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PROGRESS REPORT

MASTER

on

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

by

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(DOE Contract #DE-AS02-79ER10421.A000)

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I. REVIEW OF PROGRESS TO DATE

It was originally proposed to carry out the following program using mainly scanning and transmission microscopy:

- (a) an investigation of the crystallization process in cross-linked polyethylene both in stress-free and under stressed conditions;
- (b) the determination of the interfacial region between the conducting layer and the insulation;
- (c) The examination of the interfacial region between the conducting layer and the insulation;
- (d) the examination of treed cables to determine the most important morphological causes of tree initiation;
- (e) the examination of trees to determine the relation of the discharge channels to the morphological structure;
- (f) the production of "miniature cables" as a function of
 - (i) steam or gas cure
 - (ii) temperature and pressure during cure
 - (iii) cross-linking agent
 - (iv) extrusion temperature and die geometry
 - (v) quenching conditions

in order to determine the effects of these variables on

- (i) detailed morphology
- (ii) electrochemical treeing
- (iii) dielectric loss spectra.

For the purpose of review these different sections will be grouped together as follows:

1. Crystallization and Morphology

2. Cable Production
3. Electrical Properties

1. Crystallization and Morphology

In the eighteen months since the contract began there has been considerable progress in the basic areas of research. The more difficult applied areas involving controlled manufacture of cables and accelerated aging tests are just beginning.

1.1 Morphological investigations using the two etching techniques referred to in last years report have continued. In particular the permanganic acid etching process has been considerably improved over literature techniques, resulting in much more effective studies. We have also carried out exploratory studies using ceric sulfate solution as an oxidizing etch.

1.1.1 A considerable improvement in permanganic etching efficiency has been achieved through the use of ultrasonic mixing. Etching is now carried out in test tubes immersed in an ultrasonic bath. The microscopic stirring achieved using this method results in uniform etching over the entire surface instead of the pitting which results from the use of Bassett's technique (1-3).

Two important observations of general significance to crystallization in polymers have resulted. First, it is quite clear that a random distribution of spherulite sizes does not occur on a local level (Figure 1). Even though a histogram of a large area would indicate a random distribution, as has generally been assumed, etching studies show that spherulites tend to cluster according to size. Clusters of large spherulites tend to

have voids or bubbles associated with them. It is not yet known whether this clustering phenomenon, which we have named "autosegregation" is caused by an inhomogeneous distribution of heterogeneous nuclei on a local scale or by some form of molecular weight segregation. Nor do we know, as yet, whether it is influenced by the gel-sol separation reported for the first time last year. The "autosegregation" phenomenon is of such general importance that we have extended our studies to other hydrocarbon polymers such as linear polyethylene and polypropylene.

Secondly, it is also clear that regions containing large spherulites are more rapidly etched than regions consisting of small spherulites. This difference in reactivity must be a result of differences in the structure of the amorphous phase! It has long been assumed that more rapidly crystallizing systems would have more tie-chains interconnecting lamellae than slowly crystallizing regions. Molecular weight segregation is also more likely in slow crystallization. It seems reasonable therefore to infer that local differences in cross-linking density would contribute. The more extensive investigations now underway, involving both uncross-linked and cross-linked systems should permit distinction of the different contributions to reactivity.

1.1.2 An investigation of the effects of both melt temperature and crystallization temperature on morphology is now nearing completion. It was believed that the melt temperature could have a significant effect if it exceeded the gel-sol miscibility temperature (currently not known). Analyses of the spherulite size distribution have been carried out using etching studies of a sample compression molded and cured in the laboratory. The distributions have been analysed using time-consuming histograms because of the autosegregation referred to in the preceeding paragraph.

In Figure 2 can be seen histograms for samples crystallized at different temperatures for 24 hours but using a constant melt temperature. As expected, the specimens crystallized at 90°C and 95°C have slightly different peak maxima of 14 μ m and 18 μ m respectively. The samples held at 100°C and 105°C have not crystallized at those temperatures as indicated by the sharp peaks in the vicinity of 8 μ m. It would therefore appear that the crystallization range of cross-linked polyethylene is not the same as that of low density polyethylene.

