Effect of polyol excess on the electrical property of vegetable-polyurethane film

D. H. F. Kanda · H. N. Nagashima ·
J. A. Malmonge · W. K. Sakamoto ·
G. O. Chierice

Abstract Freestanding castor oil-based polyurethane (PU) film was obtained using spin-coating method. The effect of polyol content was analysed by means of thermally stimulated depolarisation current and AC dielectric measurements techniques. Two relaxation peaks were observed in the temperature range of −40 to 60 °C for PU with different polyol contents. The presence of polyol excess provides a shift to lower temperature of the α relaxation and the decrease in the activation energy of the transition in this region might be attributed to the plasticising effect of the polyol. The peak at higher temperature is due to the Maxwell–Wagner–Sillars relaxation, which also shifts in the low temperature direction as the polyol content is increased.

Introduction

Polyurethane (PU) is a well-known and widely used polymer due to its great versatility [1–3]. PU has a large range of applications, which can be attributed to the fact that it can be obtained as linear and flexible polymer or as rigid and highly cross-linked PU [4, 5]. Also, the versatile physical properties of the PU are attributed to their micro phase-separated structure arising from the thermodynamical incompatibility between the hard and soft segments [6].

D. H. F. Kanda · H. N. Nagashima · J. A. Malmonge ·
W. K. Sakamoto (✉)
Department of Physics and Chemistry, University of São Paulo
State—UNESP, Av. Brasil, 56, 31, 15 385-000 Ilha Solteira,
SP, Brazil
e-mail: sakamoto@dfq.feis.unesp.br

G. O. Chierice
Institute of Chemistry, University of São Paulo—USP/São
Carlos, Sao Paulo, Brazil

Most of the PU foams are based on 4,4′-diphenylmethane diisocyanate (MDI) and petrochemical-based polyols. Although this type of PU is inexpensive material, the oxidative stability is still under consideration [7]. Nowadays many researchers try to replace oil-based polyols with vegetable oil-based polyols [8–11] seeing that it has provide comparable mechanical and insulating properties and can be obtained from renewable source. Furthermore, the production of vegetable-based PU brings forth fewer problems to the environment hence considered ecologically correct. One such example, studied in our laboratory, is the castor oil-based PU [12, 13]. It was used as matrix of piezo and pyroelectric composites [14, 15] and conducting composite [16]. Also, it was used to make polymer blend with conducting polymer [13].

In the previous work [12], a stoichiometric vegetable-based PU was prepared and characterised in the frequency range of 10^{-5} to 10^{5} Hz. The glass transition temperature of 39 °C and activation energy equal to 1.58 eV were obtained for this natural polymer using thermally stimulated discharge current (TSDC) technique. The activation energy was determined by the initial raise method from the α-relaxation peak. The low dielectric loss of the PU indicates its insulating property. Furthermore, the formability and the facility to obtain this material from a renewable source is an attractive to continue the study on this polymer.

The aim of the present work is the study of the change of glass transition and the dielectric permittivity of the PU due to the change of polyol contents. By changing the dielectric constant, the electrical conductivity is also modified. The effect of polyol excess is analysed using TSDC and AC dielectric spectroscopy. Two different sample compositions (different polyol contents) were studied. For both samples two relaxations were observed in the temperature range of −40 to 60 °C.

Experimental

Sample preparation

Castor oil-based PU was prepared using the pre-polymer F-329, which is based on the 4,4'-diphenylmethano-diisocyanate (MDI) and vegetable-based polyol (21 L), which is a polyhidroxilated active component of PU, supplied by Poliquil Araraquara Polímeros Química Ltda. Film of ∼200 μm thickness was obtained by the spin-coating method. Two different polyol proportions were used, designated 10/11 and 10/12. In the sample 10/11, there are 1 part of pre-polymer and 1.1 part of polyol and the other one has 1:1.2. Aluminium electrodes (1×10^{-2} m in diameter) were evaporated onto both faces of the film for electrical contact. Stoichiometric PU is 10/10, i.e. one part of pre-polymer and one part of polyol, according to PU supplier.

