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Polymer 42 (2001) 5679–5687

polymer

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Dielectric and dynamic mechanical relaxation behaviour of poly(ethylene 2,6 naphthalene dicarboxylate). I. Amorphous films

L. Hardy[a], I. Stevenson[a,*], G. Boiteux[a], G. Seytre[a], A. Schönhals[b]

[a]*Laboratoire des Matériaux Polymères et Biomatériaux (UMR CNRS 5627), Université Claude Bernard, Lyon 1, ISTIL 43, Boulevard du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France*
[b]*Bundesanstalt für Materialforschung and -prüfung, Unter den Eichen 87, D-12205 Berlin, Germany*

Received 1 June 2000; received in revised form 1 January 2001; accepted 8 January 2001

Abstract

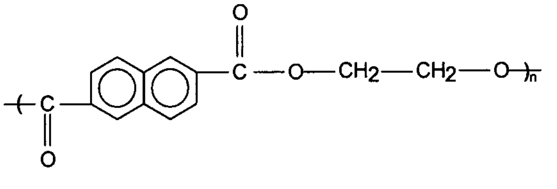
The dielectric and dynamic mechanical behaviour of amorphous poly(ethylene 2,6 naphthalene dicarboxylate) (PEN) and of thermally annealed samples is reported as a function of the morphology. During the treatment at temperatures close to the melting temperatures the samples become semi-crystalline. differential scanning calorimetry (DSC) shows that the glass transition temperatures do not change significantly with the thermal treatment. However the degree of crystallinity as well as the melting temperatures increase with the annealing temperature. Both dielectric (DEA) and dynamic mechanical (DMA) analysis display three relaxation processes. In order of decreasing temperature the α-relaxation due to the glass transition, the β^*-process assigned to the out of plane movements of the naphthalene rings or aggregates of it and the β-relaxation due to local molecular motions of carbonyl groups. The α-relaxation process shifts to higher temperatures for the semi-crystalline samples compared to the amorphous one. On the contrary, at a fixed frequency the temperature associated to β^*-relaxation is higher for the amorphous sample than for the semi-crystalline ones. The associated apparent activation energies are rather high and depend on the thermal treatment and also surprisingly on the method of measurement. It is concluded that the β^*-relaxation is probably due to cooperative molecular motions of the naphthalene groups which aggregate in the amorphous state and that these aggregates are prevented from forming when the degree of crystallinity changes due to the thermal treatment. Finally, the activation energy for the β-process is nearly independent of the thermal treatment and the value agrees with that found for poly(ethylene terephthalate) (PET).

Keywords: Poly(ethylene 2,6 naphthalene dicarboxylate); Dielectric relaxation spectroscopy; Dynamic mechanical analysis

1. Introduction

Poly(ethylene 2,6 naphthalene dicarboxylate) (PEN) is a thermoplastic polyester which combines thermal stability, degradation resistance, low permeability, with excellent mechanical and dielectric properties [1]. In general, PEN has more favourable properties when compared to poly(ethylene terephthalate) (PET). Like PET, PEN can be used in the packaging industry (bottles). But because it can be also obtained as very thin (1 μm) films, PEN can be used as a base film support for very thin gauge electromagnetic tapes such as audio, video and computer tapes [2,3] and also in capacitors. In this field, it should be mentioned that PEN has a dielectric permittivity smaller and dielectric loss factor lower than that of PET.

In general the properties of PEN depend strongly on the morphology of the sample. Therefore, to tailor the properties of PEN to a given application it is very important to know the structure-property relationships and to control the morphology. During the last two decades, relatively few papers about PEN have been published, which deal mainly with semi-crystalline bi-axially stretched samples. The general formula of PEN is:



The chain structure of PEN is close to that of PET but PEN has a naphthalene instead of a phenyl group in the repeating unit which leads to a stronger rigidity of the macromolecular chain.

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* Corresponding author. Tel.: 00-33-4-7244-6213; fax: 00-33-4-7243-1249.

E-mail addresses: steven@matplast.univ-lyon1.fr (I. Stevenson), andreas.schoenhals@bam.de (A. Schönhals).

0032-3861/01/$ - see front matter
PII: S0032-3861(01)00028-3

PEN crystallises in two triclinic forms [4]: the α and the β form which have been investigated [5] by WAXS. The β form is characterised by four chains per unit cell and can only be obtained under very special conditions which include rapid quenching and annealing procedures. Therefore generally, PEN is crystallised in the α form which corresponds to one chain per unit cell. During annealing the crystallinity increases and additionally during the stretching the crystallites will be oriented. This includes also, an orientation of the chains in the amorphous regions of the sample, therefore the properties become anisotropic and an orientation of the chains in the machine (MD) and the transverse direction (TD) has been observed [6,7]. Typical differences in characteristic values of the mechanical properties for biaxially stretched PEN and PET films are reported elsewhere [8].

The first study on PEN dealing with dielectric properties was undertaken by Bellomo et al. [9] for semi-crystalline samples. Three relaxation processes: α-, β^*-, and β- were observed in order of decreasing temperature. The high temperature relaxation was associated with the glass transition which is due to the micro-Brownian motions of the chain segments, originating from a conformational rearrangement of the chains in the amorphous regions of the sample. If amorphous or semi-crystalline PEN samples are thermally treated at temperatures higher than T_g, the amplitude of the α-relaxation peak decreases due to the decrease of the amount of the amorphous phase, due to an increase in crystallinity which induces further structural changes [10].

