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CHARACTERIZATION OF POLYMERIC DIELECTRIC INSULATION BY THERMOMECHANICAL ANALYSIS

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ABSTRACT

Use of a thermomechanical analyzer, TMA, affords a rapid, precise method for determining linear expansion coefficients and linear expansivities of cross-linked polymeric insulation material. Completed cable samples were dissassembled and insulation specimens were cut longitudinally and examined with repeated temperature cycling: ethylene–propylene copolymer rubbers and filled and unfilled crosslinked polyethylenes. The TMA results indicated that all specimens were oriented, likely incurred from extrusion processing. The facility of TMA for investigating potential anisotropic behavior from prior orientation is illustrated by examples of TMA measurements on radial specimens, similarly free of mechanical constraints.

INTRODUCTION

Thermomechanical analysis, TMA, is a method of determining the change in length of a sample as a function of temperature. A sample is placed in a furnace with a temperature controller that can be programmed to raise or lower the temperature at a series of fixed linear rates. An electrical transducer is used to provide a signal that is proportional to the change in length. The instrument is calibrated by running samples of known expansion coefficients. The temperature and change in length are recorded on an X–Y plotter[1,2]. A DuPont 941 thermomechanical analyzer was used throughout this work.

In 1969, Williams et al.[3] discussed the importance of the thermal expansion and contraction of crosslinked polyethylene in joint design. In Fig. 17 of that paper, it was shown that on initial heating there was a contraction at about 98°C. Upon cooling and reheating, this contraction disappears and the material behaves normally. In the discussion following the paper by Williams et al., Blodgett et al. also presented data given as Fig. 21 on expansion and contraction of a number of polymers including both filled and unfilled crosslinked polyethylene.

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A number of theoretical aspects of the thermal expansion and contraction for polymers have been given by Mandelkern[4]. He concluded that a crosslinked polymer should have a greater expansion coefficient than a non-crosslinked polymer of the same composition. Since the advent of modern TMA equipment, which permits precise rapid measurement of the linear expansion coefficient on small samples, there does not appear to be any studies reported on crosslinked polyethylene.

EXPERIMENTAL

Samples for the TMA were cut with the ends flat and parallel from sections of large cable insulation. The ends were then polished with a fine grit to make them smooth. The sample length, parallel to the conductor, was between 0.5 and 1.0 cm. When the specimen was cut perpendicular to the conductor, its length was less than 0.5 cm. The sample length is determined using a micrometer.

The TMA was operated in the expansion mode which uses a probe with a flat end, 0.100 in. in diameter. The weight tray used in penetration mode studies was removed from the instrument to minimize loading and a bell jar was used to protect against drafts. The entire DuPont 941 TMA was placed on a vibration table to eliminate external vibrations.

To determine the glass transition temperature of samples 1 and 2 the run was started at −120°C. Many of the other runs were started at 30°C and run to 130°C. Liquid nitrogen in a Dewar which surrounds the furnace was used as a coolant for low temperature runs. The heating rate was 5°C min^{-1} with a usual Y-axis scale of 0.08 mV in.^{-1}. A complete run consists of heating to 130°C and then cooling at 5°C min^{-1} to below the glass transition temperature followed by a second heat to 130°C.

DEFINITIONS AND CALCULATIONS

A polyethylene specimen, illustrated in Fig. 1, is formed by being drawn parallel to the X-axis while being constrained in the Y direction. The letters a, b, and c, refer to the distribution of crystal axes around XYZ. Single crystal linear high density polyethylene, in an oriented form, has been shown to have three different linear thermal expansion rates depending on the direction of the crystalline axis[5].

