

Electrical Properties of Poly(propylene terephthalate)

ANTONIO MOTORI, ANDREA SACCANI, LAURA SISTI

Dipartimento di Chimica Applicata e Scienza dei Materiali, Viale Risorgimento 2, Bologna, Italy

Received 27 August 2001; accepted 20 November 2001

ABSTRACT: Direct current (dc) and alternating current (ac) electrical behavior of a laboratory-synthesized semicrystalline poly(propylene terephthalate) is investigated. The dc charging/discharging currents and electrical conductivity are studied as a function of temperature and time of applied voltage. The conduction mechanisms are pointed out and related to the structural characteristics of the polymer. The ac properties (dielectric constant and loss factor) are investigated over a wide temperature and frequency range. The relaxation processes, which take place in the material, are disclosed and their origin is analyzed. The electrical behavior of poly(propylene terephthalate) is finally related to that shown by other thermoplastic polyesters. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2271–2275, 2002

Key words: poly(propylene terephthalate); electrical conductivity; dielectric relaxations and properties

INTRODUCTION

Engineering thermoplastic polyesters are a widely used family of materials, due to excellent physical, thermal, mechanical, and electrical properties combined with satisfactory processing characteristics. Among these polyesters, poly(propylene terephthalate) (PPT), first industrially synthesized at the beginning of the 1990s,^{1,2} did not reach widespread use, mainly due to its high cost. Its use was chiefly confined to the production of fibers^{2,3}; therefore, its mechanical properties have been deeply investigated and several sources of data can be found in literature. On the contrary, no investigation on the electrical behavior has been performed until now. Recently, a new method of synthesis of 1,3-propanediol has offered new possibilities in the marketing of this material.²

The purpose of this paper is thus to investigate the dc and ac electrical properties of PPT over a wide range of temperature and (for ac properties) of frequency, in order to check the suitability of this polymer for new engineering applications, mainly in the electrical and mechanical industries, where poly(ethylene terephthalate) (PET) and poly(buthylene terephthalate) (PBT) are already widely used.

EXPERIMENTAL

Material and Samples

The investigated PPT, free from additives and stabilizers and only containing the catalyst [Ti(OBu)₄] residuals, had the following characteristics⁵: glass transition temperature $T_g = 40^\circ\text{C}$ and melting point $T_m = 226^\circ\text{C}$, measured by differential scanning calorimetry (DSC) with a scanning rate of 10 °C/min; number-average molecular weight $M_n = 34,500$ and weight-average molecular weight $M_w = 81,600$ determined by size

Correspondence to: Antonio Motori (antonio.motori@mail.ing.unibo.it).

Journal of Applied Polymer Science, Vol. 85, 2271–2275 (2002)
© 2002 Wiley Periodicals, Inc.

exclusion chromatography (SEC); carboxyl end groups content: 25 meq/10⁶ g.

Specimens were molded under vacuum at 250°C in the form of disks 0.3–1.0 mm thick and 60 mm in diameter. At this temperature, neither significant thermal degradation phenomena occur, nor are memory effects of the previous structure present.⁵ Before electrical measurements, specimens were vacuum annealed at 150°C for 48 h. After this treatment, the polymer exhibited a crystallinity of about 60 wt %, as determined by DSC measurements, assuming a heat of fusion of 30 kJ/mol for the crystalline PPT.⁶

Electrical Measurements

The dc charging currents were measured as a function of time by the voltmeter-ammeter method, according to ASTM D257 Standard; a constant electrical field of 10 kV cm⁻¹ was applied over the temperature range 25–130°C. Hence, current-voltage characteristics, as well as dc electrical conductivity as a function of temperature, were obtained. After charging, discharging currents were also measured as a function of time, to detect possible dielectric relaxation effects in the ultralow frequency range (<10⁻² Hz) by the Hamon data treatment method and its improvements.⁷ Discharging currents measurements were started when quasi-steady-state values of the charging currents were obtained, in order to avoid systematic errors in the analysis of discharging transients.⁸

The ac measurements were performed according to ASTM D150 Standard over the frequency range 10²–10⁵ Hz and the temperature range –100–170°C. Relative dielectric constant and loss factor as a function of frequency and temperature were thus obtained.