According to Bellomo, the relaxation process called β^*-relaxation is probably associated to out-of-plane motions of the naphthalene ring [11]. The reported value of the activation energy estimated from dielectric measurements is rather high at 118 kJ/mol. This suggests that the underlying motional process is cooperative in nature. The β-relaxation is related to local fluctuations of the ester groups [12] because the chain position and the activation energy of this process is quite similar to the β-relaxation of PET [13].

More recently Cañadas et al. have comparatively studied the amorphous and partially crystalline PEN samples by TSDC, dielectric analysis (DEA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) [1,14]. They reported an α- and a β^*-process and in particular the influence of the thermal treatment on the activation energy of the α^*-process was studied. They found activation energies between 29 and 77 kJ/mol depending on the thermal treatment of the samples. The higher the annealing temperature, the lower is the activation energy. These values do not agree with the activation energies given by Bellomo. Moreover these values seem to be rather low for such a relaxation process. Ageing investigations on copolymers of PET and PEN are also published [15], but surprisingly no β^*-process was described even for pure PEN. This indicates again the complexity of the structure–properties relationships of PEN and the importance of the thermal history of the sample, including the orientation and therefore the processing conditions.

To summarise, all the discussed results concerning mechanical and dielectric relaxation experiments, the understanding of the structure–properties relationships does not appear complete. Moreover, a certain amount of contradictory results exist in recent literature. It is clear that the morphology of such a material is quite complicated depending on the treatment. Therefore, it appears necessary to re-investigate the properties of PEN, by initially considering a study of the amorphous state. Secondly, it is important to produce defined structures where these amorphous samples are annealed under controlled conditions at different annealing temperatures to obtain different degrees of crystallisation. Since fully amorphous isotropic samples have been used to obtain the crystalline ones, orientation effects on the properties can be excluded in this study. The influence of orientation will be the subject of a subsequent paper. Dielectric and dynamic mechanical relaxation spectroscopy is used, considering the molecular mobility as a probe for structure. These investigations are supplemented by thermal analysis. Further work concerning SAXS and WAXS studies [16] as well as IR investigations [17] to investigate the structure directly are in progress.

2. Experimental

PEN samples were obtained from Du Pont de Nemours in the form of amorphous films with a thickness of 300 μm. Studies were made on the virgin amorphous material and three semi-crystalline samples obtained by annealing the amorphous one at annealing temperatures of 240, 250 and 260°C. It should be mentioned that the annealing temperatures are close to the melting temperature obtained by DSC (see below) and so they are therefore higher than those applied by Cañadas et al. [14]. The thermal treatments were performed in the oven of the dynamic mechanical instrument described further on to achieve the same controlled conditions for each sample. The films were heated from room to the annealing temperatures at a rate of 10 K/min. For the corresponding DSC experiments, a similar heating rate was chosen to quantify the structure obtained by the annealing procedure. The annealing time was one hour and after that period the sample was slowly cooled down to room temperature at a rate of 5 K/min. During the whole thermal treatment the samples undergo cold crystallisation (heating up to the annealing temperature) and melt partially depending on the selected annealing temperature. As a consequence this leads to a modification of the initial amorphous state

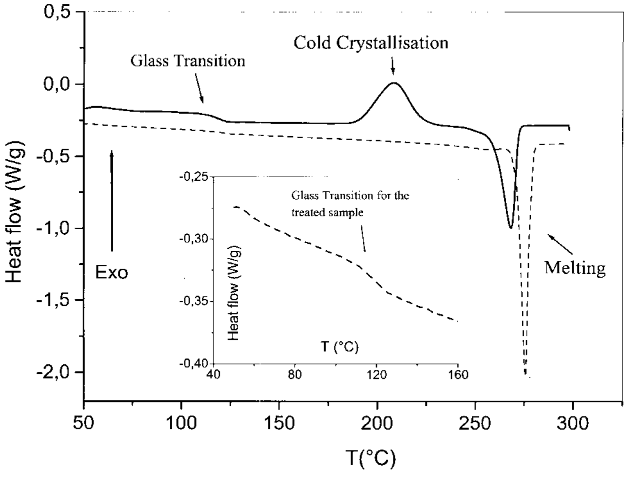

Fig. 1. DSC thermograms of PEN samples. Solid line is for amorphous sample, dashed line for thermal treated sample at 240°C. The inset shows glass transition for the thermal treated sample.

of the samples which become semi-crystalline with a spherulitic structure.

DSC measurements were carried out using a 2920 TA Instrument between 50 and 300°C with a heating rate of 10 K/min. Sample weights were approximately 10 mg. Temperature calibration was made using indium. All samples were sealed in aluminium pans and the measurements were performed under a high purity nitrogen atmosphere. The glass transition temperature T_g has been estimated from the onset temperature. Crystallisation and melting temperatures were taken from the maximum positions of the peaks. The corresponding enthalpies were calculated by the area under the peak using standard procedures.

