Analysis of dipolar relaxation in polyurethane/polyaniline blend

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Thin films of blend made up of castor oil-based polyurethane (PU) and polyaniline (PANI) were obtained by casting. The molecular mobility was studied using dielectric spectroscopy and thermally stimulated depolarization current (TSDC) for blends with two different compositions (90/10, 80/20) and the results were compared with PU pure. The peak located around $-60°C$ in TSDC thermograms of PU/PANI blend has dipolar behavior and might be attributed to the change in the molecular chain due to the interaction between isocyanate and the solvent. Vogel-Fulcher Tammann fits was performed on the observed relaxation and the result shows a α-relaxation-like. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Nowadays processing conducting polymers in form of blends and composites with commercial polymers is a well-established alternative as material for technological applications [1–6]. By combining the high electrical conductivity of one with thermal stability, good mechanical properties and processability of conventional polymer, several blends have been produced with interesting properties. The conductivity has been the main property focused in such blends [7–9].

Among conducting polymers, polyaniline (PANI) has been extensively used because of the low cost of raw material, ease of synthesis, environmental stability and because it can be blended with a variety of polymers [10, 11]. The variety of possible blend that can be obtained together of the doping control of conductive phase have opened the possibility of use such blends as dielectric material in capacitors where low conductivity and high permittivity are desired.

The aim of the present work is a comparative dielectric and TSDC studies of molecular mobility in PU/PANI blend, using a vegetable-based polyurethane as thermal stable matrix. The use of a raw material vegetable-based could be other great advantage of this blend in comparison with blends using oil-based matrix.

2. Experimental

2.1. Polymer synthesis

Esmeraldine salt form (conductive state) of PANI was chemically synthesized by the conventional route. The ammonium peroxydisulfate was dissolved in 200 cm³ of 1.0 M HCl solution cooled at 0°C. The aniline monomer was dissolved in 300 cm³ of 1.0 M HCl solution also cooled at 0°C. Both solutions were slowly mixed. The esmeraldine salt obtained was equilibrated in 0.1 M of ammonium hydroxide for 16 h at room temperature thereby producing esmeraldine base, i.e., undoped form of PANI.

2.2. Blend preparation

Castor oil-based polyurethane was used as received from Grupo de Química Analítica e Tecnologia de Polímeros—GQATP, from University of São Paulo—USP, i.e., the polymer was prepared using the pre-polymer F329 (isocyanate-based) and polyol 21 L (castor oil-based) in the rate 1/0.7, respectively.

Two composition of PU/PANI blend were studied: 90/10 and 80/20, that means 90 wt.% of PU and 10 wt.% of PANI and 80 wt.% of PU and 20 wt.% of PANI, respectively. Stock solution of conducting polymer (2 wt.%) in N-metilpirrolidone (NMP) was prepared separately. These polyaniline solutions were mixed at the desired proportions with the polyol and with the pre-polymer previously dissolved in NMP. After mixing both solutions, films (90–150 μm thick) were prepared by casting the blend solution on glass slide placed in an oven (70°C) with air circulation during 15 h for solvent evaporation.

2.3. Polyurethane films

The polyurethane films with 20 μm of thickness were obtained by casting. The pre-polymer (10 g) and polyol (7 g) were mixed with NMP separately and then mixed to obtain the final solution which was dropped on glass slide also placed in an oven at 70°C during 15 h for solvent evaporation.

3. Characterization
3.1. Dielectric measurement

AC dielectric measurements, in the frequency range 10^3–10^6 Hz, were carried out using an impedance analyzer HP model LF 4192A. For electrical contact, circular gold electrodes (1.0 cm diameter) were evaporated onto both sides of the blend. The film was placed in a temperature-controlled chamber and the dielectric data were taken with a microcomputer.