A study has also been carried out of the effect of melt temperatures on spherulite size distribution. The data are summarized in Figure 3 where it can be seen that the spherulite size at the peak fraction remains constant between 140°C and 190°C. The half width points of the distribution also remain relatively constant. It is likely that the upswing at lower temperatures is due to the proximity of the melting point although this would normally be expected to reduce the spherulite size. The slight upswing at 200°C may be due to the gel-sol miscibility temperature and is being investigated further.

1.1.3 The morphological structure of extracted and unextracted samples from 21mm and 5mm thick insulation from cables has been investigated as a function of distance from the conductor. Along with the now-standard scanning electron microscopy of etched surfaces, differential scanning calorimetry and X-ray diffraction studies have been carried out to estimate crystallinities and d-spacing.

The extractions were carried out using either p-xylene or carbon tetrachloride using a soxhlet. Carbon tetrachloride extracts about 13% by weight (Figure 4) and p-xylene about 16%. Xylene is a better solvent

and so it is believed the CCl_4 extracts are indicative of the lower molecular weight fractions present. The two differ most ($\sim 5\%$) at the outer skin region of the insulation. The crystallinity of the unextracted cable ranges from 46% at the outside to 40% at the conductor. Extracted samples range from 40% at the outside to 37% (xylene) and 30% (CCl_4), implying that the lower molecular weight species removed by the CCl_4 are of higher intrinsic crystallinity. This would be reasonable.

Recently we have begun to study the effect of cross-linking on the unit cell parameters. This was prompted largely by recent papers of Ungar and Keller (4-6) on the effect of radiation cross-linking on high density polyethylene. We had expected effects to be minimal in our samples since the cross-linking occurs in the melt followed by the a crystallization process in which, presumably, the cross-links are excluded from the crystals. Exactly the opposite was observed! Unextracted samples showed (110) and (200) d-spacings a little smaller than those normally observed in both low density and high density polyethylene. Samples extracted with carbon tetrachloride showed a quite marked reduction in both parameters with distance from the outside (Figures 5, 6), i.e. the largest reduction near the conductor. It is useful to compare these figures with Figure 4 where it will be seen that there appears to be an inverse correlation between percent extractables and d-spacings. Assuming a uniform dispersion of cross-linking agent throughout the polymer this would be a reasonable observation if cross-links were preferentially incorporated into the crystal rather than excluded. The effects observed are much greater than those observed by Ungar and Keller, and require considerably more investigation.

1.1.4 In order to quantify any observed effects of cross-links

on morphology or physical properties it is necessary to develop a reliable method of estimating the concentrations of cross-links produced during cure. Currently used techniques do not quantify but only estimate percent extractibles or viscosity indexes. A spectroscopic technique seemed most convenient and the possibilities of Fourier Transform Infrared Spectroscopy and ^{13}C Nuclear Magnetic Resonance were investigated. Due to the non-polar nature of polyethylene the NMR seemed most appropriate. Mandelkern and co-workers (7-9) had already performed a very thorough analysis of low density or branched polyethylenes following on research of other workers and so it was possible to identify and estimate the concentrations of branches. Butyl and ethyl are the main types of branch present.

We cannot go into the details of ^{13}C NMR analyses here, however, the peaks of interest are those which will be affected by production of a cross-link nearby. Branches are usually single butyl or two ethyls separated by a methylene group. Peaks are referenced relative to the peak of a standard and are expressed in parts per million.

Cross-links are likely to be produced at the branch points (B) due to the higher reactivity of a tertiary carbon, and will influence carbons several atoms away (eg. β). The table gives observed positions of peaks for the uncross-linked material and calculated positions for the cross-linked material. (GP and LA are two different computational methods). There are two important effects relevant to our observed spectra (Figures 7 and 8). First the peak at 27.3 decreases as the peak at 25.7 increases. Such an effect (see table) would be caused by a cross-link at B affecting the 2 and

β carbons. Secondly, a new peak is observed at 30.9 as a spur to the main peak. We believe that this reflects the effect of a cross-link at B on carbon γ . We can therefore designate the major cross-link site as the branch carbon (B). Quantification of the intensities to obtain an accurate count of the number of cross-links is still proceeding. This problem is complicated by the fact that more than one carbon contributes to the peak at 25.7.

