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THERMAL OPTICAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY OF CHEMICALLY CROSSLINKED POLYETHYLENE*,**

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ABSTRACT

Differential scanning calorimetry (DSC) and thermal optical analysis (TOA) were applied as part of a series of characterization methods to solid chemically crosslinked polyethylene insulation. The DSC was used to study the melting and recrystallization. The ΔH of fusion has a lower value than expected. The TOA shows premelting behavior and is more sensitive to crystalline charges, on cooling, than DSC.

INTRODUCTION

Homopolymer and copolymers of ethylene may be crosslinked by irradiation or chemical reaction. Both techniques create free radicals and form inter- and intramolecular bonds to create a network polymer. Thus crosslinked polyethylene behaves as a semicrystalline polymer below the melting point and as a rubber above the melting point.

Crosslinked polyethylene has found its widest application in power cable insulation. Formulations based on low density polyethylene are well suited for most low voltage applications such as line and building wire, service entrance cable, and similar uses. As part of an ongoing study to characterize dielectric polymeric insulation, thermal optical analysis, TOA, and differential scanning calorimetry, DSC, were applied to crosslinked polyethylene.

The samples studied were low density polyethylene (melt index ~2.7) crosslinked with 3% dicumyl peroxide. The formulation including 0.5% antioxidant is extruded over a copper conductor and cured in steam at above 200°C. The extent of crosslinking is 0.78 based on xylene extractables. The crosslinking does not materially change the crystallinity of the polyethylene. None of the samples are filled. Sample A is a commercial 15 kV cable insulation and samples B and C are insulations from No. 14 wire conductor.

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EXPERIMENTAL

Differential scanning calorimetry

The differential scanning calorimetry, DSC, of the crosslinked polyethylene was performed on a Perkin-Elmer DSC-1B. The specimens were prepared by cutting a disk from a microtomed piece of large cable insulation. Care in sample preparation is necessary in order not to alter the polymer morphology. This disk fits into a DSC sample pan which was then sealed using a pan top and a device designed to cold weld the two. In the case of small wire samples, the insulation was stripped and then sliced into a thin disk. The most important aspect of sealing the pan was being sure that the pan bottom was flat to provide good thermal contact with the sample holder. Specimen weights were determined to four figures with a Cahn electrobalance and ranged from 2 to 10 mg.

