

Dielectric Properties of Halar, an Alternating Copolymer of Ethylene and Chlorotrifluoroethylene

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Synopsis

Dielectric properties of Halar, a predominantly alternating 1:1 copolymer of ethylene (E) and chlorotrifluoroethylene (CTFE), have been obtained as a function of temperature (-100 to $+175^{\circ}\text{C}$), frequency (10^2 – 10^6 Hz), and thermal history. The dielectric loss index (ϵ''), related to heat dissipation in electrical applications, shows no major change between 25 and 175°C . However, a significant increase in ϵ'' between $+25^{\circ}\text{C}$ and -100°C is not considered detrimental for the applications. Activation energies (ΔE) for the three major relaxations (α -, β -, and γ -) in both mechanical and dielectric experiments are similar, thus suggesting a similar phase origin of the molecular relaxations in the two techniques. In dielectric analysis, the lowest temperature γ -relaxation is the strongest while it is the weakest in mechanical technique. It is proposed that, in dielectric experiments, only the CTFE groups participate and due to restricted mobility at low temperatures (i.e., γ -relaxation), the dissipation factor or relaxation strength is maximum.

INTRODUCTION

Halar is the trademark for Ausimont-USA's copolymer products made from ethylene (E) and chlorotrifluoroethylene (CTFE). At present the major application of standard Halar (50E:50CTFE, alternating copolymer) is in the electrical cable-coating industry where this material could be exposed to a wide range of temperatures. Accordingly, we have studied thermal/mechanical and molecular relaxation behavior of Halar over a wide temperature range.¹⁻⁵ Molecular relaxations occur in polymers at characteristic temperatures which dictate the product applicability. Recently we published a study of the molecular motions in Halar using dynamic mechanical techniques.³ These molecular relaxations occurring in Halar will affect the dielectric properties at certain characteristic temperatures. The dissipation factor, which is temperature-dependent and dictated by relaxation phenomena, is directly related to the heat buildup in an insulating material under an electrical field. As a result, we have undertaken a study to evaluate the dielectric properties of Halar over a wide temperature range and also to relate the molecular relaxations studied dielectrically to those previously studied by thermal/mechanical techniques.¹⁻⁵

EXPERIMENTAL

Material and Sample Preparation. Halar 500 is a commercially available (Ausimont-USA), 1:1 copolymer of E/CTFE with about 85% alternating (crystallizing) units; the remaining units consist of noncrystallizable short blocks of E and CTFE.⁵ All the experimental work was carried out on compression molded films of 5–10 mil thickness. A variation in thermal history was achieved by quick-quenching the molded films in ice/water, slow cooling of the mold, or by vacuum annealing (175°C)/17 h) of the quick-quenched films.

Dynamic Dielectric Analysis (DDA). A Polymer Laboratories DETA unit attached to a Hewlett-Packard 216 computer was used in obtaining the dielectric data. A film of 2.5 cm diameter, sputter coated with Au/Pd, was sandwiched between the electrodes under an electrical field oscillating (amplitude = 1 V) at a constant frequency in the 1–100 kHz range. The analysis was carried out from –100 to +175°C at a heating rate of 3°C/min in a dry helium atmosphere.

RESULTS AND DISCUSSION

Dielectric Analysis. Dielectric data on a particular material depend upon the test frequency as well as temperature. For a polymer, thermal history which controls its crystalline content, is another variable. We have attempted to study the effect of these variables, i.e., frequency, temperature, and thermal history, on the dielectric behavior of Halar. For a quick-quenched film and a frequency of 1 kHz, the temperature dependence of the dielectric constant or permittivity (ϵ'), dielectric loss or loss index (ϵ''), and dissipation factor ($\tan \delta = \epsilon''/\epsilon'$) are shown in Figures 1–3 and Table I.