The dynamic mechanical properties of PEN samples were studied with a DMA 2980 TA Instruments analyser applying tensile stress. The complex elastic modulus $E^* = E' + iE''$ (E', real part or storage modulus; E'', loss part; $\tan \delta_{\mathrm{DMA}} = E''/E'$; $\mathrm{i} = (-1)^{1/2}$) was measured at frequencies of 1, 3, 5, 7, 10, 12 and 15 Hz. During the measurement the temperature was increased from −90 to 230°C at a rate of 1 K/min. The dimensions of the samples were 15 mm in length and 5 mm in width.

DEA was carried out using a DEA 2970 TA Instruments spectrometer. Its measures the complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$ in the frequency range from 10 to 50 kHz (ϵ', real part; ϵ'', imaginary or loss part; $\tan \delta_{\mathrm{DEA}} = \epsilon''/\epsilon'$). Sputter coated ceramic sensors (electrodes) were used and 25×25 mm samples were metallised by evaporation with aluminium to insure a good electrical contact. A 300 N compression force between the ceramic electrodes was also applied. Samples were placed in a glass bell jar under a nitrogen gas flow to avoid oxidation during the increase of the temperature. The dielectric properties were measured in the temperature range from 100 to 230°C with a heating rate of 2 K/min.

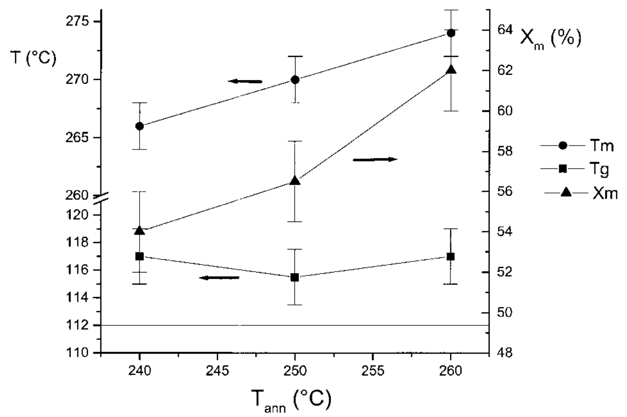

Fig. 2. Dependence of the glass transition temperature T_g (■), the melting temperature T_m (●) and the degree of crystallisation X_M (▲) on the annealing temperature T_{ann}. The lines are guides for the eyes. The horizontal line represents the glass transition temperature for the amorphous sample.

3. Results and discussion

3.1. Thermal behaviour

The DSC trace of the amorphous PEN sample is displayed in Fig. 1 together with the thermogram of a thermal treated sample annealed at 240°C. For the amorphous sample the glass transition temperature is obtained at 112°C, the maximum of cold crystallisation at 189°C and the melting temperature at 266°C. The degree of crystallinity X has been calculated using the crystallisation enthalpy of a 100% crystalline sample $\Delta H_{f,\ 100\%} = 103.4$ J/g [18]. For the annealed sample the cold crystallisation process is strongly depressed. Furthermore, the glass transition is barely visible in the original scan but the inset of Fig. 1 shows that it can be easily identified for the annealed samples. For the three temperature annealed samples, the melting temperature and degree of crystallinity are plotted in Fig. 2 as a function of the annealing temperature. As expected, the melting temperature and the degree of crystallinity increase with the annealing temperature which can be explained with an increase of the size of the crystalline entities and/or perfecting of these if annealing temperature increases (see Fig. 2). On the contrary, the variation of the glass transition temperature with the annealing temperature is not significant (±1 K which is within the range of experimental error). There is only approximately a 4 K difference in the glass transition temperature between the amorphous and the annealed samples.

3.2. Relaxation behaviour

In the Sections 3.2.1 and 3.2.2, the results obtained by each relaxation method are presented separately, where within the section each relaxation process is described in order of increasing temperature.

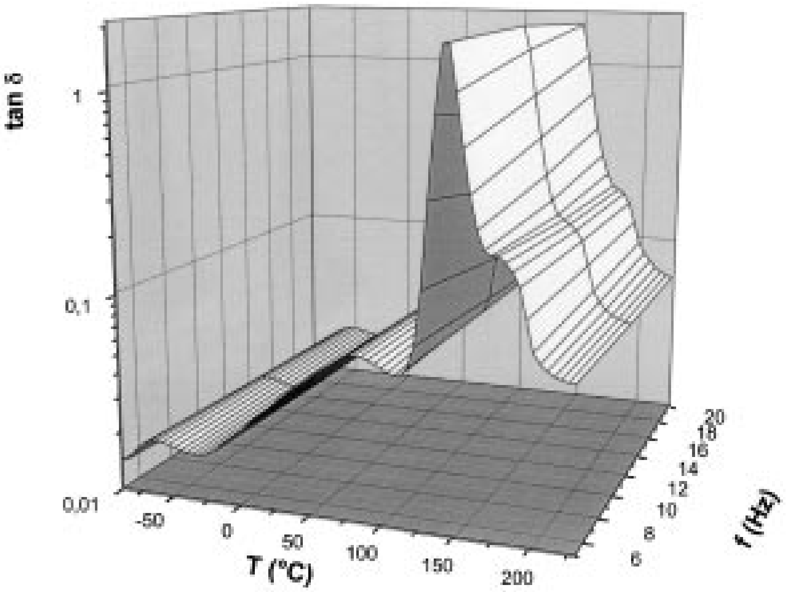

Fig. 3. tan δ_{DMA} for the amorphous sample as a function of frequency (ranging from 1 to 15 Hz) and temperature.