Considering Fig. 1 as an example, the following definitions hold for the general case of an anisotropically expanding solid. The linear temperature coefficients are given by equations of the form

$$\alpha_{XT} = \frac{1}{L_{XT}} \frac{\delta L_{XT}}{\delta T} \tag{1}$$

In this equation α_{XT} is the linear expansion coefficient in the X direction of the polymer. L_{XT} is the length of the polymer at a given temperature, T, for a given direction. ∂L_{XT} is the partial derivative of the length for a given direction at a given

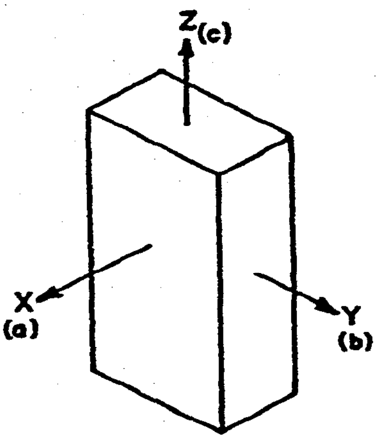

Fig. 1. Coordinates of a polyethylene specimen showing direction of preferred alignment of crystal axes.

temperature and ∂T is the partial derivative of the temperature. Similar expressions are used for α_{YT} and α_{ZT}.

The linear coefficients of expansion can readily be determined from straight line portions of the thermogram where the thermal expansion is linear with respect to temperature. For portions of the thermogram which are curves, an equation must be developed to fit the curve. A computer program to fit a polynomial to a curve was used.

The more commonly measured quantities are thermal expansions averaged over some selected temperature range. These are referred to as linear thermal strain or linear expansivity. This paper will refer to expansivity rather than strain.

Linear expansivity, E_X, for an anisotropic solid can be defined by eqn (2):

$$E_X = \frac{L_{TX} - L_{OX}}{L_{OX}} \tag{2}$$

where E_X, is the linear expansion in the X direction. L_{TX}, is the length at a temperature T cut from the X direction of the polymer. L_{OX}, is the length at a temperature of 0°C cut from an X direction of the polymer.

RESULTS AND DISCUSSION

Table 1 lists the samples and their properties. Values in the first column of Table 2 are the change in expansion from 40–130°C divided by the sample length at room temperature. The second column is the same quantity listed for a second heating. A plus sign indicates expansion, and minus sign shows contraction. On the first heating, samples 1 and 2 expanded. The crosslinked polyethylenes contracted on first heating. All samples expanded on second heating. The results indicate that the samples which are along the conductor are under tension, which one can assume occurs in the fabrication process. Samples designated 3-R and 4-R were prepared

TABLE 1

SAMPLE IDENTIFICATION

Sample	
1	A 15 kV cable with Neoprene jacket made by Manufacturer A insulated with an ethylene–propylene copolymer filled with mineral filler and carbon black.
2	A 15 kV cable insulated with an ethylene–propylene copolymer filled with mineral filler and carbon black made by Manufacturer B.
3	A 15 kV cable made by Manufacturer A insulated with a mineral filled cross-linked polyethylene.
4	A 15 kV cable made by Manufacturer C insulated with unfilled crosslinked polyethylene.

with their long axis in a radial direction perpendicular to the conductor. Both the initial and second heating expanded in contrast to the contraction exhibited by the longitudinal samples on first heating. The magnitude of the change on first and second heating is significantly greater for the radial samples than for the longitudinal samples. This would be consistent with the crosslinked polyethylene being under compression in the radial direction.

The repeatability improves on the second heating. It is possible that the somewhat larger variation in results on intial heating is real and a function of the location at which a sample was taken. A statistical evaluation of the TMA based on replicate runs on the initial polyethylene before crosslinking showed an average reproducibility of ±2.5%.

Table 3 gives values for linear expansion coefficients at 125°C for ethylene–propylene rubbers and at 125°C and 60°C for crosslinked polyethylenes. These values are average values based on the multiple measurements of Table 2.

The temperatures 60 and 125°C were chosen to be far enough from the melting transition in polyethylene as to be unaffected by it. The ethylene–propylene rubbers did not have a crystalline melting.

The EP rubbers are both under tension during the first heating relative to the second heating. The longitudinal crosslinked polyethylenes are under tension in both the solid and rubber states on first heating relative to second heating. The radially cut crosslinked polyethylenes are under compression on first heating at 60°C but only sample 4-R shows this behavior into the melt.

The glass transition of a well-behaved polymer is easily determined by TMA. The TMA trace shows a definite break between two straight line portions of the curve. The straight line portions are extrapolated and the intersection is the glass transition temperature. The crosslinked polyethylenes are not well behaved in this sense and their T_g was not determined. Samples 1 and 2 are well behaved and their T_g value of -51.7 ± 1.6°C was the same within 95% confidence limits.