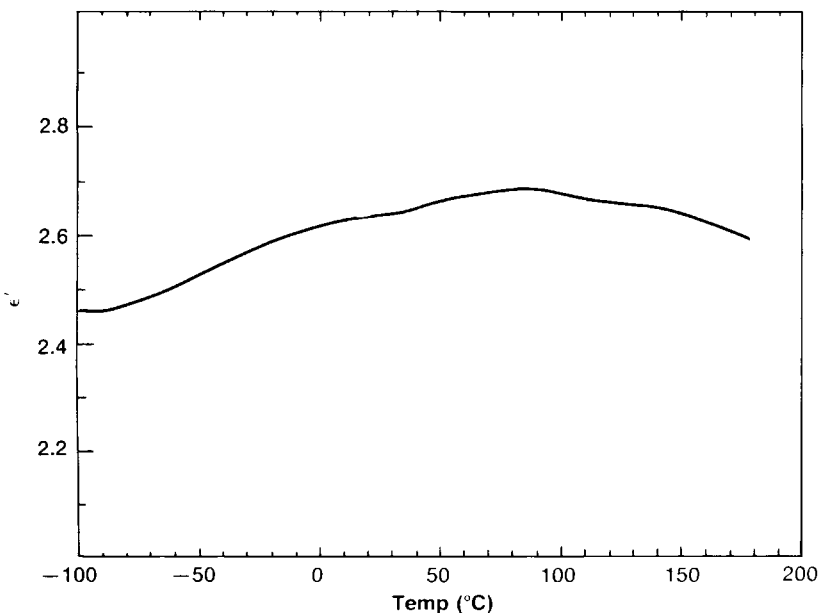


Fig. 1. Dielectric constant (ϵ') vs. temperature for a quick-quenched film of Halar at 1 kHz frequency.

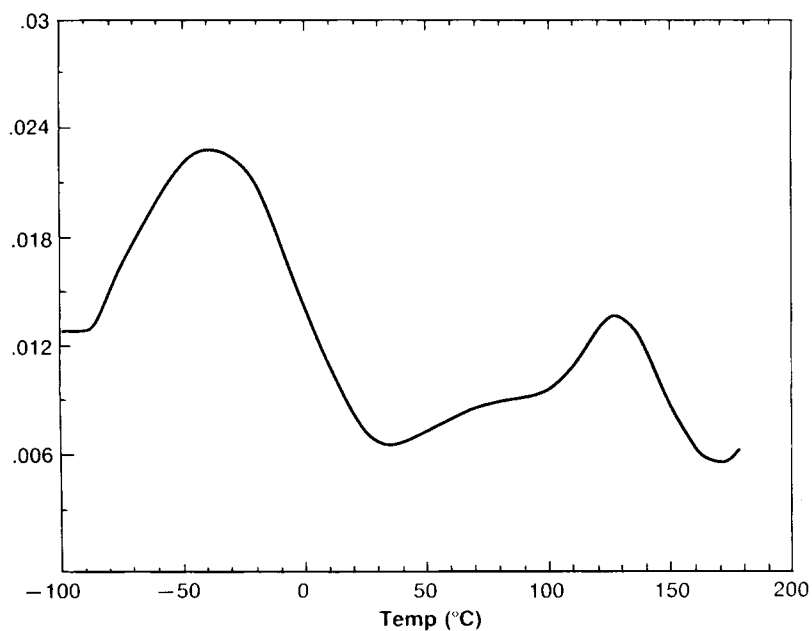


Fig. 2. Dielectric loss (ϵ'') vs. temperature for a quick-quenched film of Halar at 1 kHz frequency.