3.2.1. Dynamic mechanical analysis

Fig. 3 shows the 3-D plot of tan δ_{DMA} vs. temperature and frequency. Three relaxation processes indicated by peaks of tan δ_{DMA} are observed. They are called β-, β*-, α-relaxation in order of increasing temperature or decreasing frequency. Moreover a cold crystallisation region is visible on the high temperature side as a shoulder of the main amplitude α-relaxation peak at 190°C (in agreement with the DSC experiment). Fig. 4 shows tanδ_{DMA} vs temperature at 10 Hz for the amorphous sample. Furthermore, the behaviour of the amorphous sample is compared to a film which is treated at 240°C (see Fig. 4). Due to the crystallisation process, the intensity of the β-, the β*-and the α-relaxation decreases significantly because the content of the amorphous phase is decreased.

For each relaxation process the temperature of maximal loss can be extracted and plotted with corresponding frequency in the Arrhenius map. Each relaxation process is analysed separately.

3.2.1.1. β-Relaxation:

In Fig. 5 the Arrhenius or relaxation map for the β-relaxation is given. The data can be described by an Arrhenius equation express as:

$$f = f_{\infty} \exp\left[-\frac{E_{\mathrm{A}}}{kT}\right], \tag{1}$$

where E_{A} is the activation energy, f_{∞} is the pre-exponential factor, k is Boltzmann constant and T is temperature. The estimated activation energy is collected in Table 1.

An alternative approach to describe the data is the Eyring theory [19] which gives

$$f = \frac{kT}{2\pi h} \exp\left[-\frac{\Delta H^{*}}{kT}\right] \exp\left[-\frac{\Delta S^{*}}{kT}\right], \tag{2}$$

where as usual h is Planck's constant, ΔH^{*} and ΔS^{*} denote the activation enthalpy and the entropy respectively. Applying the general relationship $E_{\mathrm{A}} = \Delta H^{*} + kT$, the quantities ΔH^{*} and ΔS^{*} can be estimated from Eqs. (1) and (2) as given in Table 1.

Compared to the α- and the β*-relaxation, the intensity or the strength of the β-process is quite low. The thermal treatment causes a further decrease in the amplitude of tan δ in the temperature region of the β-process (Fig. 4). The decrease in the intensity of this relaxation process is clearly due to the reduced amount of the amorphous phase since, as previously stated, the thermal treatment leads to a crystallisation of the polymer. Nevertheless, a β-relaxation peak can be detected even for the annealed samples and the activation parameter can be estimated. For all annealing

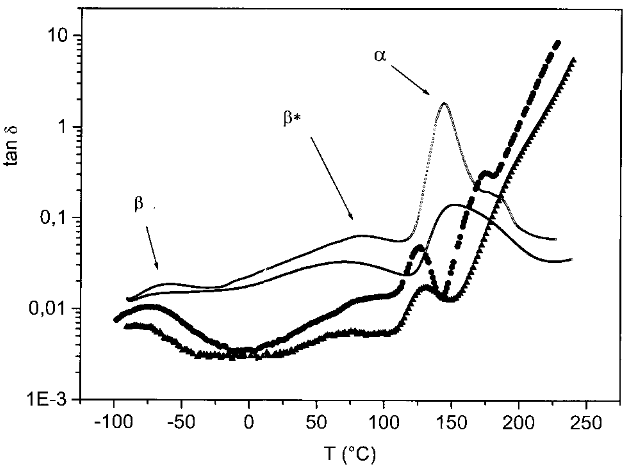

Fig. 4. tan δ_{DMA} vs. temperature at a frequency of 10 Hz. Amorphous sample DMA (○) and DEA (●); thermal treated sample at 240°C DMA (△) and DEA (▲).

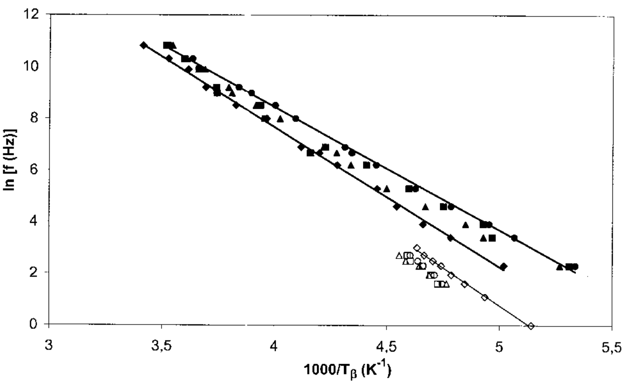

Fig. 5. Relaxation map for the β-relaxation. Open symbols DMA data, filled symbols DEA data. (◇, ◆) — amorphous sample, (□, ■) — thermal treatment at 240°C, (△, ▲) — thermal treatment at 250°C, (○, ●) — thermal treatment at 260°C.

temperatures the activation energy appears to be slightly higher than the activation energy for the non-treated sample (Table 1). However, the significance of this difference cannot be confirmed on the limited frequency range which is available from the mechanical measurements. Fig. 5 shows that the data for the thermal treated samples can be also described by the same activation energy as the data for the non-treated sample.

