Macromol. Symp. **2004**, *212*, 479-484

Influence of Morphological and Conformational Changes on the Molecular Mobility in Poly(ethylene naphthalene-2,6-dicarboxylate)

Didier Colombini,[1] *Noureddine Zouzou,*[2] *Juan Jorge Martinez-Vega**[2]

[1] Department of Polymer Science & Engineering, Lund University, Lund Institute of Technology, Box 124, SE – 22100 Lund, Sweden
[2] Laboratoire de Génie Electrique de Toulouse (UMR-CNRS 5003) Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France
E-mail: juan.martinez@lget.ups-tlse.fr

Summary: Dynamic electric (DEA) and mechanical (DMA) analyses were combined to explore the relaxational processes in amorphous and semicrystalline poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) samples. Differential scanning calorimetry measurements were carried out to investigate the crystallinity of the samples following isothermal annealing treatment at 443 K. The two secondary relaxations β and β*, the main α relaxation, as well as the ρ-relaxational process, were revealed by both electric and mechanical viscoelastic responses of the PEN samples. DMA results clearly identified the above T_α loss factor peak, ρ, as a probe of the cold crystallization. However, the association of both DMA and DEA investigations pointed out that electric and non-electric aspects might govern the ρ-process.

Keywords: cold crystallization; dynamic electric analysis; dynamic mechanical analysis; PEN; ρ-relaxation

Introduction

Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) is of particular interest in electrical applications, since its aromaticity leads to advantageous mechanical properties and to chemical and thermal stability. Recently, the microstructure/property relationship in amorphous and various semicrystalline PEN samples has been investigated[1-4], and four distinct relaxational processes (β, β*, α, and ρ, with increasing temperature) were reported. The present work deals with both dynamic mechanical and electric analyses to explore the influence of the crystallinity on the molecular mobility in PEN.

DOI: 10.1002/masy.200450861

Experimental

Amorphous PEN supplied by DuPont de Nemours (Luxembourg) was used. As previously detailed[3,5,6], as-received amorphous PEN samples were maintained at 443 K for 5, 15, 30, 45, 60, 120, and 180 min in order to reach various crystallinities, which were then estimated by differential scanning calorimetry DSC 2010, TA Instruments). Thus, following their respective isothermal annealing treatment (performed at 443 K under nitrogen atmosphere), the samples were cooled down to 303 K (10 K/min), and the DSC traces were recorded from 303 K to 573 K (10 K/min).

The DMA 2980 (TA Instruments) was used operating in tensile mode under isochronal conditions (10 Hz, from 173 K to 513 K with a heating rate of 2 K/min) to measure the temperature dependence of mechanical viscoelastic properties of PEN samples.

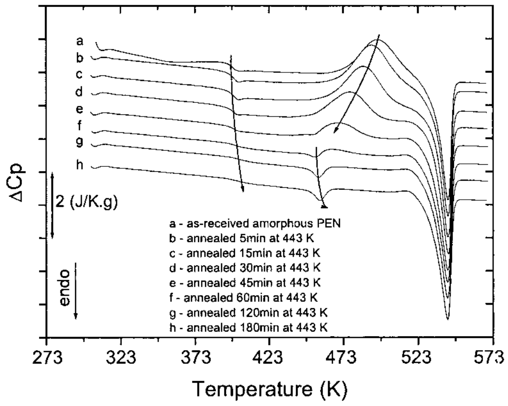
The dynamic electric analysis was carried out by using the DEA 2970 (TA Instruments) under isochronal conditions (10 Hz, from 173 K to 453 K with a heating rate of 2 K/min) to measure the temperature dependence of complex permittivity ε^*.

In order to achieve same controlled conditions for all the samples, the isothermal annealing treatment (at 443 K) was systematically performed in the furnace of the three instruments.

Results and Discussion

The DSC traces of as-received and annealed PEN samples are given in Fig. 1. First, the glass transition of the amorphous phase can be seen (around 398 K): obviously, the change of ΔC_p baseline becomes less pronounced when the isothermal annealing time increases. A cold crystallization exothermic peak is then clearly visible in curves a to e in Fig. 1.

Following the increase in the amount of the crystalline phase resulting from the increase of the annealing exposure, the area of this exothermic contribution significantly decreases going from curves a to e. After 45 min at 443 K (curves f - h), the cold crystallisation peak cannot be detected any longer and a small pre-melting peak is observed instead. As expected, at higher temperatures (around 443 K), the melting peak of PEN does not appear to be affected by the duration of the isothermal annealing treatment. In addition, on the basis of melting enthalpy results, it equals 103.4 J/g[7] for a 100 % crystalline PEN sample. The crystallinities of the annealed samples were estimated and are given in the table in Fig. 1.