TSDC measurements

The TSDC method consists of recording the thermally activated current. The sample is placed between the plates of a capacitor and poled by an applied electric field (E_P) at a fixed temperature (T_P) for a time (t_P) large compared with the relaxation time of the process to be studied. With the electric field applied, the sample is cooled down to a temperature low enough to prevent depolarisation by thermal agitation. Further, the sample is short-circuited and reheated at a constant rate.

TSDC is a powerful technique to study electrical properties of polymers when previously aligned dipoles trend to orientate at random as the increasing temperature enhances the mobility of the system [17]. This technique provides high resolution and is very sensitive, hence allowing detecting α relaxation and solves neighbouring process, i.e. due to the low heating rate possible superposed process can be observed and its deep analysis might be realised using thermal windowing technique [18]. In this work, the polarisation was conducted using a high voltage supply Keithley model 247, the thermal current was detected through a Keithley model 610C electrometer, and the sample temperature was controlled with a Toyo Seiki KP-1000 thermo controller unit. The heating rate was 2 °C/min. The polarisation conditions were: E_P from 0.5 to 2.0 MV/m; $T_P = 90$ °C; $t_P = 15$ min.

AC dielectric measurements

The dielectric loss (ε'') was measured as a function of frequency (10^3–10^6 Hz) in the temperature range of 0–90 °C. The measurements were carried out using an HP 4129A impedance analyser. A two-terminal parallel-plate capacitor dielectric cell with gold-plated electrodes temperature-controlled (Toyo Seiki) was used in association with the analyser.

Results and discussion

The depolarisation currents were monitored from −40 to 80 °C for samples pre-poled with four different electric fields (0.5, 1.0, 1.5 and 2.0 MV/m). Figure 1 shows the TSDC thermograms measured on PU 10/11 and 10/12 poled with 2.0 MV/m. Two peaks can be seen in the temperature range used here. For the sample 10/11 (1.1 parts of polyol), the first peak is located at around 13 °C, while the second one is located at 43 °C. For the 10/12 samples (1.2 parts of polyol), the peaks were shifted towards the low temperature direction yielding 10 and 32 °C for the first and second peaks, respectively.

A close analysis of the first peak at lower temperature is shown in Fig. 2. The maximum of the depolarisation current was plotted as a function of applied electric field. For both samples, the linearity between current and electric field can be observed in the first peak. As stated by Van Turnhout [19], the linear behaviour of the maximum depolarisation current with the poling electric field is an indicative of the fact that the relaxation is dipolar and is related with the glass transition of the sample. Hence, the glass transition temperature, T_g, of 10/11 samples is 13 °C and for sample with 10/12 composition is 10 °C, indicating a shifting to the lower temperature direction as the polyol contents is increased. The value of T_g for PU with 10/10 compositions was found equal to 39 °C using the same method as reported in previous work [12]. The difference with the values obtained in the present work might be attributed to the plasticising effect of the polyol. Similar
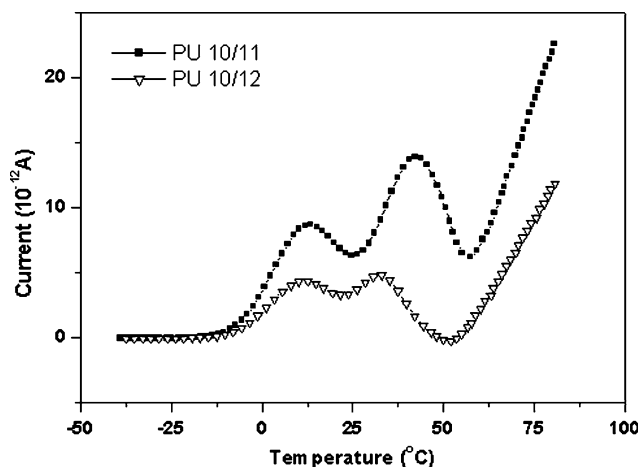

