

# Dielectric relaxation of vegetable-based polyurethane

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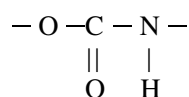
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Vegetable-based polyurethane (PU) was prepared in the thin film form by spin coating. This polymer is synthesised from castor oil, which can be extracted from the seeds of a native plant in Brazil called mamona. This polymer is biocompatible and is being used as material for artificial bone. The PU was characterised by dielectric spectroscopy in a wide range of frequency ( $10^{-5}$  Hz to  $10^5$  Hz) and by thermally stimulated discharge current (TSDC) measurements. The glass transition temperature ( $T_g = 39^\circ\text{C}$ ) was determined and using the initial rise method the activation energy was found to be 1.58 eV. © 2003 Kluwer Academic Publishers

## 1. Introduction

The name polyurethane is used to identify polymers that belong to a class of polymers with urethane link. Typical polyurethanes can contain aliphatic or aromatic sequences along the chain together with ester, ether or amide groups [1, 2]. Polyurethane is commercially used in diverse applications in industrial projects, such as automotive seating, shoe soles, etc., due to its great versatility. The chain flexibility, the intermolecular force and cross-linking can be widely varied and the product obtained can be in the range of a linear and flexible polymer to rigid and highly cross-linked polyurethane [3, 4].

One the most important components to synthesise polyurethane is isocyanate. The polyurethane may be obtained through the reaction of polyhydroxy compound and di-isocyanate. The castor oil, used in this work, is a very good natural source to synthesise polyurethane because it is a triester of ricinoleic acid. That acid, with 18 carbons with double bond between carbon 9 and 10 and one hydroxyl group on carbon 12, is structurally very suitable for urethane linkage which has the general characteristic chain group as shown below:



This vegetable-based polyurethane is biocompatible [5] and it has been used as a material for artificial bone [6]; also, it has good water resistance and is a good

insulator [7]. To obtain a better understanding of the electrical characteristics of this material a systematic study is in progress in our laboratory because this PU has been used as matrix for ceramic/polymer composites [8, 9]. Although the vegetable based polyurethane combined with ferroelectric ceramics such as PZT and BaTiO<sub>3</sub> has shown good results and some advantages in comparison with others polymeric matrix [10], its electrical properties are still not well known.

The present work reports the results and analysis of dielectric measurements of the polymer in the frequency range of  $10^{-5}$  Hz to  $10^5$  Hz using bridge and time-domain techniques. Furthermore, information about the glass transition temperature ( $T_g$ ) and activation energy ( $E_a$ ) were obtained by thermally stimulated discharge current (TSDC) measurements.

## 2. Experimental

### 2.1. Sample preparation

Transparent polyurethane films in the range of 50 to 100  $\mu\text{m}$  thickness were obtained by spin coating, from the reaction between castor oil with 4,4'-diphenylmethanodiisocyanate (MDI). The mixture was placed on a glass substrate and then on a spin coating system. To remove the film the substrate was immersed in pure water for a day. The PU film obtained was impermeable and the water used to remove the film from the glass substrate did not go into the film. To make sure that the water could not affect the dielectric measurement, the samples were dried in a vacuum chamber. Fig. 1 describes

\* Dilip Das-Gupta died during the preparation of this paper. His co-authors dedicate it to his memory.