<u>Uncross-linked</u>			<u>Cross-linked at B</u>		
	(GP)	(LA)		(GP)	(LA)
A	38.69	38.48	A	37.15	35.89
B	35.23	--	B	34.00	--
1	11.49	11.36	1	10.26	9.84
2	<u>27.79</u>	<u>27.41</u>	2	<u>26.25</u>	<u>24.82</u>
α	34.70	27.52	α	33.16	31.88
β	<u>27.80</u>	<u>27.52</u>	β	<u>26.57</u>	<u>25.58</u>
γ	<u>30.29</u>	<u>30.21</u>	γ	<u>30.93</u>	<u>30.46</u>

1.1.5 Studies of the crystallization kinetics are now being carried out on two fronts. As planned last year, a temperature controlled cell is being used in conjunction with wide angle X-ray diffraction studies to obtain bulk crystallization rates. The (110) peak intensity is being monitored for this purpose.

The radial growth rates of spherulites are being obtained using laser light scattering and a TV monitoring system. The position (10) of the scattering maximum of a clover-leaf scattering lobe (Figure 9) is monitored as a function of time and the spherulite growth rate obtained directly. Experiments are more difficult than for the uncross-linked polymer since the scattering intensity is lower and the pattern less distinct (Figure 9). This may be caused by the cross-links causing the lamellae to be diverted from the usual radial symmetry.

1.1.6 Experiments are being carried out on the use of ceric sulfate as a much safer etch than the permanganate in sulfuric acid. Etching does occur, but much more slowly than the permanganate. It appears to attack the intra-lamellar material more effectively than the permanganic etch, leaving behind a mass of rod-like species (ca. $1\mu\text{m}$ thick) which may be lamellae or stacks of lamellae. The technique is still being evaluated.

2. Cable Production

2.1 Computer Simulation. The bulk of the computer simulation study was reported last year. Since then we have carried out an amendment to the program to investigate the possibility of preheating of the metallic wire to enhance the rate of cure. In Figure 10 is shown the effect of the conductor temperature on the time needed for cure expressed as a function of the length of travel of the cable. As can be seen, preheating to the cure temperature reduces the time for cure by a factor of almost three. The effect on the temperature profile across the cable is shown in Figure 11. Because the polyethylene has such a poor thermal conductivity, cross-linking in the extruder only extends out from the conductor to about one half of its thickness preventing any possibility of setting in the extruder.

2.2 Laboratory Scale Production. The majority of the parts needed for the laboratory scale manufacturing facility have now arrived and the line is in the process of assembly. It is being built with a sufficient number of thermocouple points and pressure gauges for accurate monitoring of processing conditions. To obtain maximum versatility it has been designed for both dry and steam curing. The boiler needed for steam generation will be requested in the accompanying renewal proposal. We should therefore be in the position to begin manufacture in the very near future.

3. Electrical Properties

3.1 Dielectric Constant and Loss. We have now begun measurements of dielectric constant and loss of cross-linked polyethylene over the temperature range -120°C to $+100^{\circ}\text{C}$ and the frequency range 10 Hz to 10 kHz. An example of the loss curves obtained is given in Figure 12 for various frequencies plotted as a function of temperature. The spectrum is very different from that of oxidised low density polyethylene since the dipoles are present in the organic byproducts and not in the main chain of the polymer. There are two major low temperature peaks close to each other. These may be due to the libration at the glass transition of isolated organic molecules present in the amorphous phase of the polymer. A small peak at $20 - 30^{\circ}\text{C}$ is due to the melting of acetophenone bulk particles. The analogous peak for 2-phenyl-2-propanol at 40°C is absent, perhaps indicating totally different environments for the two impurities. The high temperature peak ($\sim 80^{\circ}\text{C}$) is related to conductivity and probably due to enhanced mobility as the melting point of the polyethylene is approached.

These studies are continuing in more detail and will be extended to examples of extruded polymer in the near future. In order to study these extruded samples, a special co-axial cell is being constructed.

3.2 Dielectric Aging and Breakdown Studies. We are still in the process of assembling this equipment. As mentioned in an earlier letter, the equipment we originally wished to purchase is no longer available. This was a fortunate occurrence from the long term point-of-view since we have designed our own equipment in such a way as to be more versatile. It will permit us to carry out several types of tests whereas the equipment originally desired would have been useful only for accelerated aging. Funds were

actually saved from this procedure and the excess has been diverted into instrumentation for the cable production facility thus saving the agency about \$5,000.00.

