Physical aging in Poly(ethylene naphthalene-2,6-dicarboxylate) in relation to sorbed water, enthalpic relaxation and mechanical properties

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Abstract

Amorphous Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) films ($\sim 220\mu\text{m}$ thick), stored in ambient atmosphere for different periods of time and after annealing at different temperatures below $T_g = 123^\circ\text{C}$, for different times, have been investigated by infrared spectroscopy, (FTIR), microhardness and differential scanning calorimetry (DSC). FTIR spectroscopy and weight measurements reveal the presence of water which is easily removed by annealing of the films. Films recover again their initial weight and absorption bands after 1–2 days-storage in ambient atmosphere. Samples annealed at different temperatures T_a for different times t_a show an increasing microhardness for relatively short times of t_a . The microhardness passes through a maximum at an annealing time depending on T_a , and it decreases towards values somewhat larger than the initial ones. The changes observed in the microhardness and in the values of the excess enthalpy with storage time of the samples at room temperature depend on the physical aging as well as on the content of water of PEN films.

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Introduction

It is well known that the physical properties of amorphous polymers held below their glass transition temperature, T_g change as a function of storage time [1]. Changes in properties can be related to chemical degradation and physical aging of the material. Physical aging below T_g is attributed to a continuous slow relaxation of the glass from its initial non equilibrium state towards its final thermodynamic equilibrium state [1]-[4].

Physical aging and structural relaxation phenomena in a wide set of amorphous polymers and particularly in polyethylene terephthalate (PET) have received increasing interest in the last years [5]-[8]. Microhardness measurements have shown to be a promising technique to provide information on microstructure variations and molecular reorganization as a result of physical aging [7],[9]. Differential scanning calorimetry has proved, as well, to be a convenient technique for studying physical aging processes in polymer glasses [3,10,11].

The aim of the present study is to investigate the variation in microhardness of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) stored in ambient atmosphere for different times and after annealing at different temperatures below T_g for different periods of time. This material has molecules stiffer than PET due to the presence of a naphthalene ring instead of the benzene ring:

PEN is a material which is becoming of increasing interest as a replacement of PET because of its higher glass transition temperature of 123°C . It crystallizes in two different crystal modifications [12]. Under usual conditions both modifications melt at 272°C . However, after adequate annealing procedures the melting point of both modifications can be raised up to 290°C . The kinetics of crystallization and the influence of morphology on the surface mechanical properties of PEN have been recently discussed elsewhere [12],[13]. Transmission infrared spectra of PEN films reveal the presence of sorbed water which must be responsible for the unexpected microhardness behavior observed in the

annealed samples. The excess enthalpy values for samples stored at room temperature and after annealing are presented. Furthermore the influence of sorbed water on the mechanical properties of PEN will be highlighted. The experiments reported here represent an example in which physical aging is notably affected by the presence of water.

Experimental

Samples of PEN were synthesized in our laboratory as described elsewhere [12]. The intrinsic viscosity measured in hexafluoro isopropanol was 0.5334 g/dl. The apparent molecular weight obtained by the relation [14]:

$$[\eta] = 5.2 \times 10^{-4} M_w^{0.695} \quad (1)$$

which was probed to be valid for PET, was $M_w = 121,000$. Films ($\sim 220\mu\text{m}$ thick) of amorphous PEN, obtained by melt pressing at about 290°C and quenching in ice water were stored for different periods of time at room temperature (Table I).

Physical aging of these PEN samples was enhanced by means of annealing at different temperatures T_a below $T_g = 123^\circ\text{C}$, for selected annealing times t_a .

The samples were annealed under three different conditions:

- (a) At ambient atmosphere under N_2 flow using a Mettler hot stage device. $T_a = 80, 90, 105$ and 115°C respectively. In this case one has to assume that water vapor is not completely excluded.
- (b) In sealed glass tubes which were previously evacuated using a rotary pump and which were placed in a controlled temperature bath. $T_a = 80^\circ\text{C}$ and 105°C respectively. Here the water vapor exposure is strongly reduced.
- (c) *In situ* inside a vacuum line (high vacuum, $\approx 2.10^{-5}\text{torr}$) after evacuation for 24 hours at room temperature. $T_a = 85$ and 105°C respectively. Here we can consider water to be practically removed.

Water sorption experiments were carried out by keeping the sample in water for 24 hours.

