwise contaminating the surface of the sheet.

Sheets of Kraton were made by solution casting. Kraton was dissolved in cyclohexane until the viscosity

of the solution was similar to corn syrup. Glass plates, placed on the bottom of a pan shaped from aluminum foil, were used to provide a smooth surface. A double layered glass mat was placed on the glass surface, and the solution was poured over it. During testing the mat prevented the Kraton from deforming and nicking which would have created an imbalance in the stresses at the peel interface. The solvent was removed in a vacuum oven at 35°C and 6 inches of vacuum for 24 hours.

Three window templates of 0.125 inches in thickness were used during lamination to assist in maintaining the thickness of each sheet. The sheet of PS was located as the center sheet in all tests of adhesion of PS to another material. In the laminations of Kraton to HDPE, the HDPE was the center sheet. A thin edge, 10 mils, of aluminum was inserted between each sheet part way to leave a lip of material that could be grasped by the grips of the Instron (see Figure XVIII). The lamination was performed at 400°F and 1500 psi; again water was used to cool the mold after the temperature and pressure had stabilized for 5 minutes.

Lamination of HDPE to PS did not have any measurable surface adhesion, and in many cases the act of taking

Figure XVIII. Lamination Technique for Peel Tests.

the mold apart pulled the HDPE sheets from the PS. The Kraton sheets were laminated to the sheets of HDPE, PS and the 50/50 blend. Upon testing the two Kraton sides were placed in the grips of the table model Instron, and the crosshead speed was set for one inch per minute traverse. For the HDPE, 50/50 blend and PS the peel strengths were 9.4, 2.5 and 4.4 pounds per inch. Based upon the evidence of the peel tests and the improved ductility of the blends with Kraton, a strong case can be made for supporting the conclusion that Kraton does act as an adhesive between the two components of the blend.

Effect of Compatibilizer Molecular Weight

One additional experiment was conducted to determine the effect of the Kraton molecular weight. Kraton G 1650, which is an SEBS copolymer with the same configuration as 1652 but of higher molecular weight, was used in a 50/50 blend of the same materials; the chain ends of PS constituted 30% of the chain. The results of the mechanical tests proved that the modulus and yield strength still decreased, but the improvement in the elongation at break was not as large. Kraton G 1650 improved the elongation

at break only 60% of the improvement made by the 1652 grade material. In this case it would appear that increasing the molecular weight of the compatibilizer decreases the number of crosslinks between the HDPE-PS which lowers the ductility of the blend.

Blends With Weld Lines

Blends of HDPE-PS with and without Kraton were prepared under the same processing conditions as the single gated specimens previously described. In these cases, however, the second runner in the mold was opened, filling the mold from both ends and thereby locating a weld line approximately in the center of the sample. The specimens were tested for yield strength and elongation at break.

The results of these tests are plotted in Figures XIX and XX vs. weight percent PS. In the graph of yield strength, it is noted that in every case the weld line strength in the material containing Kraton was less than the strength of the blends and pure materials. There could be two explanations for this effect. First, the yield strength of Kraton may show up in the results as a lower adhesive strength and, secondly, the addition of a third component at the surface of the weld line presents

Figure XIX. Weld Line Strength for Blends of HDPE-PS.

Figure XX. % Elongation for HDPE-PS Blends With Weld
Lines and Kraton G.

more opportunities for mismatch of the components across the interface. The lines on the graph are the yield strengths that are calculated from the yield strength of the pure materials in accordance with the theory outlined in Appendix E. From the graph of elongation, the observation is made that Kraton did increase the ductility of the blends. The binary blends elongated less than one percent before failure.

Thermal Analysis

As in the blends of ABS-HIPS, differential thermal analysis of this system was also performed. The T_g of the PS was found to be 98.8°C , and the T_m of the HDPE was approximately 144°C . It is known that the area under an endothermic peak on a DTA plot represents the heat of melting for the material and is directly proportional to the amount of crystallinity in the material. The area under the curve for the blend was ratioed to the area under the curve of the pure HDPE and multiplied by 100 to obtain the percent of crystallinity of the HDPE retained based on the total blend mass. Figure XXI is a plot of percent crystallinity vs. weight percent HDPE. A line has been struck between the origin and the point (100,100) which

Figure XXI. % Crystallinity of HDPE-PS Blends.

represents the change in crystallinity for the HDPE-PS blends without Kraton. The 50/50 HDPE-PS blend was tested and the percent crystallinity was 51% as plotted on the graph. All of the blends below 80% HDPE contain 20% Kraton with the additional mass composed of PS. See Table 1 for a complete listing of composition and percent of crystallinity. There appears to be two lines of crystallinity effects. As Kraton is added to the HDPE without PS the crystallinity decreases significantly faster than the rate that would be caused by a simple reduction in the HDPE mass in the system. Then at 80% HDPE, the slope changes as PS is added to the system and the line passes through (0,0). It is apparent that the Kraton is interfering with the crystallization of the HDPE.

Kraton G 1652, as noted earlier, has the lowest molecular weight styrene endblocks made commercially by Shell that will form PS domain. It has been suggested (36) that if the PS domains are small enough, enough shear stress may be generated during blending that the domains break up. If this is happening in the blends with HDPE, then the possibility exists that, due to the dilution of the Kraton by the HDPE, enough PS chain ends cannot find each other to form PS domains again and are

Table 1
Relative % Crystallinity for HDPE-PS Blends

Composition			Relative % Crystallinity
% HDPE	% PS	% Kraton	
100	--	--	100
90	--	10	81
80	--	20	56
60	20	20	45
50	50	0	50
40	40	20	29
20	60	20	15
--	80	20	0
--	100	--	0

left suspended in HDPE. These PS chain ends then would be interrupting the continuous phase of HDPE and might, therefore, be hindering the crystallization. However, it should be noted that these ideas have no direct proof and are only speculation.

CHAPTER V

SUMMARY AND RECOMMENDATIONS

Immiscible blends of HDPE with PS and ABS with HIPS were prepared in an extruder. From the literature it was shown that the morphology and, therefore, mechanical properties of the blend depend upon the processing parameters of shear rate, temperature and composition. Also from the literature the optimum blending temperature appears to be one at which the viscosity of the major component is greater than the viscosity of the minor components.

Kraton G was found to improve the ductility of blends of HDPE with PS and, therefore, meets the criteria established in Chapter II as a compatibilizer for this system. The elongation at break improved as the amount of Kraton added to the system was increased but the modulus, yield strength and weld line strengths decreased. It was noted that Kraton G 1652 appeared to lower the crystallinity of HDPE which PS did not. This depression in the crystallinity is significant in that recent work (35) has shown that the degree of crystallinity in polypropylene

will affect the mechanical properties of polypropylene blends. Further work should explore the effect of the degree of crystallinity of HDPE upon the properties of the blend and the mechanism by which Kraton appears to hinder the crystallization of HDPE.

Blends of ABS and HIPS display a linear relationship between the mechanical properties of the blends and pure materials and the composition. The weld line strengths of the blends are less than the strengths of the pure materials and passes through a minimum at approximately 60% HIPS. Kraton G did not improve the mechanical properties of the blend.

APPENDIX A

MATERIALS

The manufacturer's product specifications are given in the tables of this appendix. Table 2 shows the properties of HDPE grade DGDA-6084 used in the HDPE-PS blends. The physical properties of both Kraton G-1650 and Kraton G-1652 are given at 25°C in Table 3 (39). Abson ABS-89120, Cosden's Polystyrenes 550, 825 and 825-E are listed in Tables 4, 5, 6 and 7 respectively. The crystal PS was 550.

Table 2. Physical Properties of HDPE from the Union Carbide 1977-78 Materials Catalogue.

UNION
CARBIDE

CHEMICALS AND PLASTICS

BAKELITE² POLYETHYLENES FOR FILM EXTRUSION (Continued)

Typical Properties		
FDA STATUS (a)	ASTM Test Method	DGDA-6084 Natural 7
CHARACTERISTICS		
Description		General purpose
Applications		Merchandise bags
Density at 23°C., g./cm. ³	D 1505	0.960
Melt Index at 190°C., g./10 minutes	D 1238	0.3
Secant Modulus at 1% Elongation, plaque, psi.	D 638	135,000
FILM PROPERTIES (1.5-mil tubular)		
Dart Impact, F ₅₀ , g./mil	D 1709, Method A	(c)
Tensile Strength, psi.	D 882	
Machine Direction (MD)		5,300
Transverse Direction (TD)		4,500
Elongation, %	D 882	
Machine Direction (MD)		700
Transverse Direction (TD)		450
Coefficient of Friction (COF)		
Rating, measured		
24 hours after extrusion	D 2103	
Haze, %	D 1003	
Gloss, Gardner Glossmeter	D 523	
50° Polished Background		
45° Dull Background		
Product Modification (f)		UM
Stock Temperature, °F.		475

Table 3. Physical Properties of Kraton G.

Material	KRATON G-1650 Rubber	KRATON G-1652 Rubber	KRATON 1101 Rubber
Specific Gravity	0.91	0.91	0.94
Solution Viscosity* cp			
15%w Solids	350	150	300
25%w Solids	8500	2500	4000
Films Cast from Toluene Solution			
Appearance	clear, water-white	clear, water-white	clear, water-white
Tensile Properties:**			
Tensile at Break (T _B) psi	6000	6500	4600
Elongation at Break (E _B) %	500	500	880
100% Modules (M ₁₀₀) psi	950	730	400
Hardness, Shore A	75	75	71
Approx. Styrene Rubber Ratio	30/70	30/70	30/70
*Brookfield, see also Fig. 6 **Measured on films cast from toluene. INSTRON jaw separation rate 10 inches per minute, temperature 23°C, dumbbell specimens cut with ASTM Die D.			

Table 4. Physical Properties of ABS.

Abson®

ABS MATERIALS

89120

Injection Molding Compound

Abson 89120 ABS is characterized by:

High surface gloss

High strength

High heat distortion

Medium impact

Excellent processibility

Typical Value		Typical Value	
Tensile Properties, ASTM D 638		General Properties	
Strength, MPa (psi)	48 (7,000)	Specific gravity, ASTM D 792	1.05
Modulus, MPa (psi)	2600 (380,000)	Specific volume, cm ³ /g (in ³ /lb)	0.95 (26.4)
Elongation, %	20	Mold shrinkage, ASTM D 955 cm/cm (in/in)	0.003-0.004
Flexural Properties, ASTM D 790		Hardness, Rockwell R, ASTM D 785	113
Strength, MPa (psi)	94 (13,700)	Melt Index, Condition I, ASTM D 1238, g/10 min.	5
Modulus, MPa (psi)	2800 (400,000)	<p>All test results were obtained on injected molded specimens according to the appropriate ASTM Standard. All data shown is for unpigmented natural compound. Heat deflection temperature values on injected molded samples are usually 5.6 to 8.3°C (10 to 15°F) lower than the values obtained on compression molded samples of the same material.</p> <p>Appearance: Pellets or cubes.</p> <p>Color availability: Any opaque color.</p> <p>Chemical properties: Resistant to aqueous acids, alkalies and salts; insignificant changes from exposure to low KB solvents, alcohols and animal, vegetable and mineral oils. Ketones, esters and alkylhalides are solvents.</p>	
Impact Properties, ASTM D 256			
Notched Izod, J/m (ft lbf/in)			
23°C (73°F)	187 (3.5)		
-29°C (-20°F)	80 (1.5)		
-40°C (-40°F)	53 (1.0)		
Thermal Properties			
Heat Deflection Temperature, ASTM D 648			
1.82 MPa, °C (264 psi, °F)	91 (196)		
Annealed Heat Deflection Temperature, ASTM D 1788			
1.82 MPa, °C (264 psi, °F)	99 (211)		
Vicat, ASTM D 1525, °C (°F)	103 (218)		
Coefficient of Thermal Expansion, ASTM D 696			
cm/cm °C (in/in °F)	4.5x10 ⁻⁵ (8.1x10 ⁻⁵)		

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Table 5. Physical Properties of Crystal PS.

Cosden Polystyrene 550

Product Description
Cosden High heat 550 is designed for injection molding applications requiring maximum heat distortion and increased strength characteristics. For example high quality cutlery. In addition 550 is a proven polymer for use in foam sheet. 550 has good flow and excellent clarity even in heavy injection molded sections.

TENSILE PROPERTIES

ASTM D 638-72	typical value
Strength, psi	7500
Modulus of elasticity, psi (10 ⁵)	3.6

FLEXURAL PROPERTIES

ASTM D 790-71	
Strength, psi	14,600
Modulus of elasticity, psi (10 ⁵)	4.3

THERMAL PROPERTIES

ASTM D 648-72	
Heat distortion, °F	
unannealed	174
annealed	204
ASTM D 1525-70	
Vicat softening point, °F	224

OTHER PROPERTIES

ASTM D 785-65	
Rockwell hardness	
L	90
M	60
ASTM D 1238-73	
Flow, grams/10 minutes "G"	2.5
ASTM D 792-66	
Specific gravity	1.05

All tests were run under laboratory conditions. ASTM (where applicable) testing procedures. The data are intended as a general guide only and do not necessarily represent results that may be obtained elsewhere. The use of Cosden's products must be guided by the user's own methods for selection of the proper formulation. Cosden disclaims any responsibility for misuse or misapplication of its products.

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Table 6. Physical Properties of HIPS-825.

Cosden Polystyrene 825

Product Description
High Flex 825 is not just another high impact polystyrene. For years 825 has been the leader among shock resistant polystyrenes. Its outstanding flex properties resist cracking and splitting. Used in appliance parts, hobby horses, tackle boxes, furniture applications, containers, and blow molded parts.

TENSILE PROPERTIES

ASTM D 638-72	typical value
Strength, psi	3000
Elongation, %	40
Modulus of elasticity, psi (10 ⁵)	2.4

FLEXURAL PROPERTIES

ASTM D 790-71	
Strength, psi	5600
Modulus of elasticity, psi (10 ⁵)	2.8

IMPACT PROPERTIES

ASTM D 256-73	
Gardner Impact	
Izod, ft/lbs/in. of notch	2.0
Falling dart, inch pounds	60

THERMAL PROPERTIES

ASTM D 648-72	
Heat distortion, °F	
unannealed	155
annealed	185
ASTM D 1525-70	
Vicat softening point, °F	200

OTHER PROPERTIES

ASTM D 785-65	
Rockwell hardness	
L	65
M	10
ASTM D 1238-73	
Flow, grams/10 minutes "G"	7.0
ASTM D 792-66	
Specific gravity	1.04

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Table 7. Physical Properties of HIPS-825E.

Cosden Polystyrene 825 E

Product Description
A highly specialized formulation that extrudes into uni-form gauge sheeting that form easily into thin wall coffee cups or thick wall refrigerator door liners. 825 E offers a combination of high heat resistance, high impact strength, outstanding stress crack resistance and exceptional processing characteristics.

TENSILE PROPERTIES

ASTM D 638-72	typical value
Strength, psi	4000
Elongation, %	46
Modulus of elasticity, psi (10 ³)	2.6

FLEXURAL PROPERTIES

ASTM D 790-71	
Strength, psi	6800
Modulus of elasticity, psi (10 ³)	3.0

IMPACT PROPERTIES

ASTM D 256-73	
Gardner Impact	
Izod, ft/lbs/in. of notch	2.0
Falling dart, inch pounds	60

THERMAL PROPERTIES

ASTM D 648-72	
Heat distortion, °F	
unannealed	162
annealed	194
ASTM D 1525-70	
Vicat softening point, °F	210

OTHER PROPERTIES

ASTM D 785-65	
Rockwell hardness	
L	68
M	20
ASTM D 1238-73	
Flow, grams/10 minutes "G"	4.0
ASTM D 792-66	
Specific gravity	1.04

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APPENDIX B

EQUIPMENT

1. Extruders:

a. Brabender Plasticorder Model 2003

Screw:	0.75 inch
L/D Ratio:	20
Feed Depth:	0.15 inch
Compression Ratio:	3/1
Helix Angle:	20°
Maximum RPM:	112
Maximum Torque:	5000 gr-mtrs
Circular Die Diameter:	0.125 inch
Two primary heating zones and die	

b. Killion Laboratory Extruder

Screw:	1.0 inch
L/D Ratio:	25
Feed Depth:	0.2 inch
Compression Ratio:	3/1
Helix Angle:	20°
Maximum RPM:	140
Circular Die Diameter:	0.125 inch
Three Heating Zones and Die	

2. Brabender Mixing Head:

Mixing Bowl:	60 ml
Blades:	2 Roller
Maximum RPM:	112
Maximum Torque:	5000 gr-mtrs

3. Injection Molding Machine

Van Dorn Model H-150

Capacity:	2 oz.
Clamps:	50 Ton
Maximum Pressure:	2000 psig
Two Heating Zones and Nozzle	

4. Compression Molding Machine

Greenerd Press, Hydrolair

Usable Surface Area:	100 sq. inches
Temperature Range:	ambient-700°F
Maximum Pressure:	10,000 psig
Water and Air Cooled	

5. Tensile Testing Instrument

a. Instron Floor Model TT-C

Load Cell:	"F"
Full Scale Range:	40-10,000 lbs.

