Polymer Recycling; Potential Application of Radiation Technology

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Overview

Management of solid waste is an important worldwide problem, which is becoming progressively worse as a byproduct of continuing economic growth and development. Polymeric materials (plastics and rubbers) comprise a steadily increasing proportion of the municipal and industrial waste going into landfill. Development of technologies for reducing polymeric waste, which are acceptable from the environmental standpoint, and which are cost-effective, has proven to be a difficult challenge due to a whole range complexities inherent in the reuse of polymers. Establishing optimal processes for the reuse/recycling of polymeric materials thus remains a worldwide challenge as we enter the new century.

Due to the ability of ionizing radiation to alter the structure and properties of bulk materials, and the fact that it is applicable to essentially all polymer types, irradiation holds promise for impacting the polymer waste problem. Three main possibilities for use of radiation in this application are: 1) enhancing the mechanical properties and performance of recovered materials or material blends, principally through crosslinking, or through surface modification of different phases being combined; 2) treatment causing or enhancing the decomposition of polymers, particularly through chain scission, leading to recovery of either low molecular weight mixtures, or fine powders, for use as chemical feedstocks or additives; 3) production of advanced polymeric materials designed for environmental compatibility. This paper documents the growth and magnitude of the polymer recycling problem, outlines major obstacles to the implementation of recycling technologies, and discusses some of the approaches taken. A review of radiation-based recycling research is then provided, followed by a discussion of future directions for this area of investigation.

The Polymer Recycling Problem

The United States generates more than 200 million tons of solid waste each year. Of that ~16% is incinerated, ~22% is recycled or recovered, and ~62% is put into landfill [1]. Approximately 25 million tons of plastic appeared in the municipal solid waste of the
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United States in 1996 [2]. Most of it was buried in landfill. The percentage of polymers in the overall municipal waste stream in the United States has grown steadily as polymers find ever-increasing use in consumer products. In 1960, polymers accounted for only 0.5% of total solid waste. By 1980 that figure had grown ten fold, to 5.0%. By 1996, the figure had reached 12.3%[2]. In order to target specific polymers for recycling research, it is instructive to compare the relative quantities of the main polymer types in the municipal waste stream. In the U.S., five main types of polymers dominate the solid waste stream. The highest polymer waste results from low density polyethylene (LDPE), at 5 million tons per year. High density polyethylene (HDPE) is second, at 4.1 million tons. Polypropylene (PP) constitutes 2.6 million tons, followed by polystyrene (PS) at 2 million tons, and polyethyleneterephthalate (PET) at 1.7 million tons [2].

In Germany, about 11 million tons of polymers were produced in 1995 (which is about 10% of total world production)[3]. Polymers accounted for about 8% of the municipal waste stream - about 3 million tons in all. Nearly half of the waste stream came from packaging; other significant contributions came from polymer manufacturing, electronics, automobiles, and building[3].

Basic Approaches to Recycling/Reuse of Polymeric Materials

It is important to consider a suitable definition of the loosely-used term of “recycling” as applies to polymers, and to discuss what constitutes success in achieving recycling. One possible objective for polymer “recycling” would be any process which diverts polymer waste to any place or use, other than landfill. However, certain “recycling” options may be far from optimal, or even undesirable. For instance, if a certain method of eliminating polymer waste requires extremely high energy consumption, this may basically amount to substituting one environmental problem for another. Even if environmentally sound, if the process is very expensive, it will be an overall burden on economic conditions and is not the most desirable solution. The ideal solution would be both environmentally acceptable, and would ideally operate as a profitable enterprise, as with the recycling of aluminum. As outlined in the next section, however, the nature of macroscopic materials presents special challenges to effective recycling, and at this point in time, the door remains open to possibilities of major advances in recycling technology.