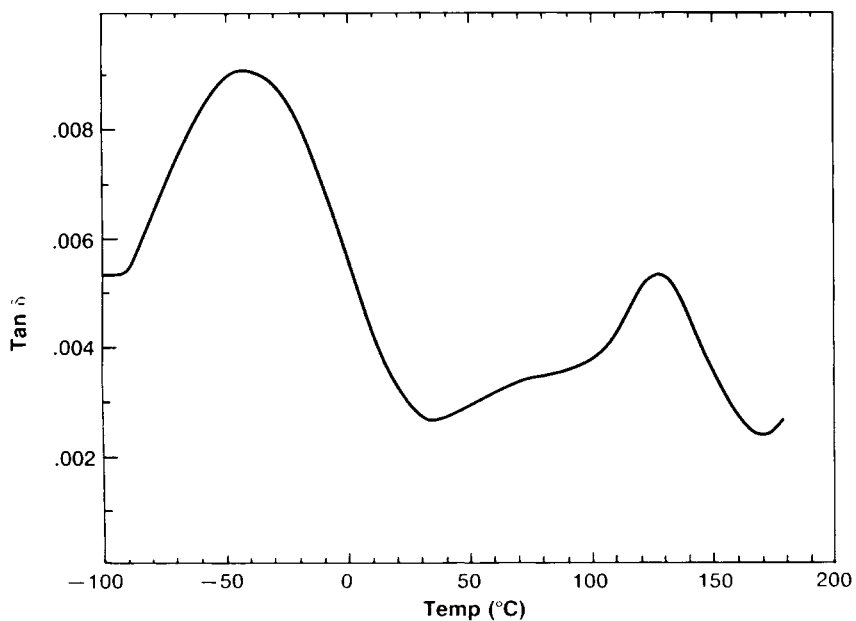


Fig. 3. Dissipation factor ($\tan \delta$) vs. temperature for a quick-quenched film of Halar at 1 kHz frequency.

TABLE I
Dielectric Properties of Halar (Quick Quenched)
at Various Temperatures

Approximate temperature (°C)	Dielectric constant ϵ'		Dielectric loss $\epsilon'' \times 10^2$		Dissipation factor $\tan \delta$	
- 50	2.54		2.20		0.0090	
	2.45		2.10		0.0089	
	2.48	2.51	2.10	2.16	0.0086	0.0088
	2.56		2.40		0.0094	
	2.54		2.00		0.0080	
0	2.62		1.30		0.0051	
	2.54		1.50		0.0062	
	2.58	2.52	1.50	1.24	0.0059	0.0056
	2.66		1.80		0.0069	
	2.63		1.00		0.0041	
25(RT)	2.63		0.70		0.0028	
	2.55		0.80		0.0035	
	2.60	2.62	0.80	0.76	0.0033	0.0032
	2.69		1.00		0.0040	
	2.64		0.50		0.0022	
50	2.67		0.80		0.0030	
	2.58		0.90		0.0035	
	2.62	2.65	0.70	0.76	0.0030	0.0031
	2.71		0.90		0.0036	
	2.66		0.50		0.0022	
100	2.68		1.00		0.0038	
	2.60		1.10		0.0043	
	2.62	2.66	0.90	0.98	0.0038	0.0039
	2.72		1.20		0.0046	
	2.66		0.70		0.0030	
150	2.64		0.80		0.0033	
	2.57		1.00		0.0041	
	2.57	2.61	0.90	0.88	0.0037	0.0036
	2.67		1.10		0.0043	
	2.61		0.60		0.0026	

The importance of studying the temperature dependence of dielectric properties is apparent when we consider that the power loss (P) in an insulator in form of heat is expressed as⁶

$$P = 0.555fv^2\epsilon'' \times 10^{-6}$$

where P = heat generated (W/cc), f = frequency (MHz), v = applied voltage, and ϵ'' = dielectric loss. Thus, under otherwise similar conditions, the heat buildup (P) in electrical cable coatings made of Halar, will vary with the use temperature in accordance with the ϵ'' vs. temperature curve (Fig. 2). For comparative purposes we have normalized the changes in ϵ' , ϵ'' , and $\tan \delta$ with reference to those at room temperature (Figs. 4-6). Using this normalization procedure, the effect of thermal history is presented in Figures 7-9. As the temperature is lowered from RT to -100°C , the ϵ' decreases but the decrease is least for the annealed, i.e., more crystalline sample (Fig. 7). Increasing the