Crosshead Speed Range:	0.02-20. inch/min
Chart Speed Range:	0.2-50. inch/min
Maximum Traverse:	25 inches

b. Instron Table Model

Load Cell:	"C"
Full Scale Range:	1-50 lbs.
Crosshead Speed Range:	0.02-20. inch/min
Chart Speed Range:	0.2-50 inch/min
Maximum Traverse:	25 inches

6. Differential Thermal Analysis-Instrument

Tracor Stone Model JP202

Reference: Al_2O_3 - 10 mg.

Pans: Aluminum

Thermocoupler: Chromel Alumel (K)

Range: Ambient to 250°C

APPENDIX C

TESTING PROCEDURES FOR MECHANICAL
PROPERTIES

Samples of blends and pure materials were prepared for testing on a Van Dorn injection molding machine in accordance with the procedure outlined in Chapters III and IV. In preparing the mold American Society for Testing Materials (ASTM) D638 was used. Specimens conformed to type I specifications; the actual dimensions are listed in Table 8 on the next page.

Testing was performed on an Instron for their tensil properties, i.e. modulus, yield strength and elongation at break in compliance with ASTM D638. In order to insure that the applied stress was concentrated in the neck of the specimen, the crossheads were located in the widest portion of the sample a short distance outside of the radii. The gage length was established at 4.25 inches. Although the majority of deformation of the sample occurred in the neck, deformation of the radii and a small part of the gripping section of the test bar was observed. Since these deformations lowered the values of the tensil

Table 8
Dimension of Tensile Test Specimens

<u>Dimension</u>	<u>Abb.</u>	<u>Inches</u>
Width Overall	WO	0.75
Width at Neck	WN	0.5
Length Overall	LO	8.5
Length of Neck	LN	2.50
Radius of Fillet	RF	3.00
Thickness		0.125

Figure XXII. Test Bar Specimens.

properties, an allowance was made for these changes by calculating a modified gage length using graphical integration. It is known that:

$$S = \frac{F}{E} \int_0^L \frac{dx}{A(x)}$$

where: S is the deflection,

F is the applied force,

$A(x)$ is the crosssectional area as a function of the distance down the bar,

L is the distance between grips,

and E is Young's modulus.

If we set:

$$S = \frac{FL'}{EA_0}$$

where: A_0 is the crosssectional area of the neck

and L' is the gage length;

then:

$$L' = \int_0^L \frac{A_0 dx}{A(x)}$$

The adjusted gage length, L' , was determined by the graphical integration of the above function. The distance between

the grips, L , was set at 4.25 inches, the crosssectional area of the neck, A_0 , was 0.0625 inches and the adjusted gage length was calculated to be 4.17 inches.

Mold shrinkage was observed in the HDPE-PS system. To correct for shrinkage the actual crosssectional area of the neck was obtained. Using a fine tooth saw, a sample was crosssectioned in the neck and the rough edges carefully smoothed with a fine grain sandpaper. Black India ink was applied to the crosssectional surface of the sample and several impressions were made on blotter paper. The impressions had three flat surfaces and the other surfaces had a peak in the center that was almost as high as the sides. On either side of the peak was an indentation or trough. The depth of the trough was obtained using a magnifying glass and a fine ruler and the area calculated treating the trough as a triangle (see Figure XXIII). The actual crosssectional area was calculated by subtracting the areas of the two triangles from the area of a rectangle having the same width and depth as the straight sides of the impression.

The softness of some of the blends tested which included Kraton required separate testing conditions for modulus from those for yield strength and elongation.

Figure XXIII. Injection Mold Shrinkage.

When testing for modulus the full scale load was set at 40 pounds. The crosshead and chart speeds were set for 0.2 and 50 inches per minute respectively. These settings permitted close observation of the recorded stress vs. strain rate thereby reducing the error in obtaining the initial slope of the curve. Several samples of each blend and the pure materials were tested. Each sample was stressed to a load of forty pounds at least four times in succession; each time the recorder reached the upper limit, the crossheads were returned to the initial gage length manually. Two or three minutes elapsed between tests to permit the sample to recover most of its original shape. A forty pound load did not stain any samples to the extent of causing irreversible damage.

In analyzing the modulus from the recorded record a curve was utilized to smooth fluctuations in the curves that appeared to be slippage in the gripes. From the curve a 0.5 percent secant modulus was obtained by locating a point on the curve that reflected a change in the length of the sample of approximately 0.5 percent of the initial gage length. A straight line was passed from the origin of the test through this point and the slope was calculated. The modulus was then obtained allowing for

differences in the chart and crosshead speeds, a corrected gage length and mold shrinkage (see Figure XXIV).

After testing each composition for modulus, fresh specimens were used to determine the yield strength and percent elongation at break. Full scale load was reset at 200,500 or 1000 pounds as appropriate for the material tested and the chart and crossheads speeds were reset at one and two inches per minute respectively. In the case of brittle materials the yield strength was read from the chart at maximum load. The yield strength for ductile materials was read from the apex of the stress-strain curve at yield. In all cases the percent elongation at break was calculated from the break point as follows:

$$\% \text{ Elongation} = \frac{\Delta L}{L_0} \times 100$$

Yield strength was calculated as follows:

$$Y.S. = \frac{\text{Stress}}{A_0}$$

The data were corrected for differences in chart speeds, crosshead speeds and full scale loads (see Figure XXV).

Figure XXIV. Measurement of Initial Slope on Stress-Strain Diagram.

Figure XXV. Measurement of Yield Load and Elongation on Stress-Strain Diagrams.

APPENDIX D

MARKET SHARES FOR PLASTICS

The following information reflects the current share of the market that each major group of polymers has: (1)

<u>Polymer</u>	<u>Percent</u>
Low Density Polyethylene	17.6
High Density Polyethylene	9.5
Polyvinyl Chloride	14.4
Polystyrene	9.8
Polypropylene	8.5
Styrene-Butadiene	7.8
Nylons	6.3
Polyesters	4.1
Polybutadiene	2.1
Acrylics	1.9
Others	8.0
Total	100.0

APPENDIX E

WELD LINES STRENGTHS

In any molding process weld lines are formed where the melt flows meet producing the weakest point in the fabricated part. Whenever possible molds are designed in such a manner to reduce the number and size of weld lines but normally they cannot be altogether eliminated. This inherent weakness is due in part to orientation effects as the melt flows through the mold. As discussed in Chapter IV, flows into a cold mold will harden at the wall causing the mold to fill from the center as depicted in Figure XXVI. Flows meeting head-on will be oriented in the traverse directions creating interfaces (12, 13).

A method has been proposed by Paul (38) for predicting the weld line strengths of immiscible blends. If a blend is injected into a dog bone mold through both ends by double gating, then the composition of each side of the weld line should be the same as the blend itself. Let F_i^l and F_i^r be the surface fraction of component; on

Figure XXVI. Flow Profile of a Hot Melt Into a Cold Mold (13).

the left and right sides of the interface respectively and let A_{ij} be the adhesive strength of polymer i to j . The total adhesive strength then across the interface would be:

$$TS = \sum_{ij} A_{ij} F_i^{\ell} F_j^r$$

For a binary system this equation becomes:

$$TS = A_{11} F_1^{(\ell)} F_1^{(r)} + A_{12} F_1^{(\ell)} F_2^{(r)} + A_{21} F_2^{(\ell)} F_1^{(r)} + A_{22} F_2^{(\ell)} F_2^{(r)}$$

Because the stream was split to form the weld line $F_1^{(\ell)} = F_1^{(r)}$ and $A_{21} = A_{12}$ the equation becomes:

$$TS = A_{11} F_1^2 + 2A_{12} F_1 F_2 + A_{22} F_2^2$$

If component 1 does not adhere to component 2, $A_{12} = 0$, this equation further reduced to:

$$TS = A_{11} F_1^2 + A_{22} F_2^2$$

where A_{11} and A_{22} are the adhesive strengths of the pure materials. This same equation might be used for blends containing a compatibilizer if its mass concentration

in the blends is constant for every blend and if A_{ii} is taken to be the adhesive strength of component i containing the compatibilizer.

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POLYMER COMPATIBILITY STUDIES IN HYDROGEN
BONDING SYSTEMS

DISSERTATION

Submitted in Partial Fulfillment of
the Requirements for the
Degree of

DOCTOR OF PHILOSOPHY (Chemistry)

at the

POLYTECHNIC INSTITUTE OF NEW YORK

by

Sai-Pei Ting

June 1980

Approved:

Department Head

Date

Copy No. _____

ACKNOWLEDGEMENT

The author would like to acknowledge the guidance, encouragement, and expert advice of Professor Pearce and Dr. Kwei during the course of this study.

Many useful suggestions from Professors Bulkin and Winter for FT-IR and thermal analysis, respectively, are sincerely appreciated.

The author also wants to express his thanks to Professor Erickson for his assistance in the use of the Instron, and Dr. Chu for the preparation of the proposal under this subject.

Many valuable discussions with Drs. Cheng and Lee in relation to the synthesis of the polymer are acknowledged.

The financial assistance from Professor Okamoto during his first year at the Polytechnic Institute of New York and from the Plastics of America, Inc. for the subsequent two years are gratefully appreciated.

ABSTRACT

"POLYMER COMPATIBILITY STUDIES IN HYDROGEN BONDING SYSTEMS"

by

Sai-Pei Ting

Advisors: Professor Eli M. Pearce, Dr. T. K. Kwei

Submitted in Partial Fulfillment of the Requirement for
the Degree of Doctor of Philosophy (Chemistry)

A series of styrene and hydroxyl containing styrene copolymers were prepared. Poly(styrene-co-vinylphenyl trifluoromethyl carbinol)(PFA), poly(styrene-co-vinyl hexafluorodimethyl carbinol)(PHFA), and poly(styrene-co-vinylphenyl methyl carbinol)(PMA) were prepared by the post-reaction of polystyrene(PS, $M.W.=3 \times 10^5$). Copolymer of styrene and p-vinyl phenyl trifluoromethyl carbinol(COPFA), and copolymer of styrene and p-vinyl phenol(COPVOH) were prepared by the copolymerization of styrene and the respective monomers. Copolymers prepared by the post-reaction of PS were high molecular weight ($\eta_{inh} = 0.97 \sim 1.07$) whereas those prepared by the copolymerization were low molecular weight ($\eta_{inh} = 0.31 \sim 0.32$). The glass transition temperatures of these copolymers ($105 \sim 109^\circ C$) were slightly higher than that of PS ($104^\circ C$). The mole % of hydroxyl group in each copolymer used in this study were 15.6(PFA), 40.5(COPFA), 22.1(PHFA), 44.2(PMA), and 86.9(COPVOH), respectively.

A crystalline polymer, poly(ethylene oxide)(PEO, M.W.= 1×10^5), was chosen as a model polymer for blending with the copolymers because of its previously shown capability to engage in hydrogen bonding.^{23,24} Blends were prepared by a solution casting method.

The compatibility of these blends were defined by the use of glass transition criteria determined by differential scanning calorimetry(DSC). The compatible ratio of these copolymers with PEO were in the order COPVOH(86.9 mole % of OH) > COPEA (40.5) $\approx$ PHFA(22.1) > PFA(15.6) >> PMA(44.2). The melting depressions of PEO in the blends were found with a similar trend as in the compatible ratio, COPVOH > COPFA $\approx$ PHFA > PMA > PFA.

Hydrogen bonding formation in the copolymer/PEO blends were studied by dispersive infrared spectroscopy. The two copolymers, PFA and PHFA, used in this study showed no significant inter- and/or intramolecular hydrogen bonding in the pure polymers. The infrared spectra showed that hydrogen bonding was formed as these two polymers were blended with small amounts of PEO, and then gradually separated into two peaks, - free and hydrogen bonded hydroxyl, as the concentration of PEO was increased to more than 50% by weight. The spectroscopic data were further analyzed by the use of

Fourier Transform Infrared Spectroscopy(FT-IR). The $-CH_2$ symmetric stretching absorption peaks of PEO were also shifted down to lower wavenumbers as the blends had higher concentration of copolymer. Hydrogen bonding occurring in the compatible blend, e. g., PFA/PEO(4/1, W/W) or PHFA/PEO(4/1), could be partially broken and then completely reformed when the blend was heated to 175 °C and then gradually cooled to room temperature. Interactions occurring in the incompatible blend, PS/PEO(8/1), and in the compatible blend, PFA/PEO(8/1), were studied by comparing their experimental and computer-generated synthetic spectra, respectively.

The coupling effect of these copolymers in ternary systems with PS and PEO were evaluated by DSC. The compatibility of PS and PEO were improved by adding certain amounts of the copolymers.

The mechanical properties of the ternary blends were preliminarily evaluated by stress-strain measurement(Instron tensile testor). PS and its modified polymer, PHFA, showed the expected higher modulus and tensile strength, as well as lower elongation at break than PEO. As PS was gradually replaced by PHFA in PS and PEO blends, the modulus and tensile strength were proportional decreased whereas the elongation at break showed little or no change.

PHFA also was shown to have potential compatibility with other types of polymers. Only a single, composition-dependent T_g was observed in the blends of PHFA with bisphenol-A polycarbonate, poly(n-butyl methacrylate), and poly(2,6-dimethyl-1,4-phenylene oxide). The plots of T_g 's of these compatible blends vs. the concentration of the latter polymers showed an abnormal positive deviation in the PHFA rich blends.

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I. INTRODUCTION

1. OBJECTIVE

Research on polymer compatibility can be related to important areas having wide application and potential among which are- (1) the recycling of waste polymers with the resultant conservation of energy-related materials derived from a petroleum base and which also requires the expenditure of energy in its manufacture. Waste disposal of polymers is an increasingly important problem¹. Recycling can be accelerated by the development of compatibilization approaches. The ability to utilize these materials without requiring a complicated separation of polymeric species could be accomplished by compatibilization systems^{2,3}; (2) the opportunity for preparing materials from readily available polymers with an unusual combination of properties related to diffusion-solubility barrier parameters, mechanical strength and modulus, as well as these and other properties which can be related to transition temperature phenomena; (3) alternate approaches to materials defined by specific end-use properties. This becomes increasingly important in two spheres- (a) the short supply of certain materials on various occasions-this would allow an alternate approach to meeting specific needs, and (b) the possibility that because of potential public health problems related to some polymers and/or additive systems, substitutes that are readily available and economical will be required in a relatively short time frame.

The objective of this study was as follows-

(1) The preparation of a series of hydroxyl containing vinyl copolymers with the general structural formulas in (Ia-c) and (II) below.

(a) $R=H$, $R'=CF_3$

(b) $R=H$, $R'=CH_3$

(c) $R=CF_3$, $R'=CF_3$

(2) The investigation of structural effects, such as inductive effects (Ia vs. Ib), and the hydroxyl group content (Ia with different mole % of OH) of these copolymers on the compatibility with a "model" polymer, poly(ethylene oxide).

(3) The exploration of the relationship between the compatibility of these copolymer/PEO blends utilizing hydrogen bonding interactions as well as the conformational changes of the constituent polymers and the strength of hydrogen bonding as a function of temperature by the use of Fourier transform infrared spectroscopy.

(4) The evaluation of these copolymers as good blending or coupling agents for the improvement of the PS/PEO blend properties. The preliminary evaluation of the mechanical properties, such as modulus, tensile strength, and elongation at break, of these copolymers used as coupling agents added

to PS/PEO blends.

(5) The assessment of the potential compatibility of these copolymers with other commercially available polymers, such as bisphenol-A polycarbonate, poly(n-butyl methacrylate) and poly(2,6-dimethyl-1,4-phenylene oxide) for future study.

2. BACKGROUND

2-1. Compatibility of Polyblends

Polyblends are physical mixtures of structurally different homo- or copolymers. A compatible polyblend is defined as a single entity of materials containing within its physical boundary at least two thoroughly mixed polymers which are not linked covalently⁴. Polyblend compatibility may be judged by measuring certain properties as the composition varies from 100% A to 100% B⁵ : (1) Compatible homogeneous blends should form a single-phase system and behavior very much like random copolymers; as composition varies from poly-A to poly-B, properties should change gradually, following a straight line or a simple monotonic curve, depending on the units used to express concentrations and properties, and the choice of arithmetic or logarithmic methods for plotting the results. (2) Semi-compatible blends should form micro-phases in which the polymer present in lesser amount disperses as discrete particles in the continuous matrix of the polymer present in greater amount, with most of the properties determined by the continuous matrix. When the two polymers are present in fairly comparable amounts, properties should go through a transition region, producing an S-shaped curve. (3) In-compatible blends should form separate phases with little adhesive strength at the interface, causing early failure under low stress, and thus producing a U-shaped curve.

