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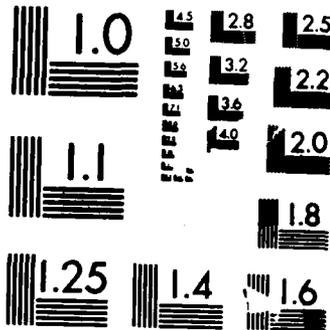
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DR, TSDC, DSC, TMA, and DMA Studies in Polymers
Complexed with Inorganic Salts

by

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<p>In the present note, the relationship between audio frequency dielectric relaxation (DR) and thermally stimulated depolarization current (TSDC) techniques is described. In addition, those methods are compared with differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA). The discussion will proceed using data taken on cast film samples of PAREL elastomer.</p>			
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DR, TSDC, DSC, TMA, AND DMA STUDIES IN POLYMERS COMPLEXED WITH
INORGANIC SALTS

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In the present note, the relationship between audio frequency dielectric relaxation (DR) and thermally stimulated depolarization current (TSDC) techniques is described. In addition, those methods are compared with differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA). The discussion will proceed using data taken on cast film samples of PAREL¹ elastomer.

1. Dielectric Relaxation

Audio frequency DR studies at various temperatures were taken over the frequency range 10 to 100,000 Hz. The equipment used to make the measurements is the latest in a long series of capacitance bridges developed by one of the authors (CGA). Results from early versions of the apparatus appeared in the literature as early as 1970.² The key element of the present system is a CGA-83 capacitance bridge which is fully automated for measurements over the range 10 to 100,000 Hz. This bridge is more sensitive and accurate than any commercially available bridge. Electrodes are either sputtered or evaporated onto the samples in two- or three-terminal configurations, and the sample holder can accommodate eight samples simultaneously. The sample holder is then bolted to the cold finger of a Precision Cryogenics CT-14 dewar. The temperature is controlled by a Lake Shore Cryotronics DRC-82C temperature controller using a silicon diode temperature sensor. The overall system is controlled by an Apple II+ microcomputer.

The results of a typical data run are shown in Fig. 1a, in this case for a sample of uncomplexed PAREL. Data are normally

taken isothermally at seventeen frequencies in approximately equal logarithmic intervals, where the capacitance, C, and the conductance divided by the frequency, G/ω are measured. Values of the real part of the complex dielectric constant, ε* = ε' - jε'', at 1000 Hz and room temperature are calculated from the usual expression for a perfect parallel plate capacitor:

$$\epsilon' = Cd/\epsilon_0 A \quad (1)$$

where A is the area of the plates, d is the sample thickness, and ε₀ is the permittivity of free space. Next, since thermal expansion coefficients were not measured, values of ε' at other temperatures and frequencies were calculated using the approximation that the relative shift in ε' is proportional to the relative shift in capacitance. Finally, values of ε'' are generated from:

$$\epsilon'' = \epsilon' G/\omega C \quad (2)$$

The results for PAREL elastomer using these procedures are shown in Figs. 1a and 1b. The strong alpha relaxation associated with the glass transition can be clearly seen. The 1000 Hz data have been shown previously.³ In fact in that paper, data at 1000 Hz are also shown for pressures up to 0.3 GPa (3kbar). The high pressure data allowed the shift in glass transition temperature with increase in pressure to be determined. Data are not usually analyzed in the variable temperature format although for some systems such techniques have been developed.⁴ It is more usual to analyze the data in terms of the frequency variation.⁵ This type of analysis shows that for PAREL the maximum of the loss peak, ω_p, varies with temperature according to the WLF⁶ or VTF⁷ equations:

$$\log_{10}(\omega_p) - 1.076 = 11.6(T-211)/(38.3+T-211) \quad (3)$$

$$\omega_p = 10^{12.68} \exp(-1023/(T-172.7)) \quad (4)$$

where T is in Kelvins and the WLF equation utilizes the "central" glass transition temperature of 211K.⁵ For the present purpose, these results are of interest as they relate to the TSDC as discussed in the next section.

2. Thermally Stimulated Depolarization Currents

The equipment used to carry out the TSDC studies has been described elsewhere.⁸ Briefly, the technique consists of placing a voltage across a sample, cooling it down and removing the voltage. The temperature is then increased and the current flowing through a large resistor connected across the sample is monitored. In the experiments discussed here, a linear heating rate is achieved using digital techniques. The results for a

typical TSDC run are shown in Fig. 1c. Two peaks are observed. The position of the higher temperature peak depends strongly on the polarization temperature and hence is attributed to space charge effects. This is to be expected as PAREL is relatively conductive, presumably due to ionic trace impurities. Further evidence of these impurities can be seen in the DR results, since the low frequency (10 Hz) values of ϵ'' rise rapidly at high temperatures. This reflects the electrical conductivity, σ , because:

$$\sigma = \epsilon_0 \epsilon'' \omega \quad (5)$$

In fact, related behavior is the motivation for studying PAREL, which is primarily poly(propylene oxide) (PPO), as it represents a prototype amorphous, ionic conductor or solid electrolyte. The authors have carried out several studies of PPO containing Li and Na salts^{3,9} and in one case have found a significant relationship between the DR and the ionic conductivity.⁵

