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Crystallization kinetics of poly(ethylene naphthalene-2,6-dicarboxylate) as revealed by microhardness

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Abstract

The microhardness technique has been used to follow the crystallization of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) from the glassy state. The crystallization temperatures investigated ranged from 423 to 448 K. Results are analyzed on the basis of the Avrami equation. Avrami parameters are discussed in the light of the morphology developed during the isothermal crystallization of PEN, as revealed by preceding electron microscopic studies [Baltá Calleja et al. J Macromol Sci Phys 1998;37:411]. The temperature dependence of microhardness for amorphous PEN has been also investigated from room temperature up to ~30 K above the glass transition temperature, T_g, of the material. From these measurements, the T_g value has been derived in agreement with preceding calorimetric data [Buchner et al. Polymer 1989;30:480]. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene naphthalene-2,6-dicarboxylate); Microhardness; Crystallization kinetics

1. Introduction

The various mechanisms occurring during the crystallization of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) have been widely investigated using transmission electron microscopy (TEM) [1], wide angle and small angle X-ray scattering (WAXS, SAXS) [2–4], light scattering (LS) [3], differential scanning calorimetry (DSC) [2,4] and dielectric spectroscopy [5]. Simultaneous WAXS, SAXS and LS measurements using synchrotron radiation were carried out to study the structural changes occurring during the isothermal crystallization of PEN from the melt [3], where it was shown that during primary crystallization of polymers the degree of crystallinity within the developing spherulites is constant. Hence, one can apply the theory of Avrami to the growth of these morphological units. During the course of secondary crystallization, various mechanisms may occur [3,6]: crystal thickening, formation of new crystals between the old ones and formation of new lamellar stacks. Recent studies on the crystallization of PEN from the glassy state using DSC, SAXS and WAXS highlight the influence of the crystallization conditions on the mechanisms of secondary crystallization [4]. The kinetics of crystallization of PEN, from the glassy state and from the melt, has been further investigated using X-ray scattering synchrotron radiation [2].

The close relationship that exists between microhardness and the degree of crystallinity in polymers [7,8] shows that the microhardness technique is a convenient means to investigate the kinetics of crystallization. The indentation hardness technique has been proven to be a valuable tool to investigate the isothermal crystallization of poly(ethylene terephthalate) (PET) and PET/PEN blends at various crystallization temperatures, T_c [9,10]. The crystallization of PEN at $T_c = 418$ K was also investigated in comparison with the crystallization behavior of the PET/PEN blends [10]. The microhardness technique has been further employed to investigate the influence of physical aging and water content on the surface mechanical properties of PEN [11]. Microhardness measurements on PEN have been also performed at room temperature after the material was crystallized from the glassy state at various temperatures for different time durations [12]. The influence of the degree of crystallinity and the crystalline lamellar thickness developed at each T_c and crystallization time, t, was investigated [12].

The present paper aims at the study of the 'in situ' isothermal crystallization of glassy PEN at various crystallization temperatures ranging from 423 to 448 K using the microindentation technique. In order to characterize the hardness

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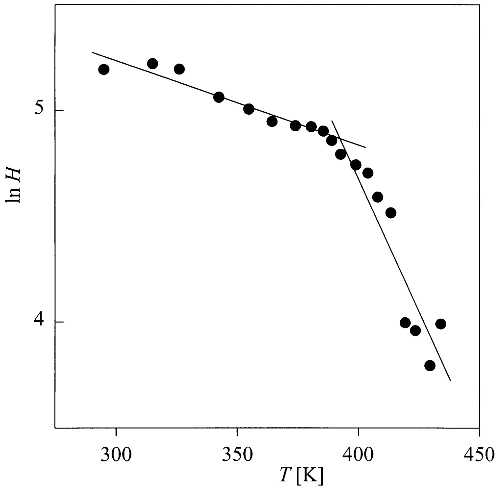

Fig. 1. Microhardness variation as a function of temperature for amorphous PEN.

value, at high temperature, at the beginning of the crystallization process, the temperature dependence of hardness from room temperature up to ~30 K above T_g was studied.

2. Experimental

2.1. Samples

Samples of PEN were synthesized from 2,6-dicarboxymethyl naphthalene and ethylene glycol using antimony trioxide and manganese acetate as catalysts [2]. Amorphous films were obtained by melt pressing above the melting point and quenching in ice water.

2.2. Techniques

Microindentation experiments were carried using a Vickers square-based diamond pyramid (included angle between opposite faces $2\alpha = 136°$). Vickers hardness, H, is calculated according to the expression:

$$H = k\frac{P}{d^2} \tag{1}$$

where P is the applied load, d the measured diagonal of the residual impression and k a geometric constant. A value of $k = 1.854$ is used when P is in N and d in mm to give H in MPa. A loading cycle of 0.1 min to minimize the creep [7] and a load of 0.25 N were employed.