Few polymers form compatible polyblends^{6,12,16,17,26,50} and this can be explained on a thermodynamic basis.^{4,7,8} For a potential compatible mixture, the free energy of mixing, ΔG^m , should have a negative value. ΔG^m can be determined by the enthalpy of mixing, ΔH^m , and the entropy of mixing, ΔS^m , in the relationship, $\Delta G^m = \Delta H^m - T \Delta S^m$. For a high-molecular-weight polymer mixture, the change of ΔS^m is always positive but is very small or negligible. Therefore, ΔG^m is primarily dependent on ΔH^m . For a quantitative calculation of the heat of mixing, the Hildebrand-Scatchard equation⁹ gives:

$$\Delta H^m = \phi_1 \phi_2 V^m (\delta_1 - \delta_2)^2$$

where V^m is the total volume of the mixture, ϕ is the volume fraction of the component polymer, and δ is the solubility parameter of the respective polymer. δ is related to the heat of vaporization and is dependent on the attractive forces between molecules. Unless the solubility parameters of the individual polymers are very close, in other words, they have very similar force fields in the mixture, the ΔH^m is always positive and results in phase separation. For most compatible blends, except for strong interaction forces such as hydrogen bonding, the $\Delta \delta$ are smaller than 0.5¹⁰ (Table 1).

Table 1. Solubility Parameter Difference Between
Some Compatible Blends.¹⁰

Component A	Component B	Wt % A	$\Delta\delta^a$
poly(vinyl chloride)	butadiene-acrylonitrile copolymer	90-20	0.5
poly(vinyl acetate); natural rubber	poly(methyl acrylate) polybutadiene	50 0-100	0.7 0.2-0.3
styrene-acrylonitrile copolymer (80/20)	butadiene-acrylonitrile copolymer (65/35)	70-100	~0
poly(vinyl acetate)	vinyl chloride-vinyl acetate copolymer (90/10)	40-50	<0.3
butadiene- acrylonitrile copolymer (60/40)	cellulose acetate butyrate	20-90	<0.3
polystyrene	butadiene-styrene copolymer (45/55)	≥ 40	<0.3
polystyrene	poly(2,6-dimethyl-1,4- phenylene oxide)	0-100	<0.3
poly(acrylic acid)	poly(ethylene oxide)	0-100	~2.3
poly(methyl methacrylate), isotactic	poly(methyl methacrylate), syndiotactic	0-100	0
poly(α -methyl L- glutamate)	poly(α -methyl D- glutamate)	0-100	0

^a Difference in solubility parameters between components A and B.

If polymer compatibility is to mean a single homogeneous phase and is associated with nearly complete mixing of molecules at the molecular level as it does for simple liquids, no truly compatible blends are known. Various methods have been used to determine compatibility of polyblends and each method has its own relative interpretation. The methods used are-^{4,10-13}

(1) phase separation in solution- miscible solutions indicate that the polymers are compatible. Brodsky¹⁴ has discussed this approach in detail.

(2) optical appearance-a clear, transparent film may indicate a compatible blend. This method is limited to component polymers with different refractive indices and do not form multiple layer films.¹²

(3) glass transition temperature(T_g)- if the polyblend shows one single composition-dependent T_g , it is compatible. If the polyblend shows two distinct T_g 's corresponding to the parent polymers, the system is incompatible. Advantages for this method are rapid measurement, small sample sizes (typically 5-30 mg), permitting the study of heat sensitive materials(e.g. PVC), and powder form samples(e.g. coprecipitation blends). Resolution of T_g 's in blends containing

polymers which less than a 22 °C difference in T_g is poor.¹⁵
Definition of compatibility for some crystalline/amorphous blends are ambiguous when the crystalline polymer is the matrix.¹⁶

(4) dynamic mechanical analysis- If the modulus-temperature curve of a polyblend is between those of the two parent polymers, the polyblend is compatible. If the modulus-temperature curve shows multiple transitions, the polyblend is incompatible. Advantages of this method are that additional information on the moduli (shear modulus or tensile modulus), and the low-temperature secondary relaxations of the parent polymers and the polyblend are obtained. However, only films or fibers (i.e. not powders) made from the blends can be studied. Resolution for blends of polymers having close transition temperatures is also poor.

(5) microscopy- this is a powerful tool for visually studying the distribution of two phases in the polyblend. Heterogeneity as revealed by microscopy is a relative property. A polyblend with finer domain size will be more compatible than one with a larger size. Advantage of this method over glass transition temperature and dynamic mechanical testing is that there are no limitations in regard to the closeness of the transition

temperatures of the parent polymers. However, no completely unambiguous criteria for defining compatibility or incompatibility is available.

(6) melting point depression- this method is widely applied to the crystalline/amorphous polyblends (e.g., PVF₂/PMMA, PVF₂/PEMA) developed by Nishi, Wang, and Kwei.^{16,17} They have derived an equation more appropriate for polymer diluent system from Scott's equation¹⁸ for thermodynamic mixing of two polymers based on an extension of the Flory-Huggins lattice theory.¹⁹ This equation can be used to calculate the polymer-polymer interaction parameter and to predict whether the polyblend is compatible or not.

(7) nonradiative energy transfer- a new method, developed by Morawetz and Amrani in 1978,²⁰ promises to measure a wider range of blend-states of polymer combination from complete miscibility to the relatively minor interpenetration between the parent polymers. They synthetically prepare copolymers with small amounts of two different chromophores and measure the strength of energy transfer by fluorescence techniques. If the wavelengths of the light emitted by one chromophore overlaps the absorption range of another, and if the two are placed close together, then light absorbed by the first

may be emitted by the second. Hence the strength of energy transfer will depend on the actual distance between the two polymer chains. Advantage of this method is that it is not limited by any closeness of polymer transition temperatures and makes available a more quantitative index of the degree of blending that has occurred.

2-2. Polyblends through Hydrogen Bonding Systems

Hydrogen bonding is an especially strong kind of dipole-dipole attraction, in which a hydrogen atom serves as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely electrostatic forces.⁸¹ Compounds of fluorine, oxygen, nitrogen, and sometimes chlorine are capable of forming hydrogen bonds. Hydrogen bonds can exist in solid, liquid, and in solution. Even in the gas phase, compounds which form particularly strong hydrogen bonds may be still be associated.²¹ Except for the $\text{FH} \cdots \text{F}^-$ bond (bond energy ≈ 40 Kcal/Mole), the strengths of hydrogen bonds are approximately in the range of $2 \sim 8$ Kcal/Mole. Typically, hydrogen bonds range between 2.4 to $3.2 \text{ \AA}$ in length.²²

The first compatible polyblend through a hydrogen bonding system was reported by Smith et. al. in 1959.²³ They found that when aqueous solutions of poly(ethylene oxide)(PEO) and poly(acrylic acid)(PAA) were mixed in approximately equal proportions, a precipitate formed immediately which could be recovered by filtration, dried and pressed out to form clear, almost water-insoluble flexible films. The mechanical properties of this molecular association complex were quite different from those which might be predicted on the basis of either component alone. The solubility parameter difference, ΔS , between these two polymers is large having a value of 2.5 (Table 1) which is far beyond the scope for

most compatible polymer pairs where the $\Delta\delta$ are usually smaller than 0.5. It also should be noted that this combination is composed of a polar polymer, PAA, and a relatively non-polar polymer, PEO. The large difference between polarities and solubility parameters in the PAA/PEO pair indicate that compatibilization can be achieved by utilizing hydrogen bonding effects. The favorable mixing of hydrogen bonding pairs can be also found in other blending systems, such as poly(methacrylic acid)/poly(ethylene oxide)²⁴, poly(methacrylic acid)/poly(vinyl pyrrolidone)²⁵, and poly(butylene terephthalate)/poly(hydroxyether of bisphenol A)²⁶. Even the weakly "acidic" proton-donating characteristic of the α -hydrogen in poly(vinyl chloride)(PVC), has been proposed to enhance miscibility with a number of polymers - including syndiotactic poly(methyl methacrylate)²⁷, poly(ϵ -caprolactone)^{28,29}, and poly(butylene terephthalate)³⁰. Specific hydrogen bonding interactions have also been credited to yield miscibility in blends of homopolymers and various copolymers such as nylon-6/poly(ethylene-co-acrylic acid)³¹, PVC/ethylene-vinyl acetate-sulfur dioxide terpolymer³², and PVC/poly(ethylene-co-N,N-dimethyl acrylamide)³³. It is also noteworthy that among the known polymeric alcohols, only nitrocellulose has been reported to be compatible with cellulose acetate propionate, poly(vinyl acetate), poly(methyl methacrylate), poly(styrene-co-methyl methacrylate), and poly(ester-co-urethane)³⁴. Poly(vinyl alcohol), however,

has been reported to be incompatible with methyl cellulose, or poly(acrylic acid)³⁶, but, it was described as "almost compatible" with poly(methacrylic acid).^{37,38}

The interaction between constituent polymers as a result of hydrogen bonding has only been postulated and not directly proven. In some systems, such as PVC/poly(ethylene-co-N,N-dimethyl acrylamide)³³, the interaction was postulated based on infrared studies using di-substituted amides and model compounds similar to PVC³⁹. No direct evidence was presented on the polymers and their blends. The inter- and/or intramolecular hydrogen bonding occurring in the respective proton-donor polymers, such as poly(acrylic acid),²³ was very difficult to differentiate with respect to the hydrogen bonding which occurred between the constituent polymers in the blend. Therefore, if a polymer only has small quantities of hydroxyl group, where the inter- and/or intramolecular hydrogen bonding occurred in the polymer itself is decreased, the intermolecular hydrogen bonding interaction between this proton-donor polymer and the other proton-acceptor polymer could probably be studied.

Hydrogen bonding can be detected either by infrared spectroscopy or by nuclear magnetic resonance spectroscopy.⁴⁰ In infrared spectroscopy, hydrogen bonding always shifts the proton donor(e.g., -OH) and the proton acceptor(e.g., C=O) peaks toward lower wavenumbers, although the shift is greater for the former. In many cases there is partial hydrogen bonding, and in such cases two peaks appear. Intramolecular hydrogen bonding may be distinguished from intermolecular hydrogen bonding by its constancy when the concentration is varied. In NMR spectroscopy, hydrogen bonding can be detected because it usually produces a shift to lower field.

2-3. Preparation of Blends

The principal methods of preparing of polyblends are by melt mixing, latex mixing, and solution mixing.^{4,10,11,41}

(1) Melt mixing: Preformed polymers are mixed by an extruder²⁶, a roll mill⁴², or by a Brabender Plasticorder⁴³. The extent of mixing is dependent on the rate of diffusion of the chain molecules⁴⁴. The establishment of equilibrium is influenced by the time of mixing, the shear gradient, the temperature, and the rheological properties of the polymers.⁴⁵⁻⁴⁸ Strong shearing forces often decompose or degrade polymers, and the resulting radicals can often participate by cross-linking or by the formation of a graft or block copolymers leading to a new structure in the polyblend.⁴⁹ Mixing in the melt must be restricted to thermally stable polymers and to polymers not readily sensitive to a shearing force.

(2) Latex mixing: In a latex, polymers are present as suspended microspheres. Interaction of neighboring spheres are prevented by the suspending medium (soap). The polyblend is obtained by coagulating the latex or evaporating the dispersing agent (H_2O). Melt mixing is often employed for compounding and pelletizing the latex-blended materials, and necessary precautions in this stage must be taken to avoid degradation or decomposition as in the previous method.

(3) Solution blending: Polymers are mixed by dissolving in a common solvent, followed by precipitation and/or drying. Advantages for this method are low temperature mixing, normally without the difficulties with shearing and polymer degradation, and usually leads to mixing at the molecular level. Coprecipitation sometimes gives a heterogeneous material if the components have different solubilities. Vaporization of the common solvent sometimes enhances phase separation if the interactions between the solvent and the respective polymers are quite different. For example, polystyrene/poly(vinylmethylether) blends are compatible when films are cast from toluene and are incompatible when cast from chloroform.⁵⁰ Therefore, compatibility evaluations of samples prepared by solution blending have to be done with care.

2-4. Mechanical Properties of Polyblends

Compatible polyblends generally exhibit good mechanical properties. For example, the tensile strength appears to be minimally as a function of the weight average of the values corresponding to the two respective component in a compatible blend¹² but often shows enhanced tensile strength in certain blend compositions.⁵¹⁻⁵³ In contrast, incompatible polyblends have a broad minimum in tensile strength which is a function of blend composition.^{52, 54-56} The modulus of rigidity of compatible polyblends are approximately linearly dependent on the blend composition whereas this relationship is not predictable in the incompatible blends.⁵⁷ Other properties such as impact strength can be greatly improved by blending the dispersed particles of a rubbery phase into a glassy material, e. g., rubber modified high impact polystyrene^{58,82}, and ABS⁸². However, a quantitative relationship between the impact strength and blend composition is still not available.

2-5. Improvement of Polymer Compatibility by Adding

Coupling Agent

Block or graft copolymers have been used as coupling agents to improve the compatibility between the corresponding homopolymer blends. Riess et. al.⁵⁹ compared random, block, and graft copolymers for improving the compatibility (judged by optical clarity) for PS/PMMA and PS/1,4-cis-polyisoprene blends, respectively. They found that the random copolymer did little to improve the blend compatibility while much improvement was obtained using block and graft copolymers, the block being more effective than the graft. Locke and Paul^{3,83} have found that a block-like copolymer, chlorinated PE, greatly improved the properties of blends containing PE and PVC, and a graft copolymer of poly(ethylene-g-styrene) improved the properties of PE/PS blends. The domain size of blends containing these additives were found to be smaller and more uniform in size than in blends which did not contain additive copolymers. Kwei et. al.⁶⁰ blended poly(vinylidene fluoride)(PVF₂) with the incompatible blend of PMMA and PEMA since PVF₂ showed compatibility with PMMA¹⁷ and PEMA¹⁶, respectively. They found that the mixtures containing 40 to 70 % by weight of PVF₂ showed a single homogeneous phase as studied by DSC.

Compatibility improvement through hydrogen bonding interactions between the coupling agent and one constituent polymer and through dispersion interactions between the coupling agent and the other constituent polymer has not been previously reported.

2-6. Polymer Synthesis

Preparation of copolymers of styrene and hydroxyl containing styrene with the general structure, Ia and Ib, can be approached either by copolymerization of the ketone form of the respective monomers or by the post-reaction of PS with the Friedel-Crafts acylation reaction. The ketone containing polymer can be reduced to the alcohol

Copolymerization of styrene and p-vinyl trifluoromethyl acetophenone has been reported by Chu and Pearce⁶¹, and Cheng and Pearce⁶² while copolymerization of styrene and p-vinylmethyl acetophenone is unknown. Post-reaction of PS with trifluoroacetyl chloride has been reported by Cheng and Pearce⁶² while post-reaction of PS with acetyl chloride is a known procedure reported by Kenyon and Waugh.⁶³

Preparation of the copolymers of styrene and p-vinylphenyl hexafluorodimethyl carbinol(Ic) can also be approached by two ways.

Synthesis of p-vinylphenyl trifluorodimethyl carbinol, or p-(2-hydroxyhexafluoro-2-propyl)styrene, and its homopolymer has been reported by Middleton.⁶⁴ The copolymer of styrene and this monomer should be readily prepared by free radical polymerization. Post-reaction of PS with hexafluoroacetone has not been reported whereas the model reaction, toluene and hexafluoroacetone, has been reported by Farah et. al..⁶⁵

Copolymers of styrene and p-vinylphenol(II) can be prepared either by copolymerization of styrene and p-vinylphenol as reported by Sovish⁶⁶ and Kato⁶⁷ or by copolymerization of styrene and p-vinylphenyl benzyl ether followed by removal of the benzyl group similar to the procedure reported by Ferruti and Fere.⁹⁷

2-7. Characterization Techniques

There are many techniques that can be used to characterize polymeric materials with each technique giving insight into different properties. The techniques used in this study involve thermal analysis(DSC), infrared(dispersive IR and FT-IR), and bulk mechanical properties(stress-strain behavior).

(1) Differential Scanning Calorimetry(DSC)^{68,69}

DSC is a technique for studying the thermal effects accompanying physical or chemical changes in a sample as the temperature is varied through a region of transition or reaction by means of programmed heating or cooling. The instrument (DSC) maintains the sample temperature isothermally to a reference substance by supplying heat to the sample or reference material. The amount of heat required to maintain these isothermal conditions is then recorded as a function of time(or temperature). The area under a thermogram peak is directly proportional to the heat energy absorbed or liberated in the particular transition occurring with a material.

A typical thermogram of a polymer with glass transition (T_g), crystallization(T_c), and melting(T_m) is shown in Fig.1. The T_g can be defined either as the inflection temperature

Fig. 1. Typical DSC thermograms.⁶⁸

* C_p : Heat capacity at constant pressure.

point which occurs at the discontinuity in C_p^* at the glass transition, the intersection point of the projection of the baseline with the tangent to the discontinuity (intersection method), or the temperature corresponding to the midpoint of the discontinuity ($1/2 \Delta C_p$). The melting point of a polymer is difficult to determine since the material can melt over a wide range which can be greatly dependent on the thermal history of the sample. T_m also can be defined either as the onset point or as the return point of the melting curve.