Fig. 1 TSDC thermograms for PU with different polyol content (■, 10/11; ▽, 10/12). Samples poled at 90 °C during 15 min with 2.0 MV/m
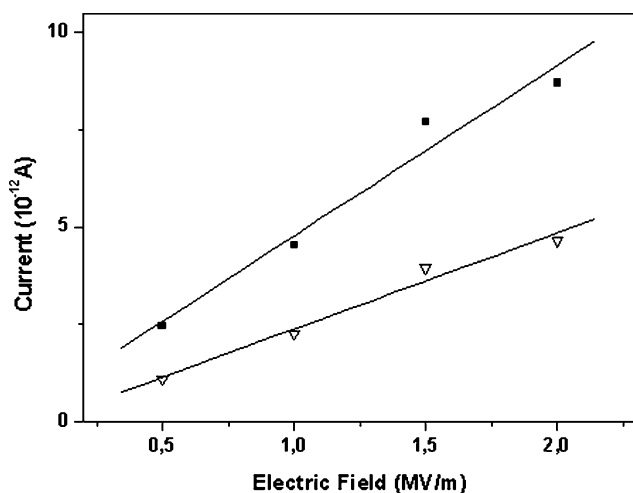
Fig. 2 Linear relation between the maximum current and the applied electric field for the first peak (■, for PU 10/11; ▽, for PU 10/12)

thermograms were obtained for all electric field used to pole the samples.

The relation between the maximum current and the electric field for the second peak (higher temperature) is shown in Fig. 3. The non-linear behaviour was observed for both samples. In segmented PU films, the existence of micro domains resulting from the separation of hard and soft segments of PU chains can accumulate charges at its interfaces during polarisation. Such charge accumulation can be attributed to the different conductivities between soft and hard micro domains [20]. The non-linear behaviour observed in Fig. 3 is an indicative that this relaxation is not only due to induced dipole, but there also is a contribution of the charge migration blocked at the interfaces between the two media (Maxwell–Wagner–Sillars characte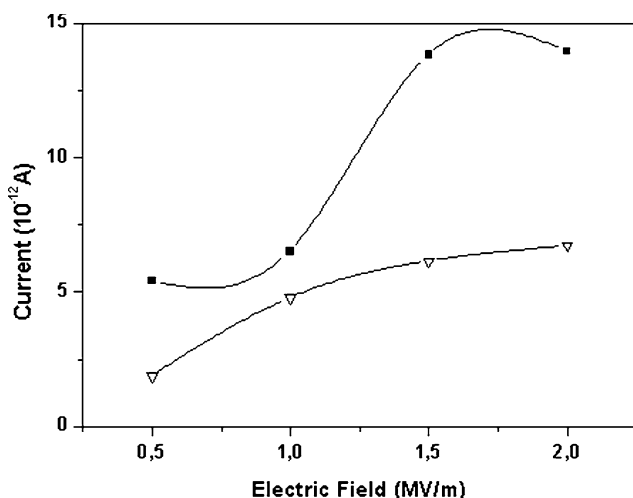ristic). The second peak is related to the relaxation due to interfacial MWS polarisation at the interface between soft and hard micro domains of the sample. The charge migration causing interfacial polarisation occurs mainly through the soft phase and the MWS-relaxation TSDC peak can be considered as a measuring of the interfacial polarisation. Several authors studying PU systems reported similar results [21, 22]. The polyol excess makes easy the reduction of the interfacial polarisation due to more uniform distribution of the hard micro domains into the continuous soft phase [20]. This effect is similar to the effect of the isocyanate excess observed by Spathis et al. [23]. The reduction in the amplitude of the measured current as the polyol content increases is in agreement with the fact that the polyol excess provides an insulation characteristic to the sample.

The thermal windowing technique was used around both α and MWS relaxation temperatures. The relation between the temperatures of current maximum (T_m) of PU 10/11, in the temperature range of -15 to 45 °C on polarisation temperature (T_P) is shown in Fig. 4. A linear relationship between T_m and T_P can be observed, with slope near to unity in the temperature region of both relaxation processes. According to Kyritsis et al. [24], the linear relationship suggesting that both peaks are due to bulk effects and not due to space charge polarisation related to electrode effects, which depends on polarisation time and polarisation temperature. Hence, the second relaxation observed in the TSDC thermogram for both samples is the α' relaxation and not the ρ peak related with the space charge, which should appear at higher temperature as suggested in Fig. 1.