The real-time microhardness variation during isothermal crystallization was measured using a heating stage. The temperature at the surface of the heating stage was calibrated against several standards. Sputtering of the sample surface using gold was performed to improve optical contrast during indentation.

3. Results and discussion

3.1. Temperature dependence of microhardness

Hardness is known to exponentially decrease with temperature, T, following [7]:

$$H = H_0 \exp[-\beta T] \tag{2}$$

where H_0 is the hardness of the material at 0 K and β the so-called coefficient of thermal softening, which may be derived from the slope of a semi-logarithmic plot of H versus T. Fig. 1 shows the plot of $\ln H$ versus T for amorphous PEN. At room temperature, the hardness value obtained ($H = 180$ MPa) is consistent with other reported values for glassy PEN ($H = 180$–210 MPa) [12–14]. From Fig. 1 one can draw two straight lines which intersect at $T = 392.4$ K, a value which is in good agreement with T_g values determined from calorimetric measurements (393 K) [2].

For $T < T_g$, a β value of 3.98×10^{-3} K^{-1} is obtained. This value is in the range of the β values reported for

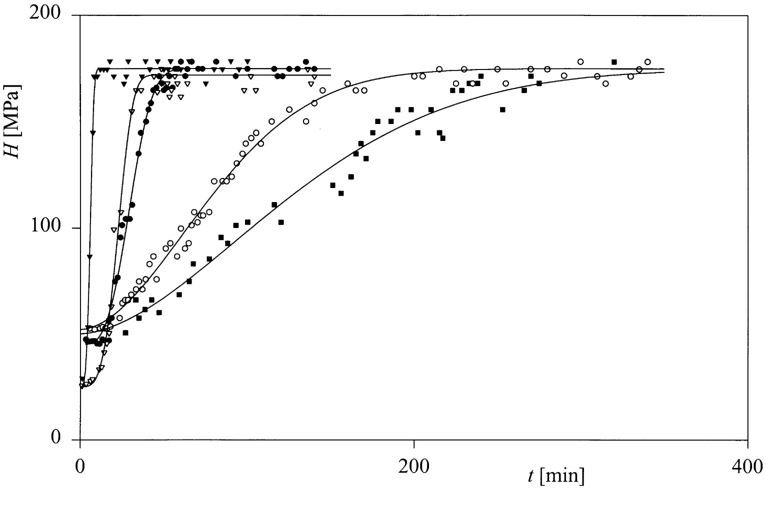

Fig. 2. Variation of microhardness as a function of crystallization time for various crystallization temperatures: ■, 423 K; ○, 428 K; ●, 433 K; ▽, 438 K; ▼, 448 K.

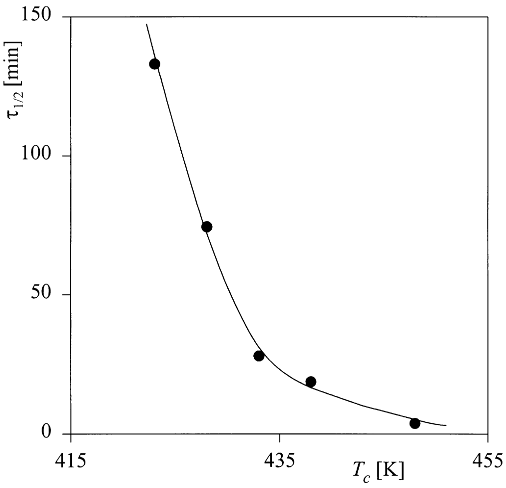

Fig. 3. Dependence of the half-time crystallization upon T_c.

various amorphous and semicrystalline polymers below T_g [15–17]. The decrease of hardness with T is well known to be directly related to the thermal expansion of the sample [15–17]. Moreover, the β coefficient has been shown to be directly proportional to the thermal expansion coefficient of the crystalline and non-crystalline regions on liquid crystalline copolyesters [16].

For $T > T_g$ a steeper rate of hardness decrease is observed, leading to a higher β value of 2.51×10^{-3} K^{-1}. The β value derived is of the order of magnitude of those obtained for $T < T_g$ in other polymeric materials [15,17]. Above T_g, the higher free volume available for the liquid-like motions leads to a faster H decrease with T [15].