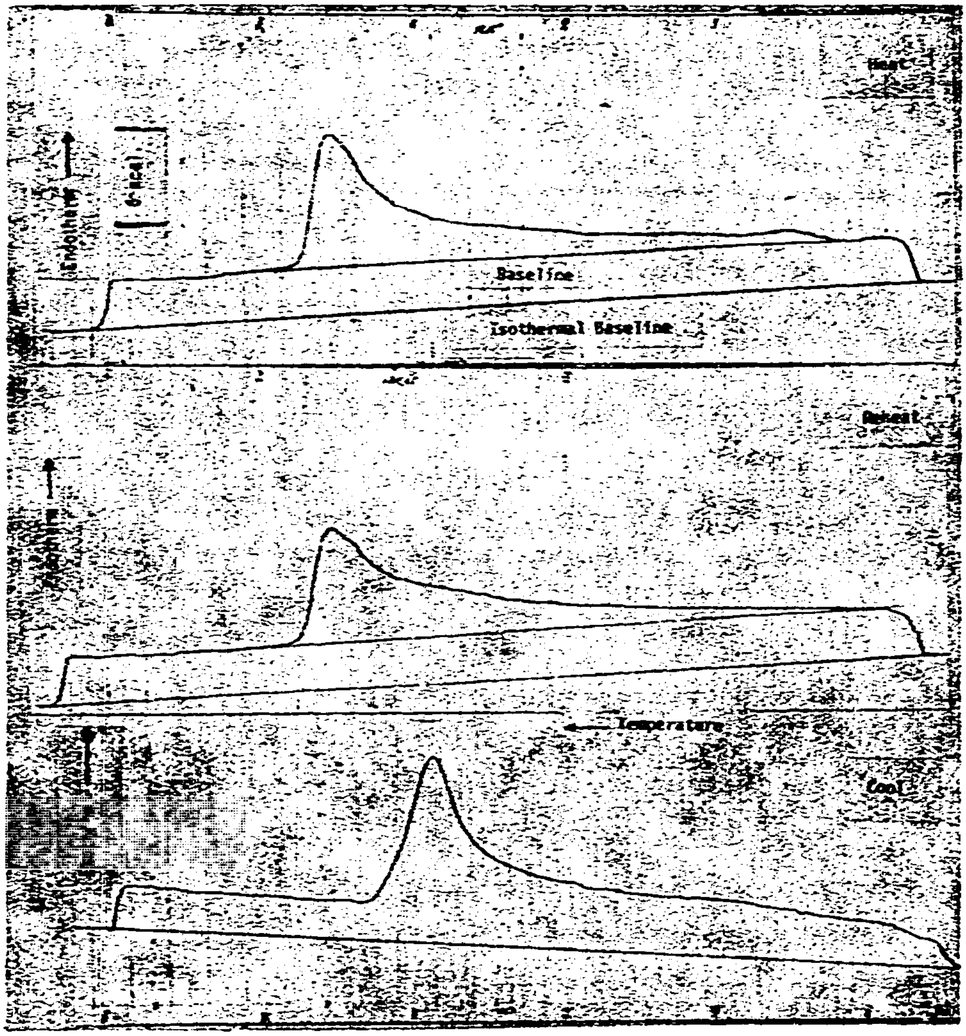

Fig. 1. DSC traces for sample C.

The run was started below room temperature by using a low temperature cover filled with ice water. A high purity nitrogen purge of 50 ml min^{-1} was used. The specimen was heated at 5°C min^{-1} and then cooled at 5°C min^{-1} to give a known thermal history. After cooling to slightly below room temperature, the specimen was heated for a second time at 5°C min^{-1} through the transition.

The premelting baseline is always wandering and occasionally there is multiple endotherm behavior. This phenomenon has been explained in semi-crystalline polymers by Sweet and Bell[1]. Consider that the baseline after the melt is the true baseline. The baseline before the fusion peak represents melting, supercooling and recrystallizing of small imperfect crystals while the calorimeter is heating. At some point, namely, the first endotherm, all these small imperfect crystallites melt, but part of the melt recrystallizes into more perfect crystals. At the second endotherm, this more perfect recrystallized region melts. Thus, the first endotherm may represent either original crystals or crystals formed in the instrument. The higher endotherm is almost always not a true characteristic of the material, but the result of recrystallization in the instrument.

Figure 1 shows a typical trace for heating, cooling, and reheating of a crosslinked polyethylene. Sample B has sharper and better formed peaks than samples A and C.

Table 1 presents the results of DSC determinations. The melting temperatures are peak temperatures extrapolated back to the isothermal baseline using the slope of leading edge of the indium calibration standard. The onset of melting was taken to be a few degrees above room temperature. The temperature and enthalpy calibrations were based on an indium standard. The percent crystallinity at room temperature was determined by X-ray crystallography with a Philips powder diffractometer and copper radiation. The 110 and 200 crystalline reflections and amorphous scatter were recorded. The reflections were resolved into Gaussian peaks and converted to intensities.

TABLE 1

DSC AND CRYSTALLOGRAPHIC DATA ON CROSSLINKED POLYETHYLENES

Sample		T_M (°C)	ΔH (*mcal* mg^{-1})	*Relative*[a] *% cryst.*	*Crystallinity by X-ray* (%)
A	1st heat	97.6	21.33	29.6	
	2nd heat	96.4	20.05	27.8	53
	cool	85.0			
B	1st heat	103.3	27.29	37.9	51
	2nd heat	104.0	24.61	34.2	
	cool	93.5			
C	1st heat	99.2	23.92	33.2	55
	2nd heat	99.0	23.07	32.0	
	cool	88.3			

[a] A value of 72 mcal mg^{-1} was used as the value for 100% crystalline polyethylene[2].

Thermal optical analysis

The intensity of polarized light transmitted by an anisotropic material measured as a function of temperature has been used in polymer research since Magill's[3] work in 1960 on the crystallization rate of nylon. This technique has been described as depolarized light intensity, thermal depolarization analysis and thermal optical analysis, TOA. Changes in crystal structure, melting, or mechanical strain result in changes in optical anisotropy. These changes result in changes in the intensity of light transmitted by an optically anisotropic material when examined between crossed polarizers.

The instrumentation for TOA, shown schematically in Fig. 2, consists of a regulated light source, a polarized light microscope, a heating stage with controlled heating rates and a photometer system for intensity measurement. The system used in this work is similar to that proposed by Barrall and Johnson[4]. The system used a Leitz ortholux pol microscope with a specially designed heating stage, a Varian multilinear temperature programmer and a photo diode light photometer. The details of this system will be reported in a separate paper.