3.2. Thermally stimulated depolarization current (TSDC) measurement

TSDC method consists of measuring the thermally activated release of frozen-in polarization. The pre-poled sample is inserted in a temperature-controlled chamber (Toyo Seiki) with its electrodes short-circuited. The current released is recorded using a Keithley 610 C electrometer while the temperature is increased at a constant rate. The temperature was measured with a Chromel-Alumel thermocouple, mounted in the sample holder and adjacent to the film.

4. Results and discussion

Fig. 1 shows the TSDC currents for PU and PANI films poled with 10 kV/cm at 120°C for 30 min. Before polarization the sample was thermally treated at 120°C during 1 h to provide an enhancement of repeatability of the measured data. It can be seem from Fig. 1 only one peak of relaxation at -62°C in the temperature range of -100 to -40°C for PU film. For PANI films there is no relaxation in that temperature range.

A close analysis of the first peak indicates linearity between the maximum intensity of depolarization current (I_{max}) and the polarization field (E_p). It was observed that the relaxation occurs at the same temperature independent of the field intensity [12]. The linear relation between I_{max} and E_p is a characteristic of dipolar relaxation [13, 14] and it was associated with the glass transition of the polymer [12]. The relaxation observed around -60°C could be stated as α-relaxation. Sakamoto and co-workers have reported the value of glass transition temperature of castor oil
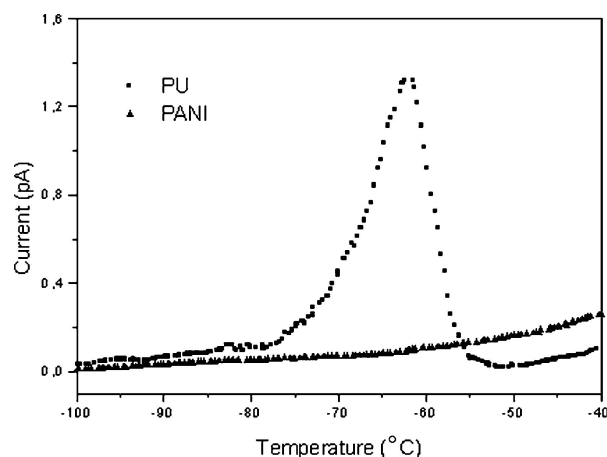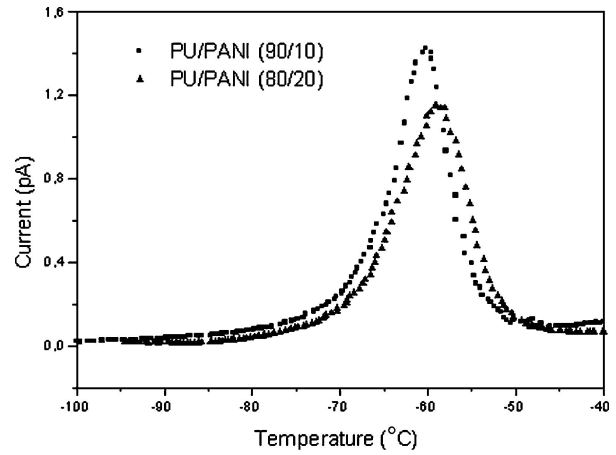

Figure 2 TSDC of polyurethane/polyaniline blend in the composition in weight 90/10 and 80/20. Heat rate $\beta = 2$°C/min., polarization temperature $T_p = 120$°C, polarization field $E_p = 10$ kV/cm and polarization time $t_p = 30$ min.

based polyurethane as around 39°C [15], obtained without any solvent. PU reported here was obtained using NMP that could change the polymer chemical structure by interacting with the isocyanate and the shift of the α relaxation must be related with that change. TSDC spectrum from a film obtained of the mixture of prepolymer and NMP did not show any relaxation peak in the range of -100 to -40°C. This result suggest that relaxation can be due to the polyol structure, which could be in excess within the PU because some isocyanate group reacted with NMP or with some water that can be in the solvent.