TABLE 2[a]

LINEAR EXPANSIVITIES FROM TMA

+ = Expansion; − = contraction.

Sample	*ΔL (%) 1st heat 40–130°C*	*ΔL (%) 2nd heat 40–130°C*
1	+1.05	+1.30
1	+0.81	+1.31
1	+0.71	+1.26
1	+0.97	+1.53
1	+1.11	+1.43
1	+0.86	+1.35
2	+0.66	+1.20
2	+0.22	+1.39
2	+0.50	+1.48
3	−0.49	+2.98
3	−0.55	+2.82
4	−1.99	+4.41
4	−1.83	+4.28
4	−1.17	+4.05
4	−1.49	+3.97
3-R	+8.20	+5.45
4-R	+13.04	+5.08

[a] It is emphasized that these values represent the insulation specimens free of the mechanical constraints of the completed cable; whose design, processing, and assembly play a major role in determining expansion behavior of the end article.

TABLE 3

AVERAGE LINEAR EXPANSION COEFFICIENTS

See also footnote to Table 2.

Sample	*α 60°C ($\times 10^4$)[a] 1st heat*	*α 60°C ($\times 10^4$) 2nd heat*	*α 125°C ($\times 10^4$) 1st heat*	*α 125°C ($\times 10^4$) 2nd heat*
1			1.21	1.47
2			0.97	1.33
3	0.88	2.83	1.49	1.63
4	2.71	4.03	2.04	2.65
3-R	6.98	4.10	2.74	2.73
4-R	8.42	3.94	4.59	3.29

[a] The coefficient of linear expansion of the first sample, first heat at 125°C is $1.21 \cdot 10^{-4}$/°C.

The melting transition is also a break between straight line portions of the trace. This is especially dramatic for crosslinked polyethylene on first heating as shown by the TMA trace of sample 4 in Fig. 2. Table 4 lists the average crystalline melting points on first heating defined as the temperature of the mid point of the expansion or the contraction and the percent charge in length during the transition.

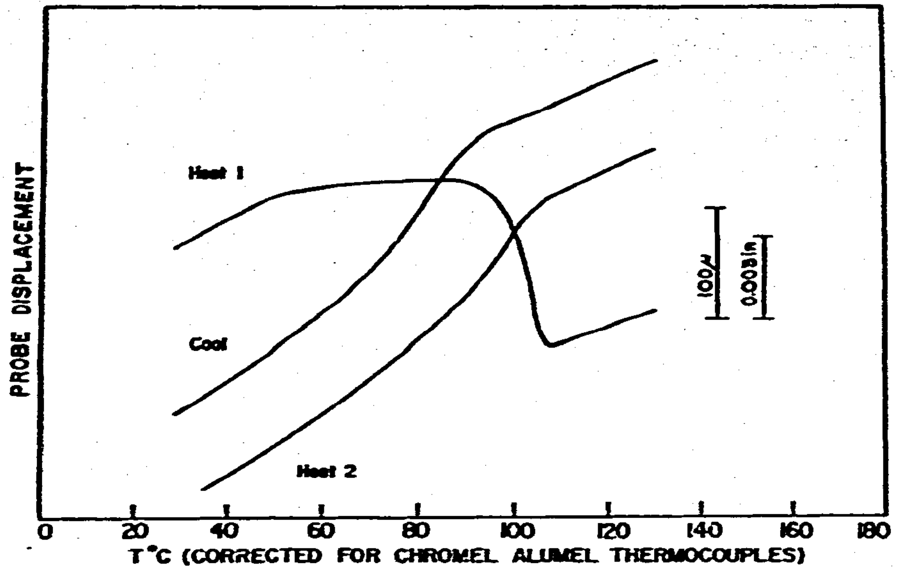

Fig. 2. Sample 4-OL, heated, cooled, and reheated at 5 °C min^{-1} showing a contraction near the transition temperature on the first heating.

TABLE 4

TRANSITION TEMPERATURES FROM TMA

+ = Expansion; − = contraction.

Sample	*Crystalline melting (°C)*	*ΔL (T) during transition*
3	96.9	−1.55
4	96.7	−2.80
3-R	95.0	+4.17
4-R	97.3	+6.98

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