The peak area in the DSC thermogram is proportional to the enthalpy change associated with the transition. It is useful in determining the heat of fusion of a semi-crystalline polymer which may then be used to calculate the crystallinity of the polymer using the relationship,⁷⁰

$$X = \frac{\Delta H_f}{\Delta H_f^0} \times 100$$

where X is the fraction of crystallinity, ΔH_f is the heat of fusion of the polymer tested and ΔH_f^0 is the heat of fusion of a 100 % crystalline polymer.

Several equations have attempted to correlate the observed T_g of a compatible blend with the blend composition as is frequently done with random copolymers. They are -
(a) the Fox equation,⁷¹

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where $W_{1,2}$ represents the weight fraction of the respective components and T_g , T_{g1} , and T_{g2} are the T_g 's of the blend, component 1 and component 2, respectively.

(b) the Gordon-Taylor equation,⁷²

$$W_1(T_g - T_{g1}) + kW_2(T_g - T_{g2}) = 0$$

where k is an empirical constant and can be determined from the slope of the T_g vs. $(T_g - T_{g1})W_1/W_2$ with $-1/k$, or as the slope of the T_g vs. $(T_g - T_{g2})W_2/W_1$ with k .

(c) the Kelly-Buche equation,⁷³

$$T_g = [T_{g1} + (kT_{g2} - T_{g1})\phi_1] / [1 + (k-1)\phi_2]$$

where ϕ_1 and ϕ_2 are the volume fractions of each component and k represents the ratio of the thermal expansion coefficient difference above and below the T_g 's for component 2 and 1 ($k = \Delta\alpha_2/\Delta\alpha_1$).

(2) Fourier Transform Infrared Spectroscopy(FT-IR)^{74,75}

FT-IR consists of an optical component(spectrometer) which has an infrared source, the Michelson interferometer,⁷⁴ a sample chamber, an infrared detector, and all of the necessary transfer optics and electronics to transmit the infrared radiation from the source, through the interferometer and sample, to the detector and out to the other major component(data system); and a data processing component(data system) which

has a mini-computer used for data collection, computation, and storage.

The main advantages of FT-IR over conventional dispersive IR⁷⁴ are (a) the increased energy throughput, (b) the improved accuracy of the frequency scale, (c) the computer capabilities for processing the digitized spectral data, and (d) the multiplex or Fellgett's advantage⁷⁶ (an interferometer receives information from all frequencies in the spectrum simultaneously during each scan).

(3) Stress-Strain Properties^{22,68}

The stress-strain curve of a polymer provides many important clues as to its mechanical behavior. This measurement is usually made on polymers by stretching the material but it can also be done by compression or shear. Fig. 2 is a schematic stress-strain curve which is useful in defining these properties- the modulus of elasticity obtained from the initial slope of the curve; the yield stress; the elongation at yield; the elongation at break; and the ultimate strength (stress at failure). Stress-strain curves for other classes of polymeric materials are shown in Fig. 3. A detailed discussion of these methods and models for polymer stress-strain behavior have been reported by Winding⁷⁷ and Nielsen.⁷⁸

Fig. 2. Generalized stress-strain curve for polymers.⁶⁸

Fig. 3. Stress-strain curves for several types of polymeric materials.⁶⁸

II. EXPERIMENTAL

1. Materials

PS(Dow Chemical Co., Styron-685D, $M.W.=3 \times 10^5$) was purified by precipitating a methylene chloride solution of PS into methanol. PEO(Aldrich Co., $M.W.=1 \times 10^5$) and PPO(Aldrich Co., $M.W.=3-4 \times 10^5$) were additive-free powders, and used directly without further purification. PBMA(Aldrich Co., $M.W.=3-4 \times 10^5$) and BAPC(Polyscience Inc., $M_v=5.6 \times 10^5$, measured in CH_2Cl_2 at $25^\circ C$) were purified by the same method as used for PS. Tri-fluoroacetyl chloride(Fairfield Chemical Co., b.p.= $-18^\circ C$) and hexafluoroacetone(E. I. Du Pont de Nemours and Co., b.p.= $-28^\circ C$) were liquified gases stored in steel containers. p-Chloracetophenone(Aldrich Co.) and acetyl bromide(Eastman Kodak) were used without purification. p-Hydroxycinnamic acid (Aldrich Co.) was purified by recrystallization from a water/methanol mixture(3/1, V/V).

2. Polymer Synthesis

2-1. PHFA(Poly styrene-co-vinylphenyl hexafluorodimethyl carbinol)

PHFA was prepared by the following route which was analogous to the procedure described by Farah et. al.,⁶⁵ used for the preparation of (2-hydroxyhexafluoro-2-propyl) benzene.

PS, 15.6(0.15 mole), was dissolved in 240 g of carbon disulfide(CS_2) in a reaction flask equipped with a stirrer, a gas inlet tube, a thermometer, two reflux condensers cooled with dry ice-acetone mixture, and an external cooling bath. About 6 g of aluminum chloride(AlCl_3) was added as a catalyst. The external cooling bath temperature was kept at about 5°C by an ice-water mixture. Hexafluoroacetone was gradually added to the stirred $\text{PS-CS}_2\text{-AlCl}_3$ mixture at a rate of 0.5-1 drop/sec. About 30-40 minutes were required for the addition of 12-14 g of hexafluoroacetone. Excess hexafluoroacetone did not increase the extent of reaction because the product becomes insoluble and separates from the solvent CS_2 . The reaction mixture was then poured into an excess of water

(300-400 ml) to effect hydrolysis. CS_2 was gradually removed by boiling the water. The light yellow crude product was then purified by precipitating the polymer from a CH_2Cl_2 solution into excess hexane. A white fluffy polymer was obtained with the yield of 110-100 % (W/W). The mole ratio of styrene to vinylphenyl hexafluorodimethyl carbinol was determined by fluorine elemental analysis. About 22.1-31.0 mole % of the latter unit was found. The material used in this study contained 22.1 mole % of the fluorinated unit. The infrared spectrum showed absorptions at 3600-3520 (ν O-H's) and 1230-1169 cm^{-1} (ν C-F's) indicating that the hexafluorodimethyl carbinol as attached to the phenyl rings of PS.

2-2. PFA(Poly styrene-co-vinylphenyl trifluoromethyl carbinol)

PFA was prepared by the following route;

(I) was prepared by reacting PS with trifluoroacetyl chloride and aluminum chloride in the presence of carbon disulfide as a solvent, analogous to the procedure reported by Simons et. al.^{79,80} and by Cheng and Pearce.⁶² The reaction

apparatus was the same as for the preparation of PHFA. Since the model reaction of toluene with trifluoroacetyl chloride gave the p-isomer, (I) was assumed to be predominately para-substituted. (I) is a random copolymer of styrene and acetylated styrene characterized by the IR, 1715 (ν C=O's) and 1169-1129 cm^{-1} (ν C-F's) and by the elemental analysis of the products. About 15 mole % of the phenyl rings were substituted with trifluoroacetyl moieties. Attempts to achieve higher conversions (> 15 mole %) resulted in a crosslinked product which was insoluble in common organic solvents. Table 2 indicated the data for the conversion of PS to (I) at varying reaction time.

PFA(II) was obtained by the reaction of (I) with lithium aluminum hydride(LAH) in THF as solvent. The reaction was essentially complete as indicated by the disappearance of carbonyl absorption (1715 cm^{-1}) and the appearance of hydroxyl group (3550 cm^{-1}) in the IR.

2-3. COPFA(Copolymer of styrene and p-vinylphenyl trifluoromethyl carbinol)

Higher mole ratios of vinylphenyl trifluoromethyl carbinol in the copolymer could be achieved by an alternate approach-

p-Vinyl trifluoroacetophenone(III) could be prepared either by the reaction of 1 mole of trifluoroacetic acid with 3 mole of p-vinylphenyl magnesium chloride⁶¹ or by the reaction of 1.1 mole of lithium salt of trifluoroacetic acid and 1 mole of p-vinylphenyl magnesium chloride.⁶² The yield by the latter method was higher since the first mole of Grignard reagent was used up by the reaction with the -OH group of trifluoroacetic acid. The yield was about 35 % based on the lithium salt. The mechanism for this reaction has been reported by Cheng and Pearce.⁶² Copolymer(IV) was prepared by the copolymerization of styrene and (III) with azobisbutyro-

nitrile(AIBN) as the initiator(0.5 wt./total wt. of the monomers). The degassed polymerization ampoules containing various mole ratios of styrene and (III) were heated at 60 °C for 24 or 72 hrs.(Table 3) The white polymeric products were purified by dissolving in THF and precipitating in petroleum ether. The infrared spectra of these copolymers showed absorptions at 1715 (ν C=O's) and 1169-1129 cm^{-1} (ν C-F's) indicating that the trifluoroacetyl group was present in the copolymers. COPFA(V) was obtained by hydrogenation with LAH. The appearance of hydroxyl absorption at 3550-3400 cm^{-1} (ν O-H's, broad) and the disappearance of carbonyl absorption at 1715 cm^{-1} indicated that the reaction was complete.

2-4. PMA(Poly styrene-co-vinylphenyl methyl carbinol)

PMA was prepared by a similar route as PFA.

(VI) was prepared according to the procedure reported by Kenyon and Waugh.⁶³ The reduction of (VI) was by the same procedure as for PFA. The infrared spectrum of (VII) showed absorptions at 3550-3400 (ν O-H's, broad) and 1155-1000 cm^{-1} (ν C-O's). The reaction of PS with two different mole ratio of acetyl bromide are reported in Table 4.

2-5: COPVOH (Copolymer of styrene and p-vinylphenol)

COPVOH was prepared by the following route

p-Vinylphenol(VIII) was obtained by the pyrolysis of p-hydroxycinnamic acid in a sublimator at 220°C under vacuum (0.01 mmHg) by the same procedure reported by Overberger et. al.;⁸⁴ m.p. 72°C (lit.⁶⁶ $71\text{--}72.5^\circ\text{C}$). The infrared spectrum showed the absorptions at 3350 cm^{-1} ($\nu\text{O-H's}$, broad) and $1220\text{--}1170\text{ cm}^{-1}$ ($\nu\text{C-O's}$). NMR spectrum showed resonance peaks at 2.12 ($-\text{OH}$, 1H), 3.18–3.88 (aromatic H, 4H), 3.94–4.13 ($\text{H}=\text{C}$, 1H), and 4.84–5.60 τ ($\text{H}_2\text{C}=\text{}$, 2H).

COPVOH(VIX) was prepared by the copolymerization of styrene and p-vinylphenol in bulk at two different mole ratios with AIBN as the initiator (0.5 wt./total wt. of the monomers). The degassed polymerization ampoules were heated at 70°C for 21 hrs. (Table 5). The infrared spectra of the copolymers gave absorptions at 3350 cm^{-1} ($\nu\text{O-H's}$, broad) and $1220\text{--}1170\text{ cm}^{-1}$ ($\nu\text{C-O's}$). The polymer was purified by dissolving in THF and precipitating in hexane.

Table 2. Chemical Modification of PS with Trifluoroacetyl Chloride at Various Reaction Time.

Sample No.	Reaction Time(hr.)	Mole % of $\text{CF}_3\text{CO-}$ in Product
1	2.5	12.3
2	3.0	15.6
3	6.0	23.7(crosslinked)

a. Equal mole ratio of PS and trifluoroacetyl chloride were used.

Table 3. Composition of Copolymer(A) of Styrene and VTFA

Sample No.	Styrene/VPTFA (mole/mole)	Reaction Time(hr.)	Wt. Conv. (hr.)	Mole % of $\text{CF}_3\text{CO-}$ in A
1	0.75/0.25	24	24.3	49.8
2	0.50/0.50	24	36.8	73.7
3	0.25/0.75	24	64.0	95.2
4	0.75/0.25	72	67.8	40.5
5	0.50/0.50	72	75.3	60.2

a. VPTFA: p-Vinyl trifluoroacetophenone.
 b. Initiator: AIBN, 0.5 %(wt./wt. of monomers).
 Solvent: Benzene, 3/1(wt./wt. of monomers).
 Polymerization temperature: $60 \pm 0.1^\circ \text{C}$.

Table 4. Chemical Modification of PS with Acetyl Bromide at Various Mole Ratios.

Sample No.	Styrene/ CH_3COBr (mole/mole)	AlCl_3 (mole)	Reaction Time (hr.)	Mole % of $\text{CH}_3\text{CO-}$ in Product
1	1/0.5	0.6	3	44.2
2	1/0.25	0.3	3	22.1

Table 5. Composition of Copolymer (B) of Styrene and p-Vinyl phenol Prepared in Bulk.

Sample No.	Styrene/p-Vinyl phenol(mole/mole)	Reaction Time (hr.)	Wt. Conv. (%)	Mole % of -OH in B
1	0.80/0.20	21	47.0	34.5
2	0.55/0.45	21	72.6	86.9

a. Initiator: AIBN, 0.5 %(wt./wt. of monomers).
Polymerization temperature: $70 \pm 0.1^\circ \text{C}$.

3. Preparation of Blends and Films

For copolymer/PEO blending systems, the blends were prepared by weighing appropriate amounts of copolymers and PEO at ratios of 8/1, 4/1, 2/1, 1/1, 1/2, 1/4, and 1/8, then dissolving the mixtures in a common solvent at a initial concentration of 0.025 g/ml (wt./solvent). THF was used as a common solvent for the COPVOH/PEO blends and CH_2Cl_2 for the others. The solutions were cast onto a Teflon plate at room temperature. After the solvent was slowly evaporated, the resulting films were dried under vacuum at 50 °C for 24 hrs., to remove trace amounts of water and solvent before characterization. In some mixtures, such as COPFA/PEO (4/1, 2/1, 1/1,) and PHFA/PEO (4/1, 2/1), the solutions were vigorously stirred before pouring onto Teflon plate to prevent premature hydrogen bond complex precipitation.

In order to evaluate the compatibilizing effect of the copolymers as coupling agents in the PS and PEO blends, three types of ternary blends were prepared according to the following procedures.

(1) Two step blending: We prepared the known compatible copolymer/PEO binary blend by solvent casting methods using CH_2Cl_2 as a common solvent. PFA/PEO and PHFA/PEO at a weight ratio of 4/1 were used due to their known compatibility based on the results in the copolymer/PEO binary system. By assuming this

blend acted as a single component, it was mixed with PS at weight ratios of 3/1, 1/1, 1/3, respectively, using the same common solvent. These ternary blends were noted as copolymer/PEO//PS. The blends prepared by this method were convenient for the compatibility studies between the hydrogen complex and PS.

(2) Two step blending: PS, copolymer, and PEO were mixed simultaneously in the common solvent at weight ratios of 8:x:1, where x was the weight percentage of copolymer based on the total weight of PS and PEO and was 2, 5, 10, 15 %. These ternary blends were noted as PS/copolymer/PEO. COPFA and COPVOH have been used in this method. The advantage of this method was that the copolymer could be more randomly dispersed in both PS and PEO.

(3) One step blending: Ternary blends of PS, copolymer, and PEO were prepared similar to the type(2); but, the weight ratio of PS:copolymer:PEO was changed to (8-x):x:1, where x was 0.25, 0.5, 1 and 2 respectively. The advantage of this method was that it kept the total weight of the blend as a constant and thus the changes of crystallinity of PEO in the blends could be calculated through the relationship $X = \Delta H_f / \Delta H_f^0$ (pp. 24). PFA and PHFA have been used in this method.

The blends of PHFA with BAPC, PBMA, and PPO, respectively, were prepared and dried in the same manner. CH_2Cl_2 was used as a common solvent for the PHFA/BAPC and PHFA/PBMA blends, whereas toluene was used for the PHFA/PPO blends.

4. Thermal Analysis(DSC)

A Du Pont Thermal Analyzer, Model 990 with DSC cell, was used to study the transition data for all the blended systems. DSC samples were cut from the cast films and sealed into an aluminum pan . An empty aluminum pan was used as a reference. The sample weight was about 3-5 mg.

The thermograms of copolymer/PEO binary blends and PS/copolymer/PEO ternary blends were taken after annealing the samples in the DSC cell at 125 °C for 1 min. followed by fast quenching to -150 °C by liquid nitrogen. The samples were heated at a programmed rate of 20 °C/min. under a nitrogen atmosphere. This treatment was an attempt to control the thermal history of each measurement so that the results would be more reproducible. This also allows the detection of the PEO T_g more readily, since it was not normally easy to detect because of its high crystallinity. In the low temperature range (-100 to 0 °C), a high sensitivity (0.2 mcal/in) was used for the detection of the PEO T_g . In the high temperature range (0 to 125 °C), a low sensitivity (2 mcal/in) was adequate for the measurement of the T_m of the PEO. If the T_g of the blend occurred in the high temperature range, the thermogram was repeated in this range at the higher sensitivity.

For blends of PHFA and BAPC, PBMA, and PPO, respectively, thermograms were obtained at a programmed rate of $20^{\circ}\text{C}/\text{min}$ with a sensitivity of 0.5 mcal/in. For the PHFA/PAPC and PHFA/PBMA systems, thermograms were taken after the samples were preheated to 125°C for 1 min. and then quenched to -20°C by a dry ice-acetone mixture. The PHFA/PPO thermograms were taken after the samples were heated to 270°C and then quenched to 50°C . All measurements were done under a nitrogen atmosphere.