Using the initial rise method [19], the activation energy related to the α-relaxation peak was calculated for both samples with polyol excess. Figure 5 shows the Arrhenius

Fig. 3 Relation between the maximum current and applied electric field for the second peak (■, for PU 10/11; ▽, for PU 10/12)
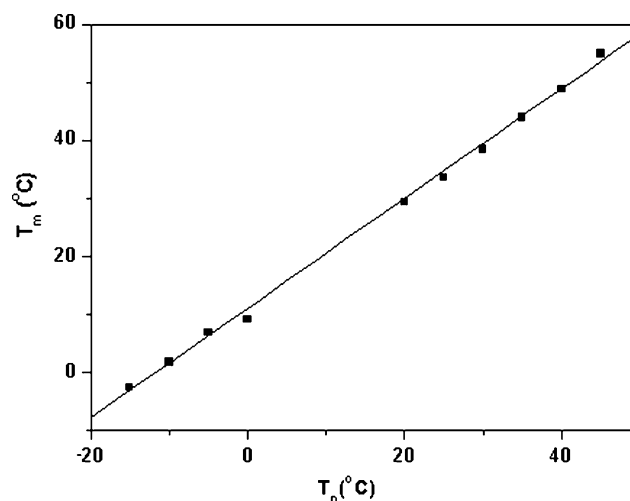

Fig. 4 Peak temperature T_m of the thermal sampling responses near both relaxations observed in the TSDC thermogram for PU 10/11 vs. polarisation temperature T_p
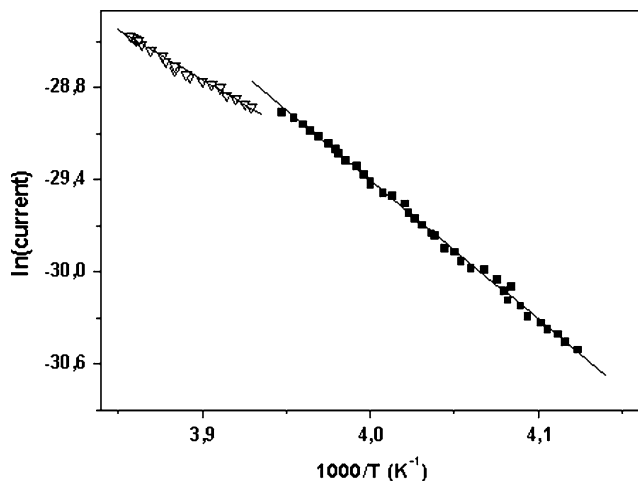
Fig. 5 Arrhenius plotting for both samples in the temperature region of α relaxation (■, for PU 10/11; ▽, for PU 10/12)

plotting for the thermally stimulated current. The decrease in activation energy can be seen as the polyol content increases in the sample. The values of the activation energy are 0.78 and 0.56 eV for PU 10/11 and PU 10/12, respectively, indicating that less energy is required to release frozen-in polarisation as the polyol content is increased because the presence of polyol excess reduce the PU molecules interaction.

The dielectric data were taken in the frequency range of 10^3 to 10^6 Hz at different fixed temperatures. The behaviour of the dielectric loss is shown in Figs. 6 and 7. It can be seem an evidence of a peak in the frequency range of kHz, which shifts to higher frequency for increasing temperature indicating a thermally activated process. From these measurements, the dielectric loss behaviour with temperatures in both samples was plotted. Figure 8 shows
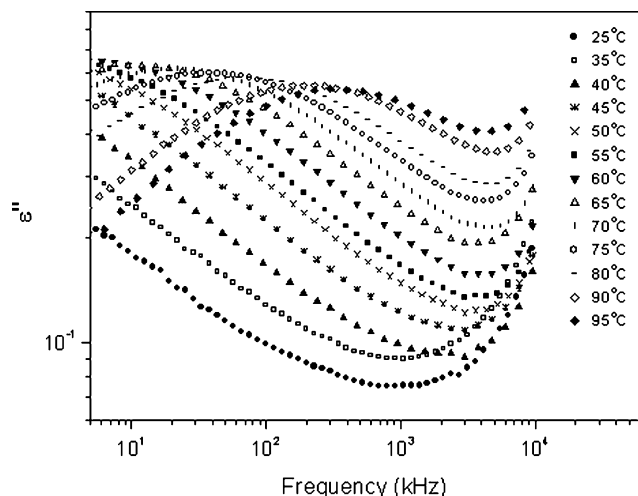