The position of the lower temperature peak, at 206 K, is independent of the polarization temperature and corresponds to the α -relaxation. These results demonstrate that TSDC can be related to low frequency DR. Specifically, the position of a TSDC peak is about where a DR peak would be expected at low frequency. For the present case, the VTF or WLF equations predict that the 206 K DR peak would appear at a frequency of about 34 mHz. This is similar to the situation described for an ionic crystal.¹⁰

3. Thermal Analysis

The TSDC result is particularly important in the light of DSC, TMA and DMA studies, the data for which were obtained using Dupont 910, 943, and 982 cells which were controlled by Dupont 990 consoles which were interfaced with Apple II+ computers. Results for all four techniques are shown in Fig. 2. In each case, an event is seen in the vicinity of 206 K. This is not at all surprising since the heating rates in all four experiments are similar. In some experiments, the variety of thermal analysis techniques has proved invaluable. For example, in the presence of an extraneous thermal absorption in the DSC, perhaps due to water, the DMA or TMA will be usually be unaffected. Similarly, when the contribution to the DR signal from DC ionic conductivity masks the α -relaxation, in the case of ion containing materials for example, alternative techniques are essential to identify the glass transition temperature. These results, then, emphasize some of the relationships between low frequency DR and thermal analysis.

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Figure 1. Real (a) and imaginary (b) parts of the dielectric constant at five frequencies (features from left to right): 10 Hz-short dashed lines; 100 Hz-long dashed lines; 1000 Hz-solid lines; 10,000 Hz-dot dash (chain) lines; 100,000 Hz-dotted lines. Straight line segments connect the datum points. Curve (c) is a TSDC spectrum. A voltage of 200 V was applied to the sample for 15 min at a polarization temperature of 190K and the heating rate was 6 K/min.