3.2.1.2. β^*-relaxation: Fig. 6 displays the relaxation map for the β^*-relaxation. As for the β-process, the data for the β^*-process too, can be described by an Arrhenius equation. Hence, the activation energy as well as the activation enthalpy and the entropy can be calculated. The corresponding values are shown in Table 2. The activation energy for the β^*-process is essentially higher than the value obtained for the β-relaxation. Also the values of the estimated activation entropy ΔS^* and enthalpy ΔH^* are high (Table 2). This indicates that the molecular motions which are responsible for the β^*-process are cooperative or at least coordinative to some extent.

For the thermal treated samples, the β^*-relaxation region is shifted to lower temperatures (see Fig. 4). The data can be analysed and the activation parameters (E_A, ΔS^* and ΔH^*) can be extracted (see Table 2). Comparing these values with those for the non treated samples, it can be seen that the annealing procedure causes a drastic decrease of the activation energy. The corresponding values of ΔS^* and ΔH^* are also essentially lower. This can be regarded as an indication that the cooperativity of the molecular motions responsible for the β^*-relaxation decreases with thermal treatment.

3.2.1.3. α-relaxation: The relaxation map of the α-relaxation is presented in Fig. 7. The corresponding trace in this plot is curved and cannot be described by the Arrhenius formula. However the Vogel/Fulcher/Tamman-(VFT-) equation [20,21] which is characteristic for the dynamics of the glass transition can be used to fit the data.

Table 1

Activation energies calculated with Arrhenius equation, variation of enthalpy and entropy calculated with Starkweather formalism in the case of the β relaxation for the amorphous and the three annealed at 240, 250, and 260°C samples obtained from viscoelastic and dielectric measurements

	Ea(β) (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
DMA			
PEN 300 μm amorphous	49 ± 5	47 ± 5	15 ± 2
PEN 300 μm annealed 240°C, 1 h	64 ± 6	62 ± 6	72 ± 7
PEN 300 μm annealed 250°C, 1 h	52 ± 5	50 ± 5	22 ± 2
PEN 300 μm annealed 260°C, 1 h	56 ± 5	54 ± 5	42 ± 4
DEA			
PEN 300 μm amorphous	45 ± 5	43 ± 4	8 ± 1
PEN 300 μm annealed 240°C, 1 h	39 ± 4	37 ± 4	− 13 ± 2
PEN 300 μm annealed 250°C, 1 h	41 ± 4	39 ± 4	− 3.3 ± 1
PEN 300 μm annealed 260°C, 1 h	40 ± 4	38 ± 4	− 7 ± 1

The VFT-equation is given by

$$\log f = \log f_\infty - \frac{A}{T - T_0}, \tag{3}$$

where $\log f_\infty$ is the prefactor, A is a constant and T_0 is the ideal glass transition temperature. Due to the limited range of frequencies available for the mechanical measurement the parameter of the VFT-equation could not be estimated reliably. At low frequencies it is in reasonable agreement with the glass transition temperature measured by DSC.

For the annealed samples the curve $\ln f$ vs. $1/T$ shifts to higher temperatures which corresponds to the increase of the glass transition temperature with annealing.

3.2.2. Dielectric relaxation spectroscopy

In a similar way to the mechanical relaxation behaviour

Table 2

Activation energies calculated with Arrhenius equation, variation of enthalpy and entropy calculated with Starkweather formalism in the case of the β^*-relaxation for the amorphous (obtained from viscoelastic and dielectric measurements) and the three annealed at 240, 250, and 260°C samples in the case (DMA measurements only)

	Ea (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
DMA			
PEN 300 μm amorphous	269 ± 27	266 ± 27	530 ± 50
PEN 300 μm annealed 240°C, 1 h	127 ± 13	124 ± 13	147 ± 15
PEN 300 μm annealed 250°C, 1 h	138 ± 14	135 ± 14	183 ± 18
PEN 300 μm annealed 260°C, 1 h	138 ± 14	135 ± 14	182 ± 18
DEA			
PEN 300 μm amorphous	152 ± 15	150 ± 15	227 ± 23

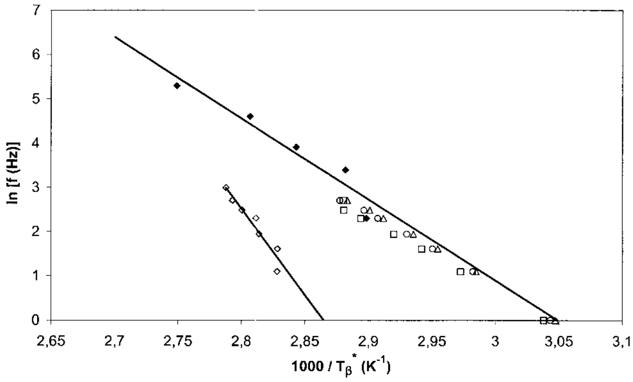

Fig. 6. Relaxation map for the β*-relaxation. Open symbols DMA data, filled symbols DEA data. (◇, ◆) — amorphous sample, (□, ■) — thermal treatment at 240°C, (△, ▲) — thermal treatment at 250°C, (○, ●) — thermal treatment at 260°C.

