

# Characterization of Castor Oil Based Polyurethane Films Prepared with *N*-Methyl-2-pyrrolidinone as a Solvent

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**ABSTRACT:** Molecular mobility in castor oil based polyurethane was investigated with thermally stimulated depolarization current (TSDC) measurements and alternating-current (ac) dielectric relaxation spectroscopy. Three peaks could be observed in TSDC thermograms from 173 to 373 K. The relaxation located at 213 K could be attributed to the change in the molecular chain due to the interaction between the isocyanate and the solvent, and it was well

fitted with the Vogel–Fulcher–Tammann equation. The other two peaks were located at 274 and 365 K and could be attributed to interfacial polarization and space charge, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 746–749, 2005

**Key words:** glass transition; polyurethanes; dielectric properties

## INTRODUCTION

Polyurethane (PU), characterized by —NH—CO—O— groups, can be obtained as a thermoplastic, thermoset, or elastomer according to the chemical structure and functionality of the reagents used in the polymer formulation. PU is a typical copolymer composed of a relatively long and flexible soft segment and a highly polar hard segment. This PU consists of an ester of ricinoleic acid (castor oil) and a diisocyanate extended with a polyol.

Because of its flexibility, formability, and mechanical strength, PUs are often used in multicomponent polymeric systems, such as polymer matrices for piezo and pyroelectric composites<sup>1,2</sup> and interpenetrating polymer networks,<sup>3</sup> and because of its thermal stability, castor oil based PU has been successfully used for blending conductive polymers.<sup>4</sup> In this study, PU films were prepared via casting with *N*-methyl-2-pyrrolidinone (NMP) as a solvent, and the relaxation process was studied with thermally stimulated depolarization current (TSDC) and ac dielectric relaxation.

Dielectric relaxation spectroscopy and TSDC are very sensitive techniques and are very attractive for molecular mobility studies of polymeric materials. The use of NMP as a solvent is advantageous because it is a good solvent for polyaniline, which can be blended with PU.<sup>5,6</sup> Hence, it is interesting to fully comprehend the influence that PU prepared with this solvent has on the electrical behavior.

## EXPERIMENTAL

### Sample preparation

PU films 60  $\mu\text{m}$  thick were obtained via casting from the reaction between a 4,4'-diphenylmethane diisocyanate based prepolymer (F329) and a castor oil based polyol (21L) supplied by Grupo de Química Analítica e Tecnologia de Polímeros from Instituto de Química de São Carlos (São Carlos, Brazil). The prepolymer (10 g) and polyol (7 g) were mixed with NMP separately and then blended. The final solution was put on a glass slide and placed in an oven at 343 K with air circulation for 15 h for solvent evaporation.

### Characterization

#### Dielectric measurements

The ac dielectric measurements, in the frequency range of  $10^3$ – $10^6$  Hz, were carried out with an HP model 4192A impedance analyzer. For electrical contact, circular gold electrodes (1.0 cm in diameter) were

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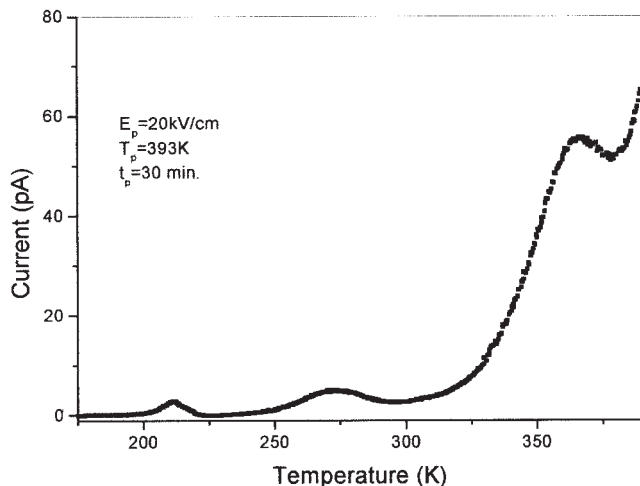


Figure 1 TSDC of PU (heating rate = 2 K/min).