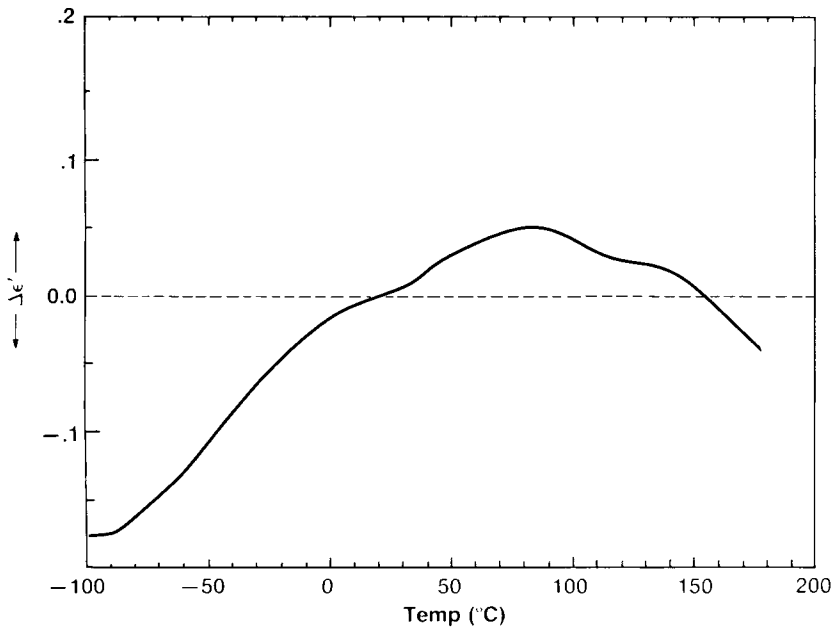


Fig. 4. Change in dielectric constant ($\Delta\epsilon'$) vs. temperature relative to 25°C for a quick-quenched Halar film at 1 kHz frequency.

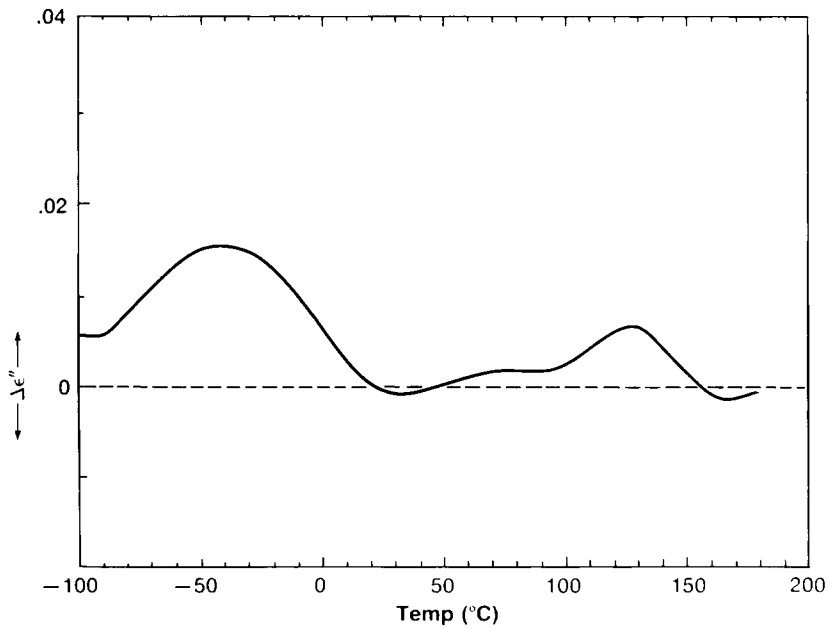


Fig. 5. Change in dielectric loss ($\Delta\epsilon''$) vs. temperature relative to 25°C for a quick-quenched Halar film at 1 kHz frequency.

