

DETECTION OF THERMAL STRESS IN INSULATORS BY THERMOMECHANICAL ANALYSIS*^{***}

JOSEPH L. HABERFELD^{***}, JULIAN F. JOHNSON, EDWARD M. BARRALL II[§]
AND RICHARD C. GASKILL

*Institute of Materials Science and Department of Chemistry, University of Connecticut,
Storrs, Conn. 06268 (U. S. A.)*

ABSTRACT

The expansion properties of samples of filled and unfilled, crosslinked low density polyethylene and ethylene-propylene insulation material have been studied by thermomechanical analysis. Both axial and radial expansion coefficients of the preformed insulation were evaluated. Release of the frozen in strains in the axial direction was noted. Reheating directly after cooling of a sample did not indicate rapid recovery of frozen in strains. Axial strains were found to be translated to the radial direction as would be expected. However, in crosslinked material the return of axial stress was noted in as little as a week after heating. Holding the sample at elevated temperatures (below the melting or glass point) was found to accelerate the rate of stress build up. It is postulated that this effect may be due to interaction between crosslinks and crystallizing regions.

INTRODUCTION

Thermomechanical analysis, TMA, is a rapid method for the determination of the change in length of a material as a function of temperature. The results can be obtained with little expended man power and have good precision¹. The use of thermomechanical analysis and a description of the apparatus used is given in a previous article in this series².

There appears to be little reported data on the thermal expansion of crosslinked polyethylene used as wire and cable insulation. Williams et al.³ have discussed the usefulness of such data in joint design and Blodgett et al.⁴ have also presented data on both filled and unfilled crosslinked polyethylene.

EXPERIMENTAL

As discussed in a previous paper² the expansions were determined using a DuPont 941 thermomechanical analyzer. Table I lists the samples and their properties.

*Presented at the 6th North American Thermal Analysis Society Conference, Princeton, N. J., June 20-23, 1976.

**Part II of a series of *Characterization of Polymeric Dielectric Insulation*.

***Present address: Uniroyal, Oxford Research Center RG-20, Middlebury, Conn. 06749, U. S. A.

§On leave from IBM Research Laboratories, San José, Calif.

TABLE 1
SAMPLE IDENTIFICATION

<i>Sample</i>	
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.

The specimens tested will be identified by the sample number followed either by an "O" or an "A" which means as received from the manufacturer, or after air oven aging of 500 h at 130°C, respectively. This code letter will then be followed by either an "L" or an "R" to signify if the specimen was cut parallel to the conductor or radial to the conductor, respectively.

Specimens were cut with flat, parallel ends which were then polished with a fine grit to make them smooth. Typical sample lengths parallel to the conductor were between 0.5 and 1.0 cm. Sample lengths radial to the conductor were necessarily less than 0.5 cm. The length of the specimen was determined using a micrometer.

The thermomechanical analyzer was operated in the expansion mode using a 0.100 in. diameter flat end probe. The weight tray for penetration was removed from the instrument to minimize loading and a bell jar placed over the probe to protect against drafts. The DuPont 941 TMA module was placed on a vibration damping table to eliminate external vibrations.

RESULTS AND DISCUSSION

The graphical output of the thermomechanical analyzer is shown in Figs. 1, 2, and 3. In Fig. 1 the specimen is sample 4, the unfilled crosslinked polyethylene, as received from the manufacturer and cut in the longitudinal direction along the conductor. On the initial heating at 5°C min⁻¹ there is a major contraction around the transition temperature of low density crosslinked polyethylene. The specimen is then cooled at 5°C min⁻¹ back to room temperature. The run is completed by a second heating of the sample at 5°C min⁻¹. The second heating takes place about one hour after the first heating. The second heating shows no marked contraction near the melting temperature but rather a change to a new linear expansion coefficient at temperatures above the transition.

