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

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FIRST YEAR REPORT

MASTER

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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 detailed morphology of a series of cables of differing diameters and extrusion conditions;

(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 purposes of review these different sections will be grouped together as follows:

A. Crystallization and Morphology [(a), (b), (c)]

B. Treed Cables [(c), (d)]

C. Cable Production [(e), (f)].

A Crystallization and Morphology

In the seven months since the contract began there has been considerable progress in some areas. Research in other areas is just beginning. Morphological investigations have concentrated until recently on the use of the already established techniques of scanning electron microscopy of polished surfaces etched with carbon tetrachloride vapor, differential scanning calorimetry and X-ray diffraction. We have recently applied the technique of permanganic acid etching (5 - 7) to cross-linked polyethylene specimens with unexpected and quite exciting results.

(a) A series of cables of varying diameter and, hence, insulation thicknesses was obtained from several manufacturers and processors. The carbon tetrachloride etching (8) was first used and a clear relationship of grain diameter to insulation thickness obtained (figure 1). Diameter increases with thickness as would be expected from quenching efficiency considerations. Basically, since the polymer is a poor conductor of heat, crystallization will take place at progressively higher temperatures as the polymer thickness is increased. When these experiments were well advanced a former student attempting to apply our techniques in industrial research advised us that he had carried out successfully exploratory research on the use of permanganic etching with the result that he was able to resolve the lamellar structure of the spherulites in cable samples.

We have now carried out some experimentation using this technique and indeed it is possible to resolve the internal structure as well as to identify the locations of the amorphous material since the etchant specifically attacks non-crystalline material. The surprising result of these experiments is that the spherulites detected by this technique are about a tenth of the

FIGURE 1

3

Gel particle size (O) and spherulite size (●) versus the thickness of the insulation for a series of XLPE cables

size of the grains detected using the carbon tetrachloride etch (figure 2). This must mean that what were previously described as spherulites were some kind of superstructure associated with the cross-linked molecules. Although gel-sol separation is well known in swollen cross-linked systems it is unheard of in solid polymers. Since these structures are present in both steam-cure and dry-cure systems the separation must be related to the presence of the by products of the cross-linking agent and not the absorbed water. Presumably something similar to a spinodal decomposition is resulting from a perturbation of the normal equilibrium existing in a molten cross-linked polymer.

This phenomenon introduces an additional complicating factor, namely that of a separation of uncross-linked molecules from the cross-linked network prior to the crystallization process. It also helps to explain some of the puzzling results of recrystallization studies obtained prior to this discovery and which will be described below. As can be seen in figure 1 both spherulite size and gel particle size vary in a similar manner with insulation thickness.

(b) In order to begin crystallization studies it was decided to use samples of polymer from a standard cross-linked polyethylene cable. The specimens were melted and the temperature raised to 130°C, maintained there for 30 minutes and then crystallized at a series of constant temperatures between 80°C and 110°C for two days. They were then polished and etched with carbon tetrachloride. The surprising result was a decrease in "spherulite" size of at most 10% regardless of the crystallization temperature. Such an insensitivity of size to temperature is uncharacteristic of crystallizable polymers. There were changes, somewhat difficult to quantify, in the microstructure of the boundary regions and also of the interiors of the grains.

If the suggestion made in the previous section is correct, namely that the grain structures revealed by carbon tetrachloride vapor are symptomatic of a phase separated melt then changes would not be expected in those structures

FIGURE 2A

Gel particle structure revealed by carbon tetrachloride etching (magnification X100)

FIGURE 2B

Spherulite structure revealed by permanganic etching (magnification X1,210)

provided the temperature was not raised above the critical miscibility temperature. Such a temperature is probably related to the θ temperature (9) for polyethylene in acetophenone/cumenol. Such data are not available in the literature, however, the θ point for polyethylene in nitrobenzene is 230°C; in benzylphenyl ether, 191.5°C; and in anisole, 153.5°C. Since these chemicals are related in some aspects of their molecular structure to acetophenone/cumenol it seems likely that such a situation is indeed occurring.

The recrystallized samples will shortly be etched using the permanganic acid technique in order to determine the dependence of the actual spherulite size on crystallization temperature.

(c) A very important practical point to be investigated relates to the variation of both cross-linked fraction and crystallinity with depth in the insulating layer. Accordingly, for a specimen of 150kV cable we have determined the overall crystallinity, percentage extractable (i.e. uncross-linked) polyethylene and the crystallinity of unextractable (i.e. cross-linked) polyethylene as a function of distance from the conductor. As expected the outer regions which are exposed to the steam temperature for longer periods of time are more highly cross-linked. The overall crystallinity drops somewhat towards the outside presumably due to more effective quenching.