II. REFERENCES

1. R. H. Olley, A. M. Hodge and D. C. Bassett, *J. Polym. Sci., Polym. Phys. Ed.*, 17, 627 (1979).
2. D. C. Bassett and A. M. Hodge, *Proc. Roy. Soc., A*, 359, 121 (1978).
3. D. C. Bassett and A. M. Hodge, *Polymer*, 19, 469 (1978).
4. G. Ungar and A. Keller, *Polymer*, 21, 1273 (1980).
5. G. Ungar, *Polymer*, 21, 1278 (1980).
6. G. Ungar, D. I. Grubb and A. Keller, *Polymer*, 21, 1284 (1980).
7. F. A. Bovey, F. C. Schilling, F. L. McCracken and H. L. Wagner, *Macromolecules*, 12, 41 (1979).
8. D. E. Axelson, G. C. Levy and L. Mandelkern, *Macromolecules*, 12, 41 (1979).
9. J. J. Dechter and L. Mandelkern, *J. Polym. Sci., Polym. Lett. Ed.*, 17, 317 (1979).
10. M. R. Rhodes and R. S. Stein, *J. Appl. Phys.*, 31, 1873 (1960).

Figure 1. Cross-linked polyethylene, etched, showing autosegregation of spherulites.

Figure 3. The effect of melt temperatures on spherulite size distribution.

Figure 4. Carbon tetrachloride extraction by weight.

Cable; radial cross-section (medium sized)

Figure 6

Cable; radial section (large sized)

Figure 5

D-spacings in terms of distance from the outside of a cable for samples extracted with carbon tetrachloride and for unextracted samples.

Figure 7. ^{13}C NMR of original low density polyethylene.

Figure 8. ^{13}C NMR of original cross-linked polyethylene.

Figure 9.

Laser
Light
Scattering
Patterns

Low Density Polyethylene

Cross-Linked Low Density Polyethylene

Figure 10a. The effect of the initial wire temperature on the cross-linking rate of an intermediate size copper cable assuming condensation curing; $\dot{m}_{EXT}=135\text{kg/hr}$, $T_{POLY}=120^\circ\text{C}$, $T_{CURE}=200^\circ\text{C}$.

Figure 10b. The effect of the initial wire temperature on the cross-linking rate of full-size copper cable considering condensation curing; $\dot{m}_{EXT}=200\text{kg/hr}$, $T_{POLY}=120^\circ\text{C}$, $T_{CURE}=200^\circ\text{C}$.

Figure 11. The effect of the initial wire temperature on the profile across a full-size cable as it transits curing stage: $\dot{M}=200\text{kg/hr}$, $T_{CURE}=200^{\circ}\text{C}$, $T_{POLY}=120^{\circ}\text{C}$.

Figure 12. Loss curves of cross-linked polyethylene for various frequencies plotted as a function of temperature.

III. LISTS OF PUBLICATIONS AND PRESENTATIONS

Research has now progressed to the stage where papers can be submitted to regular high quality scientific and engineering journals. Presentations of the work at conferences have continued and several abstracts and conference preprints have appeared in the past year. During a trip to England last autumn the research funded by this contract was the most requested seminar subject, a total of six seminars being given on the subject in the space of two weeks.

As a result of this research funded by the Department of Energy, the Electrical Power Research Institute will sponsor a two day workshop on the subject with the principal investigator giving an invited lecture.

A. Publications (preprints attached)

(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*, accepted for publication.

(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*, accepted for publication.

(v) D. V. Brower, K. L. Naylor and P. J. Phillips, "The Two-Tiered Morphology of Chemically Cross-Linked Polyethylene", *Journal of Materials Science*, submitted.

(vi) C. A. Kodres, "The Use of Wire Preheating to Increase Curing Rates of Polyethylene Cables", *I.E.E.E. Transactions*, submitted.

(vii) L. C. Winterton and P. J. Phillips, "Extraction Studies of Cross-Linked Polyethylene", in preparation.

(viii) D. L. Buerger and P. J. Phillips, "¹³C NMR Studies of Cross-Linked Polyethylene", in preparation.

B. Conference Presentations

(i) "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).

C. 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.

APPENDIX: PREPRINTS OF PUBLICATIONS

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