Measurements of dc and ac properties were performed with the three-terminal cells and instrumentation elsewhere described,⁹ in a dynamic vacuum from the highest to the lowest temperature, to minimize the effects of accidental adsorption of gases or vapors on the samples surfaces. Before measurements, specimens were gold coated by vacuum deposition, in order to obtain the suitable three-terminal electrode configuration.

RESULTS AND DISCUSSION

The dc electrical conductivity (γ) at 1, 10, and 60 min after the application of a step voltage is plot-

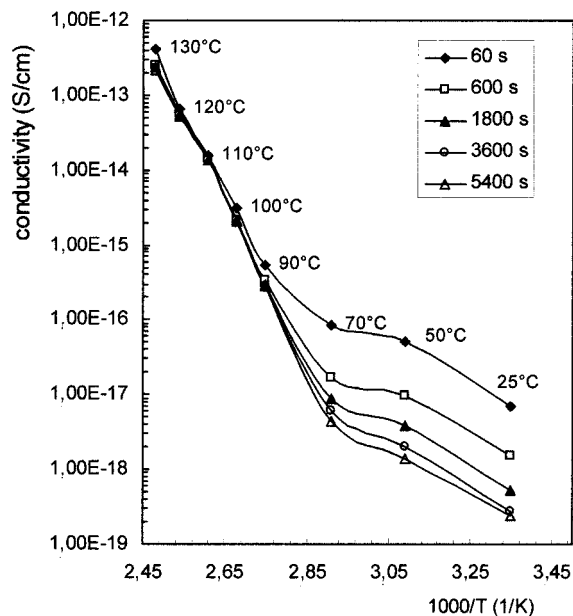


Figure 1 Isochronal electrical conductivity vs the reciprocal absolute temperature.

ted in Figure 1 as a function of the reciprocal absolute temperature.

The conductivity values fall approximately between 10⁻¹³ S/cm at 130°C and 10⁻¹⁸ S/cm at room temperature. These values are typical of excellent insulating materials and match those previously found for PBT in the same temperature range.¹⁰ A quite linear behavior can be observed only above 70°C, where transients are practically absent and steady-state values are quickly reached. Below this temperature, remarkable transient phenomena are present and the steady state is not observed even at the longest times investigated; this can be ascribed to strong polarization processes.

These results show that a transition takes place in the electrical behavior of PPT at about 70°C, which can be related to the glass transition of the polymer. Indeed, the glass transition detected by DSC measurements is slightly lower, but this is not unusual when different techniques are applied. Above the glass transition, conduction can be ascribed to the presence of ionic charge carriers, arising from the carboxyl end groups and characterized by high mobility. In fact, if an electrical field is applied, carboxyl end groups can ionize after dissociation of the existing hydrogen bond, according to the same mechanism proposed for PET and PBT,^{10,11} thus providing protons for conduction. This mechanism is also

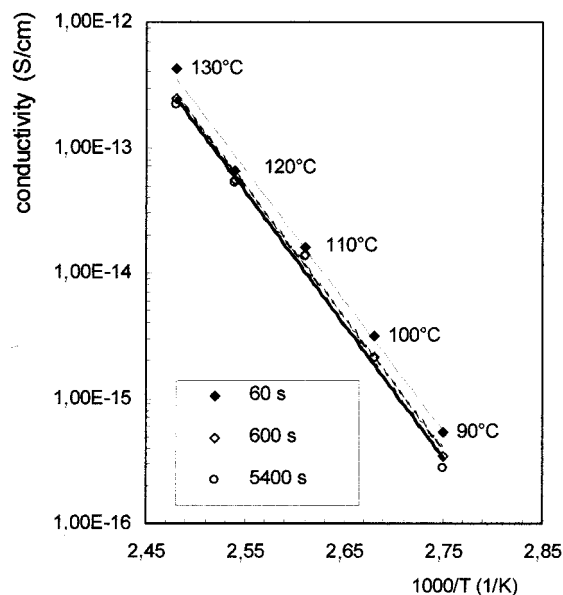


Figure 2 Isochronal electrical conductivity above the glass transition.

