DOE/ER/10421--T2

DOE/ER/10421--T2

DE82 011712

MASTER

PROGRESS REPORT

on

THE EFFECTS OF PROCESSING CONDITIONS ON THE RELIABILITY
OF CROSS-LINKED POLYETHYLENE CABLE INSULATION

by

Paul J. Phillips
Professor of Materials Science and Engineering

(DOE Contract #DE-AC02-79ER10421)

I.	Review of Progress to Date.....	1
II.	References.....	17
III.	List of Publications and Presentations.....	18

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MGW

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

I. REVIEW OF PROGRESS TO DATE

The overall long-term objective of the program remains the determination of the influence of processing on the electrical properties of cross-linked polyethylenes through its effect on morphological variables. Although aimed at an understanding of failure processes in heavy walled insulation, the basic morphological studies are of direct relevance to the many varieties of cross-linked polyethylenes now becoming amongst the most reliable of engineering plastics.

There are three basic studies involved, each of which has posed different experimental problems. These areas are:

- (i) an investigation of the crystallization process in cross-linked polyethylenes using isotropic and strained melts,

- (ii) an investigation of the effect of processing conditions on the morphology of miniature extruded cables,

- (iii) an investigation of the effects of morphological and processing variables on dielectric loss and dielectric breakdown (specifically "treeing" behavior).

Our investigations to date have concentrated mainly on the first of these areas. Although some dielectric loss research is now complete we are only now in a position to really move ahead on the second and third areas of investigation. These different sections will now be reviewed in some detail.

1. Crystallization Studies

1.1 Crystallization Kinetics

Considerable progress has been made in this area over the past year. Bulk crystallization rate studies using transmitted light intensity are now complete for the standard commercial vulcanizable low density polyethylene

which contains 2% cross-linking agent. We have studied the polymer in its cross-linked state in order to quantitatively estimate the effect of cross-link density. Using $t_{1/2}^{-1}$ versus crystallization temperature plots (figure 1) we can see that the small number of cross-links produced (~ 0.2 mole percent of backbone atoms) results in a considerable drop in crystallization rate as well as a drop of 5°C in the highest temperature at which crystallization can occur. The data have also been analyzed using log time plots in order to obtain Avrami exponents (figure 2). We have used the same light transmission technique to measure the melting points as a function of crystallization temperature. The melting point behavior is typical of a polymer (figure 3), however there are two interesting differences in behavior between the polymer before and after cross-linking. First for high supercoolings a 2°C depression occurs, however, for low supercoolings the cross-linked polymer appears to have a higher melting point. This latter point needs to be investigated further and more datum points obtained.

The use of wide angle X-ray scattering to monitor crystallization rates through measuring the growth in intensity of particular diffraction lines was severely impeded by the abrupt departure last summer of the graduate student involved, who decided to switch to the biomedical area. We had anticipated a second student going off the project because of his completion of the dielectric loss work and so had arranged for his replacement ahead of time. This replacement student was put onto the crystallization work on arrival last September and so progress has been slow as he learns the techniques. The temperature control cell is now functioning well on the X-ray diffractometer, however, some fine tuning on the temperature control may still be needed. Nevertheless, useful data is now being generated (figure 4) and we have already carried out a preliminary comparison of the kinetics from the X-ray

and light transmission techniques (see figure 1). The X-ray experiment is, of course, a difficult one because of the low maximum crystallinity (40%) and the low intensities normally obtained from polymers.

The above techniques produce bulk crystallization data. We also wish to study the spherulitic or lamellar growth rates in order to be able to estimate separately the effects of cross-linking on crystal growth and nucleation. Laser light scattering will be used here since the growth rates are much too fast and the spherulites too small for good data to be obtained from light microscopy. Scattering patterns of final spherulite size have been determined for the crystallization temperatures used in the bulk studies (figure 5). Specimens crystallized at 94°C and below show a double clover leaf pattern indicative of a bimodal distribution of spherulites (figure 6). This effect is a new one and may be related to the gel-sol phase separation suggested earlier as operative in this system.

Because the spherulites are so small ($\sim 1\mu\text{m}$) and the light scattering pattern (1) is inversely proportional to spherulite size we have encountered a problem in obtaining the kinetics of spherulite growth. The pattern at most stages of growth is so large that it is cut off by the specimen heater plate. We are currently attempting to overcome this problem by boring a conical opening in the plate and expect to obtain data before the end of the current grant period.

We are now in a position to consider the effects of variations in cross-linking density on kinetics and we plan on making our own formulations of low density polyethylene and cross-linking agent (dicumyl peroxide). It is also an appropriate time to begin studies of the crystallization process in pre-strained films.