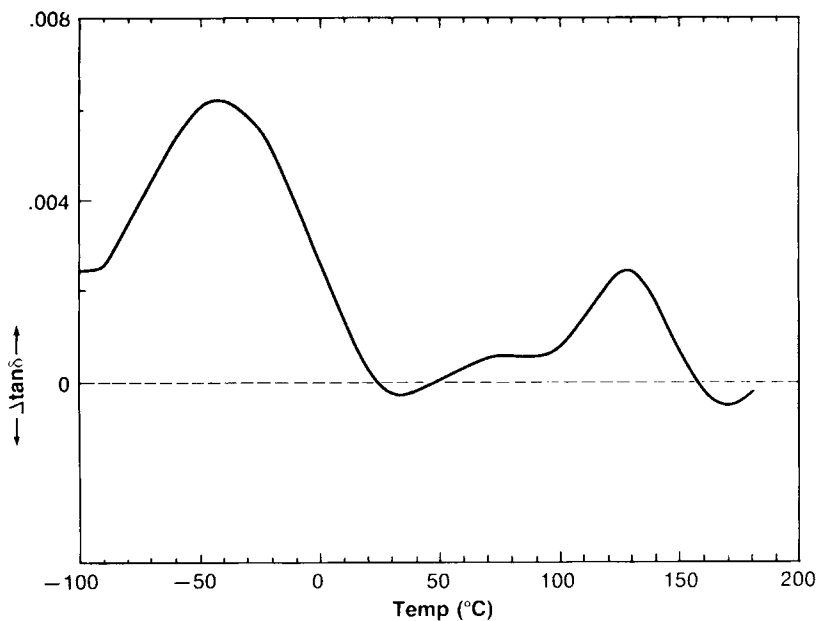


Fig. 6. Change in dissipation factor ($\Delta \tan \delta$) vs. temperature relative to 25°C for a quick-quenched Halar film at 1 kHz frequency.

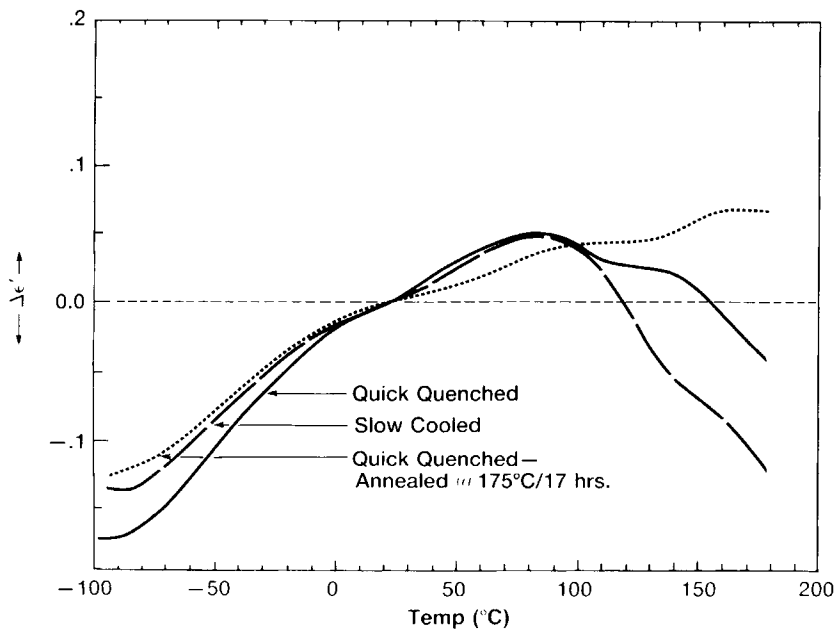


Fig. 7. Effect of thermal history on ϵ' vs. temperature for Halar.

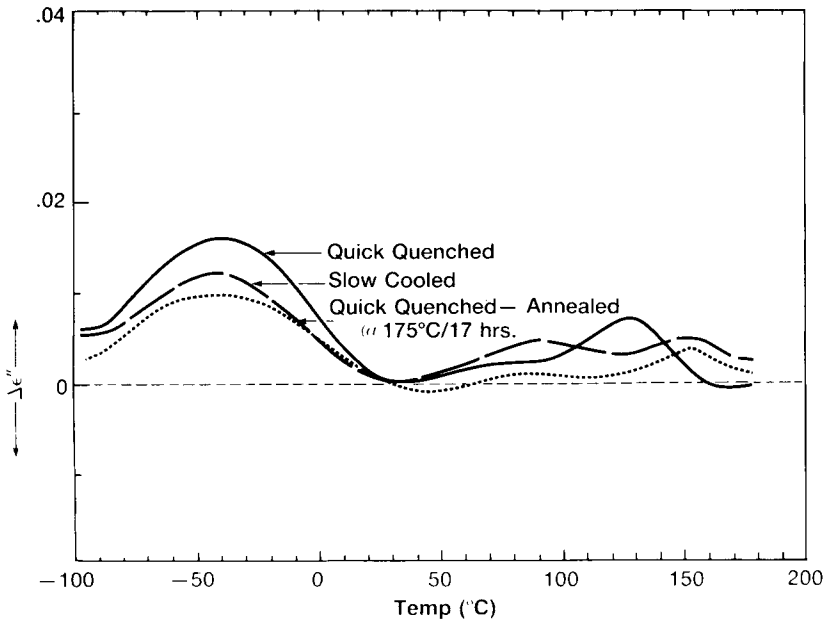


Fig. 8. Effect of thermal history on ϵ'' vs. temperature for Halar.