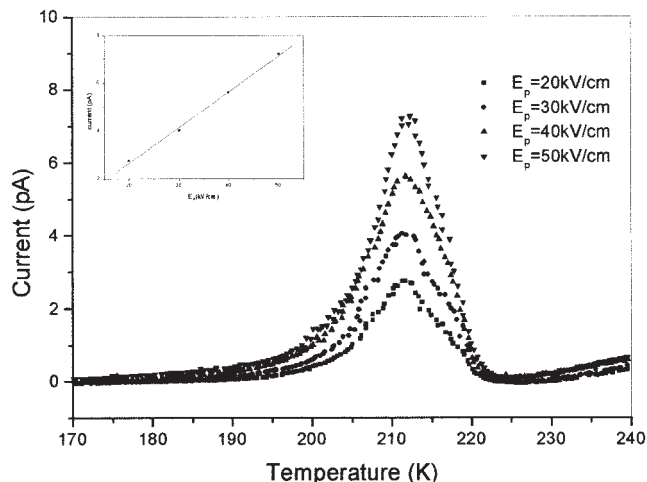


Figure 2 TSDC of PU for different poling fields. The inset shows the maximum current dependence on  $E_p$ .

evaporated onto both sides of the film. Dielectric data were obtained with the sample placed in a temperature-controlled chamber.

TSDC measurements

The TSDC technique has been very useful for studying the relaxation of polymeric materials.<sup>7,8</sup> This method consists of measuring the thermally activated release of frozen-in polarization. A prepoled sample is placed in a temperature-controlled chamber with its electrodes short-circuited. The current released is recorded while the temperature is increased at a constant rate.<sup>9</sup> In this work, the thermal current was detected through a Keithley model 610C electrometer, and the sample temperature was controlled with a Toyo Seiki KP-1000 thermocontroller unit.

RESULTS AND DISCUSSION

Figure 1 shows TSDC currents for PU film poled with 20 kV/cm at 393 K for 30 min. Before polarization, the sample was thermally treated at 393 K for 1 h to provide an enhancement of repeatability of the measured data. Figure 1 illustrates three relaxation peaks in the temperature range of 175–390 K.

A close analysis of the first peak indicates linearity between the maximum intensity of the depolarization current ( $I_{max}$ ) and the polarization field ( $E_p$ ), as shown in Figure 2 for five different electric fields. The relaxation occurs at the same temperature, independently of the field’s intensity. The linear relation between  $I_{max}$  and  $E_p$  can be seen in the inset of Figure 2. These results are characteristic of dipolar relaxation.<sup>10,11</sup>

The relaxation observed around 213 K could be called an  $\alpha$  relaxation. Sakamoto et al.<sup>12</sup> reported the value of the glass-transition temperature of castor oil based PU, obtained without any solvent, as being

around 313 K. The PU reported here was obtained with NMP, which could change the polymer chemical structure. The shift of 100 K was high, and consequently we suggest that the relaxation could be due to the polyol structure, which could be in excess within PU because some isocyanate groups reacted with NMP or with some water that might have been in the solvent.

Figure 3 shows the behavior of a real part of the complex permittivity of PU in the frequency range of  $10^3$ – $10^6$  Hz for various fixed temperatures. The increasing permittivity ( $\epsilon'$ ) with increasing temperature could be indicative of space charge polarization and free-charge motion within the material.<sup>13</sup> The behavior of the dielectric loss ( $\epsilon''$ ) is shown in Figure 4. A broad peak in the kilohertz frequency range can be observed, which is shifted to a high frequency to increase the temperature; this indicates a thermally activated process that is related to the  $\alpha$  relaxation.