The T_g was taken as the intersection of the extrapolated low temperature base line with the tangent to the heat capacity fall endotherm (intersection method). The T_m was determined as the onset temperature of thermal melting

5. Infrared Studies (IR and FT-IR)

Preliminary hydrogen bonding studies occurring in the PFA/PEO and PHFA/PEO blends were done on the dispersive IR (Perkin-Elmer 457). Sample films were prepared as previously described and were cut into $1 \times 2.1 \text{ cm}^2$ rectangles with a thickness of $\sim 0.05 \text{ mm}$. The PEO spectrum was taken using a KBr pellet because of its high crystallinity and the difficulty in casting a self-supporting film. The wavenumber of the absorption peaks were calibrated by the aromatic C-H stretching peak of a PS standard film (ν C-H's, 3027 cm^{-1}).

A Digilab FTS-20B infrared spectrometer was used to study hydrogen bonding as a function of temperature. An environmental chamber designed by Bulkin, Pearce, and Huang⁸⁵ (Fig.4) was used in this study. The sample was a solution cast film on a polished aluminum plate which was set into the environmental chamber under a nitrogen atmosphere thereby preventing thermal oxidation during the heating process. The samples were heated by a controlled miniheater and the temperature was monitored by a Tele-Thermometer, YSI model 42 SC with a thermocouple. Spectra was taken at different temperatures- 25, 75, 125, and 175°C , respectively, by the use of the external reflection method.

The reassociation of hydrogen bonding in the blends after heating was investigated by the use of the difference spectra for the heated and unheated samples.

The interaction in the incompatible or compatible blends were studied by comparing the difference spectra of these blends with their synthetic spectra, the addition spectra of the corresponding parent polymer after properly adjusting to the same weight ratios.

The subtraction technique was used to subtract the spectrum of one component in the blend to show the spectrum of the remaining polymers. Most commonly, the 760 cm^{-1} (out-of-plane hydrogen deformation), or 700 cm^{-1} (out-of-plane phenyl ring deformation) of the copolymers could be selected as "key bands".⁸⁶ These were the characteristic bands of the copolymers due to their aromaticity and were not seriously overlapped with the band of PEO and thus could be mathematically removed from the spectrum of the blend. The difference spectrum could indicate the conformational change of PEO in the blend.

Hydrogen bonding occurring in the PHFA/BAPC blends were studied by FT-IR. Samples were solution cast films on a polished aluminum plate and spectra were measured in the chamber at room temperature.

The experimental conditions for the FT-IR studies were 32 scans, 4 cm^{-1} resolution, a sensitivity scale of 1, and double precision.

Fig. 4. Diagram of the environmental chamber, M_1 , M_2 , and M_3 are reflection mirrors.⁸⁵

6. Mechanical Properties Measurements

PS/copolymer/PEO ternary blends were used to investigate the change of mechanical properties with various amounts of coupling agent by using the Instron tensile testor. Samples were cut from solution cast thin films having a thickness of 0.06-0.08 mm using a steel die (dog-bone shape, ASTM-D638 Type V specimen; $0.125 \times 0.375 \text{ in}^2$, $W \times L$). The thickness of each sample was measured with a micrometer. Five samples were used for each measurement.

A very low rate of strain (0.04 in/min) was used. The true stress and strain in % elongation has been calculated from the experimental load-deformation curves with the use of the following equations:

$$\Delta L = \text{Chart length} \times \frac{\text{Head Speed}}{\text{Chart Speed}}$$

$$\epsilon = \frac{\Delta L}{L_0} \times 100\%$$

$$\sigma = \left(\frac{F}{A} \right) \times \frac{L_0 \Delta L}{L_0}$$

$$E = \left(\frac{d\sigma}{d\epsilon} \right)_{\epsilon=0}$$

where head speed was the rate of deformation, ΔL was the increase in sample length, L_0 was the original sample length, ϵ was the % elongation, F was the required force for a given

deformation, σ was the true stress at any deformation assuming that the density of the sample remained constant during deformation, and E was the initial rigidity modulus of the material.

III. Results and Discussion

1. Compatibility Studies of Copolymer/PEO Blends

The hydrogen bonding formation between the copolymers and PEO are of two kinds - blends of PFA, COPFA and PHFA with PEO in which the hydrogen bonding strength is affected by the inductive effects resulting from the substituent group adjacent to the respective hydroxyl group; blends of COPVOH and PEO in which hydrogen bonding formation is probably due to the strong acidity of phenol groups of COPVOH as a result of resonance effect with the benzene ring. In the first category, PFA with 15.6 mole% of hydroxyl group has the highest mole ratio we could obtain through the post-reaction of PS and trifluoroacetyl chloride without obtaining a crosslinked polymer. The affect of increasing the concentration of hydroxyl groups on compatibility with PEO is studied by using COPFA (40.5 mole% of -OH). PMA containing the electron donating methyl groups is intentionally adjusted to a similar ratio (44.2 mole% of -OH) as in COPFA to examine the influence of different substituents. The hexafluorodimethyl carbinol group in PHFA, with two strong electron withdrawing substituents, has a stronger affinity for hydrogen bonding than the trifluoromethyl group in COPFA. The concentration of the hexafluorodimethyl carbinol group in this polymer, 22.1 mole% is approximately half that the hydroxyl group in COPFA. By comparing the results of COPFA with PHFA blends,

we hope to assess the relative importance of the strength vs. the number of hydroxyl groups in promoting miscibility. In the second category, the COPVOH with 86.9 mole% of hydroxyl group was selected to study the compatibility with PEO.

1-1. General Properties of Copolymers

The structure, T_g , η_{inh} , and mole% of hydroxyl group for the copolymers used for the compatibility studies with PEO are shown in Table 6. The T_g 's of these five copolymers are not very different from the value for PS. Apparently, the bulky side phenyl rings are the dominant factor in the positions of the T_g 's of these polymers and additional substituents on the ring exert very little effect. Inherent viscosities, η_{inh} , measured in THF at 30 °C at a concentration of 0.5 g/dl, show that the PFA, PMA, and PHFA, prepared from the post-reaction of PS, have a higher molecular weight whereas COPFA and COPVOH, prepared by copolymerization, have a relatively lower molecular weight. The low molecular weight of COPVOH is due apparently to hydrogen transfer of vinylphenol during the polymerization process.⁸⁷ The low molecular weight of COPFA is not understood at this time.

Table 6. Properties of Copolymers.

structure	abbreviation name	$T_g (^{\circ}\text{C})$	η_{inh}	mole-% of OH
PFA	107	0.97	15.6
COPFA	108	0.31	40.5
PMA	104	0.98	44.2
PHFA	109	1.07	22.1
COPVOH	105	0.32	86.9

a. T_g and η_{inh} of PS (Styron-685D) are 104°C and 0.96 respectively.

b. Inherent viscosities were measured in THF at $30 \pm 0.1^{\circ}\text{C}$ with concentration of 0.5 g/dl.

1-3. Thermal Analysis

Fig. 5 shows the thermograms of PEO measured with different thermal histories. Sample 5-A was cooled from room temperature ($\sim 25^{\circ}\text{C}$) by liquid nitrogen to -150°C , then heated at a programmed rate of $20^{\circ}\text{C}/\text{min}$. No clear T_g could be detected. Sample (5-B) is annealed in the DSC cell at 125°C for 1 min, quick quenched to $\sim 150^{\circ}\text{C}$ by liquid nitrogen, and subsequently heated at the same rate of $20^{\circ}\text{C}/\text{min}$, and gave a detectable T_g at -56°C . The latter sample, quenched from the melt, contained a higher proportion of amorphous material compared with 5-A, as can be seen from the diminished area under the fusion endotherm. The T_m of PEO also varied as a result of different thermal treatments. It was shifted from 61°C to 58°C (onset) or from 68°C to 63.5°C (peak). The T_m 's of PEO in the blends determined in the following are relative values based on the same thermal histories.

The thermograms for PS/PEO blends are shown in Fig. 6 and their characterization data are reported in Table 8. Two clear T_g 's which correspond to the T_g 's of their respective parent polymers could be detected in most blends. At two critical ratios, 3/1 and 1/8, the T_g 's of the low concentration component escaped detection, but the T_g of the major phase is very close to that of the corresponding parent polymer. The T_m 's of PEO in the blends are nearly identical to that of the pure PEO.

Fig. 5. DSC thermograms of PEO. (A) Sample is quenched by liquid nitrogen from 25 °C, then heat at a programmed rate of 20 °C/min.. (B) Sample is annealed at 125 °C for one min., then quenched and heated as in (A).

Fig. 6. DSC thermograms of PS/PEO blends in weight ratios.

Therefore, we conclude that no significant interaction can be found in the mixtures of PS and PEO.

When p-trifluoromethyl carbinol substituents are attached to PS, miscibility with PEO is noticeably improved (Fig. 7 and Table 9). At COPFA/PEO ratios of 8/1, 4/1 and 2/1, PEO did not crystallize and a single T_g was found for each mixture. Upon lowering the COPFA content in the mixture to 1/1, a low temperature T_g is observed at -48°C , followed by a broad crystallization exotherm between -20 and 25°C and a melting endotherm near 51°C . The thermogram of the 1/2 mixture has qualitatively similar characteristics. When the blend ratio is low in COPFA, 1/4 or 1/8, the T_g of PEO is about -52°C and the T_m is about 50°C .

Except for the three amorphous mixtures whose thermograms are typical of those of single phase systems, the other four mixtures have complex phase structures. Two distinct phases can be identified from the thermograms- a crystalline PEO phase and an amorphous phase very rich in PEO (T_g near -50°C). There should be at least one more phase containing substantial amounts of COPFA. However, its presence eluded our repeated thermal scans. We are forced to speculate that the missing phase may have a T_g near 60°C and is hidden by the melting

Fig. 7. DSC thermograms of COPFA/PEO blends in weight ratios.

Table 8. DSC Characterization Data of PS/PEO Blends.

PS/PEO	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$
pure	104	-	-
8/1	104, -	57.5	-
4/1	103, -55	57.5	-
2/1	104, -56	58	-
1/1	104, -56	58	-
1/2	102, -53	57.5	-
1/4	103, -55	57.5	-
1/8	- , -56	58	-
pure	-56	58	-

Table 9. DSC Characterization Data of COPFA/PEO Blends.

COPFA/PEO	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$
pure	108	-	-
8/1	37	-	-
4/1	58	-	-
2/1	27	-	-
1/1	-48	51	4
1/2	-51	53.5	-18
1/4	-52	56	-
1/8	-53	57	-
pure	-56	58	-

endotherm. In this regard, similar difficulties in phase identification have also been encountered in the thermal analysis of poly(vinylidene fluoride)/poly(ethyl methacrylate) mixtures.⁴³ Only in certain cases have all the coexisting phases been accounted for in detail.¹⁶

When the melting endotherms of COPFA/PEO mixtures are examined more closely (Fig. 8), the onset, the peak, and the end of the fusion process have all moved to lower temperatures in comparison with the values for PEO. Both the imperfection of PEO crystals and the interaction between PEO and COPFA are likely to contribute to the depression of the melting point.

The calorimetric data for the PFA/PEO, PHFA/PEO, and COPVOH/PEO blends resemble those of COPFA/PEO mixtures (Tables 10-12). When a mixture contains a minor part of PEO, crystallization of the latter is suppressed and the mixture shows a single T_g . At high concentrations of PEO, crystallization of PEO prevails. A PEO-rich phase can be identified in the mixture but again there appears to be a missing phase, the T_g of which is not detectable. Blends of PMA and PEO are essentially incompatible at all compositions (Table 13).

Fig. 8. Melting endotherms of COPFA/PEO blends at weight ratio of (A)1/1, (B)1/2, (C)1/4, (D)1/8, (E) PEO(pure).

Table 10. DSC Characterization Data of PFA/PEO Blends.

PFA/PEO	$T_g (^{\circ}\text{C})$	$T_m (^{\circ}\text{C})$	$T_c (^{\circ}\text{C})$
pure	107	-	-
8/1	74	-	-
4/1	50	-	-
2/1	-48	54	28
1/1	-54	55	8
1/2	-53	56	-
1/4	-55	57	-
1/8	-55	57.5	-
pure	-56	58	-

Table 11. DSC Characterization Data of PHFA/PEO Blends.

PHFA/PEO	$T_g (^{\circ}\text{C})$	$T_m (^{\circ}\text{C})$	$T_c (^{\circ}\text{C})$
pure	109	-	-
8/1	80	-	-
4/1	49	-	-
2/1	23	-	-
1/1	-52	50	-4
1/2	-53	53	-
1/4	-53	55.5	-
1/8	-55	56.5	-
pure	-56	58	-

Table 12. DSC Characterization Data of COPVOH/PEO Blends.

COPVOH/PEO	$T_g (^{\circ}\text{C})$	$T_m (^{\circ}\text{C})$	$T_c (^{\circ}\text{C})$
pure	105	-	-
8/1	69	-	-
4/1	45	-	-
2/1	20	-	-
1/1	-14	-	-
1/2	-52	50	-16
1/4	-54	53	-
1/8	-55	56	-
pure	-56	58	-

Table 13. DSC Characterization Data of PMA/PEO Blends.

PMA/PEO	$T_g (^{\circ}\text{C})$	$T_m (^{\circ}\text{C})$	$T_c (^{\circ}\text{C})$
pure	104	-	-
8/1	98, -44	-	-
4/1	-45	51	28
2/1	-54	52	16
1/1	-52	54	-
1/2	-53	55	-
1/4	-54	56	-
1/8	-55	57.5	-
pure	-56	58	-

The strength of interaction between the copolymers and PEO can be judged in a qualitative way by examining (1) the lowest copolymer concentration at which a compatible, amorphous mixture with PEO is obtained, and (2) the effectiveness of PEO in lowering the T_g of the copolymer. The former occurs at 50% (weight) for COPVOH, 66.7% for COPFA and PHFA, and 80% for PFA (Fig. 9). Therefore, the miscibility of the copolymers with PEO can be arranged in the order $\text{COPVOH} > \text{COPFA} \approx \text{PHFA} > \text{PFA}$. Interestingly, the effectiveness of PEO in lowering the T_g 's of the copolymers follows the same order. When we examine the chemical structure of the copolymers, there appears to be a correlation between the above-mentioned order with the number and acidity of the hydroxyl groups. COPVOH has the highest mole % of hydroxyl groups, 86.9, and the acidity of phenol group is strong. The hydroxyl contents of COPFA and PHFA polymers are 40.5 and 22.1 mole%, respectively; but the acidity of the hexafluorodimethyl carbinol is stronger than that of trifluoromethyl carbinol group. Hence these two copolymers have approximately the same miscibility with PEO. The PFA polymer has the lowest hydroxyl content, 15.6 mole%, and the lowest miscibility with PEO.

The melting point depression of PEO in the blends shows a similar trend as that for compatibility- $\text{COPVOH} > \text{COPFA} \approx \text{PHFA} > \text{PFA}$ (Fig. 10). The larger magnitude of the T_m depression

Fig. 9. T_g 's of compatible copolymer/PEO blends vs. blend composition in weight fraction of PEO. (A)PFA/PEO, (B)COPFA/PEO, (C)PHFA/PEO, (D)COPVOH/PEO.

Fig. 10. Melting point depression in the copolymer/PEO blend as a weight fraction of PEO. (A)PFA/PEO, (B)PMA/PEO, (C)COPFA/PEO, (D)PHFA/PEO, (E) COPVOH/PEO.

of PEO in the PMA/PEO blends than that in the PFA/PEO's is probably due to the relatively higher content of hydroxyl group in PMA(44.2 mole%) even though PFA(15.6 mole%) shows a stronger affinity for forming hydrogen bonding with PEO.

1-4. Detection of Hydrogen Bonding by Infrared Spectroscopy

Fig. 11 shows the infrared spectra of PFA, PHFA, COPFA, PMA, and COPVOH respectively. The spectra of COPFA, PMA, and COPVOH are not suitable for the hydrogen bonding studies in the copolymer/PEO blends since only a broad hydroxyl absorption was observed. The more distinct hydroxyl absorption in the spectra of PFA(ν O-H's, 3550 cm^{-1}) and PHFA(ν O-H's, 3600 and 3520 cm^{-1}) indicates that hydrogen bonding in each of the two polymers is relatively low. There are two kinds of hydroxyl absorption occurring at 3600 and 3520 cm^{-1} in PHFA which are probably due to both ortho and para substitution on the phenyl ring of PS as a result of Friedel-Crafts reaction of hexafluoroacetone. In the reaction of model compounds such as toluene and hexafluoroacetone under similar conditions, Farah et. al.⁶⁵ finds both mono-(para) and bis-(para and ortho) substituted products. The less sterically hindered para position in our polymer should be more reactive and hence has the stronger peak intensity(3520 cm^{-1}). Because of the relatively low degree of intra- and/or intermolecular hydrogen bonding in PFA and PHFA, these two polymers are chosen as candidates for the study of intermolecular hydrogen bonding

A

B

C

D

E

Fig. 11. Infrared spectra of (A)PFA, (B)PHFA, (C)COPFA, (D)PMA, and (E)COPVOH, measured by dispersive IR.

with PEO.