temperature from RT to $+100^{\circ}\text{C}$ increases the ϵ' and this increase is least for the annealed, i.e., more crystalline sample (Fig. 7). Above $+100^{\circ}\text{C}$ the ϵ' increases with temperature for the annealed sample while it decreases for the unannealed samples, partly due to crystallization (Fig. 7). The ϵ'' and $\tan \delta$ values also tend to be lower for the annealed sample (Figs. 8 and 9). Our previous study using thermal/mechanical techniques has more fully examined the effect of annealing on this material in terms of the structure.³

Under otherwise similar experimental conditions, the effect of increasing the frequency is to shift the relaxation peaks to higher temperatures (Fig. 10). The temperature shift of each relaxation with frequency will vary depending upon the activation energy associated with a particular relaxation (Fig. 11). In accordance with the time-temperature superposition principle, with increasing frequency (i.e., shorter time scale) at a constant temperature (e.g., RT) the dielectric properties are expected to move in the direction of the lower temperature. Thus, from Figures 4 and 6 one would expect that at RT the ϵ' and $\tan \delta$ of Halar should decrease and increase respectively as a consequence of increasing frequency. The actual data in Figure 12 confirm this. The temperature dependence of the relaxation time is so strong that the entire relaxation peak can be observed by changing the temperature rather than frequency. In other words, a single scan of ϵ' , ϵ'' , or $\tan \delta$ vs. temperature can instantaneously reveal the magnitude of changes in dielectric properties due to frequency variations.

Dielectric Molecular Relaxations. Similarity of activation energy (ΔE) for the mechanical and dielectric experiment (Fig. 11) suggests a similarity in molecular relaxation mechanisms. Thus, based on our previously published

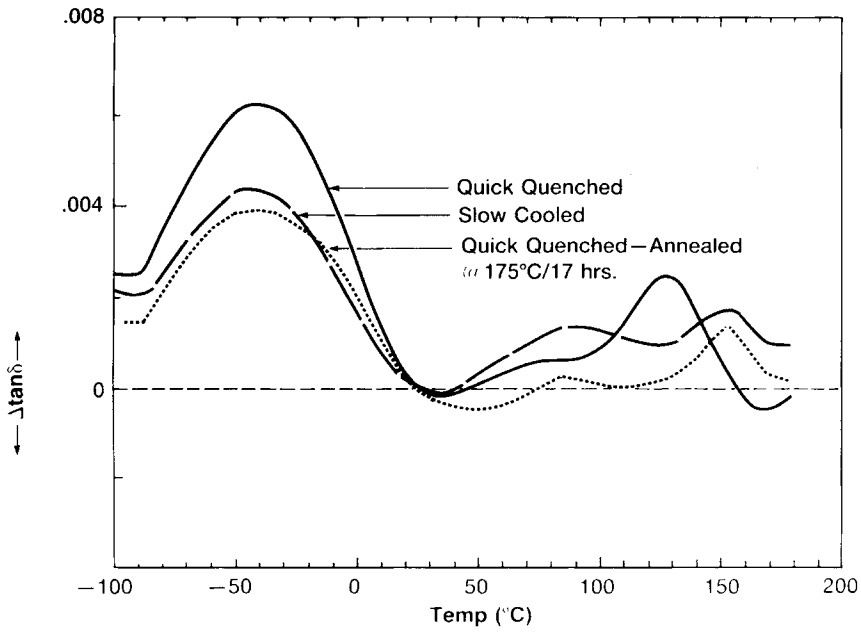


Fig. 9. Effect of thermal history on $\tan \delta$ vs. temperature for Halar.