Microhardness was measured at room temperature using a microhardness tester with a Vickers square pyramidal diamond indenter. The microhardness value (in MPa) was evaluated from the residual projected diagonal impression using the equation:

$$H = kp/d^2 \quad (2)$$

where d is the mean diagonal length of the indentation in mm, p is the applied force in N , and k a geometrical factor equal to 1.854. A loading cycle of 0.1 min to minimize creep of the material under the indenter and a load of 1N were used [15]. For each value of H , at least 10 measurements of d were carried out and the mean value was calculated. The H value was determined with an error of 2–3%

Differential scanning calorimetry (DSC) scans from 30 up to 160°C for amorphous PEN were carried out on 5 mg annealed samples, following the experimental procedure (a). A Perkin–Elmer DSC–4, previously calibrated with an indium standard was employed. A heating rate of 10K/min and a cooling rate (320 K/min) were used.

Transmission infrared spectra of thick films were recorded using a Perkin–Elmer FTIR spectrometer after 8 scans with a resolution of 2 cm^{-1} .

Results

I. Microhardness and DSC Measurements of the initial aged–samples

Table I shows the microhardness values measured on PEN samples stored in ambient atmosphere for different periods of time. An appreciable hardening of the material attributed to the physical aging of the stored material at room temperature is observed after the first months of storage. Fig. 1 shows the first DSC run for the four PEN samples investigated. They show a clear glass transition temperature at about $T_g = 123^\circ C$ and a similar specific heat capacity, $\Delta C_p = 0.048$ cal/g K. In these DSC traces, a subtle endothermic broad maximum appears located well below the glass transition interval (less than 80°C to 95°C). The area of this broad maximum was measured by drawing a smooth line through the experimental curve and defining a base line between 60 and 105°C. It is seen that, both, the peak position and the endothermic area (Table I) change with

storage time. For longer storage times this broad maximum appears closer to T_g . For the shortest time stored material (~ 1 month) no endothermic maximum was observed (Fig. 1, upper curve). Peak area measurements were estimated with an error of 5%.

II. Influence of pretreatment on the water content

Information on the water content was obtained by means of FTIR spectroscopy and weight measurements. The PEN films investigated were too thick to get useful transmission IR-spectra for much of the examined spectral region. However, they were sufficiently transparent in the $4000\text{--}2000\text{ cm}^{-1}$ spectral region allowing us to investigate some of the absorption bands related to water. In Fig. 2 the transmission IR-spectra of the initial aged-samples are shown. Infrared spectra from different pieces of each film sample reveal similar values (variations are less than 10% in absorbance) for the integrated absorbance of the doublet at $3631\text{--}3550\text{ cm}^{-1}$ associated with the OH stretching (asymmetric and symmetric) vibration mode of water [16,17]. The narrow shape of these doublet bands supports the presence of water weakly bounded to this polymer. One sees that the intensity of the peak at 3631 cm^{-1} gradually increases and that the intensity of the peak at 3550 cm^{-1} concurrently decreases with increasing storage time. The shape of the doublet after long storage time resembles the shape observed for water [17]. This change might be related to a rearrangement of the material upon aging, influencing the vibration modes of the water molecules.

Fig. 3 shows the doublet at 3631 and 3550 cm^{-1} in the original PEN film B (spectrum 1) and both, after annealing at 105°C for 20 min (spectrum 2) and after placing the sample in water for 24 hours (spectrum 3). As one can see the doublet has almost completely disappeared after annealing while a strong increase in intensity is observed after the sorption of water. It has been pointed out that the remaining band at about 3546 cm^{-1} could correspond to the band associated to hydroxy end-groups [18]. This doublet has been used in a separate study to measure the water content [19]. In case of the hydrated film the doublet appears at $3622\text{--}3549\text{ cm}^{-1}$.

In agreement with the FTIR results, after annealing a weight decrease and after hydration a weight increase of the sample were respectively observed. Annealing at $T_a = 105^\circ\text{C}$

for 20 min of the different samples A,B,C,D gives rise to a relative weight decrease ($\Delta w/w$) of 0.4–0.6%, independently of the sample storage time. The water uptake of sample B in the sorption experiment was of 0.7%.