supported by the results of measurements carried out on PPT samples, having comparable molecular weight and containing different amounts of $-\text{COOH}$ end groups ($17\text{--}55 \text{ meq}/10^6 \text{ g}$); in fact, an increase of the conductivity values with the enhancement of the end groups content was observed. Below the glass transition, the mobility of ions is much lower; the observed conduction transients can be mainly related to polarization phenomena, while in the steady state the contribution of an electronic mechanism, through hopping of charge carriers between localized states, can be hypothesized.^{10,11}

Figure 2 shows the conductivity values above the glass transition as a function of the reciprocal absolute temperature. The quite linear behavior observed in the figure allowed us to derive an apparent activation energy of 203 kJ/mol for conduction (which is practically independent of the time of applied voltage, due to the absence of transients). This linear trend was not found in PBT, for which remarkable charge transients were observed.¹⁰

The dielectric loss factor at ultralow frequency, obtained by the Hamon treatment of the dc discharging current data above the glass transition, is reported in Figure 3. A relaxation process, with its maximum shifting to higher frequencies as temperature increases, can be observed. No relaxation was shown by data at temperatures below the glass transition. The process of Figure 3 can

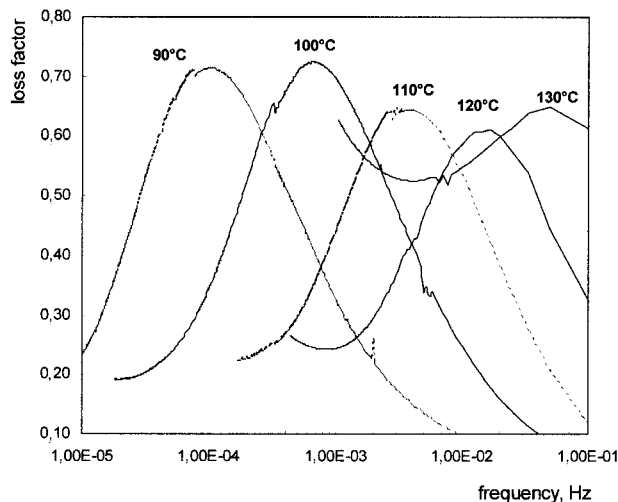


Figure 3 Loss factor at ultralow frequency.

be ascribed to an interfacial polarization of the Maxwell–Wagner–Sillars (MWS) type,^{10,12} due to the semicrystalline nature of the polymer and the different mobility of the ionic charge carriers in the ordered and disordered phases; only above the glass transition temperature ions can migrate in the amorphous regions and accumulate at the interfaces with the crystalline regions.

Figure 4 shows the transition map of the MSW polarization of Figure 3, obtained by plotting the frequency of the maxima as a function of the reciprocal absolute temperature. From the linear regression of the points an activation energy of 220 kJ/mol was calculated; the value is close to that found for dc conductivity (Fig. 2). This feature further supports the hypothesis previously made on the origin of this relaxation.

The results of ac measurements are reported in Figures 5 and 6, where the relative dielectric con-

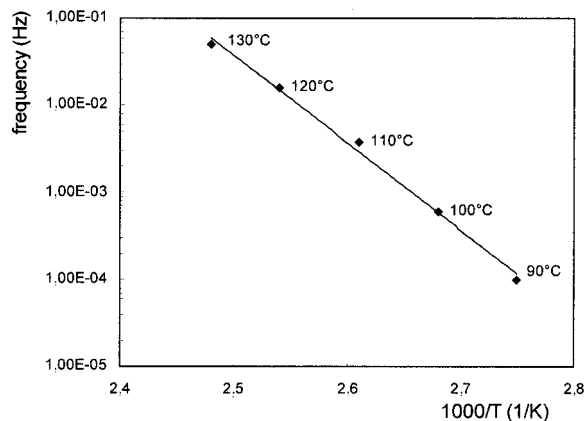


Figure 4 Transition map of the MWS polarization.