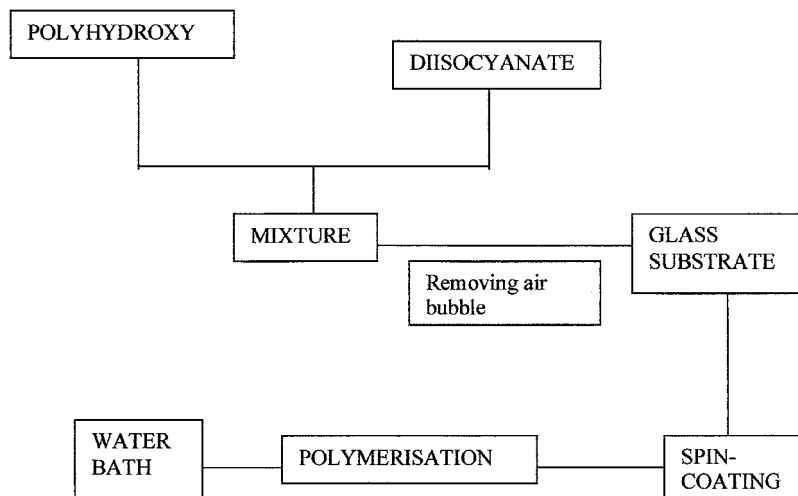


Figure 1 Schematic Diagram to obtain the PU film.

schematically the preparation of the polymer. The films were cut to an appropriate size and aluminium electrodes (diameter of 10 mm) were evaporated onto both side of the sample for electrical contact.

## 2.2. Measurements

The dielectric data were taken in the wide frequency range of  $10^{-5}$  Hz to  $10^5$  Hz. In the low-frequency range ( $10^{-5}$  Hz to  $10^{-2}$  Hz) the time domain technique of the measurement of discharge current with subsequent Hamon [11] approximation method were used while in the high-frequency range of 20 Hz to  $10^5$  Hz the measurements were made using a bridge (General Radio Bridge Model 1621) and for the medium frequency range of  $5 \times 10^{-2}$  Hz to 10 Hz, an EG&G Lock-In Amplifier model 7265 was used. For transient discharge current measurement the sample was placed in a temperature controlled chamber under reduced pressure and was charged for 27 hours with an electric field of  $10^6$  V/m. The discharging currents were taken for 3 hours.

The thermally stimulated discharge current (TSDC) spectra were obtained from  $0^\circ\text{C}$  up to  $80^\circ\text{C}$  for four different charging electric fields with range of  $1.5 \times 10^6$  to  $3 \times 10^6$  V/m. The sample was placed in a temperature-controlled chamber and reduced pressure. A Keithley model 247 power supply provided stabilised DC voltage (poling with constant electric field) and discharging currents were measured using a Keithley 610°C electrometer and recorded using a microcomputer. A Cu-Constantan thermocouple, mounted in the sample holder and adjacent to the film, allowed the temperature measurement. The heating rate used was  $1^\circ\text{C}/\text{min}$  and was done automatically by the temperature controller (Toyo Seiki).

## 3. Results and discussion

Dielectric relaxation in materials can be studied by time-domain or by frequency-domain measurements. In materials responding linearly with the amplitude of applied signal, time-domain and frequency-

domain responses are Fourier transforms of one another [12].

$$\chi'(\omega) = \int_0^\infty f(t) \cos(\omega t) dt \quad (1)$$

$$\chi''(\omega) = \int_0^\infty f(t) \sin(\omega t) dt \quad (2)$$

$$\text{and} \quad f(t) = \frac{2}{\pi} \int_0^\infty \chi'(\omega) \cos(\omega t) d\omega \quad (3)$$

$$f(t) = \frac{2}{\pi} \int_0^\infty \chi''(\omega) \sin(\omega t) d\omega \quad (4)$$

where  $\chi'(\omega)$  and  $\chi''(\omega)$  are the real and imaginary parts of the complex susceptibility  $\chi(\omega)$ , respectively,  $\omega$  is the angular frequency and  $f(t)$  is a time-dependent function.