Fig. 4 shows the time evolution of the integrated absorbance of the doublet related to water for an hydrated film ($\Delta w/w = 0.45\%$) and for an original film annealed at 105°C for 20 min. After storage of both samples for 1–2 days in ambient atmosphere the IR-spectra show absorption values which are similar to those observed for the untreated PEN films. These results clearly indicate that PEN films, far away from their equilibrium water content, by means of both treatments, absorb/desorb water spontaneously. It turns out that the time required to reach equilibrium is similar in both cases. A similar behavior was found for the annealed samples which recovered their initial weight after the first day of storage at room temperature in ambient atmosphere. Finally, it is worth noting that the water uptake and water release behavior shown in Fig 4 follows Fick's law [20].

Fig. 5 shows the variation of the integrated absorbance of the doublet at $3631\text{--}3550\text{ cm}^{-1}$ for an hydrated and an original sample B during annealing (experimental procedure (a)) at 105°C as a function of annealing time. After each annealing time the sample was quenched, between two metal plates, to room temperature in order to perform the FTIR measurement. One sees that for $t_a > 15$ min the integrated absorbance does not change.

We want to note that the time required to reach the lowest value for the integrated absorbance depends on the annealing temperature used. Thus, experiments performed in samples annealed at lower temperatures ($T_a = 90$ and 80°C) revealed that the times required to reach the lowest absorbance values are larger (45 and 55 min, respectively).

III. Influence of annealing below T_g on microhardness

Fig. 6 illustrates the variation of H for samples C and D as a function of annealing time (procedure a) for various annealing temperatures. In all cases H first increases, approximately, linearly with t_a , passes through a maximum, for a given t_a value which depends on T_a and decreases towards steady values ($\sim 190\text{ MPa}$) which are larger than the initial ones. It is noteworthy that the maximum value of hardness is similar for the

different temperatures used (80, 90, 105 and 115°C). However, the maximum level of hardening observed for the heat treated samples is very much dependent on the aging (storage time) of films investigated. This is illustrated in Fig. 7 where it can be seen that the rate of hardening for a given temperature is larger the longer the storage time. For all samples the limiting H-values, after say 60 min of annealing, are larger (5–6 MPa) than the corresponding initial values. Finally, we observed that a further annealing treatment of the “dried” samples yielded no appreciable change in the hardness of the samples.

In order to gain a better understanding about the appearance of a maximum in H with annealing time, additional experiments were carried out by changing the ambient conditions using the experimental procedures b and c. Fig 8 represents the microhardness of sample D as a function of annealing time using the annealing procedure b and c respectively at 2 different annealing temperatures; namely 80°C (below the boiling point of water) and 105°C (above it). In case of procedure b, where the influence of water is considerably smaller than in case of procedure a, for $T_a=105^\circ\text{C}$ a maximum of H appears at about 10 min. and then H decreases with t_a . On the other hand, for $T_a=80^\circ\text{C}$, H starts to increase only after the first 7 hours of annealing showing a maximum after about 60 h. Particularly, for the lower temperature the maximum H value (194 MPa) is much smaller than that observed for samples treated under N_2 flow (220 MPa). After longer annealing times (2 months) the H values are 190 and 194 MPa for 80°C and 105°C, respectively.

Since the water sorbed by polymer films and at the glass tube walls is not completely removed, after rotary pump vacuum application, annealing of sample D under vacuum levels of $2 \times 10^{-5} \text{ torr}$ were carried out (procedure c). The variation of H observed for the two temperatures investigated is also represented in Fig. 8 (open symbols). For $T_a=105^\circ\text{C}$ the relatively sharp peak observed using sealed glass tubes has now disappeared and H shows only a smaller hardening after 40 min of annealing treatment. For $T_a \simeq 85^\circ\text{C}$ an even smaller hardening than that for sealed glass tubes is observed and the H-maximum is shifted towards higher annealing times (~ 80 h).

IV. Influence of annealing on the enthalpic relaxation process

The influence of annealing temperature on the first DSC run of sample D annealed for 20 min is shown in Fig. 9a. After annealing the broad endothermic maximum is shifted by about 20°C above the T_a used. Thus, for $T_a = 90^\circ\text{C}$ the peak still appears below T_g , at about 110°C while for higher T_a values this endothermic peak appears to extend into the T_g region. Thus, in the case of sample annealed at 105°C for 20 min the endothermic peak is spread on the T_g interval. Indeed, the measured T_g for this sample is 2°C smaller in comparison to other DSC curves. Nevertheless, with increasing annealing time (80 min) (Fig. 9b) the scan at 105°C shows an endothermic peak well developed on the T_g interval.