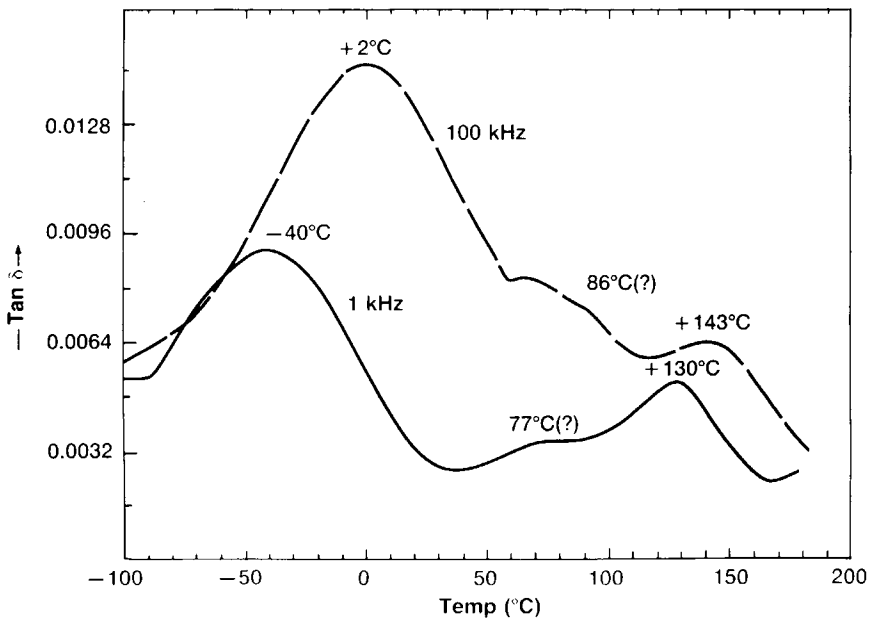


Fig. 10. Effect of frequency on the dielectric relaxations of Halar.

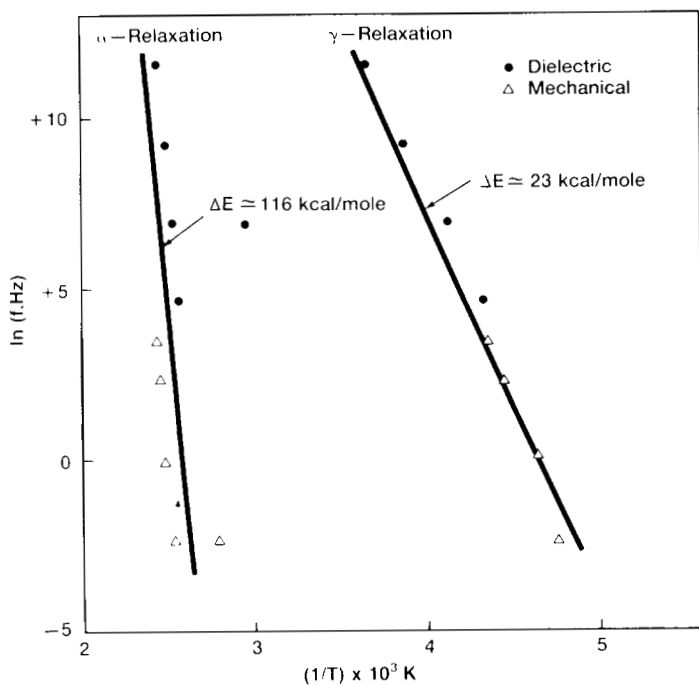


Fig. 11. Energies of activation for the α - and γ -relaxations in Halar based on dielectric and mechanical techniques.