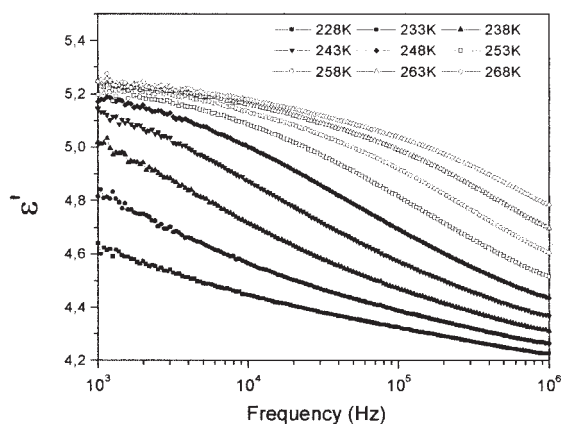
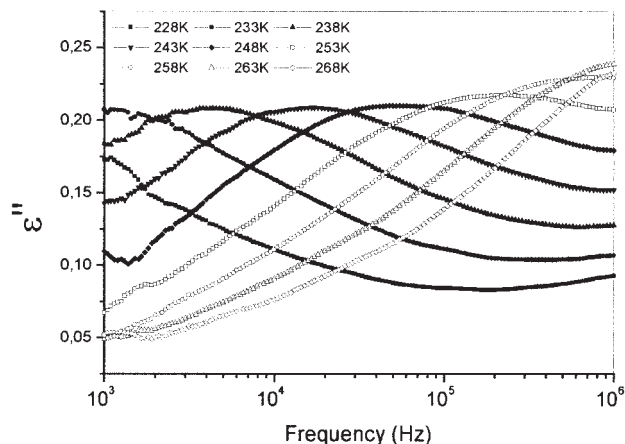


Figure 3  $\epsilon'$  plotted as a function of the frequency at different fixed temperatures. The temperature step was 5°C.



**Figure 4**  $\varepsilon''$  plotted as a function of the frequency at different fixed temperatures. The temperature step was 5°C.

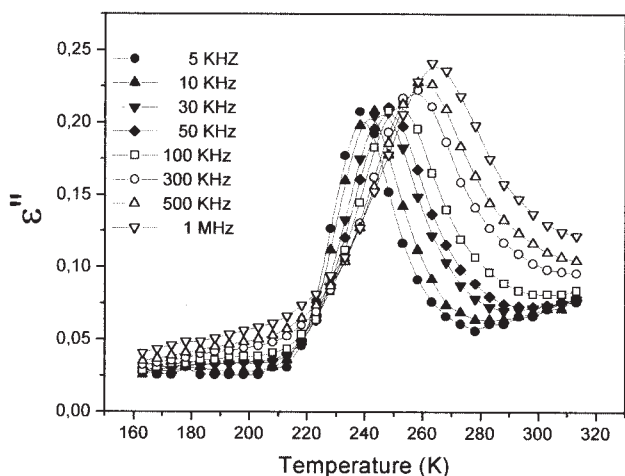
To compare the results of the ac measurements with those of the TSDC technique, Figure 5 shows  $\varepsilon''$  as a function of temperature for different fixed frequencies. The  $\alpha$  relaxation shifts to a higher temperature with increasing frequency.

The data for the  $\alpha$  relaxation in PU have been fitted with the Vogel–Tammann–Fulcher (VTF) equation:<sup>14</sup>

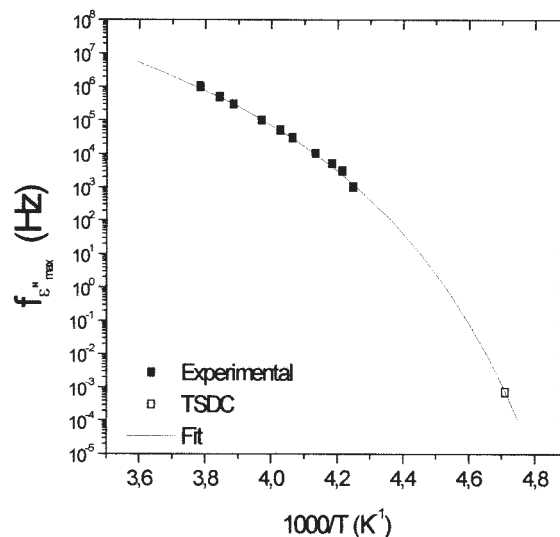
$$f_{\max} = A \exp \frac{-B}{T - T_0} \quad (1)$$

where  $A$ ,  $B$ , and  $T_0$  are temperature-independent empirical constants.  $T_0$  is called the Vogel temperature, and its value is 30–50 K below the glass-transition temperature.<sup>15</sup> The good fitting of the data with VTF allows us to state that the relaxation is related to dipolar relaxation.