The hydroxyl peak of PFA in PFA/PEO blends (Fig. 12) broadens and shifts from 3550 to 3380 cm^{-1} as the weight fraction of PEO is increased from zero to 0.5. At higher concentration of PEO, the absorption gradually returns to 3550 cm^{-1} , but the contribution of the 3380 cm^{-1} (hydrogen bonded peak) is still discernible.

In the PHFA/PEO blends (Fig. 13), the variations of hydroxyl absorptions are similar to those found in the PFA/PEO blends, but two distinct differences are noted. First, at 8/1 PHFA rich blend, both the free hydroxyl groups (3600 and 3520 cm^{-1}) and the hydrogen bonded hydroxyl (3260 cm^{-1}) are observable. Second, in PEO rich blends, the absorptions around 3260 cm^{-1} are more intense than those in the PFA/PEO blends at the same weight ratios. The two differences may be due to the nature of these two copolymers. Since PHFA has a higher hydroxyl content and stronger electron withdrawing groups than those in PFA, only a certain portion of its hydroxyl groups form hydrogen bonds with PEO in PHFA rich blends and the rest retain their own characteristics. In PEO rich blends, a significant number of hydroxyl groups are hydrogen bonded (3260 cm^{-1}) although the extent is insufficient to prevent the segregation of PEO molecules. The larger wave-number shifts of hydroxyl groups in the PHFA/PEO blends can

Fig. 12. Infrared spectra of the PFA/PEO blends in weight ratio of (A)8/1, (B)4/1, (C)2/1, (D)1/1, (E)1/2, (F)1/4, (G)1/8.

Fig. 13. Infrared spectra of the PHFA/PEO blends in weight ratio of (A)8/1, (B)4/1, (C)2/1, (D)1/1, (E)1/2, (F)1/4, (G)1/8.

also be a reflection of the stronger hydrogen bonding strength than in PFA/PEO blends.

The spectra in Figs. 12 and 13 are from dispersive infrared studies. They only give a qualitative picture of the hydrogen bonding formation. They are not scaled to remove the effects of different thickness. Moreover, source heating of the sample occurs, so that the effective temperature is $\sim 40^\circ\text{C}$. The limitations are overcome in the FT-IR spectra discussed below.

The spectroscopic data are further analyzed by using FT-IR. Infrared spectra of PFA, PHFA, PS, and PEO are shown in Fig. 14 with an absorbance unit. The assignments of the main peaks of these polymers are listed in Table 14. Fig. 15 shows one example of the difference spectrum obtained by subtracting PFA from the PFA/PEO blend(2/1), where the peak 700 cm^{-1} is chosen as the "key band". The difference spectrum is significantly different from the pure PEO(Fig. 14-A). In addition to the hydrogen bonding formation, the changes in $-\text{CH}_2$ symmetric stretching frequencies of the PFA/PEO blends are summarized in Fig. 16 and can be explained. First, the lone pair electrons of the oxygen atoms in PEO would engage in hydrogen bonding with a hydroxyl group of PFA. Thus, the force constant of the adjacent $-\text{CH}_2$ stretching vibrations is reduced and the absorption shifts down to lower

Fig. 14. Infrared spectra of (A)PEO, (B)PHFA, (C)PFA, (D)PS measured by FT-IR. Sample in (A) is a KBr pellet, in (B)-(D) are solution cast films.

Table 14. Infrared Absorption Frequencies and Assignments of the Main Peaks of PEO, PHFA, PFA and PS .

Frequencies (cm^{-1})				
PEO	PHFA	PFA	PS	Assignments
	3600			free - OH stretching (ortho)
		3550		free - OH stretching (para)
	3520			free - OH stretching (para)
	3083			
	3060	"	"	
	3027			aromatic C-H stretching
	2920			
	2850	"	"	aliphatic C-H stretching
2886				CH_2 symmetric stretching
	1602			
	1496	"	"	in plane bend stretching
	1455			vibrations of phenyl ring
1463				CH_2 scissoring
1345				CH_2 wagging
1283				CH_2 twisting
	1270	1275		O-H in-plane bending
	1230			
	1215			C-F and C-O stretching region
	1169	1169		
		1129		
1149				C-O stretching or CH_2 rocking
1102				C-C or C-O stretching
1062				C-C or C-O stretching or CH_2 rocking
	1105			O-H stretching
963				CH_2 rocking or CH_2 twisting
844				C-O or C-C stretching, or CH_2 rocking
	760	"	"	out of plane hydrogen deformation
	700	"	"	out of plane phenyl ring deformation

Fig. 15. (A) The infrared spectrum of the PFA/PEO(2/1, w/w) blend.
(B) The difference spectrum of PFA/PEO(2/1) blend and PFA.

Fig. 16. The infrared spectra of -CH₂ symmetric stretching absorption of PEO in (A) pure PEO, (B)-(E) are the spectra obtained by subtracting the spectrum of PFA from that of the PFA/PEO blends at the weight ratio of (B) 8/1, (C) 4/1, (D) 2/1, (E) 1/1.

wavenumbers. In PFA-rich blends(8/1 and 4/1), this effect becomes prominent as most ether linkages of PEO are hydrogen bonded, whereas the number of nonhydrogen-bonded ether linkages increase as the PFA concentration is lowered and it becomes obscure. Second, the frequency shift may also indicate a change from a crystalline to an amorphous state of PEO as the blend composition becomes richer in PFA. These change toward lower wavenumbers, as observed here, are associated with the appearance of trans, trans, trans conformers in addition to the trans, gauche, trans seen in the crystalline state.⁸⁹ It is possible that PFA also causes such conformational changes.

The effect of temperature on hydrogen bonding in compatible blends of PFA/PEO(4/1) and PHFA/PEO(4/1) are also studied by FT-IR. The intensities of hydrogen bonded hydroxyl peaks, 3380 cm^{-1} in the PFA-blend, and PHFA-blend, are monitored at 25, 75, 125, and $175\text{ }^{\circ}\text{C}$, respectively(Figs. 17 and 18). There is a decrease in the intensity of 3380 cm^{-1} absorption in the PFA-blend at $75\text{ }^{\circ}\text{C}$ whereas the intensity of 3260 cm^{-1} absorption in the PHFA-blend remains unchanged at that temperature. This observation is consistent with the strong acidity of the hydroxyl group in PHFA and hence stronger hydrogen bonding is formed in the latter blend. At $175\text{ }^{\circ}\text{C}$, the absorptions of hydrogen bonded

Fig. 17. Hydrogen bonding dissociation in the compatible blend of PFA/PEO(4/1, W/W) at elevated temperatures under nitrogen atmosphere. (A) 25 °C, (B) 75 °C, (C) 125 °C, (D) 175 °C.

Fig. 18. Hydrogen bonding dissociation in the compatible blend of PHFA/PEO(4/1, W/W) at elevated temperatures under nitrogen atmosphere. (A) 25 °C, (B) 75 °C, (C) 125 °C, (D) 175 °C.

hydroxyl groups decreases substantially and those of the free hydroxyl groups reappear at 3550 cm^{-1} in the PFA-blend and at 3600 and 3520 cm^{-1} in the PHFA-blend. Dissociation of hydrogen bonds in these two compatible blends at elevated temperatures is probably a result of promoting rotation of the C-O-H bond in PFA or PHFA, as well as increasing the segmental motions of PFA, PHFA, and PEO as the temperature becomes higher than the T_g 's of the respective blend (T_g : 50°C for PFA/PEO, T_g : 49°C for PHFA/PEO).

After the above samples are heated to 175°C and then gradually cooled to room temperature, the broken hydrogen bonds reform as can be seen in Figs. 19 and 20. Based on these results, we surmise that the miscibilities of the PFA/PEO and PHFA/PEO blends at lower temperatures resulting from hydrogen bonding interactions will not be affected prior treatment at elevated temperatures (up to 175°C).

As a further check of our spectroscopic data, we compared the synthetic spectrum of the incompatible PS/PEO (8/1) blend with the experimental one. The synthetic spectrum is obtained by the mathematical addition of the respective PS and PEO at appropriate weight ratio. As can be seen in Fig. 21, the synthetic

Fig. 19. Hydrogen bonding reassociation in the compatible blend of FFA/PEO(4/1, W/W). (A) Unheated sample. (B) Sample was heated to 175 °C, then gradually cooled to 25 °C. (C) The difference spectrum of (B) and (A).

Fig. 20. Hydrogen bonding reassociation in the compatible blend of PHFA/PEO(4/1, W/W). (A) Unheated sample. (B) Sample was heated to 175 °C, then gradually cooled to 25 °C. (C) The difference spectrum of (B) and (A).

spectrum is nearly identical to the experimental one. This is to be expected from an incompatible mixture having very little interaction between the constituents. However, the result is quite different in the compatible blend, PFA/PEO(8/1), as shown in Fig.22. Besides the apparent variation in the hydroxyl absorption region, or the $-\text{CH}_2$ symmetric stretching (Fig. 16-B), the absorption peaks in the fingerprint region ($1300\text{--}650\text{ cm}^{-1}$) are also different between the synthetic and the experimental spectra. These indicate that the conformations of both PFA and PEO are changed as a result of hydrogen bonding formation.

Fig. 21. (A)The infrared spectrum of the incompatible blend of PS/PEO(8/1, W/W). (B)The synthetic spectrum of PS/PEO blend at the same weight ratio.

Fig. 22. (A)The infrared spectrum of the compatible blend of PFA/PEO(8/1, W/W). (B)The synthetic spectrum of PFA/PEO blend at the same weight ratio.

2. Compatibility Studies on Ternary Blends- Copolymer, PS and PEO

2-1. Thermal Analysis

Since PEO is only compatible with the copolymers when the latter is a major part in the binary blend, the concentration of PEO in the PS, copolymer, and PS compatible ternary blends should be low. In addition, because the T_g 's of PS and the copolymers to be used as a coupling agent are close, evaluation of compatibility for the ternary blends by the glass transition criteria will not be as free of ambiguity as in the binary systems.

Two different approaches are used in these studies- (a) a mixture of compatible copolymer/PEO blend and PS, (b) a mixture of PS, copolymer, and PEO. Concentration of the blends are varied and the changes of thermal transitions are observed.

The DSC characterization data for the two step mixing, copolymer/PEO//PS blends (type 1) are listed in Tables 15 and 16. In the PFA/PEO//PS blends (Table 15), they are compatible at the ratio of 0.25/0.75 and 0.50/0.50, since only one T_g is observed between the T_g 's of the PFA/PEO and PS. Phase separation probably occurred at the ratio of 0.75/0.25, since two T_g 's are detected

Table 15. DSC Characterization Data of PFA/PEO//PS Blends

PFA/PEO	PS	T _g (°C)
pure	-	50
0.25	0.75	100
0.50	0.50	101
0.75	0.25	100, 41
-	pure	104

a. PFA/PEO=4/1 (W/W).

Table 16. DSC Characterization Data of PHFA/PEO//PS Blends

PHFA/PEO	PS	T _g (°C)
pure	-	49
0.25	0.75	100
0.50	0.50	101, 45
0.75	0.25	103, 43
-	pure	104

a. PHFA/PEO=4/1 (W/W).

as the PFA/PEO is a major part in the blend. In the PHFA/PEO//PS blends (Table 16), phase separation starts early at equal ratio of PHFA/PEO and PS (0.50/0/50). These occur probably because the compatibility between the coupling agent (copolymer) and PEO is through hydrogen bonding formation while that between coupling and PS is by Van der Waals' interaction. If the coupling agents are to play a successful role in bridging the PEO and PS molecules, the two forces would have to be balanced or equalized with each other. No doubt, hydrogen bonding should be stronger in the PHFA/PEO blend than that in PFA/PEO blend at the same composition because the PHFA has a higher hydroxyl content as well as the stronger proton-donor group. However, the hydrogen bonding in PHFA/PEO could be internally too strong and thus complete and prevent the interaction of PHFA and PS. In addition, the conformation of the coupling agent and PEO in the complex should be an important factor. If the coupling agent molecules are surrounded by the PEO, phase separation occurs through the repelling of the two completely dissimilar molecules, PEO and PS. In contrast, if PEO molecules are surrounded by the coupling agents, we can not exclude the possibility that the modified PS (coupling agents) are still compatible with PS. Since the T_g 's are lower than 104°C (T_g of PS) in the incompatible blends, and no clear phase separations are observed by visually examining these films, it seems reasonable to conclude that the two T_g 's of the blends are probably due to a partially compatible condition.

The DSC characterization data from one step mixing, PS/copolymer/PEO(type 2), are reported in Tables 17 and 18. The T_m disappears in the COPFA(15%)- and the COPVOH(10 and 15%)- blends. The T_g 's in the COPFA- and COPVOH- blends are gradually lowered as the concentration of copolymer increases. Two distinct T_g 's are observed in the COPVOH-blends(10 and 15%), one is the T_g of PS and the other (-17, -27 °C) probably is the T_g of COPVOH/PEO complex. Therefore, phase separations may be occur in these blends. The compatibilizing order of the copolymer to PEO is COPVOH > COPFA, however, the compatibilizing order of these copolymers to PS seem to be opposite. Therefore, choosing the copolymer useful for coupling both PS and PEO would be dependent on the compositions of the blends and the balance between the interactions of the copolymer-PS and copolymer-PEO. The T_g of PEO(-56 °C) in the ternary blends is not reported because it is difficult to detect. The judgement about the compatibility of ternary blends by the absence or presence of T_g for PEO is not conclusive.

Table 17. DSC Characterization Data of PS/COPFA/PEO Blends.

PS	COPFA(%)	PEO	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$
8	-	1	104	58	-
8	2	1	101	57	-
8	5	1	100	55	-
8	10	1	99	53	-
8	15	1	97	-	-

Table 18. DSC Characterization Data of PS/COPVOH/PEO Blends.

PS	COPVOH(%)	PEO	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$
8	-	1	104	58	-
8	2	1	103	57	-
8	5	1	101	55	-13
8	10	1	102, -17	-	-
8	15	1	100, -27	-	-

2-2. Crystallinity Studies of PEO in the PS/Copolymer/PEO

Blend

Fig. 23(R) and (L) show the melting peaks of PEO in the PS/copolymer/PEO blends (type 3). The T_m 's of PEO are lowered in both the PFA and PHFA added blends. PHFA seems to be a better solvent based on comparisons with PFA at the same addition ratios as shown by the faster decrease of the T_m of PEO. This result is consistent with the same trend of the T_m depression of PEO as in the copolymer/PEO blend. The degree of crystallinity of PEO in blends can be calculated by the following equation:⁷⁰

$$X = (\Delta H_f / \Delta H_f^O) \times 100$$

where X is the fraction of crystallinity of PEO in the blend, ΔH_f is the heat of fusion per gram of PEO in the blend, and ΔH_f^O is the heat of fusion of 100% crystalline of PEO. The heat of fusion of a tested material measured by the Du Pont DSC cell is calculated according to⁹⁰

$$H = A/m (60 \cdot B \cdot E \cdot \Delta qs)$$

where A is the melting peak area, m is the sample mass, B is the time base setting, E is the cell the calibration coefficient at the temperature of experiment, Δqs is the Y axis range on DSC recorder. Since the $(60 \cdot B \cdot E \cdot \Delta qs)$ is constant for any given instrument and a constant weight is used for every measurement, the heat of fusion is proportional to the peak area only.

Fig. 23. Melting thermograms of the PS/PFA/PEO blends(left) and PS/PHFA/PEO blends(right) at the weight ratio of (A)8/0/1, (B)7.75/0.25/1, (C)7.50/0.50/1, (D) 7/1/1, (E)6/2/1.

To facilitate the understanding of the relative crystallinity changes of PEO in the copolymer added blends, and for the convenience of calculation, the crystallinity of PEO in the incompatible PS/PEO blend(8/1) is assumed to be 100%. The results based on this assumption are shown in Table 19. The crystallinity of PEO decreases faster in the PHFA-blends than in the PFA-blends. This can be explained by the stronger interaction occurred in the PHFA and PEO molecules.

Table 19. Melting Point Depression and Relative Crystallinity of PEO in the PS/PFA(PHFA)/PEO Ternary Blends Measured by DSC.

PS	PFA(PHFA)	PEO	$T_m (^{\circ}\text{C})$	Rel. Crystallinity
8	-	1	58	100
7.25	0.25	1	57(56.5)	87.9(81.0)
7.50	0.50	1	56(55)	71.2(65.8)
7.0	1	1	53(51)	54.3(41.6)
6	2	1	50(-)	24.6(0)

- Blends were prepared by one step of mixing according to weight ratio(type 3).
- Data in the bracket belonged to PHFA added blends.
- Crystallinity of PEO in the PS/PEO=8/1 blend was assumed as 100%.

2-3. Mechanical Properties Measurements of PS/Copolymer/PEO Blends

Among the four useful coupling agents, PHFA appears to have the highest potential for development. It is relatively easy to prepare by a direct modification of PS through a one step reaction so that it has the same degree of polymerization as the PS in the studies. It contains an amount of hexafluoro-dimethyl carbinol groups(22.4 mole%) which forms strong hydrogen bonding with PEO.