Figures 2 and 3 are traces from experimental runs at the same heating rate and y-axis sensitivity. Figure 2 shows the heating, cooling, and reheating of sample 4 which has been thermally stressed and cut parallel to the conductor. Figure 3 shows

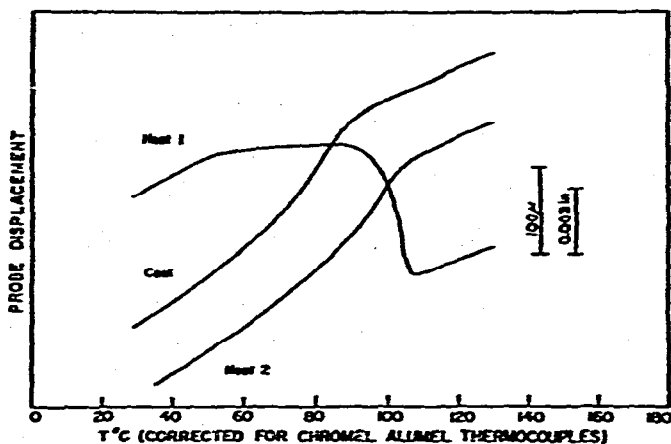


Fig. 1. Sample 4-OL, heated, cooled, and reheated at $5^{\circ}\text{C min}^{-1}$ showing a contraction near the transition temperature on the first heating.

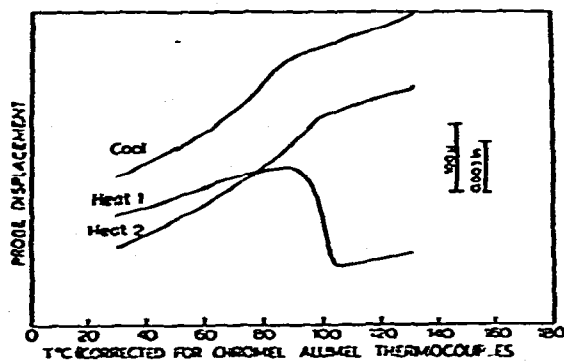


Fig. 2. Sample 4-AL, heated, cooled, and reheated at $5^{\circ}\text{C min}^{-1}$ showing a contraction near the transition temperature on the first heating.

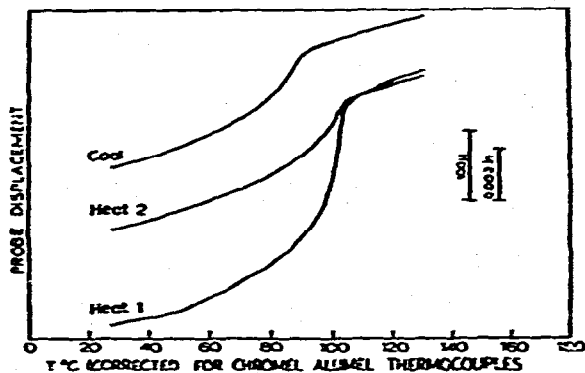


Fig. 3. Sample 4-AR, heated, cooled, and reheated at $5^{\circ}\text{C min}^{-1}$ showing an expansion near the transition on temperature first heating.

the heating, cooling, and reheating of sample 4 which has been thermally stressed and cut radial to the conductor. In this case the first heating shows a major expansion around the transition temperature. On reheating this expansion does not appear.

Data for the linear expansion coefficient, which is the change in length at a given temperature, are listed in Table 2. The linear expansion coefficients are listed at 60°C for both the first and second heating and at 125°C for the first and second heating for each sample. Samples 1 and 2 which are ethylene-propylene rubbers are almost completely amorphous and, therefore, have no crystalline melting transition. Thus, only the expansion coefficient at 125°C is reported. The values for specimens radial to the conductor in samples 3 and 4 were combined into single populations

TABLE 2
AVERAGE LINEAR EXPANSION COEFFICIENTS

Sample	α 60°C ($\times 10^{-4}$)		α 125°C ($\times 10^{-4}$) ^a	
	1st heat	2nd heat	1st heat	2nd heat
1-OL			1.21	1.47
1-AL			1.49	1.55
2-OL			0.97	1.33
2-AL			1.42	1.41
3-OL	0.88	2.83	1.49	1.63
3-AL	2.16	3.03	1.50	1.66
3R(ALL)	7.06	4.15	3.19	3.04
4-OL	2.71	4.03	2.04	2.65
4-AL	2.84	4.11	1.72	2.50
4R(ALL)	6.44	3.82	3.74	3.15

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

TABLE 3
AVERAGE TRANSITION TEMPERATURES FROM TMA

÷ = Expansion; - = contraction.