Material recycling is a term used to describe processes in which the macromolecular structure is kept basically intact, and the material is reformed into a new product. Some alteration of the molecular structure and/or morphology of the material may be made for the purpose of enhancing performance. If material recycling can be made to function effectively, this is the most desirable approach, since it may require the least amount of processing expense and energy, and potentially will result in a product having a reasonable value, possibly approaching that of the original item. It is, however, technologically the most difficult approach. A wide range of research work has been carried out on single-component polymers, on blends, and on compositions to which
other materials have been added [4-5] in an attempt to enhance properties (crosslinking agents, surfactants, reinforcing fillers, etc.). There has been some success in grinding of thermoplastic waste material for remelting/remolding of useful items where a clean good quality waste stream can be obtained [6-7]. PET and PE are examples. Usually, the reground material is mixed with virgin resin. Plastic lumber used for building benches, fences, walkways, etc, has been one application explored by many investigators [7].

Chemical recycling refers to the decomposition of the macromolecular structure to generate low molecular weight compounds. This is typically carried out under high temperature and in the presence of various types of catalysts. This approach consumes large amounts of energy, and in many cases results in rather low value products. Probably the type of chemical recycling having the highest potential value involves depolymerization. In this case, the resulting monomer can then be utilized to regenerate more polymeric material. Some polymer types that can be depolymerized are of interest in this regard. For example, PMMA [3], nylon and polyesters [2] can be depolymerized. For material types which decompose to products that are primarily not monomer, pyrolysis can be expected to result in liquids (often mixtures) which are of use as feedstocks for the petrochemical industry or as fuels. Another chemical recycling approach is high-temperature gasification using a nonstoichiometric amount of oxygen, to generate “synthesis gas” (mainly CO + H2), which is of use in the chemical industry. High-temperature hydrogenation methods using H2 gas (similar to industrial methods for processing heavy oil residues and coal), has also been employed in the chemical recycling of polymers [3]. Other creative approaches include the substitution of hydrocarbon waste for oil, in the reduction of iron ore to make steel; upon introduction into a blast furnace at 2000 C, the organic material produces H2 and CO, which act as the reducing agent in the generation of iron metal [3]. Chemical recycling is being heavily developed in Germany, which has particularly stringent governmental regulations regarding waste recycling, together with an exceptionally strong chemical industry [3]. An analysis of the economics of existing chemical recycling methods indicates that the profit margin on the products obtained is overbalanced by the current costs of collection and sorting [8]; the energy cost of these current approaches is also substantial.

Incineration is a third category of polymer waste utilization; here the product is heat, which is used in the production of electricity. Polymers, mixed with other waste, may be burned in specially designed facilities. In the United States about 112 waste combustion facilities are in operation. This approach is technologically the most simple, and requires little selectivity in terms of the composition of the waste stream being processed. However, energy is a comparatively low value commodity.

Among these three approaches, radiation may potentially provide major benefit either for material recycling or for chemical recycling. A success in material recycling could constitute a major breakthrough in demonstrating an energy-efficient and economically-attractive recycling technology. Because of its ability to penetrate solid materials, including opaque materials, and to effect chemistry in the solid phase, radiation may be uniquely suited to this purpose. Because radiation can result in degradation of materials.
depending on polymer type and environmental conditions, it may likewise be of utility in reducing energy costs by pretreatment of polymers to promote chemical recycling.

Technological Challenges of Polymer Recycling

Perhaps the most successfully recycled commodity material in the U.S. today, and possibly in the world, is aluminum. In the U.S., the aluminum waste stream comes mainly from aluminum beverage containers, which are widely used for a variety of soft drinks and other beverages. Recycling trucks are a common sight in the parking lots of large grocery stores, and a large number of Americans routinely recycle their aluminum cans – largely due to reasons of environmental consciousness, and partly because the recycling company pays cash for returned cans. One may then ask why the equally-common plastic beverage containers (used in the U.S. for soft drinks, milk, etc.), are not also extensively recycled. The answer is twofold. First, the production of aluminum from raw ore is an expensive, energy-intensive process. By comparison, remelting of aluminum metal for reforming into products is a much less expensive process. Secondly, remelted aluminum performs just as well as the original material. There are few impurities in the waste stream, and organic residues on the aluminum surfaces are volatilized or decomposed during the high-temperature process. In contrast, reuse of polymeric materials brings a whole set of problems.