Fig. 2 shows TSDC thermograms of PU/PANI 90/10 and PU/PANI 80/20. Relaxation peak can be observed around -60°C for both PU/PANI blends. A detailed study of that relaxation in PU/PANI blends indicating the same temperature of relaxation independent of the poling field can be observed in Fig. 3 for PU/PANI 90/10. Furthermore, linear relation between the peak-current intensity and the poling field could be observed as shown in the inset of Fig. 3. The same behavior was observed in 80/20 PU/PANI blend. These results
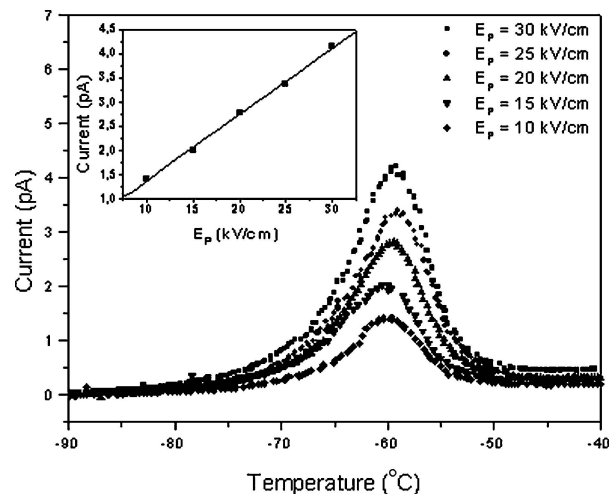

Figure 1 TSDC of polyurethane and polyaniline. Heat rate $\beta = 2$°C/min and polarization temperature $T_p = 120$°C.

Figure 3 TSDC of 90/10 blend for different poling field. The inset shows the maximum current dependence on the polarization field. Heat rate $\beta = 2$°C/min.
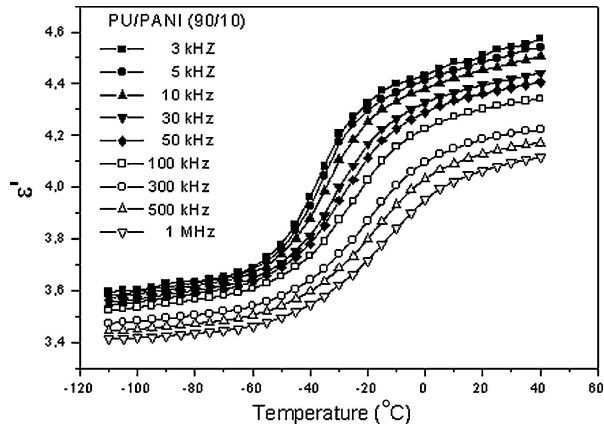
Figure 4 Dielectric constant ε' plotted as a function of temperature at different fixed frequencies.
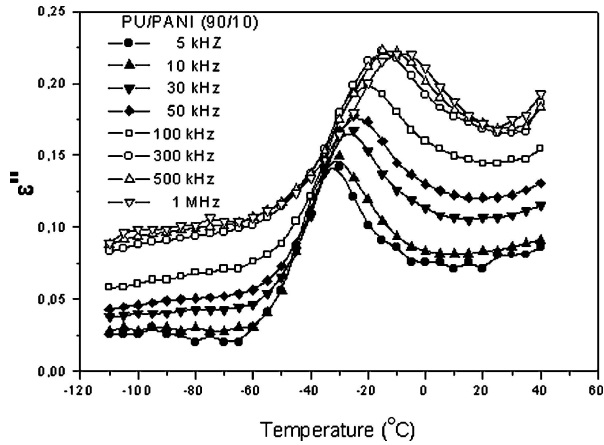

Figure 5 Dielectric loss ε'' plotted as a function of temperature at different fixed frequencies.

indicate that the relaxation occurring around $-60°$C in the blends has dipolar origin due to polyurethane (polyol phase) since polyaniline does not show relaxation in that temperature range. It can be seen from Figs 1 and 2 that there is no significant change in the dipolar temperature position, which means that polyaniline form one phase in the PU matrix.