Sample I.D.	T_g (°C)		Crystalline melting (°C)	ΔL (%) During transition
	1st heat	2nd heat		
1-OL	-54.3	-52.9		
1-AL	-47.1	-51.6		
2-OL	-46.5	-50.5		
2-AL	-50.9	-53.1		
3-OL			96.9	-1.55
3-AI			97.8	-0.22
4-OL			93.8	-2.20
4-AL			99.0	-2.11
3-OR			95.0	+4.17
3-AR			96.5	+2.80
4-OR			97.3	+6.98
4-AR			99.5	+3.96

after differences in mean values derived from individual specimens were tested for significance by the "t" test and shown not to differ significantly.

Table 3 lists the average transition temperature as determined by TMA. In the case of sample 1 and 2 the glass transition is listed for both first and second heating. Additionally, the percentage change in length during the transition is listed. The glass transition temperature for original and thermally treated specimens of 1 and 2 cannot be distinguished on first and second heating even with the moderate scatter of the values. The value of T_g for these samples is -51.7°C . The crystalline melting temperatures agree well with other thermal methods used to determine this value.

The change in length during melting shows that 3-AL contracts less than 3-OL which contracts less than 4-AL which contracts less than 4-OL. The radially cut specimens all expand during the transition. It appears that axial strain is being released to the radial direction. Heat treatment has eliminated some of the strain but not all.

The TMA testing of the specimens was done approximately three months after they were oven aged. Much of the annealing effect expected from the thermal treatment seems to have been lost in the time period at room temperature. Certainly the reheating during the TMA cycle seems to anneal out a major portion of compressive or tensile stresses. The time for return of stress in crosslinked cable insulation has been noted to be as short as one week⁵.

It appears that this is the first reported anisotropy in crosslinked cable insulation. The insulation is under tension along the conductor and under compression radial to the wire. It has been shown that uncrosslinked polyethylene has anisotropies including negative thermal expansions for such species as single crystals and extended chain polyethylene⁶⁻¹¹. Much of this work dealt with crystals of polyethylene which showed very small contractions along the chain axis as determined by x-ray diffraction.

Further research will be required to fully elucidate the causes of the anisotropy for cross-linked cable insulation. However, the similarity of this behavior with the well-known heat working of alloys cannot be passed without comment. It is possible that a combination of slow elastic recovery and recrystallization may control the rate and size of the strain recovery. The time range is certainly well within acceptable limits.

REFERENCES

- 1 R. C. Gaskill and E. M. Barrall, *Thermochim. Acta*, 12 (1975) 102.
- 2 J. L. Haberfeld, J. F. Johnson and R. C. Gaskill, *Thermochim. Acta*, 18 (1977) in press.
- 3 J. L. Williams, A. Zanona and A. R. Lee, *IEEE Trans. Power Appar. Syst.*, PAS-88, 1969, p. 157.
- 4 R. B. Blodgett, R. G. Fisher and F. McAvoy, *IEEE Trans. Power Appar. Syst.*, PAS-88, 1969, p. 164.
- 5 J. L. Haberfeld and J. A. Reffner, *Thermochim. Acta*, 15 (1976) 307.
- 6 Y. Kobayashi and A. Keller, *Polymer*, 11 (1970) 114.
- 7 E. A. Cole and D. T. Holmes, *J. Polym. Sci.*, 46 (1960) 245.
- 8 G. T. Davis, R. K. Eby and J. P. Colson, *J. Appl. Phys.*, 41 (1970) 4316.
- 9 B. H. Baughman and E. A. Turi, *J. Polym. Sci. A-2*, 11 (1973) 2453.
- 10 B. H. Kim and R. DeBatist, *J. Polym. Sci.*, B11 (1973) 121.
- 11 R. S. Porter, N. E. Weeks, N. J. Capiati and R. J. Krzewki, *J. Therm. Anal.*, 8 (1975) 547.