Compatibility: There are many types of polymers. Except in rare cases, different polymer types are not compatible – that is, they are not mutually soluble. When an attempt is made to mold a mixture of two or more polymer types, the different materials form separate phases, and the overall material sample typically has very poor mechanical properties and poor integrity. Even small amounts of an “impurity” polymer can have a negative effect on properties. Given that there are numerous different polymer types, this implies that either the waste stream must be very efficiently sorted into its different components (a timeconsuming process), or that a way must be found to compatibilize the two phases through some sort of surfactant or coupling agent at the interface.

Contamination: By their nature, polymers can absorb low molecular weight compounds, which dissolve and migrate into the bulk of the material. Thus, compounds causing discoloration, odor, or toxicity may be incorporated into the material. The remolding process would not be expected to result in destruction of dissolved contaminants; discoloration by impurities may become worse as a result of the thermal treatment. Thus, remolded material may not be usable for the original function, but may need to be employed in a less demanding (typically lower value) application. For example, reuse of materials in food applications is probably impossible. No company would be willing to manufacture plastic milk jugs using a waste stream consisting of recycled plastic milk containers. If one such container had been used for storage of a foreign substance prior to recycling (such as insecticide), and that foreign substance showed up in the remade
milk containers even in small amount, the resulting lawsuits and public reaction would almost undoubtedly put the company out of business.

Degradation: Polymers, in contrast to aluminum, are subject to changes in the macroscopic properties due to subtle changes in molecular structure that can result from environmental factors: U.V. light, thermal-oxidative processes that can occur during molding or even at room temperature, attack by pollutant gasses in urban environments, chemical interaction with liquid contents, and others.

Crosslinking: Thermoset polymers, which were crosslinked as a part of their initial processing to enhance properties, are particularly problematic for recycling. Remelting and reforming is not possible. Fortunately, most of the common (inexpensive) engineering plastics are not crosslinked.

Rubber tires, however, are an example of a highly crosslinked product which exists in large quantities. (Roughly half the world’s rubber production goes into tires) [9]. In fact, virtually all products made from rubber are crosslinked.

Relatively Low Value: In contrast to aluminum, production of raw polymeric materials from crude oil is relatively inexpensive. Given the cost of collecting, shipping, sorting, and cleaning recycled polymers, there is little financial incentive for manufacturers of polymer resins to recycle material. Basically, the combination of the low cost of virgin materials, the high cost of recycling, the low cost of putting refuse into land fill, and the low value of energy to be obtained by burning, combine to make the economics of polymer reuse marginal.

Government Regulation: One factor with the potential to drive polymer recycling is environmental regulation. Such laws vary widely from country to country, and are subject to change (becoming either more or less stringent) based on pressures from environmental groups, consumers, and corporations.

Progress in Recycling Technology

Advances in conventional recycling technologies on a number of fronts may be useful to future efforts in the area of radiation recycling. As pointed out earlier, a wide range of research has been carried out on single-component polymers, on blends, and on compositions to which other materials have been added in an attempt to enhance properties (crosslinking agents, surfactants, reinforcing fillers, etc.). Conventional methods include the use of thermally-initiated free radical initiators to promote crosslinking, addition of molecules (such as “coupling agents”) capable of bonding together two different material phases, surface grafting to alter interface characteristics, and surface treatment of particulate material using plasma or other means. These methods were originally developed for use in processing new (non-recycled) polymers.
but many such approaches involving conventional methods have been applied to recycled materials. Results of conventional studies may provide direction for use of radiation-based chemistries.