It was observed that DSC traces from a second run did not show any endothermic peak. Therefore, we used the second DSC run as reference to evaluate the excess enthalpy associated to the aging process. In Figure 10, the excess enthalpy δh so calculated for the annealed D sample at different temperatures is plotted *versus* the annealing time. For $T_a = 115^\circ\text{C}$ a sudden increase of δh for short annealing times is observed. For lower T_a values the increase of δh is smaller and occurs at longer annealing times (20–30 min).

Discussion

The time evolution of the integrated absorbance of the IR-doublet at 3631-3550 cm^{-1} (Figs. 4 and 5) and the accompanying variation of weight of the treated PEN supports the presence of “weakly bounded” water in PEN films, (0.4–0.6% in weight). Annealing of the films in the range of 80-115°C (below T_g) provokes a loss of water, which is accompanied by a reduction of the integrated absorbance of the IR-doublet, down to a minimum value of $\sim 10 \text{ cm}^{-1}$ or about 450 cm^{-2} when referred to unit film-thickness. The annealing time required to reach the minimum water content is higher the lower the annealing temperature. These limiting annealing times required to obtain the dry sample coincide with the time for which a maximum of hardening was observed (Fig. 6). After 1-2 days of storage at room temperature in ambient atmosphere the IR-spectra show that the PEN heat treated films recover their original content of water (Fig. 4).

The hardening rate observed (Figs. 6–7) for PEN samples annealed at temperatures

below T_g is notably higher than that reported for PET (namely 0.15 MPa h^{-1}) [7]. Experiments in which the presence of water is considerably reduced (Fig. 8), clearly support the relevant role of water in the hardening process of heat treated PEN films. The influence of annealing the sample below and above the boiling point of water results in a different water-vapor pressure inside the evacuated sealed glass tubes. While at 105°C most of the water evaporates from the glass-inner wall coming into contact with the sample at the beginning of treatment, at 80°C the vapor pressure of water inside the glass tube must be considerably smaller. In the first case (105°C) a well resolved maximum of H , H_{max} , is observed while in the second case (80°C) the maximum intensity of H is smaller and shifted towards longer times (60 h). In the experiments using a high vacuum line annealing is accomplished under a dynamic vacuum condition and the water vapor pressure is notably smaller than in the case of glass sealed tubes. Therefore, the observed hardening is reduced and H_{max} appears at longer times.

Physical aging, representing a change in the mechanical properties of the material, can be discussed in the light of the analysis of results deduced from Fig 7 and represented in Fig. 11. The influence of the storage (aging) on the level of hardening at room temperature follows a logarithmic increase (long time hardening) which is characterized by **straight line 1** in Fig. 11. Annealing below T_g ($T_a = 80\text{--}115^\circ\text{C}$) not only increases the hardening rate as shown for sample C and D in Fig. 6 but also yields the maximum hardness values, H_{max} , observed for $T_A = 105^\circ\text{C}$ and plotted in **curve 2**. The values of H_{max} seem to depend on the aging of the initial samples (Fig. 7) and are independent of T_A (see Fig. 6). The final hardness values, H_f , (**straight line 3**), obtained after longer annealing times are, however, larger than the H_0 values corresponding to the room temperature stored samples. Finally, after 1–2 days storage of the “dried” samples at room temperature in ambient atmosphere, the low original H_0 values (**straight line 1**) are recovered. Similar conclusions can be drawn for the other annealing temperatures.

What explanation can be given for the H_{max} values observed? In the first place, for short annealing times, the progressive loss of water, which acts as a plasticizer should contribute to a hardening of the material. After removal of the water a maximum in H should be obtained (H_{max}) since for longer annealing times one might speculate that a

decrease of H might be connected with a relaxation of the chain molecules in the 80–115°C range caused by the onset of the libration motion of naphthalene moities [21],[22].

After a storage for 1–2 days of the annealed sample at room temperature, the film recovers the original hydration degree and comes to its equilibrium state (**straight line 1** of Fig. 11). Upon further annealing at high T_a , the same hardening cycle is reproduced.