The relationship between the permittivity and susceptibility are:

$$\begin{aligned} \varepsilon(\omega) &= \varepsilon'(\omega) - i\varepsilon''(\omega) \\ &= \varepsilon_\infty + \varepsilon_0[\chi'(\omega) - i\chi''(\omega)] \end{aligned} \quad (5)$$

$$\varepsilon'(\omega) = \varepsilon_\infty + \varepsilon_0\chi'(\omega) \quad (6)$$

$$\varepsilon''(\omega) = \varepsilon_0\chi''(\omega) \quad (7)$$

where  $\varepsilon_\infty$  is the high-frequency limit of the real part  $\varepsilon'(\omega)$  of the complex permittivity  $\varepsilon(\omega)$ ,  $\varepsilon''(\omega)$  is the imaginary part of  $\varepsilon(\omega)$  and  $\varepsilon_0$  is the permittivity of free space ( $= 8.85 \times 10^{-12}$  F/m).

In the frequency range of 20 Hz to  $10^5$  Hz the values of  $\varepsilon'$  and  $\varepsilon''$  were obtained from experimental data measured with General Radio Bridge. The data in the range of 0.05 Hz to 10 Hz (medium frequency range) were measured with a Lock-In Amplifier, Model 7265 EG&G. A sinusoidal voltage from the internal oscillator of the lock-in amplifier was used to generate a current in the sample. The in-phase and  $90^\circ$  out of phase currents were then measured using the lock-in amplifier. A correction on magnitude and on phase of applied voltage must be done in this range of frequency due the mismatch of the impedance. The permittivity and dielectric

loss was calculated using the equation [13]:

$$\varepsilon' = \frac{di_y}{\omega\varepsilon_0AV} \quad (8)$$

$$\varepsilon'' = \frac{di_x}{\omega\varepsilon_0AV} \quad (9)$$

where  $d$  is the sample thickness,  $A$  the electrode area,  $V$  the corrected applied voltage,  $i_x$  and  $i_y$  are the quadrature and in phase currents respectively.

The low frequency data of dielectric loss were calculated from the transient discharging current, obtained experimentally, using the Hamon approximation [11], given by

$$\varepsilon''(\omega) = I(t)/2\pi f C_0 V \quad (10)$$

here  $C_0$  is the capacitance of measuring electrodes without the sample,  $V$  is the applied voltage,  $I$  is the charging current and  $f$  is the Hamon frequency. The Hamon approximation is valid if the charging currents were extended for a time period of at least one order of magnitude than that of the discharging current [14]. The dielectric loss in the range  $10^{-5}$  Hz to  $10^5$  Hz were then combined and fitted using the "Universal" relaxation law [15]. The low-frequency permittivity  $\varepsilon'(\omega)$  can be calculated using the Kramers-Kronig relations [16], which are

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\varepsilon''(x)}{x - \omega} dx \quad (11)$$

$$\varepsilon''(\omega) = \frac{-1}{\pi} P \int_{-\infty}^{\infty} \frac{\varepsilon'(x) - \varepsilon_\infty}{x - \omega} dx \quad (12)$$

where  $P$  is the Cauchy principal value of the integral. The low-frequency values of  $\varepsilon'$  were obtained and fitted using a computer program.

Fig. 2 shows the behaviour of the real and imaginary parts of the dielectric permittivity ( $\varepsilon'$  and  $\varepsilon''$ , respec-

tively) for three different temperatures (RT, 40°C and 60°C). It can be seen a peak in the dielectric loss in the range of 1 Hz to 50 Hz (medium frequency range) for all three temperatures. This peak shifts to a higher frequency for increasing temperature indicating a thermally activated process. The presence of the peak in this range of frequency also was observed in other polymers such as low-density polyethylene (LDPE) [16] and was related with the impurities in the polymer matrix.