The sorting problem may become less severe due to a number of developments. Enabling technologies to facilitate polymer recycling through highly automated sorting routines have been developed. At Sandia Labs, near-IR spectroscopy has been applied in a reflectance mode, using a neural network approach to spectral identification, as the basis of a device which is able to sort samples of common waste polymer types at a rate of > 10 items/sec; accuracies of >98% have been achieved [10-11].

With heightened awareness of recycling issues, commercial manufacturers are giving some attention to designing products with easier recycling in mind [2]. For example, soft drink bottles had been made of PET, but with a PE bottom, a PP or aluminum cap, and paper labels; simplified constructions are now being explored, which would help the problem of separation of different polymer types.

Some progress has been made on the difficult problem of recycling rubbers. Grinding and reuse of rubber particulate has been done to a limited extent; this approach is useful for lower performance rubber applications, and for toughening of asphalt [9]. Reports have been published claiming successful devulcanization of rubber using either chemical reagents, microwaves or ultrasonics, to selectively cleave C-S bonds but not C-C bonds [12]. The recovery of a carbon black material, thought to be useful as a filler, has been reported following the pyrolysis of carbon-black-filled rubber from tires [13].

Another approach aimed at the solid waste problem is the development or evaluation of biodegradable polymers [14]. These are based on a variety of natural products, (often structurally modified to optimize properties), or are laboratory-made polymers with structures expected to be susceptible to enzymatic attack. A rather large effort has grown up in this area. Polymer types being studied include cellulose derivatives (such as cellulose acetate) [15], polysaccharides such as chitin [16] starch, and poly(3-hydroxybutrate) [17]. A related approach to materials which break down under natural environmental conditions is the development of U.V. – degradable plastics, designed to decompose in sunlight should they become “litter” [18]. Examples include a copolymer of ethylene and carbon monoxide, and modified PET.

Approaches to Radiation-Assisted Polymer Recycling

Radiation crosslinking of single-material and binary mixed-waste compositions is being investigated. Both gamma and e-beam irradiation are being applied to recovered LDPE samples in an effort to improve properties of the recycled material [19]. Likewise, gamma irradiation has been applied in an effort to improve the properties of a blend of LDPE and HDPE mixed-waste material through crosslinking; a competing process of
oxidative chain scission has been problematic with this approach [20]. Gamma irradiation under inert atmosphere of mixed compositions of PET and PP which had been coextruded, was reported to show modest improvement in properties at low dose (5 Mrad) as a result of material crosslinking, though the data were not conclusive; significantly decreased properties were seen at higher doses (30 Mrad) [21].

The addition of agents which undergo crosslinking upon radiation exposure, to compositions representing recovered waste materials, has been investigated. Mixed materials containing HDPE, PP, and PS, with triallyl cyanurate (TAC) added, showed significant improvement in modulus at a dose of ~20 to 35 Mrad. Some positive effect was seen at 2% TAC; substantial improvement was found at 10% TAC [22]. Irradiation of PP pressurized with acetylene gas to ~6 Mrad was found to result in an increase in mechanical properties [21].

Czvikovszky and coworkers have reported a number of studies in which recycled, reinforced polymer systems were prepared using PP from reprocessed car bumpers [23, 24, 25]. A variety of fibers were used, including wood, viscose, glass, and waste cord-yarns from the tire industry. Reactive additives (such as epoxy acrylate) were used to enhance bonding between the materials. Significant improvement upon e-beam irradiation was noted for a number of materials, including those with wood and viscose reinforcement. The approach is particularly interesting since many of the fibers used are either low-cost materials, and/or materials which themselves have been recycled.

A limited amount of work has been reported on the use of radiation in chemical recycling. Yoshii and coworkers at the Japan Atomic Energy Research Institute have reported that irradiation of PP allowed its subsequent pyrolysis to be carried out at a much lower temperature, and that it was possible also to alter the nature of the compounds resulting upon decomposition. These results indicate that radiation can be useful in lowering the energy requirements for chemical recycling, as well as providing a means of controlling the nature of the products [26].