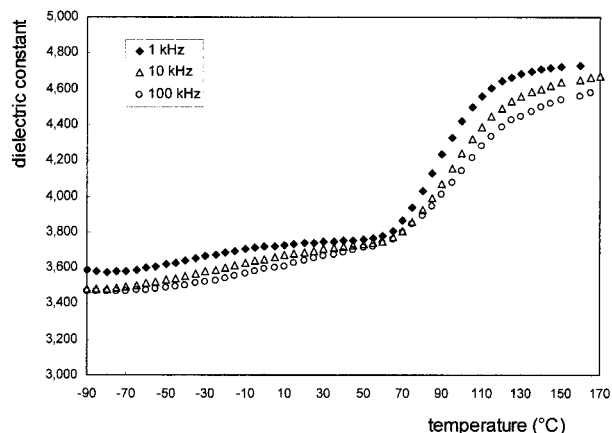


Figure 5 Dielectric constant as a function of temperature at different frequencies.

stant and loss factor, respectively, are plotted as a function of temperature at different frequencies. The dielectric constant (Fig. 5) continuously increases with increasing temperature and decreasing frequency; moreover, a steep increase is observed above the glass transition. Dielectric constant values are slightly higher than those found for PBT. Loss factor curves (Fig. 6) exhibit two relaxation peaks, both shifting to higher temperatures as frequency increases, henceforth named β (low temperature) and α (high temperature) peak. The high-temperature peak, much narrower and higher in magnitude than the β one, can be ascribed to large scale motions of the chain segments in the amorphous phase of the polymer above the glass-rubber transition. The steep increase of the dielectric constant above the glass

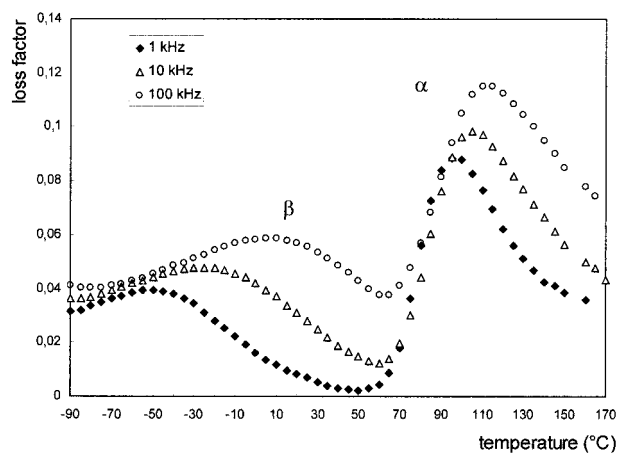


Figure 6 Dielectric loss factor as a function of temperature at different frequencies.

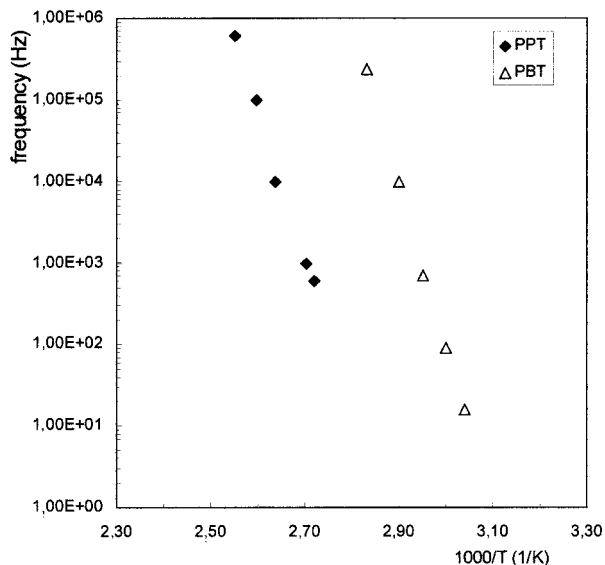


Figure 7 Transition map of the α process.

transition (Fig. 5) is also related to this relaxation. The β peak can be related to local (micro-brownian) conformational motions of the chains below the glass transition.

Figures 7 and 8 show the transition map of the α and β relaxation, respectively; the same data, previously obtained for PBT and falling in the same frequency range, are also reported for comparison. For PPT, both processes are shifted to higher values of temperature: this behavior can be ascribed to its higher glass transition temper-