(d) The investigation of the crystallization kinetics has not yet begun since it proved impossible to recruit a graduate student before December. We are in the process of carrying out exploratory experiments into the use of differential scanning calorimetry (DSC) to follow the bulk crystallization kinetics. We are also constructing a temperature control and straining cell for use on the X-ray diffractometer so that the bulk kinetics can be obtained using this second technique.

(e) The experimentation carried out in (b) also enabled us to study the

effect of melting and recrystallization on the interfacial boundary between the insulation and the semi conducting layer. A great deal of separation does indeed occur as was predicted but as yet the effect has not been quantified, and must await a correlation with spherulitic structure from permanganic etching.

B. Treed Cables

We were fortunate to obtain the cooperation of Dr. Jack Lawson of Pacific Gas and Electric for this part of the project. He maintains a collection of the "treed" parts of failed cables and has provided us with parts of specimens from his collection. Most of the specimens are polyethylene however there are a few cross-linked samples also available. Because the size of each specimen is rather small we have had to pay special attention to the development of staining techniques.

The technique originally planned and currently used in the staining of tree tracks for optical studies does not work for scanning electron microscopy. Although lead oxide and a dye containing detectable sulfur atoms are involved the lead oxide does not penetrate the polymer and the dye penetrates the entire polymer to such a degree that the concentration differences are not adequately detectable by EDAX. Alternative techniques involving the deposition of soluble metal salts in the tree tracks are currently being explored.

C. Cable Production

A mechanical engineering graduate of the University of Utah was recruited as a post-doctoral associate to assist with this part of the program. The individual concerned, Dr. Calvin A. Kodres, carried out thesis research on the computer modelling of heat transfer processes in uniaxial systems and was an ideal recruit for this stage of the research.

The new extruder and wire making attachment have now been delivered and the apparatus is in the assembly process. A short but non-critical delay has occurred here because of a necessary upgrading of the power supply to the equipment.

It will be in operation prior to the ending of the current grant period.

As an advisable first step prior to the design, construction and assembly of the scale-down manufacturing facility we decided to set up a computer simulation of the cure and quench processes to ensure that any scale down process made accurately reflects the treatment received by a full size cable. It is for these purposes that Dr. Kodres is particularly valuable.

The program written generates the time-temperature dependence of the insulation not only as a function of radial distance from the conductor but also as a function of circumferential position. It also includes thermal conduction along the axial direction. Neither of these two variables have been considered before in published wire making programs. The cross-linking reaction is also included with its known temperature dependence permitting an estimation to be made of cross-link density as a function of time and location.

Several variants of the program have already been constructed, the problem of diffusion of water and gases into the insulation having already been handled successfully. We are currently working on the quenching process and also on the possible complication of the absorbed water molecules interfering with the cross-linking reaction. An adaptation of the program to simulate the melt-down and recrystallization processes which occur under overload conditions is also underway.

The mathematical formulation of the program involves obtaining solutions to the following equations:

(i) Heat Transfer

$$\rho c \frac{\partial T}{\partial t} = \frac{k_r}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{k_\theta}{r^2} \cdot \frac{\partial^2 T}{\partial \theta^2} + k_z \frac{\partial^2 T}{\partial z^2} + Q'$$

where ρ is the density, c the specific heat, k_r , k_θ and k_z the thermal conductivities in the radial, circumferential and axial directions respectively

and Q' a heat source or heat sink.

(ii) Mass Transfer

$$\frac{\partial \omega_A}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(\frac{r}{1 - \omega_A} \cdot \frac{\partial \omega_A}{\partial r} \right) + \frac{R_A}{\rho}$$

where ω_A is the mass fraction of component A, D its diffusion coefficient in the polymer and R_A any mass change.

The equations consider the addition or subtraction of heat or mass from a volumetric element. They are transformed to eliminate the moving boundary condition (i.e. leading end) and only consider a section of polymer within a continuous section of cable. They are non-dimensionalized; the velocity of the cable being introduced as part of the non-dimensionalization through a Peclet number. The equations are then solved for a particular set of conditions over a series of discrete and non-dimensionalized volume and time units (a copy of the program which has now been copyrighted is submitted in Appendix B). Constants used for the equations correspond closely to those used in a recent simplified simulation of radiative curing which was found to predict a temperature variation very close to that found in practice (10).

Some of the results of this modelling procedure will now be summarized.

(a) Effects of Surface Heat Transfer Mode for Mini-Cable (figure 3)

The major conclusion to be made is that the mode of heat transfer between the steam environment and the cable surface is of extreme importance. Condensation of superheated water clearly is the most effective means.