Gamma radiation has been used in preparation of a new material type which would yield environmental benefit by providing biodegradable packaging. Calcium caseinate (a protein-based material derived from milk) can be cast into films, but in order to be useful, radiation crosslinking is needed to improve mechanical properties and water resistance [27, 28, 29, 30].

A final study of interest does not involve the use of radiation in recycling, but rather is a study of conventional methods for recycling crosslinked material (which was irradiated as a part of its initial processing). In this work, it was reported that when particles of radiation-crosslinked polyethylene, that had been cryogenically ground, were incorporated as an additive into a melt of uncrosslinked polyethylene, a considerable enhancement of elasticity was obtained for the composite material [31]. This observation may not only provide a very attractive solution to the problem of recycling a crosslinked material, but it may indicate the possibility of crosslinking ordinary waste polyethylene by radiation in order to prepare a value-added filler material.
Future Prospects for Using Radiation in Polymer Recycling

As mentioned before, ionizing radiation offers unique possibilities for application to the problem of recycling polymers, due to its ability to cause crosslinking or scission of a wide range of materials. Scission or crosslinking can be made to occur in the interior of bulk materials in the "as received" condition, without the necessity of dissolving the material or having some chemical initiator incorporated in the material matrix. Adhesion between particulates of different material types, or with fillers/fibers, can be promoted by coating of the particles with a radiation-activated crosslinking monomer prior to mixing and remolding of the recovered material. It would appear that crosslinking of recovered scrap polymer by radiation shows much more promise when a reactive monomer is added to the mixture, and it is recommended that this approach be more widely explored. A broad range of possibilities should be pursued using various combinations of recovered scrap of one or more materials, reactive additive, and inexpensive filler additives, in an effort to create a useful structural engineering material.

Two-phase materials, where surface-treated polymer scrap particulate is incorporated as a filler into non-recycled resins, prior to their molding, has considerable promise as a way of utilizing low-value polymer waste, to create materials having enhanced properties. For example, it may be possible to create impact resistant polystyrene by incorporation of recycled scrap particulate of other polymers. Also worth investigating is the reground rubber scrap from tires, incorporated into plastic resin or (virgin) uncured rubber resin. Can radiation-crosslinking, in which the rubber particulate becomes linked to the surrounding matrix, yield a material of high-quality properties?

Further work is also warranted in the utilization of radiation to develop chemical recycling technologies for polymer scrap. The 3 highest-volume polymers in the U.S. municipal waste: HDPE, LDPE and PP, are all very susceptible to radiation-induced degradation (chain scission) at low doses, in the presence of air. Much is known about the conditions affecting the degradation of these materials (we are so often trying to prevent it!). Low dose rate and high surface area promote oxidative scission, as does a post-irradiation thermal exposure. There is a large and successful industry based on the radiation-degradation of Teflon powder, which renders the material able to be incorporated into inks, lubricants and other formulations [32]. It would be worth performing exploratory research, in which the radiation-induced breakdown of PE and PP scrap is carried out to generate lower molecular weight micropowders, as is done with Teflon. It would then be necessary to interact with colleagues from industries using the Teflon additives to see whether the PE or PP powders can perform some of the same functions, or else can be useful in other related formulations. Besides inks and coatings, it could be possible that surfactants, cleaning fluids, and particulate fillers for roofing tar, asphalt, or tires, could be potential uses for inexpensive micropowders or oils resulting from the extensive oxidative scission of PE and PP.
Pyrolytic breakdown, using different catalysts and reactor types, of PE and PP that have been heavily radiation-oxidized is also worth pursuing further, to determine how much energy saving and how much diversity of potentially useful decomposition products having oxidative functionalities, may be usefully obtained. This may be best achieved in collaboration with existing commercial facilities for chemical recycling; many of these are located in Germany.

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References