Sample	Isothermal annealing At 443 K (min)	Crystallinity (%)
a	0	0.3
b	5	1.1
c	15	5.1
d	30	14.2
e	45	29.8
f	60	39.4
g	120	41.5
h	180	42.3

Figure 1. DSC traces of the as-received amorphous and annealed PEN samples.

Figure 2 reports the temperature dependence of the storage modulus (E') and the loss factor (tan δ) for all amorphous and annealed PEN samples. When the temperature increases, three relaxation processes – β (around 223 K), β^* (around 358 K), and α (around 413 K) relaxations – are evidenced. Their molecular assignments have been discussed in detail previously[6]. Insofar as the α relaxation is associated with the anelastic manifestation of the glass transition of PEN, the corresponding peaks of tan δ are accompanied by an important decrease in *E'* for all the samples. After passing through the glass transition, the amorphous PEN phase begins to crystallize. As a result of the cold crystallization (occurring in amorphous and short-time annealed samples), a rapid increase in the storage modulus as well as the occurrence of a shoulder in tan δ related to the ρ-process can be observed above 453 K.

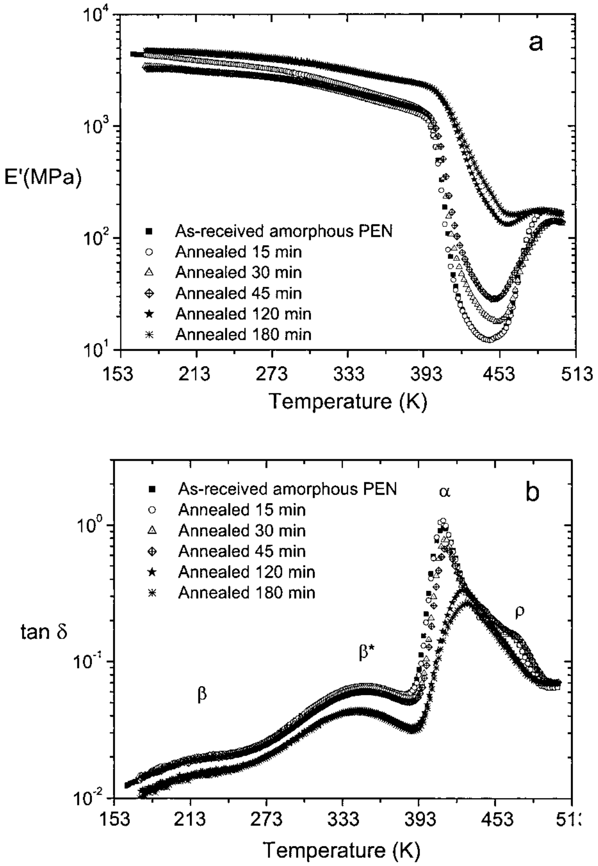


Figure 2. Mechanical viscoelastic properties of the as-received amorphous and annealed PEN samples: (a) storage modulus *E*' and (b) loss factor tan δ *versus* temperature (at 10 Hz).

Similarly to mechanical thermograms, the temperature dependence of permittivity (ε') and the loss factor (tan δ) also reveal the three β, β^*, and α relaxations of PEN, the corresponding peaks of tan δ being associated with an increase in ε' (Fig. 3). It was then deemed to be of interest to combine both mechanical and electric approaches to further investigate the molecular mobility in the amorphous and annealed PEN samples, especially for the high-temperature processes. Independently of the technique, the maxima of either the mechanical or the electric loss peaks associated with the α relaxation are shifted toward higher temperatures, when the crystallinity increases. Both decreasing values of the dielectric permittivity and increasing mechanical storage moduli are obtained, when the cold crystallization process takes place. However, the ratio of the magnitude of both α- and ρ-relaxation peaks appears to be much more important in the case of dielectric measurements than when a mechanical stress is applied to the samples. As a result, the so-called ρ-relaxation can be considered as governed by both electrical and non-electrical aspects.