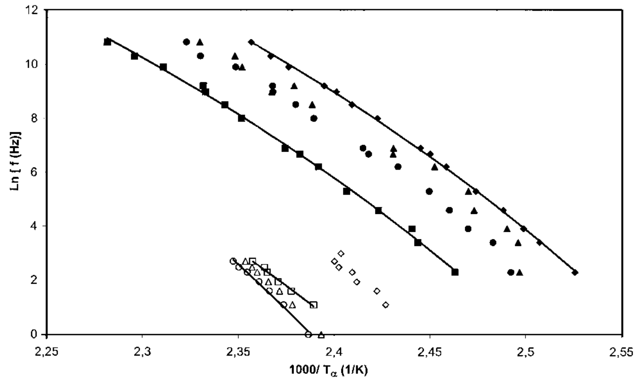

Fig. 7. Relaxation map for the α-relaxation. Open symbols DMA data, filled symbols DEA data. (◇, ◆) — amorphous sample, (□, ■) — thermal treatment at 240°C, (△, ▲) — thermal treatment at 250°C, (○, ●) — thermal treatment at 260°C.

measured by DMA, the dielectric spectra also show three relaxation processes which can be assigned similarly to the DMA measurements of the β-, β*- and α-relaxations (see Fig.4). This is demonstrated also in Fig. 8 where the dielectric loss factor tan δ_{DEA} is plotted vs. temperature and frequency. As for the mechanical measurements, the dielectric relaxation spectra will also be discussed in order of increasing temperature or decreasing frequency.

3.2.2.1. β-relaxation: In Fig. 5 the relaxation map for the dielectric β-process are plotted and compared with the mechanical results. Like the mechanical behaviour, the dielectric behaviour can also be described by an Arrhenius equation. The estimated activation energy and also the corresponding activation enthalpy and entropy are given in Table 1. It is clear that the values taken from the mechanical measurements are in excellent agreement with those extracted from the dielectric behaviour.

In addition, the strength of the dielectric β-relaxation decreases with the thermal treatment, but since the intensity of the dielectric β-process is higher than that of the mechanical one (see Fig. 4) it can also be evaluated for the annealed samples (see Fig. 5) and the activation parameter can be estimated with a higher accuracy. The corresponding data are summarised in Table 1. There is only a small decrease (around 5 kJ/mol) of the activation energy of the β-process due to the annealing. The significance of this decrease based on the presented data can only be confirmed by additional investigations. There appears to be a shift of the β-relaxation peak to lower temperatures with the thermal treatment, but this shift varies unsystematically with the annealing temperature.

3.2.2.2. β-relaxation:* In addition to the data extracted from the mechanical measurements, Fig. 6 also displays the relaxation map obtained from the dielectric measurements for the β*-process. It is difficult to extract the values for the dielectric β*-process because of its strong overlapping with the α-relaxation which is much more intense than the β*-relaxation. The data can be described by an Arrhenius law. The estimated value for the activation energy is essentially higher than the values published by Cañadas et al. [14]. Their reported values (29–77 kJ/mol) appear to be rather low even for β-relaxation processes. The values for E_{A} found in the present investigation by dielectric measurements, agree with that published by Bellomo et al. [9] which are taken also from dielectric experiments. According to Cañadas et al. [14] the value of E_{A} for the β*-relaxation should be constant for annealing temperatures higher than 200°C. This conclusion is not supported by the presented experiments.

The thermal treatment causes a strong decrease of the intensity of the dielectric β*-relaxation. In general, no clear peak can be detected in the temperature range where the β*-process is observed for the non-treated material. Only for one annealing temperature a very weak dielectric β*-relaxation process could be detected Due to the dispersion in the experimental data, it was not possible to extract reliable value for the activation parameter. This may be one reason why the β*-relaxation was not detected in reference [15] because that paper deals with annealed samples.

3.2.2.3. α-relaxation: Similarly to the mechanical measurements, the trace of the dielectric α-relaxation is curved in the Arrhenius plot. The VFT-equation can be used to describe the data. The shift of the ln$f$ vs. T towards higher temperatures for the annealed samples is consistent with the mechanical data (Fig. 7).

3.2.3. Discussion of the relaxation behaviour

For each relaxation process a small relative shift of the mechanical loss data compared to the dielectric one is observed. The mechanical relaxation processes are observed at temperatures 10–15 K higher than the corresponding dielectric loss peak (see Figs. 5–7). A similar behaviour is