A convenient property of the glassy matrix for determining extensive physical aging is the excess enthalpy. The results shown in Fig. 1. indicate that the excess enthalpy involved in the aging process due to storage of the samples appears far below T_g and not at the T_g transition, as it is often observed for other polymers with lower T_g values [3],[10]. The presence of a sub- T_g endothermic peak has been explained using a distribution of relaxation times [23]. However, after annealing near T_g for short periods of time and/or at lower temperatures for prolonged periods of time, an increased endothermic peak is resolved just at the end of the glass transition interval as it is observed for PET [6],[8] and other polymers [24],[25]. The excess enthalpy for the stored samples given in Table I and those shown in Fig. 10 for an annealed sample support the occurrence of physical aging with storage of the samples in ambient atmosphere and that this process, as would be expected, is thermally enhanced [1],[2]. Indeed, Fig. 10 indicates that the increase of the excess enthalpy is larger for a higher annealing temperature [6],[25]. Additionally, for the very short periods of time that were investigated, an increase of the excess enthalpy with annealing time was observed.

Conclusions

- Amorphous PEN under usual conditions (30% relative humidity) contains about 0.4–0.6% water. This value can be increased by placing PEN in water upon which an additional 0.7% water is sorbed.
- No enhanced crystallization behavior was observed for PEN when exposed to water vapor.
- Water combined within PEN can be removed by annealing below T_g for relatively short periods of time depending on the annealing temperature (T_a).

- During annealing of PEN below T_g water is disrobed, the relaxation enthalpy is increased and the microhardness is also increased.
- The increases in microhardness are larger for longer aging times. The annealing temperature influences the rate of hardening but not the maximum value of hardness reached.
- Annealing beyond the time where relaxation enthalpy reaches the inflexion point leads to a decrease in hardness. The latter has been suggested to be caused by the onset of motion of naphthalene groups.

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Figure Captions

- Fig. 1 First DSC run for the initial aged PEN samples investigated.
- Fig. 2 4000-2000 cm^{-1} spectral region of transmission spectra of thick ($\sim 220\mu m$) PEN films from the samples of Table I. From bottom to top: A, B, C and D samples.
- Fig. 3 4000-2000 cm^{-1} spectral region of transmission spectra of thick ($\sim 220\mu m$) PEN films. B sample: (spectrum 1); B sample treated at 105°C for 20 min (spectrum 2); Hydrated B sample with $\Delta w/w = 0.45\%$ (spectrum 3).
- Fig. 4 Variation of the integrated absorbance of the doublet at 3631-3550 cm^{-1} with storage time in air for the hydrated (open circles) and annealed (filled circles) samples of Fig. 3.
- Fig. 5 Variation of the integrated absorbance of the doublet at 3631-3550 cm^{-1} for sample B annealed at 105°C as a function of annealing time (filled circles) and for the hydrated sample B ($\Delta w/w = 0.45\%$) (open circles).
- Fig. 6 Microhardness as a function at annealing time for the aged PEN samples annealed at different temperatures T_a (°C): a) sample C; b) sample D.
- Fig. 7 Microhardness for the initial aged PEN samples, annealed at 105°C as a function of annealing time.
- Fig. 8 Microhardness as a function of annealing time for sample D annealed within evacuated glass sealed tubes ($\bigcirc, \triangle$) and in a vacuum line ($\bigcirc, \triangle$)($2 \cdot 10^{-5} torr$). $T_a(°C) = 105$: ($\bigcirc, \bigcirc$); and 80: ($\triangle\triangle$).
- Fig. 9 First DSC run for sample D before and after annealing at different temperatures for: a) $t_a = 20$ min., b) $t_a = 80$ min.
- Fig. 10 Variation of the excess enthalpy δh (cal/g) with annealing time for sample D treated at different temperatures (°C).

Fig. 11 Variation of the microhardness as a function of log time for samples, as obtained from Fig 7: 1) stored at room temperature; 2) stored and subsequently annealed at $T_a = 105^\circ\text{C}$ upto the maximum H-value ($t_a = 15$ min); 3) stored and subsequently annealed at $T_a = 105^\circ\text{C}$ to the final value of H ($t_a = 60\text{--}100$ min).

Table I

Microhardness H , and excess enthalpy δh , values observed for PEN samples with different storage time.

Sample	Storage time	$H(\text{MPa})$	$\delta h(\text{cal/g})$
A	< 1 month	177	–
B	3 months	182	0.08
C	1 year	184	0.14
D	~ 3 years	185	0.16

Fig 1

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Fig 2
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Fig. 3

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Fig. 5
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Fig 6a
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Fig 6b
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Fig 7
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Fig 8

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Fig 9a
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Fig 9b

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Fig 10
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Fig 11
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