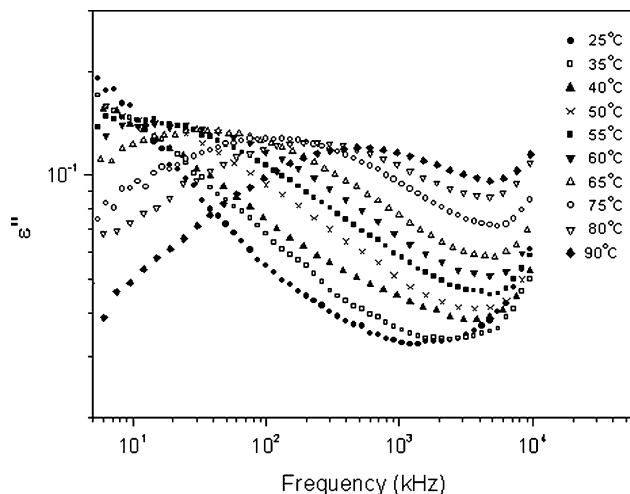Fig. 7 Dielectric loss ε'' versus the frequency for PU 10/12 at several temperatures indicated on the plot

the imaginary part of the complex permittivity (ε'') plots at 10 kHz in the temperature range of 0–90 °C. From the figure, it may be observed that there is a broad relaxation peak in both PU samples. The difference of peak position seemed to be due to polyol content employed to obtain the PU film.

The broad relaxation peak observed may be attributed to the result of the overlapping of the two peaks observed by TSDC. In order to justify, this assumption is necessary to consider that a plot of ε'' versus frequency should display both peak (α and MWS relaxation) in the frequency range of 10^{-2} Hz, which can be obtained using the relation stated by Van Turnhout [19] in Eq. 1.
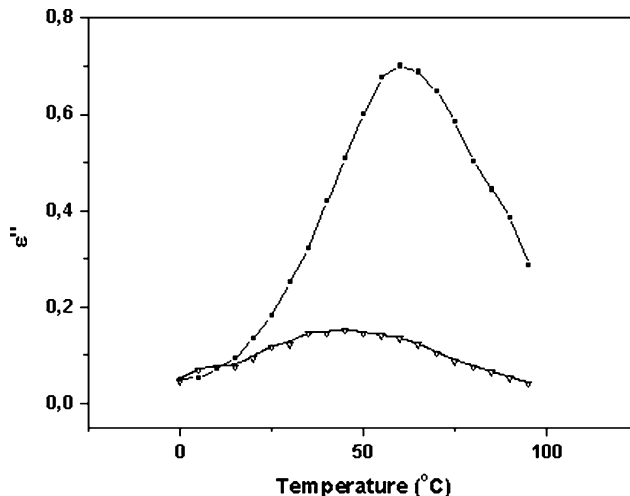
$$\omega = \frac{A}{hkT^2}, \tag{1}$$

Fig. 6 Dielectric loss ε'' versus the frequency for PU 10/11 at several temperatures indicated on the plot

Fig. 8 Isochronal plot of dielectric losses against temperature ■ for PU 10/11 and ▽ for PU 10/12, at 10 kHz

where ω is the angular frequency, A the activation energy, h the reciprocal of heating rate, k the Boltzmann constant and T is the temperature of maximum current in the TSDC. Due to the low frequency dispersion, the measurement was carried out in the high frequency range and the peaks were displayed at higher temperature. The frequency of the isochronal plot of ε'' is 10 kHz for 10/11 and 10/12 samples compositions and the peak appeared around 50 °C. In this temperature both relaxations had already occurred and the observed peak might be considered as a superposition of both relaxation. The shift of the ε'' peak to higher temperature for the 10/11 sample in comparison with the 10/12 seems to be due to the shift of the α relaxation and is in agreement with the observed TSDC result.

Conclusion

TSDC and AC dielectric spectroscopy were employed to study castor oil-based PU systems with two different polyol contents. Two relaxation peaks were observed in the TSDC thermograms related with the glass transition and the MWS relaxations. The decreases in the activation energy in the region of α relaxation can be attributed to effect of the polyol excess in the PU sample. The polyol excess also shifts the relaxations process in the low temperature direction, which might be attributed to the reduction of the PU molecules interaction. The second peak α' relaxation is related to MWS interfacial polarisation due to the existence of interfaces between soft and hard segments with different conductivities.