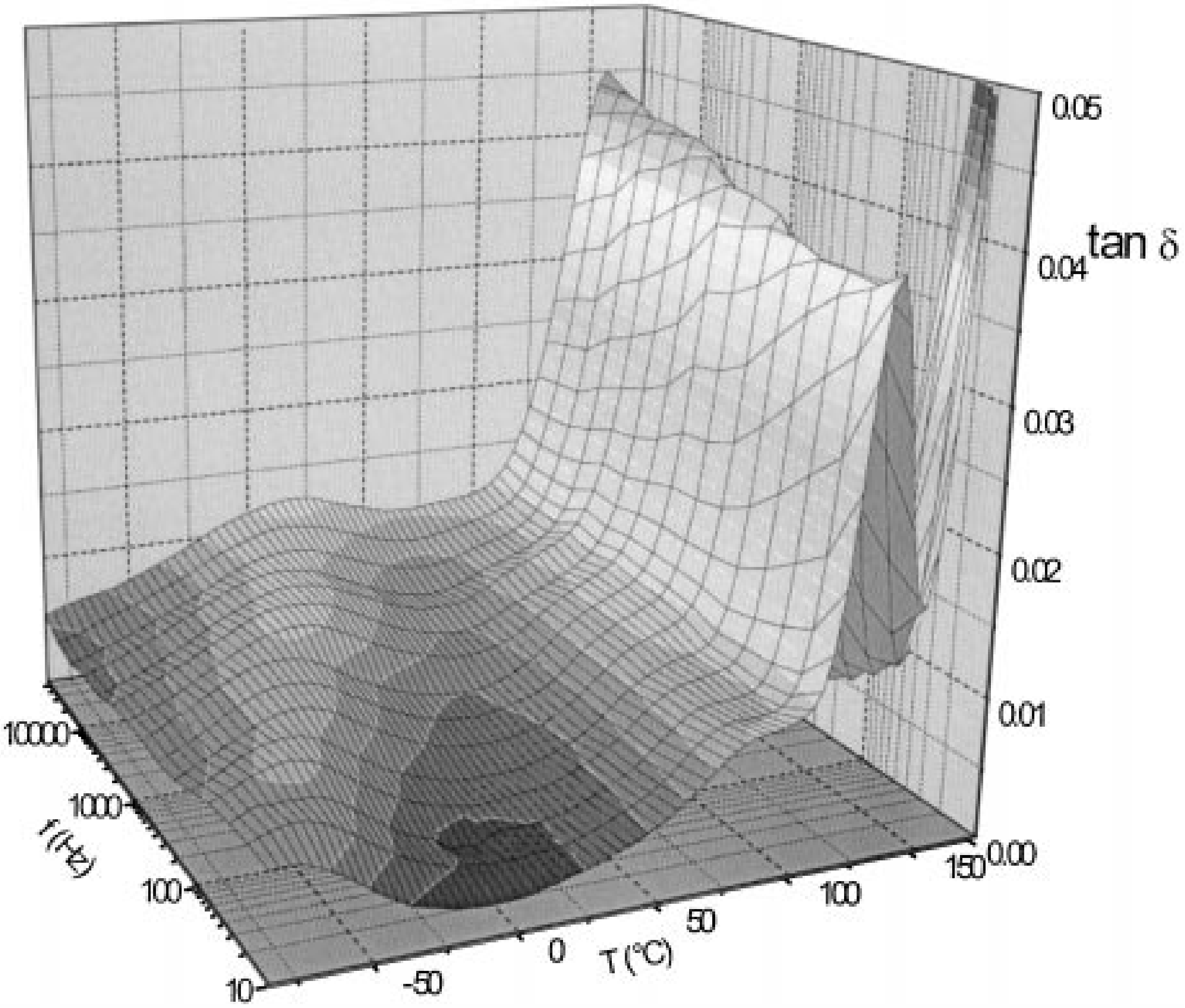

Fig. 8. tan δ_{DEA} for the amorphous sample as a function of frequency (ranging from 10 to 50 kHz) and temperature.

found, for instance, for a series of poly(alkyl methacrylate)s [22] and was mentioned previously in the literature [23,24]. In addition, Cañadas et al. [1,14] described a small shift in the temperature positions of the relaxation processes measured by DMA and DEA. In the present investigation the cold crystallisation process is observed at the same temperature with both methods. Therefore it is concluded that each method measures the same relaxation process, but different aspects of it. Moreover, a comparison of the mechanical and dielectric relaxation behaviour can give some insight into the molecular processes because dielectric spectroscopy is sensitive to fluctuations of dipole moments and mechanical relaxation monitors the fluctuations of internal stresses [25].

3.2.3.1. β-relaxation: The molecular assignment of the β-relaxation is far from being unanimous in the literature even for PET. On one hand, Maxwell et al. [26] have shown by high resolution carbon 13 and deuterium NMR experiments that the rapid 180° flip of the phenyl ring can be related more closely to the DMA β-relaxation than the molecular motions of the ethylene glycol unit which have a very weak amplitude. On the other hand, the phenyl ring is apolar and therefore its molecular motions cannot lead to a dielectric response. Hence, Maxwell et al. [26] concluded that the β-relaxation peak in PET is perhaps due to two molecular processes. Moreover, dielectric and mechanical spectroscopy have been applied to a group of three polyesters containing naphthalene groups [27]. A systematic absence of the dielectric β-relaxation is regarded as an indication that the process is associated with the naphthalene groups and neighbouring carbonyl groups undergoing a coordinated rotation motion about the main polymer axis. Furthermore, it is also known that dielectric losses for the β-relaxation of PET and PEN are stronger than the mechanical ones. This shows that there is no agreement in the literature about the assignment of the β-relaxation in PEN.

The presented results for PEN show that the activation energy for the β-relaxation is low. Also the values of ΔH^* and ΔS^* are low. Therefore it is concluded that the molecular motions responsible for the β-process are local in nature.

This reasoning is also supported by the fact that the activation parameters are nearly independent of the thermal treatment of the sample and therefore of the semi-crystalline structure. Moreover the estimated values agree more or less with those found for PET (50 kJ/mol). Also the location of the β-adsorption observed for PEN and PET corresponds to each other. For these reasons the motional processes related to the β-process should be fairly similar. Since 180° flips of the bulky and rigid naphthalene groups are unlikely, it is argued that the β-process must be assigned to fluctuations of the carbonyl (ester) group. This is further supported by the fact that the dipole moment of 1,2,3,4-tetrahydronaphthalene is only 0.49–1.67 D whereas the dipole moment estimated for $HCOOC_2H_5$ is $\mu = 1.94$–2.01 D [28].