1.2 Morphological Studies

The equivalent of metallography for polymers does not exist at the present time and so much of our time here (one undergraduate assistant) has been spent on trying to develop such a system for low density polyethylene. In previous reports we have presented data obtained using the permanganic etch developed by Olley, Hodge and Bassett (2). In the last report we mentioned a paper about to be submitted to the Journal of Materials Science. However, we made some observations last spring which raised serious questions about the etching technique and we withdrew the paper pending the outcome of further studies. The studies raising the question were in situ SEM deformation studies of etched films of cross-linked polyethylene. One of my undergraduate students, for her senior thesis project, was given the task of installing a tensile device, which had been purchased from Cambridge Instruments, and of carrying out in situ tensile-morphology studies. She found that prior to the yield point the surface produced cracks which were much deeper than any gold film. Further investigations showed that there was a relatively brittle film on the surface of thickness $\sim 1 - 3\mu\text{m}$. It therefore seemed possible that the morphologies we were observing were not indicative of the cross-linked polyethylene but of some oxidized by-product. The existence of such a film had never been alluded to by Olley et al (2). We therefore dropped all etching studies and concentrated on an investigation of the etching technique itself. Shortly afterwards I visited Bassett's group whilst in England and discussed the problem with them. They had also discovered the existence of the film and were actively investigating the effect of concentration, time and temperature on its dispersibility. We have carried out our studies independently of one another and have come to similar conclusions regarding film formation. We, ourselves, have chosen to optimize conditions first for

linear polyethylene since it has a crystallinity of 70 - 80% and spherulite sizes of up to several hundred microns which can be easily studied using transmission optical microscopy. Ideal conditions are 0.2% potassium permanganate in concentrated sulfuric acid for one hour at ambient in an ultrasonic bath. Bassett's original recipe, as being used by other interested researchers, was 7% at 90°C for two or more days. We now wash the specimen in dilute sulfuric acid in the ultrasonic bath thereby dispersing the film and revealing the true morphology (figure 7) at a detailed level. These studies have unexpectedly revealed a heretofore unnoticed detail of spherulite morphology which will cause a revolution in our thinking on polyethylene morphology. Banded spherulites have been observed for 40 years using polarized microscopy (figure 8). The maltese cross extinction patterns make difficult the tracing of any band completely around the spherulite. This banding has been ascribed to a regular twisting of the radiating lamellar crystals. Our etching studies, however, reveal that many spherulites (figure 9) are not made of concentric rings but of continuous spirals! Moreover Bassett has shown (3) that the lamellae do not twist but manifest a zig-zag growth perhaps consistent with a twinning process which for some reason or other occurs with a regular frequency as growth proceeds. We do expect to spend some more time investigating this discovery.

We have also optimized etching procedures for linear low density polyethylenes of crystallinity ca. 60% and spherulite sizes of ca. 10 - 20 μ m. Lower crystallinity means higher amorphous content and more material to be removed by the etchant for resolution of the morphology. Here we need to use a 0.4% solution then wash and repeat the whole process 3 to 5 times for optimal resolution.

Basically the conditions we use are such as to minimize film stability and we find it much more effective to remove the film as it forms and carry out repetitive etching procedures. We can now handle crystallinities down to 60% but are still optimizing the procedures for the lower crystallinity polymers which are the focus of this contract. The polymers whose etching procedure we have optimized have spherulitic structures relatively easily resolved using polarized microscopy of microtomed sections of bulk material. With the low density and cross-linked polymers we are considering here, resolution of $1\mu\text{m}$ spherulites in the optical microscope is difficult at best and so the problem is more difficult to resolve. The procedures should however be optimized within the next month or two and then the earlier morphological studies will be re-evaluated. We are very close to having developed a reliable "metallography" for polyethylenes of all known levels of crystallinity. Such a procedure, when published, should produce a major advance in studies of the morphology of molded components and permit structure-property investigations to proceed at a rate which has hitherto been inaccessible.

We do intend to make TEM studies of chlorosulphonated specimens (4,5) in order to evaluate the lamellar organization within spherulites. Individual polymer crystals are usually only 100 - 200Å thick and require TEM of stained ultramicrotomed films for their study. It is also possible that we will be able to carry out TEM studies of surface replicas of etched specimens as a corroborative study here.

1.3 Extraction Studies

Last year we reported studies of the specimens in which the uncross-linked extractable low molecular weight polymer molecules had been removed from cross-linked specimens. This part of the project has also been impacted

due to the abrupt departure of the Ph.D. student referred to earlier. It should resume shortly. The related study of the effect of cross-linking on unit cell parameters has also been similarly impacted.