Figure 6 shows the behavior of the frequency of the corresponding loss peak as a function of the reciprocal



**Figure 5**  $\varepsilon''$  plotted as a function of temperature at different fixed frequencies.



**Figure 6** Arrhenius plot of  $f_{\varepsilon''\max}$  against the reciprocal of the temperature ( $1/T$ ) for the  $\alpha$  process of PU film. The line is the VTF fit to the experimental data. The TSDC point is also showed.

of the temperature. The parameters are  $A = 1.9 \times 10^{11} \text{ s}^{-1}$ ,  $B = 1008 \text{ K}$ , and  $T_0 = 182 \text{ K}$ . The TSDC point in Figure 6 corresponds to the TSDC peak temperature of 213 K and the equivalent frequency ( $f_{\text{eq}}$ ) of  $7 \times 10^{-4} \text{ Hz}$ , defined as the frequency of ac measurements that gives a maximum in  $\varepsilon''$  at the same temperature,<sup>16</sup> according to eq. (2):

$$f_{\text{eq}} = \frac{Br}{2\pi(T_m - T_0)^2} \quad (2)$$

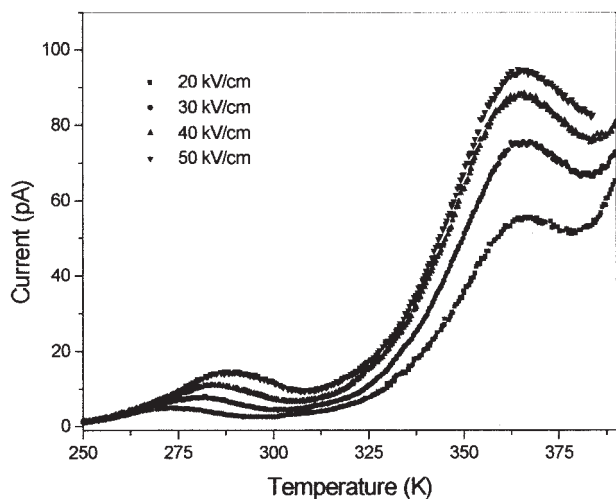
where  $r$  is the heating rate of TSDC and  $T_m$  is the peak temperature.

In the relaxation observed at 274 K, the maximum current increases linearly with the poling field, and the peak shifts to a higher temperature, as can be seen in Figure 7. Measurements with blocking electrodes, for which Teflon foils 12  $\mu\text{m}$  thick were placed between the PU sample and the electrodes, showed the same behavior as the measurements without blocking electrodes. These results suggest that the peak above the  $\alpha$  relaxation is due to interfacial polarization. Similar results were obtained with other PU systems.<sup>17,18</sup>

The peak at 365 K can be attributed to space charge because it shows a nonlinear relation between the maximum current and the poling electric field.<sup>12</sup> This behavior can be seen in Figure 7. Studies about the influence of the diisocyanate fraction on the relaxation process in PU are in progress.

## CONCLUSIONS

Dielectric and TSDC techniques were used to study the molecular mobility of a vegetable-based PU. A



**Figure 7** TSDC of PU for different poling fields (polarization parameters: temperature = 393 K, time = 30 min, heating rate = 2 K/min).

global TSDC spectrum showed three relaxation peaks located at 213, 274, and 365 K. A linear relation between the maximum intensity of the depolarization current and the poling electric field indicated the dipolar origin of the relaxation around 213 K. This was also confirmed by the VTF. The lower temperature for the  $\alpha$  relaxation obtained in this study, in comparison with the glass-transition temperature described in a previous article,<sup>12</sup> could be attributed to the effect of the solvent on the polymer chemical structure.

The second peak, located at 274 K, could be attributed to the interfacial polarization, whereas the relaxation at 365 K was due to space charge movement.

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