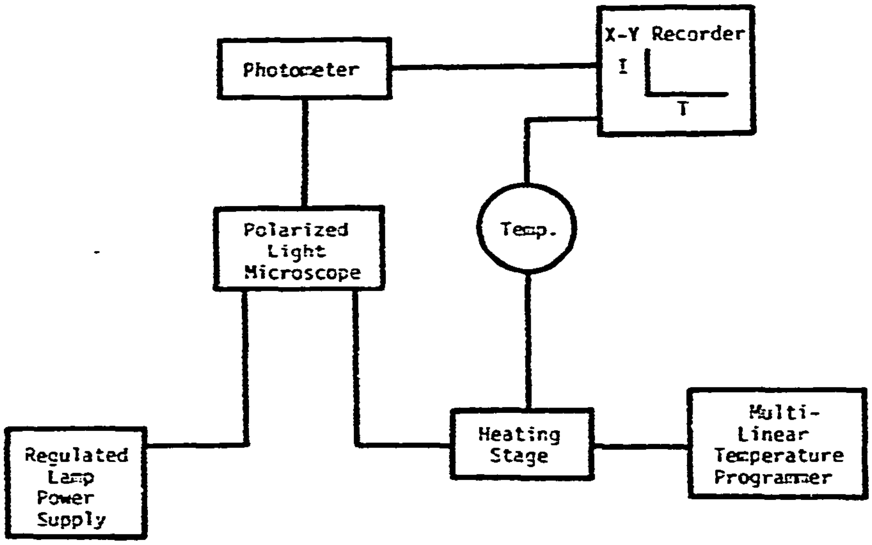

Fig. 2. Block diagram of thermal optical analysis system.

The samples of chemically crosslinked polyethylene were prepared by cutting sections 0.05 to 0.5 mm thick and placing them on clean microscope slides (2.5 × 3.8 cm) under a cover glass. The cutting is performed at room temperature and introduces a large amount of mechanical deformation which results in strain birefringence. The strain is removed by annealing during an initial heat–cool cycle. In transmission TOA, observations can only be made on thin transparent samples.

The data output is the relative light intensity as a function of temperature. The graphical data in Figs. 3–5 illustrate the nature of information determined by TOA.

The three chemically crosslinked polyethylene samples and sample C polymer prior to crosslinking were examined after cutting and after a thermal cycle of heating to 130 °C and slow cooling to 35 °C. Samples are reported at a heating rate of 5 °C min^{-1}.

The total intensity of polarized light transmitted by a thin section of material[5] results from the sum of its parts as expressed in eqn (1). Each anisotropic component results in birefringence and an increase in transmission of crossed polarized light.

$$I_{total} = I_{crystal} + I_{stress} + I_{form} - I_{scatter} \qquad (1)$$

The components of the intensity are the intensity due to the crystalline birefringence of the polymer plus the intensity due to the stress birefringence and the form birefringence less the intensity loss due to scatter. In thin sections, the form and scatter terms are negligible[6]. The scatter term depends on the number of small particles which can scatter light. The stress birefringence of these thin sections is very large due to sample preparation. By thermally annealing, mechanical stress is reduced so that the intensity from this term becomes negligible. Thick sections will show residual stress from manufacturing or mechanical work. Once the I_{stress} term is minimized, the changes in total intensity are related to the crystalline birefringence.

Figure 3 shows the TOA data obtained on the first heat-cool cycle of samples B and C. The higher intensity initially observed results from the strain introduced in sample preparation. The rate of intensity loss on first heating is related to the rate of annealing of mechanical deformation. On cooling the material recrystallizes and the rate of recrystallization and degree of undercooling can be determined.

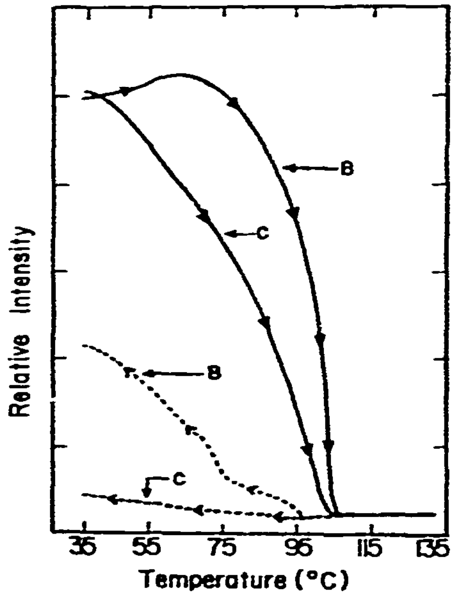

Fig. 3. TOA on initial heating and cooling cycle of samples B and C. Cut samples having large strain birefringence. ———, heating at 5 °C min^{-1}; — — —, cooling (non-linear).