Type 3 PS/PHFA/PEO ternary blends are used to investigate the change of mechanical properties with various amounts of coupling agent using the Instron tensile testor.

Table 20 shows the standard value of some mechanical properties for PS and PEO.^{95,96} PS has a higher modulus and tensile strength but a lower elongation at break than PEO. Table 21 shows the experimentally measured mechanical properties for PS and PHFA. The different values between Table 20 and 21 for for the same material, PS(Styron-685D), are due to differences in experimental conditions, sample size and shape. Therefore, the data reported here is to be interpreted on a relative basis. The mechanical properties of PS and its modified polymer(PHFA) are similar. The data for our PEO is not reported because it is too brittle for adequate sample preparation and testing.

Table 20. Mechanical Properties of PS and PEO.

	Modulus (PSI) $\times 10^{-5}$	Tensile Strength (PSI) $\times 10^{-4}$	Elongations at Break (%)
PS ^a	4.7-4.8	6.4-8.2	1.5-2.4
PEO ^b	0.3-0.7	1.8-2.4	700-1,200

a. Data obtained from the data sheet for PS-(685 D), Dow Chemical Co.

b. Data obtained from "Encyclopedia of Polymer Science and Technology, Vol. 6, p 125 (1969), - representative properties for a medium M.W. ethylene oxide polymer (Polyox WSR-301).

Table 21. Mechanical Properties of PS and PHFA.

	Modulus (PSI) $\times 10^{-5}$	Tensile Strength (PSI) $\times 10^{-3}$	Elongations at Break (%)
PS ^a	1.60	4.77	3.04
PHFA ^b	1.52	5.12	3.73

a. Same material (PS-685 D), data obtained by using thin films (0.06-0.08^{mm}), slow head speed (0.04 in/min) at ambient temperature ($\sim 25^{\circ}\text{C}$).

b. Modified PS prepared from PS-685 D, data obtained at same conditions as a.

Fig. 24 shows a preliminary examination by optical clarity for the sample in which PS is gradually replaced with an equal amount of the coupling agent (PHFA). The incompatible PS/PEO blend (8/1) is an opaque film and thus clear phase separation is observed visually. When the concentration of PHFA is gradually increased, the films become semi-transparent and finally completely transparent as the PHFA concentration in PS/PHFA/PEO is increased to 6/2/1. At that composition, no discernible phase separation can be observed visually. This indicates that appreciable improvement in the compatibility between PS and PEO through the coupling effect of PHFA has probably occurred.

Fig. 25 shows the stress-strain curves of PS/PEO (8/1) and the PS/PHFA/PEO blends where PS is gradually replaced by the PHFA. Their mechanical properties data are summarized in Table 22. The stress-strain curve of PS/PEO blend seems to reflect the distinct individuality of polymers with different mechanical properties. At low strain, the blend is stiff due to the contribution of PS, while at high strain region, its behavior is very similar to PEO. In the PS/PHFA/PEO blends, the curves are changed more uniquely as the concentration of PHFA is increased. These changes probably result from increasing the compatibility of PS and PEO. The irregular changes of the elongation at break are most likely due to the phase

separation between the PHFA/PEO complex and PS, or perhaps due to experimental deviations occurring as a result of sample preparation and measurement. A more exact explanation is not available at this time. The apparant changes of modulus, tensile strength in these PHFA added blends supported our origanal proposition that the mechanical properties of the incompatible blends are improved if a suitable coupling agent based on hydrogen bonding interaction is added.

Fig. 24. Optical clarity of PS/PHFA/PEO blends,
(a) 8/0/1, (b) 7.75/0.25/1, (c) 7.50/0.50/1,
(d) 7/1/1, (e) 6/2/1 (W/W/W).

Fig. 25. Stress-strain curves of the PS/PHFA/PEC blends at the weight ratio of (a) 8/0/1, (b) 7.75/0.25/1, (c) 7.50/0.50/1, (d) 7/1/1, (e) 6/2/1.

Table 22. Mechanical Properties of PS/PHFA/PEO^a Ternary Blends.

Composition ^b			Modulus	Tensile Strength	Elongation
PS	PHFA	PEO	(PSI) $\times 10^{-5}$	(PSI) $\times 10^{-3}$	at Break (%)
8	0	1	1.32	4.18	5.12
7.75	0.25	1	1.22	4.03	4.75
7.50	0.50	1	1.15	3.51	4.00
7	1	1	0.99	3.25	3.89
6	2	1	0.84	3.14	5.23

- Type 3 of ternary blends were prepared as described in experimental section.
- PEO obtained from Aldrich Co. with M.W. = 1×10^5 .
- Experimental conditions were the same as in Table 21.

3. Compatibility Studies between PHFA and Other Polymers

Copolymers of styrene and hydroxyl containing styrene, e.g., PFA, COPFA, PHFA, and COPVOH, are conditionally compatible with PEO depending on their respective compositions and blend ratios. It is of interest to explore the potential compatibility of these modified PS with other types of polymers having functional groups which can act as "proton-acceptors". Bisphenol-A polycarbonate (BAPC), and poly(n-butyl methacrylate) (PBMA) are of interest because they contain ester carbonyl groups, their T_g 's (147 and 26 °C, respectively) are sufficiently different from those of the copolymers ($T_g \sim 100$ °C), so that changes in the blends can be monitored by thermoanalytical techniques, and BAPC is an example of polyester with high aromatic character while PBMA is essentially aliphatic in comparison. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is also of interest not only because of its ether linkages which can act as a "proton-acceptor", and for comparison with the aliphatic polyether (PEO), but also it itself is already compatible with PS^{91,93} whereas incompatibility with some styrene-copolymers, e.g., poly(styrene-co-4-chlorostyrene) at compositions of the latter monomer higher than 32.9 mole%, has been reported.⁹¹ PHFA has been used in these studies because of its affinity for forming hydrogen bonds and its relative ease of preparation.

3-1. Optical Clarity of PHFA/Polymer Blends

Optical clarity can be used to preliminarily assess the compatibility of the PHFA/PBMA system. PS/PBMA cast films are opaque, whereas PHFA/PBMA appear to be transparent at all blending ratios. For the PS/BAPC and PHFA/BAPC systems, compatibility as judged by optical clarity could be somewhat ambiguous since the refractive index of PS and BAPC are 1.585 and 1.590,⁹² respectively. Thus, in all combination, clear films are expected. For the PHFA/PPO blends, all cast films are transparent while the PS/PPO blends are also transparent because of their known compatibilities at all ratios.^{91,93}

3-2. Thermal Analysis

The DSC thermograms of PS/BAPC mixtures (Fig. 26) show two distinct T_g 's which correspond to the values for the parent polymers. However, miscibilities are improved dramatically by using PHFA in place of PS (Fig. 27). A single T_g appearing between those of the parent polymers is found and the T_g value changes with the composition of the mixture.

The PS/PPO pair is one of the few compatible blends for which extensive calorimetric data are available.^{91,93} Our T_g results agree well with the literature values (Fig. 30). Partial substitution on the phenyl rings of PS with hexafluorodimethyl

Fig. 26. DSC thermograms of PS/BAFC blends in weight ratios. (a)PS, (b)8/1, (c)4/1, (d)2/1, (e) 1/1, (f)1/2, (g)1/4, (h)1/8, (i)BAFC.

Fig. 27. DSC thermograms of PHFA/BAPC blends in weight ratios. (a)PS, (b)8/1, (c)4/1, (d)2/1, (e) 1/1, (f)1/2, (g)1/4, (h)1/8, (i)BAPC.

carbinol groups also results in compatible mixtures(Fig. 31).

Our T_g results for the PHFA/BAPC, PHFA/PBMA, PS/PPO, and PHFA/PPO blends are plotted in Figs. 28-31. In each figure, two calculated T_g curves are also shown for comparison. Curve(C) is computed in accordance with the Fox equation,⁷¹

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where W_1 and W_2 denote the weight fraction of the component polymers and T_{g1} and T_{g2} , their glass transition temperatures, respectively. Curve C(dashed lines) represents the weight-average values. It is worth noting that (a) the experimental T_g value is always higher than that predicted by the Fox equation, and (b) for the PHFA/BAPC and the PHFA/PBMA mixtures, there are large positive deviations of the experimental results from the computed weight-average values. Such positive deviations are also reported in the PAA/PEO blends²³; but, no explanations are offered.

The magnitude of the positive deviation is substantial when a mixture is rich in PHFA. As the amount of PHFA decreases, the T_g value either approaches the weight-average value (in PHFA/PBMA blends) or falls below it(in PHFA/BAPC blends).

When the concentration of PHFA is low in its mixtures with PPO, the glass transition temperature of the mixture is lower than the weight-average value. The lowering is similar in magnitude as reported for PS/PPO. As the concentration of PHFA increases,

the transition temperature approaches the weight-average value and the two values become identical at weight fractions of 0.8 and 0.9. In the same concentration range, the T_g of PS/PPO blends remains significantly less than the weight-average value. In this sense, we can still consider the PHFA-rich mixture as having T_g values higher than what one would normally expect.

The positive deviations, which occurred in the PHFA/polymer systems, are found to be very close to 1:1 functional group stoichiometry (-OH/C=O or -OH/-O-); i.e., for the PHFA/BAPC blends, at 0.71 weight fraction of PHFA where the -OH(PHFA) and C=O(BAPC) are in a equal mole ratio. Therefore, a possible explanation for these positive deviations may arise from the strong hydrogen bonding complex formation when the blends are rich in PHFA, and thus act as a "pseudo" cross-linked product which shows a higher T_g .⁹⁴

Fig. 28. T_g 's of PHFA/BAPC blends vs. blend composition in weight fraction of BAPC. (A) Experimental curve, (B) Fox equation, (C) Weight-average curve.

Fig. 29. T_g 's of PHFA/PBMA blends vs. blend composition in weight fraction of PBMA. (A) Experimental curve, (B) Fox equation, (C) Weight-average curve.

Fig. 30. T_g 's of PS/PPO blends vs. blend composition in weight fraction of PPO. (A) Experimental curve, (B) Fox equation, (C) Weight-average curve.

Fig. 31. T_g 's of PHFA/PPO blends vs. blend composition in weight fraction of PPO. (A) Experimental curves, (B) Fox equation, (C) Weight-average curve.

3-3. Hydrogen Bonding Formation in PHFA/BAPC Blends

The hydrogen bonding association between PHFA and BAPC was studied by FT-IR(Fig. 32). At the weight ratios of 8/1 and 4/1, neither the ortho nor the para hydroxyl absorption peaks shifts in position; but, a broad shoulder appears at lower wavenumber indicating that the hydrogen bonding is gradually formed as the BAPC's concentration increases. At 2/1 and 1/1 weight ratios, the para hydroxyl peaks are shifted from 3550 to 3450 cm^{-1} while the sterically hindered ortho hydroxyl peaks remain at the same position. For the BAPC rich blends (1/2 - 1/8), the ortho hydroxyl groups begin participating in hydrogen bond formation and only a single broad hydrogen bonded absorption(3450 cm^{-1}) is observed. The spectroscopic data strongly support the idea that hydrogen bonding interaction between the proton-donor(-OH) and the proton-acceptor (C=O) overcomes the unfavorable mixing normally occurring between styrene and BAPC molecules.

Fig. 32. Infrared spectra of the compatible PHFA/BAPC blends measured by FT-IR.

IV. CONCLUSIONS

- (A) The copolymers of styrene and hydroxyl containing can be prepared either by post-reaction of PS, e.g., PFA, PHFA, PMA, or by copolymerization of styrene and the respective monomers, e.g., COPFA, and COPVOH.
- (B) The compatibility of these copolymers with PEO are dependent on-
- (1) The hydroxyl content, - increasing hydroxyl content gives higher compatible ratios, e.g., COPFA(40.5 mole % -OH) > PFA(15.6).
 - (2) The presence of strong electron withdrawing substituent groups adjacent to the hydroxyl group. These have higher compatibility ratios than electron donating substituents, e.g., COPFA(40.5 mole%) > PMA(44.2).
 - (3) The presence of two similar strong withdrawing groups has the same compatibility ratio as one of the same electron withdrawing group where the former is present in about half the amount of hydroxyl group as the latter, e.g., PHFA(22.1 mole%) $\approx$ COPFA(40.5).
 - (4) The presence of strongly acidic -OH functionality as a result of resonance stabilization-, e.g., COPVOH, also shows good compatibility with PEO.

- (C) The compatibility of these copolymers and PEO shows a similar thermal behavior-
- (1) A single homogeneous phase is formed as the blend is rich in copolymer,
 - (2) A crystallization peak of PEO appears at lower copolymer concentration, but the T_g of the blend remains higher than the T_g of the pure PEO.
 - (3) Phase separation occurs when PEO becomes rich in the blends.
- (D) PEO melting point depression occurs when it is blended with copolymers.
- (E) Hydrogen bonds are formed in the PFA- and PHFA- blends as shown by infrared. They gradually separate into two peaks representing free and hydrogen bonded hydroxyl as the concentration of PEO is increased to more than 50% by weight.
- (F) Hydrogen bonds in the PFA- and PHFA- blends with PEO are partially broken as the temperature is increased to 175 °C, and then are completely reformed on cooling to 25 °C.
- (G) Conformation changes of PEO in the copolymer/PEO blends are confirmed by monitoring the band shifts for the $-CH_2$ symmetric stretching absorption.

- (H) Interactions are found in the compatible blend, PFA/PEO(8/1), and not detectable in the incompatible blend, PS/PEO(8/1), by comparing the experimental and the computer-generated infrared spectra, respectively.
- (I) PFA/PEO(4/1) hydrogen complex is compatible with PS at weight ratios of 1/3 and 1/1, but incompatible at 3/1. PHFA/PEO(4/1) are only compatible with PS at 1/3 weight ratio.
- (J) The compatibility of a incompatible blend, PS/PEO(8/1), has been gradually improved by using COPFA as a coupling agent at adding ratio of 2, 5, 10, and 15%(based on the total weight of PS and PEO). Clear phase separation can be detected by using COPVOH as a coupling agent at the adding ratio of 10 and 15%.
- (K) The relative crystallinity of PEO in the PS/copolymer/PEO ternary blends has been measured by DSC. The magnitude of the decrease in PEO crystallinity for the PHFA-blends are larger than that of the PFA-blends.
- (L) The modulus and tensile strength of PS/PHFA/PEO blends are gradually decreased with increasing concentration of PHFA, whereas the variations of elongation at break of PHFA added

blends are random.

- (M) PHFA shows compatibility with the other types of "proton-acceptor" polymers. It appears to be completely compatible with BAPC, PBMA, and PPO, respectively.
- (N) An unusual positive deviation is observed in the PHFA/BAPC, PHFA/PBMA, and PHFA/PPO blends, respectively, when the T_g 's of these blends are plotted as a function of the respective latter polymers. Formation of "pseudo-crosslinked" hydrogen bonded complex is proposed to explain this phenomenon.
- (O) Hydrogen bonding formation is shown to occur using FT-IR in the PHFA/BAPC blends. Appropriate shifts of the hydroxyl absorption of PHFA in the blends occur.

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FOURIER TRANSFORM INFRARED STUDIES OF POLYMER BLENDS.

III. Poly(β -propiolactone) - Poly(vinyl chloride) system.

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Synopsis

Fourier transform infrared (FTIR) studies of the poly(β -propiolactone) (PPL) - poly(vinyl chloride) (PVC) blend system are presented. PPL - PVC blends are observed to be incompatible in the molten (80°C) and solid (25°C) states, over the entire range of compositions. This is in marked contrast to our previous results of the poly(ϵ -caprolactone) (PCL) - PVC blend system which was shown to be compatible in the amorphous state. The results of both studies are compared and discussed with particular reference to the detection of intermolecular interactions by FTIR and correlation with compatibility in polyester - PVC blends. The role of the chemical interactions in the compatibilization of polymer blends is discussed in terms of thermodynamic considerations. Finally, it is well known that changes in refractive index of polymer blend compositions can cause frequency shifts of infrared bands which is particularly relevant to the interpretation of residual peaks obtained by difference spectroscopy. The FTIR results of the PPL - PVC blends are germane to this subject and are discussed.

Introduction

In a recent publication we reported the results obtained from a Fourier transform infrared (FTIR) study of the poly(ϵ -caprolactone) (PCL) - poly(vinyl chloride) (PVC) blend system in the molten (amorphous) and solid states¹. Evidence supporting the existence of specific chemical interactions between the individual chains of PCL and PVC in the blends was presented and it was inferred that these interactions could play a significant role in the apparent compatibility of this blend system in the amorphous state. Additionally, an 'S' shaped curve was shown of the width at half height of the carbonyl band of PCL in the molten state as a function of PVC concentration. A saturation phenomenon was observed which was interpreted in terms of the concentration of PVC necessary to completely involve all of the carbonyl groups.