There is evidence of a peak around  $3 \times 10^{-4}$  Hz. This peak might be related with the glass transition of the polymer. Also, in this low frequency range, the dielectric loss exhibit fractional power law dependence on frequency indicating a low-frequency dispersion process (LFD) [17], may be due to space charge movement. It can be seen from Fig. 2 that the movement of charges is increased with increasing temperature. The relaxation at low-frequency due to glass transition of the polymer ( $\alpha$  relaxation) can be seen by thermally stimulated discharge current (TSDC) measurement. Fig. 3 shows the behaviour of TSDC for the PU sample with  $54 \mu\text{m}$  thickness, poled at 90°C for 15 minutes. From TSDC measurement it is clear that there are two distinct process occurring in the temperature range of 39°C and 70°C. Considering the first peak, located at  $T = 39^\circ\text{C}$ , it can be seen that the quantity of charge increases linearly within the range of electric field used ( $1.5 \times 10^6$ – $3 \times 10^6$  V/m), indicating a dipolar relaxation process ( $\alpha$  relaxation). The glass transition temperature ( $T_g$ ) of this vegetable-based (castor oil) polyurethane is comparable with that of the polyurethane prepared by solution-casting after copolymerisation of liquefied woods and polymeric methylene diphenylene diisocyanate [18].

The second peak was observed around 70°C and the non-linear enhanced amplitude as the poling field is increased and the saturation of the charge with the applied field indicate the presence of space charge. Figs 4 and 5 show the maximum current as a function of applied field for both 1st and 2nd peak, respectively.

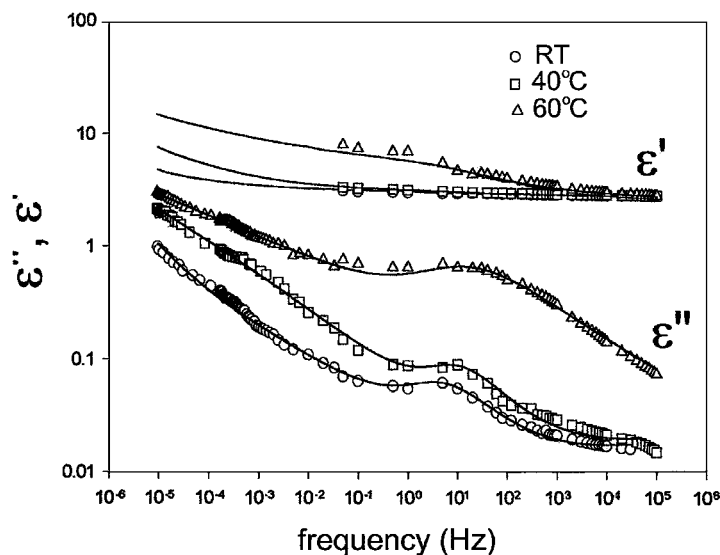


Figure 2 Real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) parts of the complex permittivity ( $\varepsilon$ ) for PU measured by: a) discharge current with subsequent Hamon approximation ( $10^{-5} - 3 \times 10^{-2}$  Hz), b) lock-in amplifier ( $5 \times 10^{-2} - 10$  Hz), (c) General Radio Bridge ( $20 - 10^5$  Hz). The low frequency values of  $\varepsilon'$  were obtained from equation 11 and fitted using a computer program.