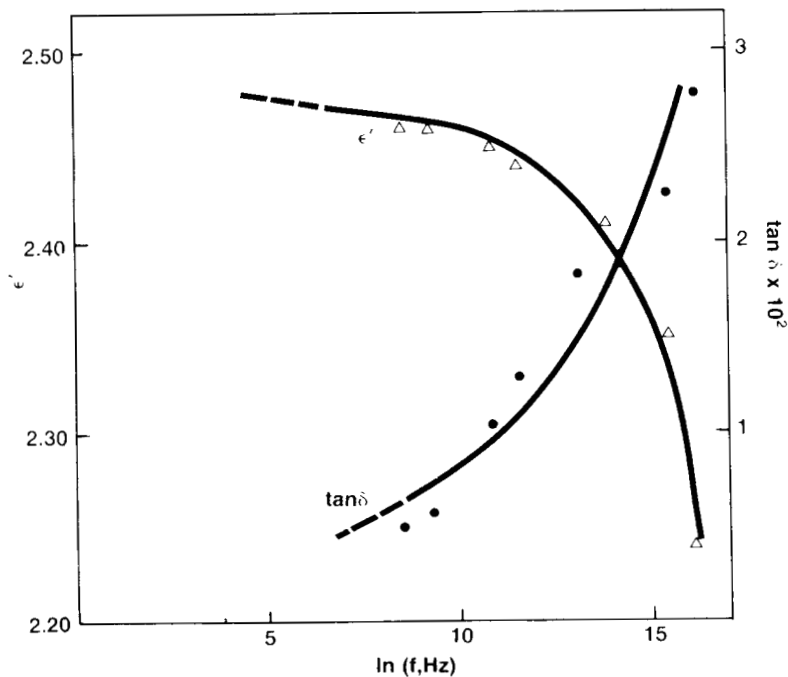


Fig. 12. Effect of frequency on the ϵ' and $\tan \delta$ of Halar at 25°C .

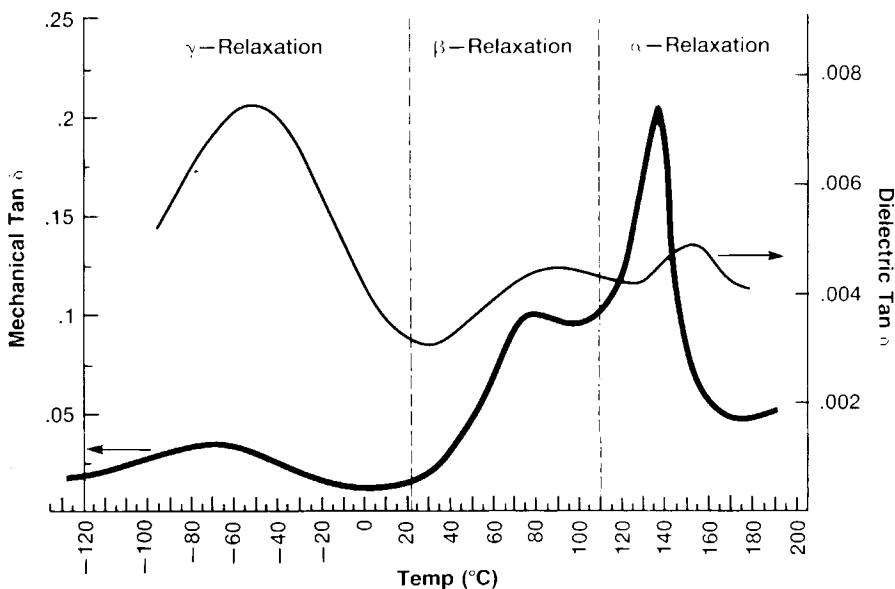


Fig. 13. Comparison of the dielectric (1 kHz) and mechanical (1 Hz) relaxation strengths of Halar.

study using thermal/mechanical techniques, α -, β -, and γ -relaxations originate from the interfacial amorphous phase, discrete amorphous phase, and the various short chain units, respectively.³ Interestingly, the relaxation strengths of mechanical and dielectric experiments are of reverse magnitude (Fig. 13). This can be explained on the basis of the principle involved in these techniques. In the mechanical experiment, it is assumed that all the molecules participate in the relaxation process. However, in the dielectric experiment, only the polar groups are active. Although our material is a 1:1 copolymer of E and CTFE, only the CTFE units are dielectrically active in all the three relaxations observed. In the temperature region of γ -relaxation, the CTFE units i.e., $[-(C(Cl)F-CF_2)-]_n$ groups would be the most dissipative due to restricted mobility. With an increase in temperature and thus molecular mobility, the dissipation of CTFE groups should be reduced. Interestingly, a similar trend in dielectric relaxation strengths is shown by the homopolymer of CTFE.^{7,8} This might explain the reduction in relaxation strengths in going from γ - to α - in dielectric experiments (Fig. 13).

The authors wish to thank G. Chomyn for her accurate and timely dielectric measurements.

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Received April 12, 1988

Accepted August, 8, 1988