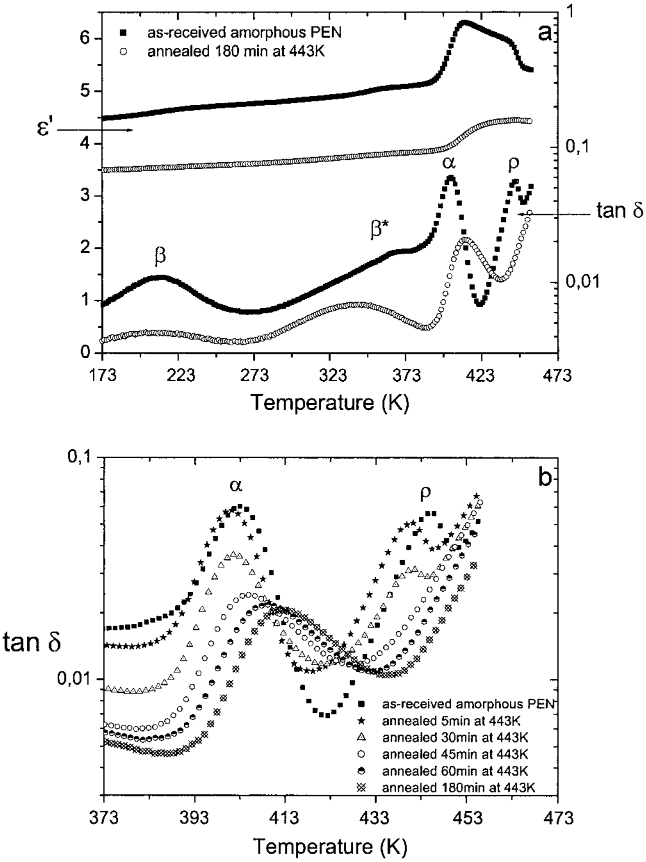


Figure 3. Dielectric viscoelastic properties of the as-received amorphous and annealed PEN samples: permittivity ε' and loss factor tan δ *versus* temperature (at 10 Hz).

Similarly to mechanical thermograms, the temperature dependence of permittivity (ε') and the loss factor (tan δ) also reveal the three β, β^*, and α relaxations of PEN, the corresponding peaks of tan δ being associated with an increase in ε' (Fig. 3). It was then deemed to be of interest to combine both mechanical and electric approaches to further investigate the molecular mobility in the amorphous and annealed PEN samples, especially for the high-temperature processes. Independently of the technique, the maxima of either the mechanical or the electric loss peaks associated with the α relaxation are shifted toward higher temperatures, when the crystallinity increases. Both decreasing values of the dielectric permittivity and increasing mechanical storage moduli are obtained, when the cold crystallization process takes place. However, the ratio of the magnitude of both α- and ρ-relaxation peaks appears to be much more important in the case of dielectric measurements than when a mechanical stress is applied to the samples. As a result, the so-called ρ-relaxation can be considered as governed by both electric and non-electric aspects.

Conclusion

In this paper, both dynamic electric and mechanical analyses were successfully associated to explore the relaxational processes in amorphous and semicrystalline PEN samples. First, differential scanning calorimetry measurements were performed to estimate the consequence of more or less long-time isothermal annealing at 443 K for the crystallinity of PEN samples. Then, the crystallinity dependence of the viscoelastic properties of the samples was investigated. In particular, DMA results clearly identified the above T_g loss factor peak as a probe of the cold crystallization (observed only for the amorphous and the short-time annealed samples). Although the influence of the cold crystallization also occurs in the dielectric response of the samples, DEA results showed that the high-temperature loss peak (associated with the ρ-relaxation) is simultaneously governed by electric and non-electric aspects. The ambiguity of this relaxation in the literature could therefore find its source in such a bimodal origin.

[1] J.C. Cañadas, J.A. Diego, M. Mudarra, J. Belana, R. Diaz-Calleja, M.J. Sanchis, C. Jaimés, *Polymer*, **1999**, *40*, 1181.
[2] A. Nogales, Z. Denchev, I. Sics, T.A. Ezquerra, *Macromolecules*, **2000**, *33*, 9367.
[3] J.J. Martinez-Vega, N. Zouzou, L. Boudou, J. Guastavino, *IEEE Trans. Diel. Electr. Insul.*, **2001**, *8*, 776.
[4] L. Hardy, I. Stevenson, G. Boiteux, G. Seytre and A. Schönhals, *Polymer*, **2001**,42, 5679.
[5] N. Zouzou, C. Mayoux, J.J. Martinez-Vega, *Rev. Int. Génie Electr.*, **2000**, *3*, 513.
[6] N. Zouzou, D. Colombini, J.J. Martinez-Vega, *Polymer*, **2002**, submitted.
[7] S. Z. Cheng, B. Wunderlich, *Macromolecules*, **1988**, *21*, 789.