(b) Effect of Cable Dimensions on Curing Rate (figures 4, 5)

For a large transmission class cable the low thermal conductivity of the polymer dominates, the mode of surface heat transfer being of minor importance. For distribution class cables both thermal conductivity and heat transfer mode are important. Also shown as vertical lines are cure times normally

used in industry for 4 inch and 6 inch extruders.

(c) The Effect of Curing Temperature (figures 6, 7)

Here it can be seen that for the smaller cables changing the cure temperature has a major effect on efficiency whereas for transmission cables the effects although significant are not so great.

(d) The Effects of Extruder Discharge Temperatures (figure 8)
and Conductor Material (figure 9)

For all cables, changing the extrusion temperature has a major effect on curing time. This is perhaps the most influential variable so far neglected by manufacturers. The core material also exerts a major effect because of its thermal conductivity and for smaller cables a change of conductor causes a doubling of the cure time.

(e) Diffusion of Water into the Cable (figures 10, 11)

The diffusion of water molecules to the conductor region is very slow for large cables but relatively rapid for small ones as might be expected. Although the concentration of water molecules is rather small the levels achieved over the outer half of the cable are, on a molar basis, comparable to the concentration of cross-linking agent and hence could exert a major effect on the efficiency of the cross-linking process.

(f) Temperature Profiles (figures 12, 13)

Here a comparison of temperature profiles for a mini-cable and transmission cable using conduction transfer are shown. It is clear that a near complete cure is achieved for the minicable in a few minutes whereas several hours are needed for the full size cable. These figures would indicate that as far as the cure process is concerned mini-cables as currently used in industrial and research institutions for evaluation of aging behavior are *in no way* a substitute for the real cable.

The effect of the surface heat transfer mode on the curing rate of a polyethylene cable insulation

Dimensions of Insulation: $RI = 0.159$ cm
 $RO = 0.238$ cm

Extruder Discharge Temperature = 120°C

Curing Environment Temperature = 200°C

$E_a/R = 9169^{\circ}\text{K}$

$k_0 = 5.4(10)^6 \text{sec}^{-1}$

Copper Core

FIGURE 4

CABLE IDENTIFICATION

1. ————— MINI-CABLE

RC = 0.150 cm
RI = 0.159 cm
RO = 0.238 cm

2. - - - - - FULL-SIZE CABLE

RC = 1.308 cm
RI = 1.549 cm
RO = 3.995 cm

3. — — — — — INTERMEDIATE

RC = 0.495 cm
RI = 0.546 cm
RO = 1.219 cm

FIGURE 5

The effect of cable dimensions on the curing rate of a polyethylene cable insulation.

Extruder Discharge Temperature = 120°C

Curing Environment Temperature = 200°C

$E_a/R = 9169^\circ\text{K}$

$k_0 = 5.4(10)^6 \text{ sec}^{-1}$

Thermal Cond. = 0.22 w/m/°K

Copper Core

FIGURE 6

The effect of curing temperature on the curing rate of a polyethylene cable insulation (convective boundary).

Extruder Disc. Temperature = 120°C

$E_a/R = 9169^\circ\text{K}$

$k_0 = 5.4(10)^6 \text{ sec}^{-1}$

Thermal Cond. = 0.22 w/m/°K

Copper Core

$h = 50. \text{ w/m}^2/\text{°K}$

FIGURE 7

The effect of curing temperature on the curing rate of a polyethylene cable insulation (condensation).

Extruder Disc. Temperature = 120°C

$E_a/R = 9169^\circ\text{K}$

$k_0 = 5.4(10)^6 \text{ sec}^{-1}$

Thermal Cond. = 0.22 w/m/°K

Copper Core

$h = 12000. \text{ w/m}^2/\text{°K}$

FIGURE 8

The effect of extruder discharge temperature on the curing rate of a polyethylene cable insulation.

Curing Environment = 200°C

$E_a/R = 9169^\circ\text{K}$

$k_0 = 5.4(10)^6 \text{ sec}^{-1}$

$k = 0.22 \text{ w/m}^\circ\text{K}$

$h = 50. \text{ w/m}^2/\circ\text{K}$ (laminar convection)

Copper Core

FIGURE 9

The effect of cable (core) material on the curing rate of a polyethylene electrical distribution cable.

Extruder Discharge Temperature = 120°C

Curing Environment = 200°C

$E_a/R = 9169^\circ\text{K}$

$k_0 = 5.4(10)^6 \text{ sec}^{-1}$

Thermal Conductivity = 0.22 w/m/°K

$h = 50. \text{ w/m}^2/\circ\text{K}$ (laminar convection)

FIGURE 10

Diffusion of water through mini-cable.

FIGURE 11

Diffusion of water through full size cable.

FIGURE 12

Typical temperature profiles through full-size cable subjected to convective curing.

FIGURE 13

Typical temperature profiles through full-size cable subjected to condensation curing.