2. Cable Production

2.1 Laboratory Scale Production

The scaled down facility is now ready to function in the dry cure mode. We expect to begin studies in the next few weeks. The boiler requested in last year's submission has not yet been purchased for several reasons. The manufacturers have now told us that several safety features will be needed because of the pressures involved and will require considerably more investment. We are currently investigating the possibility of tapping into a boiler used nearby for oil shale retorting. It is possible that purchase of a pressure control system together with new piping will be adequate. Since our present rate of progress in this part of the project is understandably slow we do not anticipate moving onto the steam cure for at least a year and so will request funding for this equipment in next year's proposal.

2.2 Computer Simulation

As reported last year our studies of computer simulation had proceeded as far as they could without crystallization rate data. We now have sufficient data available for a simulation of the crystallization during cable extrusion assuming spherulitic morphologies. These studies will be taken up again next year.

3. Electrical Properties

3.1 Dielectric Constant and Loss

We have recently improved our dielectric cell, and experiments aimed at quantitatively estimating the effects of by-products of the organic cross-linking agent have been completed with high reproducibility and accuracy. In addition to now having better data for the cross-linked polymer, we have carried out studies in which a related low density polyethylene has been 'doped' with by-products. The two by-products, acetophenone and 2-phenyl-2-propanol, produce losses at low temperatures in the kHz range (figure 10) but the two molecules exhibit very different activation energies for these loss processes (figure 11a). When extrapolated to room temperature their losses would be found in very different frequency ranges (figure 11b). These losses are of little relevance to electrical transmission but would have appreciable effects in the microwave region, in which cross-linked polyethylene is now being used in a foamed form. Experiments on stretched polyethylenes show minimal orientational effects from these effectively spherical molecules. One intriguing observation, which necessitates further more quantitative analyses of the data, is that the intensity of the peaks does not increase linearly with content. Nor does it decrease at higher concentrations as would be expected if the solubility limit had been exceeded. The student who carried out this work is investigating the behavior of small molecules dissolved in polyethylenes and has now moved onto other molecular species relevant to an Army contract but will move back to pursue the DOE interests as necessary.

3.2 Dielectric Aging and Breakdown Studies

The larger pieces of equipment are now in hand and we expect to begin studies as soon as certain safety features and devices have been installed.

Since high voltage studies are new to us we have been actively obtaining the advice of Dr. David Cooper and Dr. T. C. Cheng of the Cable Research Laboratory of the University of Southern California. Dr. Cooper is one of the most critical experimentalists involved in breakdown testing. Our aging experimentation should take shape in the immediate future. We also want to carry out less time-consuming experiments in the form of needle or discharge testing. Most people in the field seem unable to agree on which form of test is most meaningful, and so we are still actively evaluating the possibilities. In any case, the equipment we have purchased will be adequate for both aging studies and whichever form of breakdown test we opt for.

Figure 1. Recrystallization half time of crystallization vs. crystallization temperature for non-cross-linked polyethylene (N-XLPE) and cross-linked polyethylene (C-XLPE) using light transmission and X-ray intensity measurements.

Figure 2. Normalized fractional crystallization vs. log time at the temperatures indicated for (a) noncross-linked polyethylene, and (b) cross-linked polyethylene.

Figure 3. Melting point vs. crystallization temperature for noncross-linked polyethylene and cross-linked polyethylene.

Figure 4. Normalized fractional intensity of (110) line as a function of log time for cross-linked polyethylene at temperatures indicated. Data have been corrected for the contribution of amorphous scattering.

Figure 5. Ultimate spherulite size in microns as a function of crystallization temperature for cross-linked and non-cross-linked polyethylene.

Figure 6. Laser light scattering pattern of specimen crystallized below 94 °C showing double clover leaf pattern indicative of bimodal distribution of spherulites.

(525X)

(570X)

Figure 7. Banded spherulites in linear polyethylene revealed by permanganic etch at the optimal etching condition.

(2.16K)

Figure 8. A banded spherulite of linear polyethylene observed using polarized microscopy.

(2.47K)

Figure 9. A banded spherulite in linear polyethylene revealed using optimum permanganic etching. Note that the bands are not concentric rings but continuous spirals.

Figure 11a. Activation energy curves for (a) cross-linked polyethylene, (b) low density polyethylene doped with acetophenone, and (c) low density polyethylene doped with 2-phenyl-2-propanol.

Figure 11b. Data of figure 11a plotted in such a way as to extrapolate to room temperature.