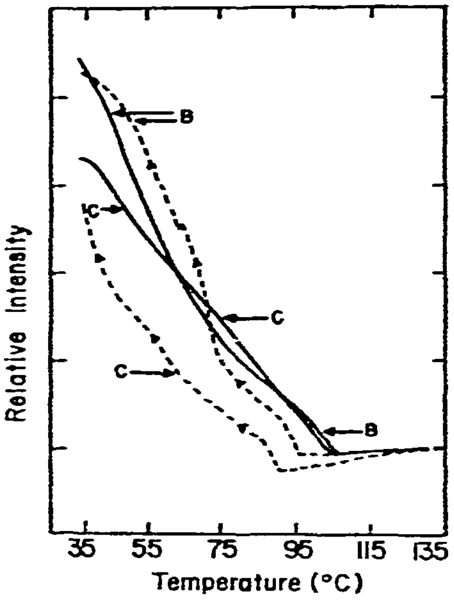

Fig. 4. TOA of samples B and C on second heat-cool cycle. ———, heating at 5 °C min^{-1}; — — —, cooling (non-linear).

The complex character of the recrystallization data is reproducible and indicates multiple recrystallization processes. Figure 4 shows the second cycle of heating and cooling for the same samples. On cooling there is a drop in intensity before the increase. This phenomenon is related to the onset of nucleation where small nuclei scatter light which results in a light loss. At a certain nuclei size there is a retardation level which results in the detection of intensity.

Figure 5 shows the second heat–cool cycle of sample C and its base polyethylene compound before crosslinking. The crosslinked polyethylene shows a broader melting and cooling behavior than the low density polyethylene.

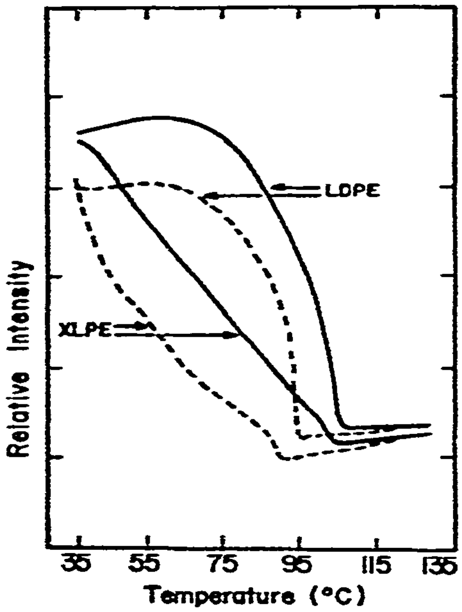

Fig. 5. TOA of sample C before and after crosslinking; LDPE is polymer with dicumyl peroxide added; XLPE is the same material after crosslinking at ~225°C.

DISCUSSION

DSC and TOA can detect substantial differences in relatively similar commercial crosslinked polyethylenes. TOA data as a function of temperature can also be used to follow the thermal recovery of mechanical deformation. DSC was used to study melting and recrystallization processes.

TOA also shows that there are long term changes in crosslinked polyethylene occurring at room temperature. Specimens that have been thermally annealed will show changes in intensity which in one to two weeks annealing at room temperature will reach a stable level.

Transmitted light TOA is restricted to transparent samples while DSC can be used to study filled, opaque, or colored samples. TOA seems to be more sensitive to crystalline changes particularly on cooling. DSC cooling exotherms are generally well behaved and without multiple peaks. The TOA cooling trace shows reproducible structure related to increasing crystallinity. The cooling rate in TOA is non-linear (exponential) while the DSC was cooled at 5°C min^{-1}. The degree of supercooling detected by the two methods seems comparable.

The relative percent crystallinity calculated from DSC differs significantly from X-ray crystallinity at room temperature. This tends to support the hypothesis that recrystallization is occurring in the DSC apparatus. The endothermic melting is in competition with the exothermic recrystallization process with an apparent lowering of the ΔH of fusion.

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