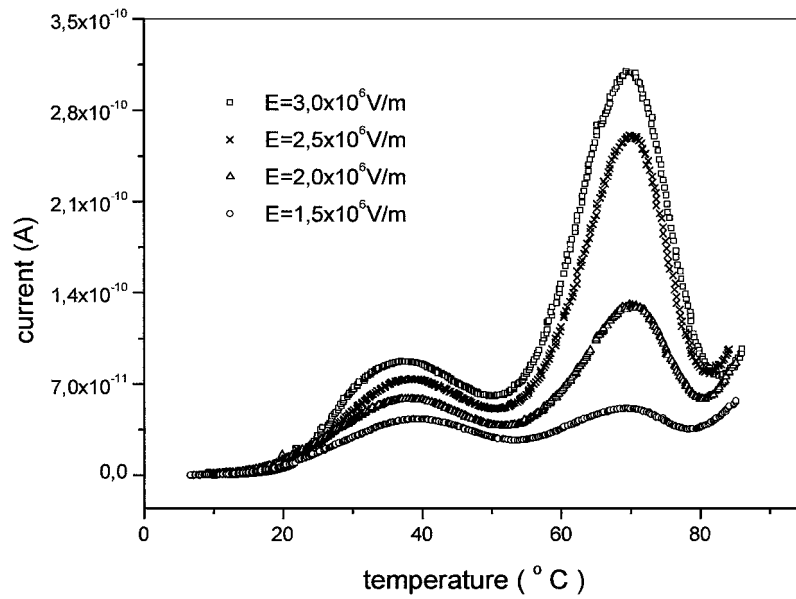


Figure 3 Thermally stimulated discharge current (TSDC) for PU for 4 different applied electric field.

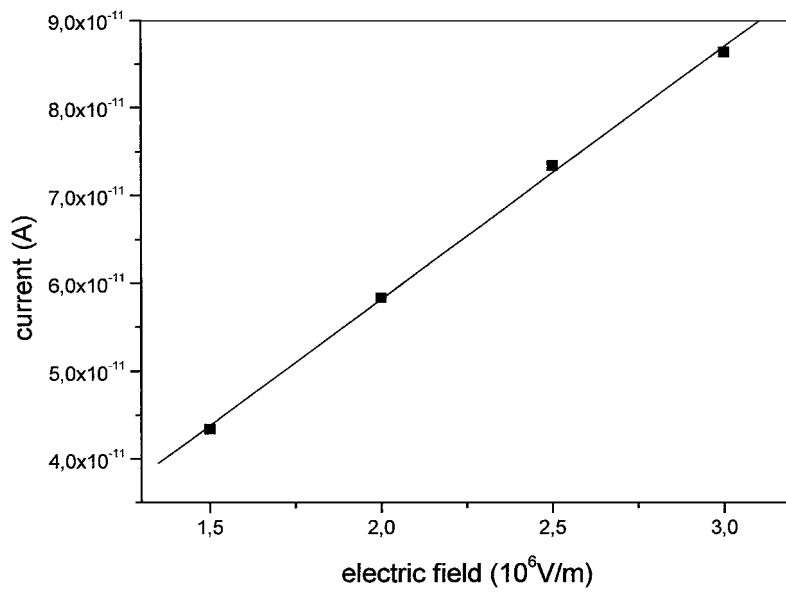


Figure 4 Maximum current as a function of applied electric field for the peak at 39°C.

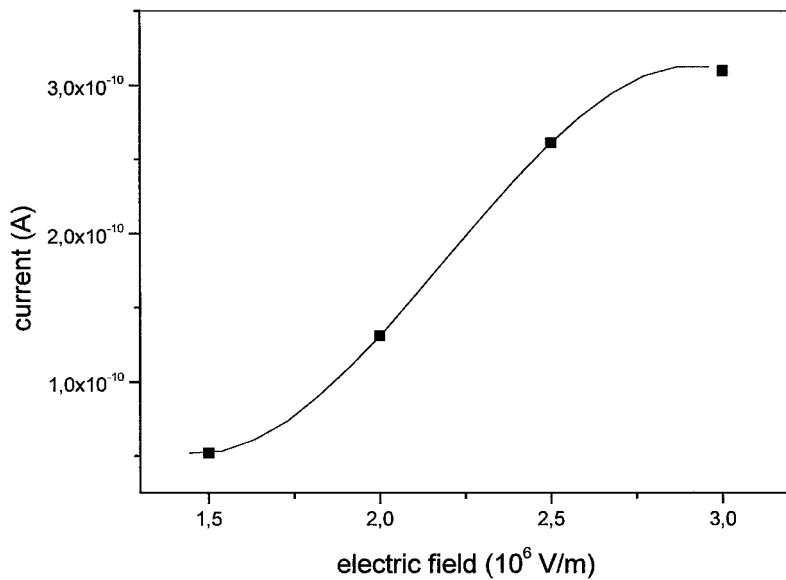


Figure 5 Maximum current as a function of applied electric field for the peak at 70°C.