II. REFERENCES

1. M. R. Rhodes and R. S. Stein, J. Appl. Phys., 31, 1873 (1960).
2. R. H. Olley, A. M. Hodge and D. C. Bassett, J. Polym. Sci., Polym. Phys. Ed., 17, 627 (1979).
3. D. C. Bassett and A. M. Hodge, Proc. Roy. Soc., A, 377 25 (1981).
4. G. Kanig, Kunststoffe, 64, 470 (1974).
5. D. C. Bassett and A. M. Hodge, Polymer, 19, 469 (1978).

III. LISTS OF PUBLICATIONS AND PRESENTATIONS

In addition to the Conference proceedings, two papers have just appeared in I.E.E.E. Transactions (reprints have not arrived), one paper is in press in Wire Journal and a review chapter written for the ASTM book "Engineering Dielectrics" is expected to be published in June 1982. Papers on the morphology, previously ready for submission, are being held pending completion of our investigation into the etching techniques referred to earlier. Other papers on NMR, crystallization kinetics, and dielectric behavior are in preparation. Two invited lectures were presented during the past year in Washington, D.C. and Stockholm, Sweden at symposia on polyethylene morphology.

1. Publications

(i) D. V. Brower, K. L. Naylor and P. J. Phillips, "Multiple Morphologies in Cross-Linked Polyethylene", 1980 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, 113 (National Academy of Sciences).

(ii) C. A. Kodres and P. J. Phillips, "Computer Simulation of Cable Processing", 1980 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, 240 (National Academy of Sciences).

(iii) C. A. Kodres and P. J. Phillips, "A Numerical Method to Simulate the Processing of Electrical Distribution Cable. Part I. (Heat and Mass Transfer)", I.E.E.E. Transactions, published January 1982.

(iv) P. J. Phillips and C. A. Kodres, "A Numerical Method to Simulate the Processing of Electrical Distribution Cable. Part II. (Curing Rates)", I.E.E.E. Transactions, published January 1982.

(v) P. J. Phillips, chapter 2, "Morphology and Molecular Structure of Polymers and Their Dielectric Behavior", in "Engineering Dielectrics", Vol. II, R. A. Bartnikas, ed., ASTM, June 1982.

(vi) C. A. Kodres, "The Use of Wire Preheating to Increase Curing Rates of Polyethylene Cables", Wire Journal, accepted for publication.

2. Conference Presentations

(1) "Morphological Studies of Cable Insulation", Invited Lecture, National Academy of Sciences Workshop on Experimental Techniques for Investigating the Degradation of Electrical Insulation, Hershey, PA, 1979.

(ii) "Morphological Studies of Cross-Linked Polyethylene", American Physical Society, New York, 1980 (with K. M. Jayakar and K. L. Naylor).

(iii) "Multiple Morphologies in Cross-Linked Polyethylene", American Chemical Society, Las Vegas, 1980 (with D. V. Brower and K. L. Naylor).

(iv) "Multiple Morphologies in Cross-Linked Polyethylene", CEIDP, Boston, 1981 (with D. V. Brower and K. L. Naylor).

(v) "Computer Simulation of Cable Processing", CEIDP, Boston, 1981 (with C. A. Kodres).

(vi) "Permanganic Acid Etching Studies of Low Density and Cross-Linked Polyethylenes", American Physical Society, Phoenix, 1981 (with D. L. Buerger, K. L. Naylor and L. C. Winterton).

(vii) Invited Lecture, EPRI Workshop on the Morphology of Polyethylene, Washington, D. C., March 1981.

(viii) Invited Lecture, Symposium on Morphology and Properties of Polyethylene, Royal Institute of Technology, Stockholm, Sweden, June 1981.

(ix) "Fact and Artifact in Permanganic Etching", American Physical Society, Dallas, 1982 (with K. L. Naylor).

3. Seminar Presentations

(i) "Morphological Studies of Electric Power Cable Insulation", National Bureau of Standards, Washington, D. C., 1979.

(ii) "Recent Studies of Polymer Crystallization", Seminar, Queen Mary College, London, 1980 (Materials Department).

(iii) "Morphological Studies of Cross-Linked Polyethylene", Seminar, Central Electricity Generating Board Laboratories, London, 1980.

(iv) "Morphology of Cross-Linked Polyethylene", Seminar, Standard Telecommunications Laboratories, Harlow (London), 1980.

(v) "Morphological Studies of Cross-Linked Polyethylene", Seminar, University of Newcastle-upon-Tyne, 1980 (Metallurgy Department).

(vi) "Morphological Studies of Cross-Linked Polyethylene", Seminar, University of Leeds, 1980 (Physics Department).

(vii) "Morphological Studies of Cross-Linked Polyethylene", Seminar, AERE Harwell, 1980.