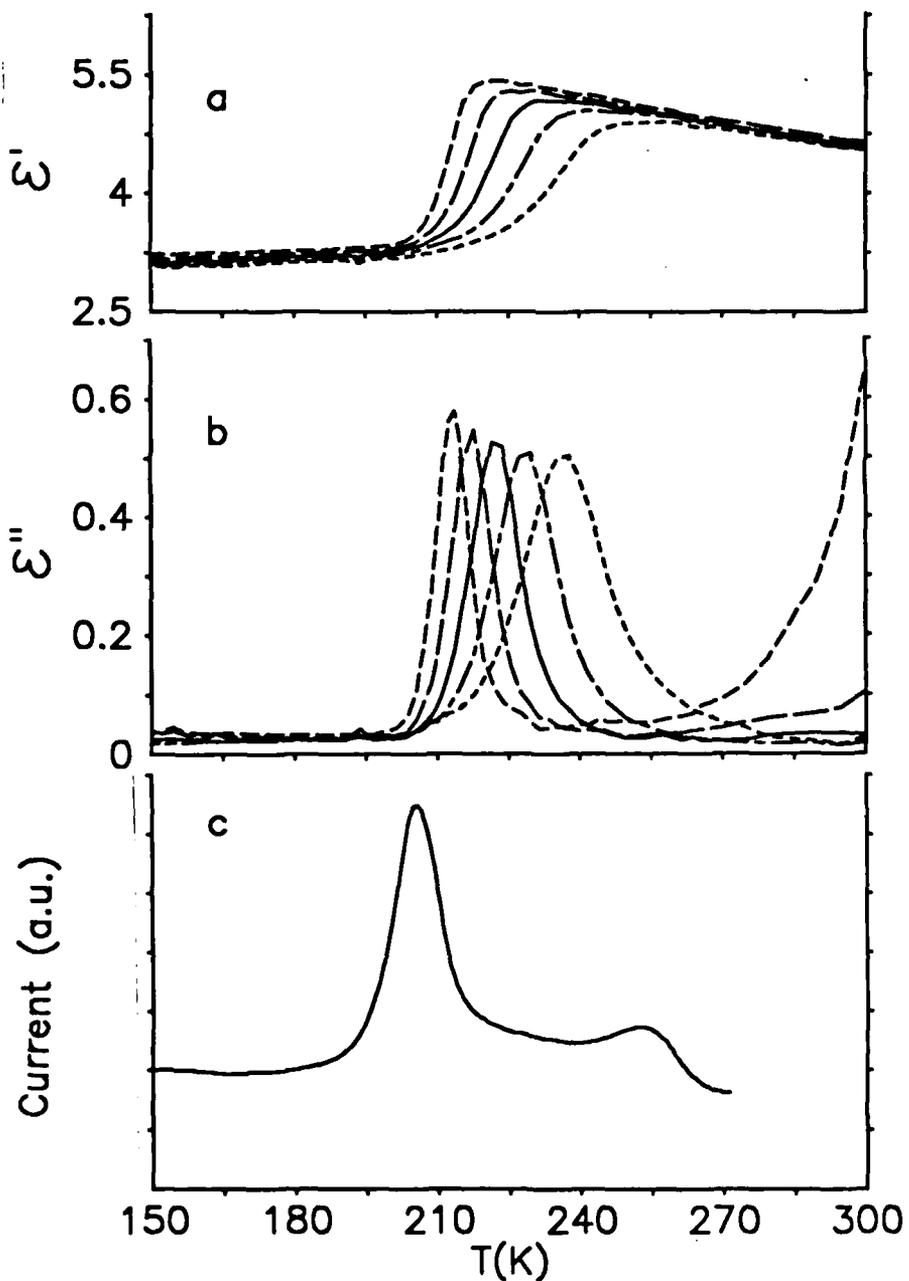
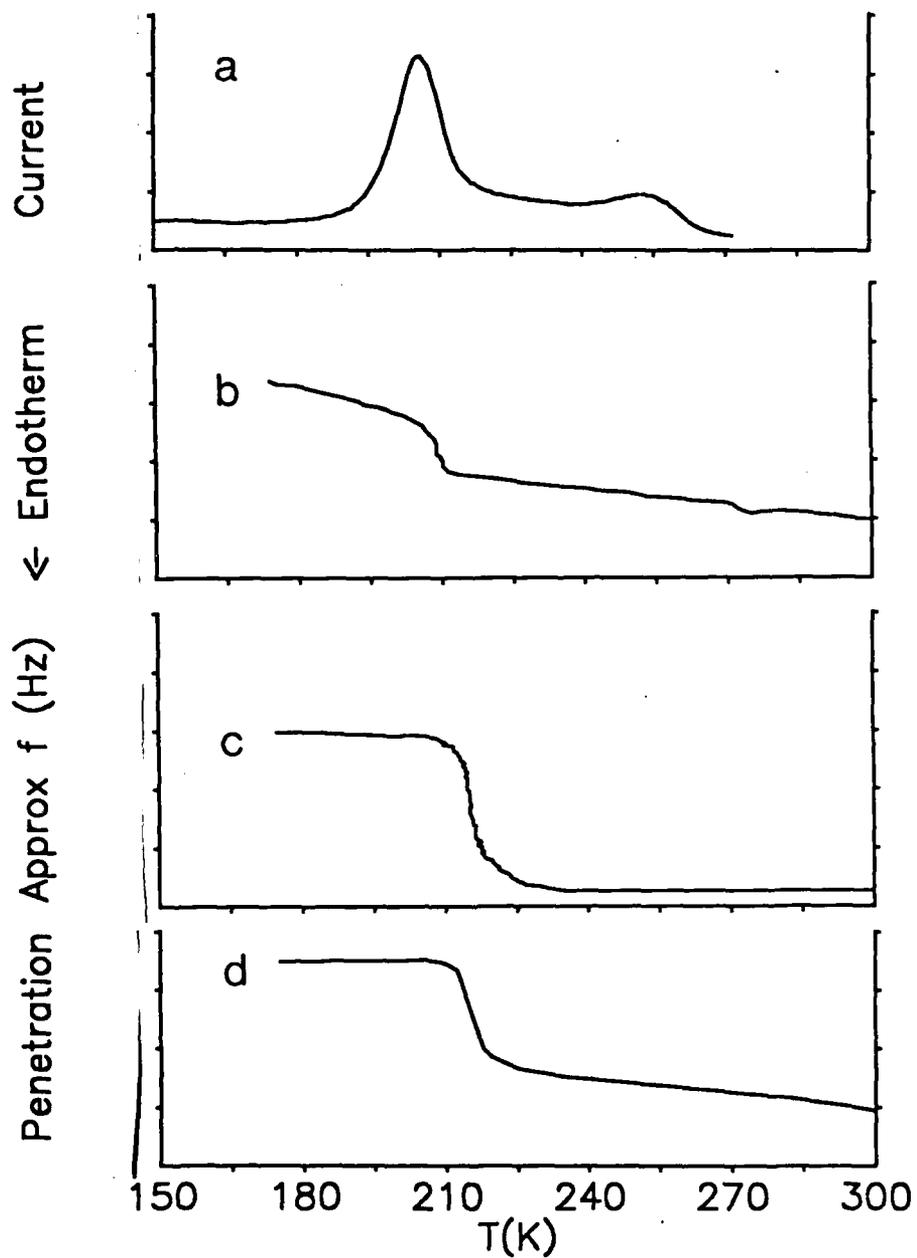


Figure 2. (a) TSDC spectrum from Fig. 1c. (b) DSC thermogram. The heating rate was 10 K/min. (c) DMA results. The heating rate was 5 K/min. (d) TMA penetration results. The heating rate was 5 K/min.



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