Fig. 4 shows the behavior of complex permittivity of 90/10 PU/PANI in the frequency range of 10^3 to 10^6 Hz for various fixed temperatures. The increasing permittivity ε' with increasing temperature is an indicative of space charge polarization and free-charge motion within the material [16].

To compare the results of ac measurements with those of TSDC technique, Fig. 5 shows the isochronal dielectric loss (ε'') plots at different fixed frequency. The α relaxation shifts to higher temperature with increasing frequency.

The data for the α-relaxation in 90/10 PU/PANI have been fitted by Vogel-Tammann-Fulcher (VTF) equation [17]:

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

where A, B and T_0 are temperature-independent empirical constant. T_0 is called Vogel temperature which
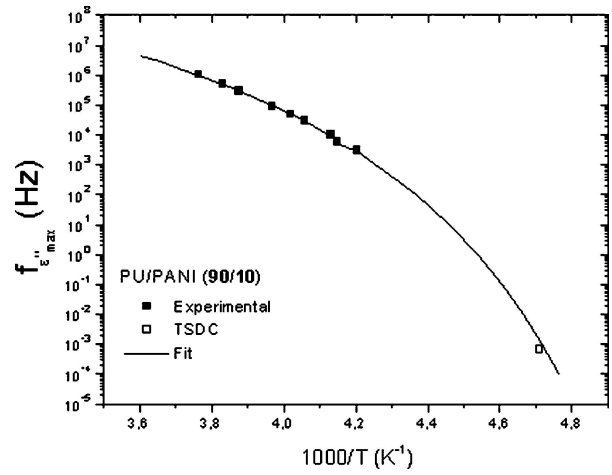

Figure 6 Arrhenius plot of frequency of maximum dielectric loss, $f_{\varepsilon''\max}$, against reciprocal temperature. The line is the VTF fit to the experimental data. The TSDC point is also showed.

value is in the range of 30–50 K below glass transition temperature [18].

Fig. 6 shows the behavior of frequency ($f_{\varepsilon''\max}$) of the corresponding loss peak as a function of reciprocal of temperature. The parameters used are: $A = 1.6 \times 10^{11}$ s^{-1}; $B = 1016$ K; $T_0 = 181$ K. TSDC point in Fig. 6 correspond to the TSDC peak temperature T_g of $-60°$C and the equivalent frequency (f_{eq}) of 7×10^{-4} Hz defined as the frequency of ac measurements, which give a maximum in ε'' at the same temperature [19], according to Equation 2:

$$f_{eq} = \frac{B\beta}{2\pi(T_m - T_0)^2} \qquad (2)$$

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

Similar results were found for the blends 80/20. The parameters obtained with the VFT fitting are: and $A = 2.0 \times 10^{11}$ s^{-1}; $B = 1088$ K; $T_0 = 179$ K. The excellent fits by Vogel-Tammann-Fulcher equation allow to states that the relaxation is related to dipolar relaxation.

5. Conclusions

Dielectric and TSDC techniques were used to study the molecular mobility of a vegetable-based polyurethane and its blend obtained with polyaniline, a conductive polymer. Global TSDC spectrum in the range of -100 to $-40°$C shows one relaxation peaks located around $-60°$C. That relaxation was also observed in PU/PANI blend in both compositions: 90/10 and 80/20 wt.%. Linear relation between the maximum intensity of the depolarization current and the poling electric field and the VTF fitting confirm the dipolar origin of the relaxation around $-60°$C. This relaxation can be related with the polyol group that were not reacted with isocyanate group. The presence of PANI in the blend does not change significantly the dipolar relaxation position indicating that polyaniline is immersed in PU matrix forming one phase.

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