The initial goal underlying this present work was to test this saturation hypothesis. It was reasoned that similar FTIR studies of a polymer blend system consisting of PVC and a poly(ester) containing a shorter translational chemical repeating unit, such as poly(β -propiolactone) (PPL, $-(CH_2)_2COO-$), should lead to a displacement of the 'S' shaped curve. In other words, the saturation effect should occur at lower molar concentrations of PVC. However, as we shall demonstrate, in contrast to the PCL-PVC blends, the PPL-PVC blends are incompatible over the whole range of compositions both in the amorphous (molten) and solid states. As is often the case, the experiments described in this paper did not yield the expected results. Nevertheless, the data is significant in terms of the application of FTIR to the study of compatibility in polyester-PVC blends. Additionally, it has forced us to reevaluate the role of specific interactions in the compatibilization of polymer blends. Finally, the results are relevant

to the recent theoretical studies of Allara² concerning the effect of refractive index changes on frequency shifts in polymer blends.

Experimental

The PCL and PVC polymers employed in this study have been described previously¹. PPL was kindly supplied by Dr. K. Holland-Moritz of the University of Koln, W. Germany. The molecular weight of the polymer was not available but is known to be relatively low ($<10,000$). The T_g and T_m of the PPL were determined by differential scanning calorimetry to be approximately -67 and 77°C respectively and the infrared spectrum is consistent with that reported previously³.

Blends of the PPL and PVC were prepared as thin films by casting onto KBr windows from a 1% (w/v) solution in cyclohexanone. In order to completely remove traces of cyclohexanone from the dried films, solvent exchange to dry acetone was found necessary. The films were then dried in vacuo at room temperature.

Infrared spectra were obtained on a Digilab FTS-15/B FTIR spectrometer. Four hundred scans at a resolution of 2 cm^{-1} were signal-averaged and stored on a magnetic disk system. The frequency scale was calibrated internally with a reference helium-neon laser to an accuracy of 0.2 cm^{-1} . Spectra recorded at elevated temperature (80°C) were obtained at an accuracy of $\pm 2^\circ\text{C}$ using a SPECAC high-temperature cell and controller mounted in the spectrometer. It was essential for spectral manipulation to ensure that films were sufficiently thin to be within the absorbance range where the Beer-Lambert law is obeyed⁴.

Results and Discussion

The vibrational spectra of PCL and PVC have been discussed previously¹. Tadokoro et al.⁵ reported the far-infrared spectrum of PPL and performed a limited normal-coordinate analysis (NCA) using a Urey-Bradley force field to assign the bands in this region of the spectrum. A more detailed study including Raman data and a NCA employing a valence force field is contained in the thesis of Kirkpatrick³. Of particular significance to this present study is the frequency of the 'crystalline' (preferred conformation) and amorphous stretching vibration of the carbonyl band, $\nu_s(\text{C=O})$. Figure 1 shows the infrared spectrum of PPL in the region of 1650 - 1800 cm^{-1} . The spectrum of the semi-crystalline polymer (A) shows a dominant contribution from the 'crystalline' band at 1733 cm^{-1} and a relatively weak contribution at 1738 cm^{-1} (amorphous). Spectrum B is that obtained at 80°C and represents PPL in the amorphous (molten) state. By subtracting spectrum B from spectrum A using an appropriate weighting factor⁴, a 'purified' spectrum of the crystalline band (C) can be obtained. The results obtained are similar to those observed for PCL¹.

Experiments on the PPL-PVC blends were initially performed at 80°C in the molten state identical to those carried out on the PCL-PVC system¹. Figure 2 shows the infrared spectra obtained for pure PPL and two blends of PPL-PVC containing 45 and 80 mole percent of PVC respectively. In contrast to the PCL-PVC blend system, where similar experiments produced significant shifts in frequency and broadening of the carbonyl band, there

appears to be no comparable effects in the PPL-PVC blend system. In fact, the carbonyl bands appear, within experimental error, to be identical in position and shape regardless of the presence of up to 80 mole percent PVC. This is further illustrated in figure 3 where a constant width a half height of the carbonyl band is observed for PPL-PVC blends in the molten state as a function of mole percent PVC. Again, this is in marked contrast to a similar plot obtained for the PCL-PVC system where a 'S' shaped curve was determined. The above results for the PPL-PVC blends are interpreted as being indicative of a two phase incompatible system in the melt.

The results of FTIR experiments conducted in the solid state at room temperature also suggest a two phased incompatible system for PPL-PVC blends over the total range of compositions. Figure 4 shows the infrared spectra in the carbonyl region of pure PPL and a PPL-PVC blend containing 70 mole percent PVC. The PPL component of the blend is obviously crystalline and there is no evidence for a significant increase in the amorphous content of PPL in the blend. This is true of all blend compositions and once again the results are in sharp contrast to those obtained for the PCL-PVC system¹.

Further evidence for the incompatibility of the PPL-PVC blends may be gained from differential scanning calorimetry (DSC). Figure 5 shows the results of a typical DSC scan obtained on a PPL-PVC blend containing 80 mole percent PVC. The sample was heated to 400°K and quenched to liquid nitrogen temperature. The scan was then recorded at a heating rate of 40°K/min. Two distinct Tg's are observed at -67°C and 87°C which correspond to the Tg's of

PPL and PVC respectively. Additionally, the crystallization and melting of PPL is readily identified. These results are entirely consistent with the observations and interpretations made from the FTIR experiments.

From the above experiments it is evident that the PPL-PVC blend system is incompatible. Of particular importance to infrared studies of polymer blends is the fact that there are major differences in the spectral results obtained from the compatible PCL-PVC and the incompatible PPL-PVC blend systems. In the former case, frequency shifts and broadening of the carbonyl band can be interpreted as being indicative of chain-chain interactions between the individual polymers. This is analogous to interactions between a plasticizer and polymer and, in fact, PCL may be viewed as a macromolecular plasticizer for PVC. Conversely, the absence of these effects in PPL-PVC blends is indicative of phase separation; i.e., in infrared spectral terms, the chains of one component do not recognize that the other component exists.

Thermodynamic Considerations

We now turn our attention to a consideration of the possible factors involved in the compatibilization of polyester-PVC blends. In particular, we wish to understand the role of specific chemical interactions of the type observed for the PCL-PVC blend system. This poses several important questions. Does the presence of intermolecular interactions between the two polymers make a significant contribution to the compatibilization of the PCL-PVC system? How much of a contribution to overall free energy of mixing do these dipolar interactions make? If these interactions are relatively weak, what is the major driving force that confers macromolecular mixing? Finally, we must rationalize the fact that the PPL-PVC system is incompatible.

The thermodynamics of macromolecular mixing has been discussed in detail by many authors and excellent reviews of the experimental and theoretical results have been published by Kraus⁶, Koningsveld et al.⁷, and Patterson and Robard⁸. In the following discussion we will restrict ourselves to only the rudimentary Flory-Huggins thermodynamic treatment of macromolecular mixing. We recognize the limitations, especially in the light of the recent Prigogine-Flory theory. However, as we shall demonstrate our results can be adequately explained on the basis of solubility parameters and we believe this simple treatment can be useful in predicting compatibility in polyester - PVC blends. The free energy of mixing, ΔF_m , may be expressed by:

$$\Delta F_m = \frac{RTV}{V_r} \left[\frac{v_A}{x_A} \ln v_A + \frac{v_B}{x_B} \ln v_B + \chi_{AB} v_A v_B \right] \quad (1)$$

where V = Total volume of the mixture.

V_r = Reference volume (molar volume of smallest polymer repeat unit).

v_A, v_B = Volume fractions of the polymers A and B in the mixture.

x_A, x_B = The degrees of polymerization of polymers A and B in terms of the reference volume V_r .

χ_{AB} = Interaction parameter.

Furthermore, in its simplest form, assuming only dispersive forces, the interaction parameter, χ_{AB} , may be related to the Hildebrand solubility parameters, δ_A and δ_B , by the following expression:

$$\chi_{AB} = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (2)$$

Macromolecular mixing will occur when ΔF_m is negative. The first two terms in the brackets of equation 1, which are related to entropy terms, are always negative. Hence, if the $\chi_{AB} v_A v_B$ term is equal to zero, i.e.

when $\delta_A = \delta_B$, macromolecular mixing is assured on thermodynamic grounds. Of particular significance to this work is the critical value of the difference in the solubility parameters, $|\delta_A - \delta_B|_{cr}$, for polymers A and B, which represents the limiting value, above which, thermodynamic mixing cannot occur. Kraus has considered this problem and by using reasonable assumptions has demonstrated that values of $|\delta_A - \delta_B|_{cr}$ of 0.35 to 0.10 $(\text{cal cm}^{-3})^{1/2}$ are applicable for polymers with $x_A = x_B$ in the range of 100 to 1000.

It is important to note that the above discussion does not consider hydrogen bonding or polar interactions occurring between the polymer molecules. If hydrogen bonding or dipolar interactions do exist there may be a positive interaction between the two polymers which results in a negative contribution to the $\chi_{AB} v_A v_B$ term. It is this consideration that led us to believe that the specific interactions detected in the PCL-PVC blends could contribute to the apparent compatibilization of this system.

The solubility parameters for polymers may be calculated approximately from a knowledge of the molar attraction constants and molar volumes of the chemical groups contained in the polymer chain. Table 1 shows the calculated values of δ for PVC, PCL and PPL based on the methods of Small and Hoy (9). It is immediately apparent that the calculated values of δ for PVC and PCL are almost identical. Conversely, there is a significant difference in the δ 's calculated for PVC and PPL. Thus we conclude that although the specific interactions detected in the PCL-PVC system may make a negative contribution to the ΔH_m , the dominant factor is the comparable solubility parameters of the two polymers. In the case of the PPL-PVC blends, the solubility parameters are sufficiently different (well outside the range implied

by Kraus for macromolecular mixing) so that random mixing of the polymers cannot occur. The specific polar interactions are not strong enough to override the difference in chemical and structural dissimilarity of PPL and PVC. It is realized that the calculations used to determine the solubility parameters are simplistic but nonetheless, the results are in remarkable agreement with the experimental observations.

Olabisi¹⁰, using inverse gas-liquid chromatography, studied polymer-polymer miscibility in the molten state. For the PCL-PVC blend system, Olabisi estimates a value of approximately -2.9 cal cm^{-3} for the exchange energy parameter, X_{ij} ⁸. This may be viewed as a measure of the interaction between the polymer molecules. The above X_{ij} value was estimated from a 6 cm^{-1} frequency shift observed by Shaw¹¹ for a PCL-PVC (50:50) blend in the solid state at 25°C. However, as shown in our previous paper¹, the carbonyl region of the spectra of PCL-PVC blends in the solid state is complicated by contributions from both 'crystalline' (preferred conformation) and amorphous absorbances. In fact, for a 50:50 weight percent PCL-PVC blend (which corresponds approximately to a 35:65 molar percent), the shift in frequency is towards higher wavenumbers due to the increased amorphous contribution¹. PCL-PVC blends in the molten state indicate that a maximum shift of only 2 cm^{-1} toward lower wavenumbers is observed for a 50:50 blend. However, we have previously shown¹ from a plot of width at half height of the PCL carbonyl band as a function of PVC concentration in the amorphous state that 'saturation' occurs at PVC levels of >65% (i.e., the point at which all the carbonyl bands in the blend are associated with PVC). The maximum shift in this case is 3 cm^{-1} towards lower wavenumbers. Accordingly, we believe that Olabisi's estimation of the X_{ij} value from spectroscopic data is a factor of two too high. Hence a X_{ij} of approximately -1.5 cal cm^{-3} is indicated for PCL-PVC blends. This contribution is evidently not sufficient to override the differences in the solubility parameters in the case of the PPL-PVC blends.

A final comment is in order which relates to the application of FTIR to the study of compatibility in polymer blends. The correlation between the observation of intermolecular interactions between the different polymers and compatibility or non-compatibility in the case of the PCL-PVC and PPL-PVC systems respectively, may be fortuitious. Whereas the detection of significant intermolecular interactions infers mixing on a macromolecular level, it is entirely possible to conceive of a compatible blend of two polymers where intermolecular interactions will not be detected. Consider, for example, two relatively non-polar polymers which have identical solubility parameters. In this case, no dipolar or hydrogen bonding interactions are necessary to ensure thermodynamic macromolecular mixing. Infrared spectroscopy will thus be limited in compatibility studies to systems involving significant interactions between the two individual polymers.

Dispersion Effects

The FTIR results discussed in this paper have a bearing on the recently published studies of Allara². The author cautions that infrared frequency shifts observed in the spectra of polymer blends^{12,13} may be due to dispersion effects resulting from variations in refractive index and not indicative of intermolecular interactions. A comparison of the FTIR spectra of the PCL-PVC and PPL-PVC blends is informative. The calculated refractive indices⁹ of PCL and PPL are identical, as shown in table 1. If the frequency shifts of the carbonyl band observed in the spectra of the PCL-PVC blends are due to dispersion effects then similar shifts should be observed for analogous compositions in the case of the PPL-PVC blends. This is not observed experimentally. We have demonstrated that the PPL-

PVC blend system is incompatible which implies a two phase system. Consequently, with the possible exception of the interfacial region between domains of the two components, intermolecular interactions between PPL and PVC are not feasible. This is consistent with the FTIR results (see figure 2) which indicates that the frequency and width of the carbonyl band is insensitive to changes in PVC concentration in the PPL-PVC blends; implying no intermolecular interactions between the two polymers. However, if we digitally subtract the infrared spectrum of pure PPL in the carbonyl stretching region from that of the PPL-PVC (1:4 molar) blend a small derivative type residue is obtained. This is illustrated in figure 6. It should be emphasized that the relative absorbances of the two spectra are comparable and well within the range where the Beer-Lambert law is obeyed⁴. This is an important consideration as derivative residues can be obtained by subtracting infrared spectra of identical samples which have significantly different absorbances⁴. The positive residual peak in figure 6, represents approximately 2.5% of the area the original carbonyl peak of the PVC-PPL blend spectrum. This is comparable to that calculated theoretically by Allara². It is tempting to conclude that the residual observed in the PPL-PVC blend system is due solely to dispersion effects. However, in this experiment we are unable to separate possible intermolecular interaction contributions between the two polymers in the interfacial regions between domains.

In the case of the PCL-PVC blends, there is an obvious frequency shift and broadening of the carbonyl band as a function of PVC concentration. The residual peak obtained by subtracting the spectrum of pure PCL from that of the PCL-PVC (1:4 molar) blend is far more definitive. The positive lobe of the derivative type residual represents approximately 9% of the

original area of the carbonyl band in the blend spectrum. As the refractive index of PCL is the same as PPL, the magnitude of the shift in frequency and broadening cannot be due solely to dispersion effects. Thus we conclude that we are definitely detecting intermolecular interactions between PCL and PVC in this blend system.

Conclusion

FTIR studies of the PPL-PVC blend system have demonstrated that there are significant differences in the spectral results obtained for compatible and incompatible polyester-PVC blends. In contrast to the PCL-PVC system, frequency shifts and band broadening of the carbonyl band in PPL-PVC blends are not observed. The latter blend has been shown to be incompatible over the entire range of compositions. From a consideration of the solubility parameters and interaction energies involved between polyester-PVC blends, it is concluded that the negative contribution to the heat of mixing from specific interactions between PPL and PVC is not sufficient to override the differences in solubility parameters of the two polymers. Finally, it has been demonstrated that the frequency shifts observed in the carbonyl band of PCL-PVC blends cannot be attributed solely to dispersion effects.

Acknowledgements

The authors would like to express their appreciation for the financial support of the Plastics Institute of America for this work.

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Figure Captions

Figure 1: FTIR spectra in the range $1650 - 1800 \text{ cm}^{-1}$.

- (A) Spectrum of PPL recorded at room temperature (semi-crystalline),
- (B) Spectrum of PPL recorded at 80°C (amorphous),
- (A-B) Difference spectrum obtained by subtracting B from A.

Figure 2: FTIR spectra in the range $1660 - 1820$ for PPL; PPL-PVC (55:45 molar) and PPL-PVC (20:80 molar) recorded at 80°C .

Figure 3. Plot of width at half-height of the carbonyl stretching frequency as a function of PVC concentration for PPL-PVC blends recorded at 80°C .

Figure 4. FTIR spectra in the range $1650 - 1820 \text{ cm}^{-1}$ for PPL and PPL-PVC (30:70 molar) recorded at room temperature.

Figure 5. DSC scan of PPL-PVC (20:80 molar) blend.

Figure 6. FTIR spectra in the range $1650 - 1850 \text{ cm}^{-1}$ for;

- (A) PPL-PVC (1:4 molar) blend,
- (B) PPL and
- (A-B) Difference spectrum obtained by subtracting B from A.

All recorded at 80°C .

Table 1

Calculated solubility parameters and refractive indices.

	Solubility Parameter $\delta_{(\text{cal cm}^3)^{1/2}}$		Refractive Index
	<u>Small</u>	<u>Hoy</u>	
PVC	9.6	9.5	1.52
PCL	9.4	9.5	1.47
PPL	10.7	10.9	1.47

FIG 1

FIG 2

FIG 3

FIG 4

FIG 6