3.2.3.2. β^*-relaxation: A relaxation process similar to the β^*-relaxation found for PEN is not present in PET. Therefore the β^*-process must be due to naphthalene units [10]. The activation energies for the β^*-process are essentially higher than the values for the β-relaxation. Also the estimated values for the activation entropy ΔS^* are high (Table 2). This indicates that the molecular motions which are responsible for the β^*-process are cooperative to some extent. Recently it has been shown by optical spectroscopy that the naphthalene groups can aggregate in solution [29] but also in the solid state [30]. At present, very little is known about the structure of such aggregates. For example, it is not known how many naphthalene groups form an aggregate and how many aggregates per volume unit are present. Because of the high value of the activation energy of the β^*-relaxation, it is assumed that the β^*-process is due to molecular motions of these aggregates or part of them. This line of argument is also supported by the experimental fact that the intensity of the β^*-process is higher for the mechanical measurements than for the dielectric one because the naphthalene unit is apolar. The dielectric intensity of the dielectric β^*-relaxation must be due to the ester groups. So it can be argued that the dielectric β^*-relaxation has to be related to fluctuations of ester groups inside or close to the aggregates. For a mechanical response the large scale motion of a whole aggregate is necessary. By adopting this scheme, the experimental fact that the activation energy for the mechanical β^*-relaxation is higher than for the dielectric one, can be understood.

If the amorphous samples are thermally treated the crystallisation occurs (see Fig. 1). Experimentally the activation energy of the mechanical β^*-relaxation decreases dramatically (see Table 2) and the peak shifts to lower temperatures. This experimental fact can be regarded as further evidence for the assignment of the β^*-relaxation to a cooperative motional processes, because local molecular motions are not generally influenced by a change in the supramolecular structure. During the crystallisation the chains will be stretched also in the amorphous regions. This process will also influence the proposed aggregation which will be more complicated in the semi-crystalline than in the amorphous state. Hence, the number, the extent and the size of the aggregates are smaller in the semi-crystalline state than in the amorphous one. Therefore the activation energy of the β^*-relaxation is decreased in the semi-crystalline state compared to the amorphous one.

3.2.3.3. α-relaxation: Due to the more rigid chain structure of PEN, the glass transition temperature is higher than the value for PET. It is also well known that the T_g for polymers with a semi-crystalline morphology is higher than for the corresponding amorphous state. This is also true for the investigated PEN sample (see Fig. 7). The DMA measurements give a systematic increase of the dynamic glass transition temperature with the annealing temperature (see Fig. 7). On the contrary, the dynamic glass transition temperature extracted from the dielectric measurements increases initially with the annealing temperature (240°C) but decreases for higher annealing temperatures (250 and 260°C).

4. Conclusions

The dielectric and dynamic mechanical behaviours of amorphous PEN and of thermal annealed samples have been reported as a function of the morphology. The DSC study shows that the glass transition temperatures do not change significantly with the thermal treatment and that the degree of crystallinity and melting temperatures increase with annealing temperatures as expected. Both DMA and DEA gives the main α-relaxation process associated to glass transition and the two processes i.e. the β^*- and the β-relaxation at lower temperatures (or higher frequencies) than the α-relaxation. These two sub-glass relaxations were analysed in terms of the activation energies (Arrhenius plot) and the variation of enthalpies and entropies (Starkweather formalism) were studied as a function of morphology (amorphous and semi-crystalline). It has been confirmed that the β-relaxation is due to local movements. The molecular mechanism should be similar to that of the β-relaxation in PET. It is argued that the β-adsorption is due to local fluctuations of carbonyl groups. The high values found for the activation energies, enthalpies and entropies of the β^*-process leads to the conclusion that this relaxation process is due to partially cooperative molecular motions. This line of argument is supported by the structure dependence of the β^*-process. It is found that the activation parameters decrease with thermal treatment which indicate that the degree of cooperativity is reduced by the crystallisation process. Summarising all experimental facts it is argued that the β^*-relaxation should be assigned to molecular fluctuations of aggregates of the naphthalene rings which were evidenced by optical spectroscopic investigations. The α-relaxation process shifts to higher temperature and the amplitude of the peak decreases for the semi-crystalline samples compared to the amorphous one as expected due to the decrease of molecular mobility.

This paper shows the complementarity of dielectric and dynamic mechanical spectroscopy for studying an aromatic thermoplastic polyester such as PEN. Each experimental method sheds light on different aspects of the molecular motions which are under investigation. A future paper will relate the study of a biaxially stretched PEN film non treated and thermally treated by these two techniques and an annealed amorphous sample will be compared with a semi-crystalline from industrial process.

Acknowledgements

The authors would like to thank the Ministry of Education and Research for its support through a PhD grant and for an associated professor position of A. Schönhals at University Claude Bernard Lyon 1. Du Pont de Nemours (R. Adam) is thanked for providing us with PEN samples. We are grateful to Olivier Gain for fruitful discussions and technical assistance. This work has been also performed in the frame of bilateral PROCOPE exchange program.

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