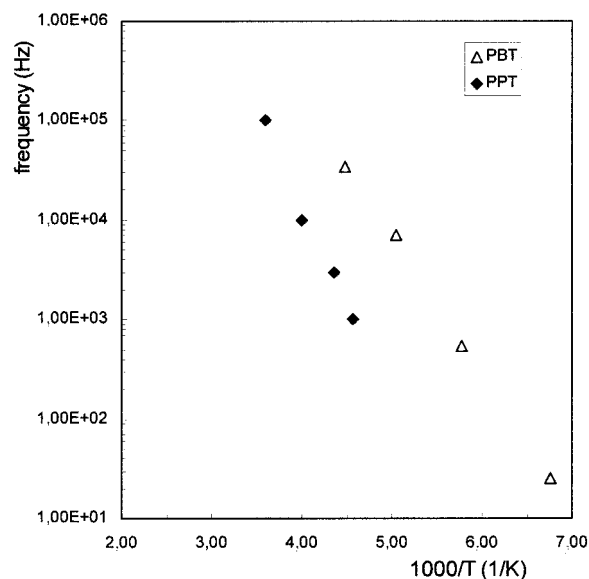


Figure 8 Transition map of the β process.

ature. By drawing a linear regression of the points in all the plots, an average activation energy of 340 and 38 kJ/mol was calculated for the α and β process, respectively. For the same relaxations, values of 360 and 26 kJ/mol were obtained for PBT, while values of 380 and 54 kJ/mol were reported for PET by other authors.¹³ For the three materials, only small differences between the energy values of the α relaxation can be observed; indeed, it can be affected by polymer features, such as the crystallinity degree and the morphology of the crystalline phase. The activation energy of the β process, increases as the number of $-\text{CH}_2-$ units in the monomer is reduced, and thus, the polyester chain flexibility is decreased; this relaxation can be considered practically independent of morphology.^{14,15}

The overall good insulating characteristics exhibited by PPT can disclose promising engineering application for this polymer, mainly in the electrical industry.

CONCLUSIONS

The dc electrical properties of poly(propylene terephthalate) exhibit a transition at about 70°C, which can be related to the glass transition of the polymer. Above the glass transition, dc conductivity can be ascribed to protons arising from ionization of the carboxyl end groups; at low temperature conduction can be mainly related to polarization phenomena.

The ac properties display three relaxation processes. Two of them, the α glass-rubber and the β subglass polarization, are ascribed to large-scale and local chain motions, respectively. The third

relaxation occurs at ultralow frequency and is related to the polarization of ionic charge carriers at the interfaces between the amorphous and crystal phases of the polymer.

The overall good insulating characteristic exhibited by poly(propylene terephthalate) can disclose new engineering applications, mainly in the electrical industry, for this material.

REFERENCES

1. Traub, H. L.; Hirt, P.; Herlinger, H.; Oppermann, W. *Ang Makromol Chem* 1995, 230, 179–187.
2. Shaunoff, S.; Shmidt, W. *Chem Fiber Int* 1996, 46, 263.
3. Chuah, H. H. *Chem Fiber Int* 1996, 46(6), 424.
4. Brown, H. S.; Chuah, H. H. *Chem Fiber Int* 1997, 47(1), 72.
5. Berti, C.; Bonora, V.; Lotti, N.; Montanari, G. C.; Motori, A.; Munari, A.; Saccani, A.; Sisti, L. *Proc ISEI 2000*, Austin, Texas, April 2–5, 2000.
6. Pyda, M.; Boller, A.; Grebowicz, J.; Chuah, H.; Lebedev, B. V.; Wunderlich, B. *J Polym Sci: Part B: Polym Phys* 1998, 36, 2499.
7. Hamon, B. V. *Proc IEE*, 99, Pt IV, 1952, p 151.
8. Wintle, H. J. *J. Non-Cryst Solids* 1974, 15, 471.
9. Marrone, G.; Nicolini, P.; Motori, A.; Sandrolini, F. *Proc 34th CIGRE*, Paris, August 1992, paper 15-402.
10. Sandrolini, F.; Motori, A.; Saccani, A. *J Appl Polym Sci* 1992, 44, 765.
11. Sacher, E. *J Macromol Sci Phys B* 1970, 4, 441.
12. Das Gupta, D. K.; Joyner, K. *J Phys D* 1976, 9, 829.
13. Hedvig, P. In *Dielectric Spectroscopy of Polymers*; A. Hilger, Ed.; Bristol, 1977; p 398.
14. Boyd, R. H. *Polymer* 1985, 26, 323.
15. Coburn, J. C.; Boyd, R. H. *Macromolecules* 1986, 19, 2238.