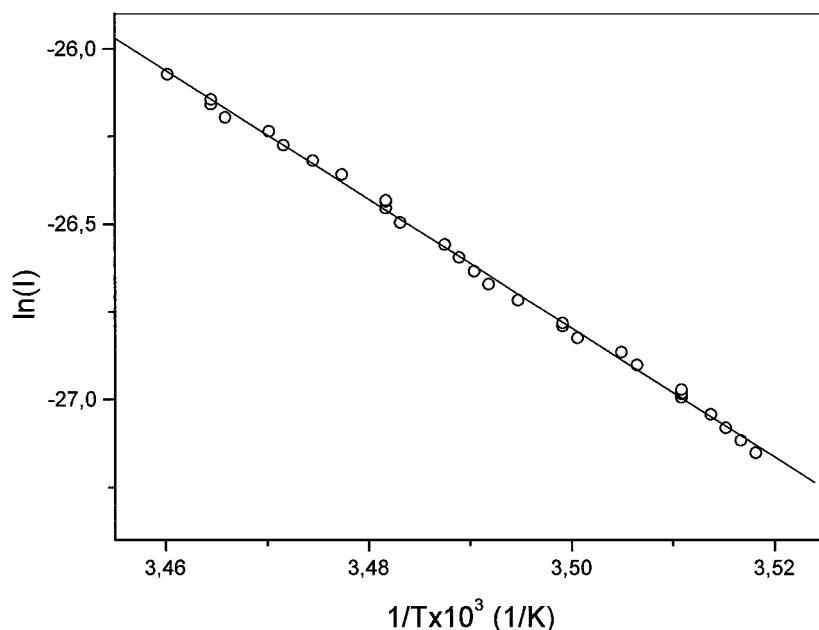


Figure 6 Plot of  $\ln(I) \times 1/T$  using the initial rise method from discharge current measurement.

According to Van Turnhout [19] the peaks observed in TSDC spectra are related with the peaks observed in the dielectric loss measurements by,

$$\omega = \frac{A}{bkT^2} \quad (13)$$

where  $A$  is the activation energy,  $b$  is the inverse of heating rate,  $k = 1.38 \times 10^{-23}$  J/K is the Boltzmann constant and  $T$  is the temperature ( $39^\circ\text{C}$ ) of the maximum in the TSDC curve. Using the value of 1.58 eV for the activation energy obtained from the slope of the  $\ln(I) \times 1/T$  plot ( $= d\ln I(T)/d(1/T)$ ) in Fig. 6 the corresponding frequency is  $5 \times 10^{-4}$  Hz. It can be seen that the evidence of the peak observed in the range of  $10^{-4}$  Hz in the dielectric loss is due to the dipolar relaxation. The movement of the space charges responsible for the low-frequency dispersion was located at  $70^\circ\text{C}$  in the TSDC spectra.

The activation energy ( $= 1,58$  eV) calculated by initial rise method is similar to the activation energy of a chemically obtained polyurethane using polyol + 1,4 butandiol + 4, 4' diphenylmethane diisocyanate [20].

#### 4. Conclusions

Transparent films of vegetable-based polyurethane were obtained from a triester of ricinoleic acid. The oil can be extracted from the seeds of a native plant in Brazil, called Mamona tree. This polymer has glass transition temperature ( $T_g$ ) of  $39^\circ\text{C}$  and the activation energy of this dipolar relaxation was found equal 1.58 eV. Frequency domain measurements show the contribution of the conductivity due to space charge in the low-frequency range ( $10^{-4}$  Hz). The low dielectric loss of the polymer indicates that it can be used as an insulator. The formability and the facility to obtain this product might be a good reason to use this natural polymer as an alternative to oil-based polymers. The study of the transport process, breakdown voltage and some mechanical tests are in progress with this poly-

mer and must be done before proposing its polymer for industrial applications.

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