References

1. Grant GT, Taft RM, Wheeler S (2001) J Prosthet Dent 85:281. doi:10.1067/mpr.2001.114089
2. Chen G, Hu JW, Zhang MQ, Rong MZ (2005) Sens Actuators B 105:187. doi:10.1016/S0925-4005(04)00423-X
3. Claudé B, Gonon L, Verney V, Gardette JL (2001) Polym Test 20:771. doi:10.1016/S0142-9418(01)00022-8
4. Woods G (1987) The ICI polyurethane books. Wiley, Holland
5. Oertel G (1994) Polyurethane handbook, 2nd edn. Hanser, New York
6. Georgoussis G, Kyritsis A, Pissis P, Savelyev Yu V, Akhranovich ER, Privalko EG et al (1999) Eur Polym J 35:2007. doi:10.1016/S0014-3057(98)00288-2
7. Chu B, Gao T, Li Y, Wang J, Desper CR, Byrne CA (1992) Macromolecules 25:5724. doi:10.1021/ma00047a025
8. Guo A, Javni I, Petrovic Z (2000) J Appl Polym Sci 77:467. doi:10.1002/(SICI)1097-4628(20000711)77:2<467::AID-APP25>3.0.CO;2-F
9. Lyon CK, Garret VH, Frankel EN (1974) J Am Oil Chem Soc 51:331. doi:10.1007/BF02632378
10. Chian KS, Gan LHJ (1998) Appl Polym Sci 68:509. doi:10.1002/(SICI)1097-4628(19980418)68:3<509::AID-APP17>3.0.CO;2-P
11. Dahlke B, Poltrock R, Larbig H, Scherzer HDJ (1998) Cell Plast 34:361
12. Sakamoto WK, Kanda DHF, Andrade FA, Das-Gupta DKJ (2003) Meat Sci 38:1465. doi:10.1023/A:1022912312657
13. Malmonge JA, dos Santos MA, Sakamoto WK (2005) J Math Sci 40:4557. doi:10.1007/s10853-005-1117-6
14. Sakamoto WK, Shibatta-Kagesawa S, Kanda DHF, Fernandes SH, Longo E, Chierice GO (1999) Phys Status Solidi A Appl Res 172:265. doi:10.1002/(SICI)1521-396X(199903)172:1<265::AID-PSSA265>3.0.CO;2-N
15. Sakamoto WK, Kagesawa S, Kanda DHF, Das-Gupta DKJ (1998) Meat Sci 33:3325. doi:10.1023/A:1013233329595
16. Sakamoto WK, Kanda DHF, Carvalho CLJ (2000) Mater Sci Lett 19:603. doi:10.1023/A:1006790530934
17. Gross B (1964) Charge storage in solid dielectrics. Elsevier, NY
18. Ahmed MT, Fahmy T (2005) Polym Plastics Technol Eng 44:1559. doi:10.1080/03602550500209507
19. Van Turnhout J (1987) In: Sessler GM (ed) Electrets, 2nd edn, chapter 3. Springer-Verlag, Germany
20. Tsonos C, Apekis L, Zois C, Tsonos G (2004) Acta Mater 52:1319. doi:10.1016/j.actamat.2003.11.015
21. Kanapitsas A, Pissis P, Estrella AG (1999) Eur Polym J 35:923. doi:10.1016/S0014-3057(98)00075-5
22. Tsonos C, Apekis L, Viras K, Stepanenko L, Karabanova L, Sergeeva L (2001) Solid State Ionics 143:229. doi:10.1016/S0167-2738(01)00858-X
23. Spathis G, Niaounakis M, Kontou E, Apekis L, Pissis P, Christodoulides CJ (1994) Appl Polym Sci 54:831. doi:10.1002/app. 1994.070540701
24. Kyritsis A, Pissis P, Gomez-Ribelles JL, Monleon Pradas MJ (1994) Polym Sci B Polym Phys 32:1001. doi:10.1002/polb. 1994.090320605