3.2. Microhardness measurements in 'real time': kinetics of crystallization

Fig. 2 shows the plot of the hardness values versus the crystallization time for the various crystallization temperatures (423 K $\leq T_c \leq$ 448 K). Data for $T_c = 443$ K are not included in Fig. 2 for the sake of clarity. However, these data are used in the analysis of the kinetics of crystallization as will be shown in Fig. 4. It is relevant to note that the initial hardness values for $T_c = 423$ K ($H \approx 50$ MPa) coincide with the H values at the end of the temperature cycle shown in Fig. 1. Lower H values at the beginning of the crystallization process are found for higher crystallization temperatures (see Fig. 2), in agreement with the hardness tendency to decrease with increasing T (see Fig. 1). Fig. 2 shows that, for all the T_c considered, there is an initial steep increase in the H values with increasing t followed by a H-plateau. The rate of hardness increase during primary crystallization tends to rise with increasing T_c. The final leveling-off value of H ($H_M = 172$–175 MPa) seems to be independent of the crystallization temperature. However, this value is slightly higher than the H_M value obtained during the isothermal crystallization of PEN at $T_c = 418$ K ($H_M = 165$ MPa) [10].

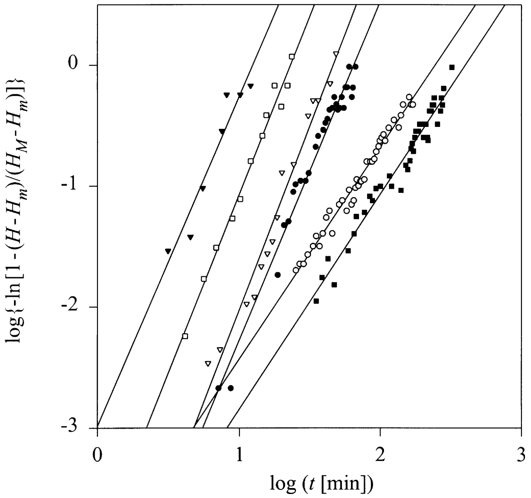

Fig. 4. Double logarithmic plot of $-\ln[1 - (H - H_m)/(H_M - H_m)]$ versus t for the various T_c studied: ■, 423 K; ○, 428 K; ●, 433 K; ▽, 438 K; □, 443 K; ▼, 448 K.

Fig. 3 illustrates the half-time crystallization values, $\tau_{1/2}$, derived from Fig. 2 as a function of crystallization temperature. We take $\tau_{1/2}$ as the time required to attain one-half the value of $H_M + H_m$, where H_m is the lowest H value for each isothermal crystallization curve. The results are in agreement with the $\tau_{1/2}$ values obtained from X-ray scattering synchrotron data for PEN crystallized from the glass [2].

Previous microhardness measurements performed at room temperature on PEN crystallized from the glassy state revealed that the hardness values during primary crystallization are directly proportional to the total emerging crystallinity in the sample [12]. Hence, the hardness evolution with crystallization can be described by the Avrami equation:

$$H(t) = H_m + (H_M - H_m)[1 - \exp(-Gt^n)]. \tag{3}$$

Indeed, the increase of H with t during the primary crystallization of amorphous PET has been shown to follow Eq. (3) [9]. Fig. 4 shows the double logarithmic plot of $-\ln[1 - (H - H_m)/(H_M - H_m)]$ versus t for the various T_c considered. From the slope and intercept of the straight lines in Fig. 4, one can derive the n and G values, respectively, for each crystallization temperature (see Table 1).

Table 1 shows n values of around 2 for the lowest crystallization temperatures ($T_c \leq 428$ K) while $n \sim 3$ within the range 433 K $\leq T_c \leq$ 448 K. Previous 'in situ' microhardness measurements on PEN crystallized from the glass at $T_c = 418$ K showed two different regimes with $n \sim 1.5$ and $n \sim 5$ [10]. Our results suggest that for higher crystallization temperatures (423 K $\leq T_c \leq$ 448 K), a unique regime is observed with n values depending on the crystallization temperature. Prior morphological studies using transmission electron microscopy during the early stages of crystallization of amorphous PEN revealed an emerging lamellar structure within a dendritic morphology for $T_c \leq 428$ K [1]. This morphology is consistent with the n values

Table 1
Avrami exponent, n, and Avrami constant, G, for the various crystallization temperatures (T_c) studied

T_c (K)	n	G
423	1.94	1.0×10^{-5}
428	1.75	6.6×10^{-5}
433	2.93	5.2×10^{-6}
438	3.04	8.7×10^{-6}
443	2.95	9.8×10^{-5}
448	2.73	1.0×10^{-3}

obtained in the present paper ($n \sim 2$). On the other hand, the electron micrographs obtained for PEN crystallized from the glass at high crystallization temperatures show a dendritic superstructure which exhibits bundles of lamellae with radial orientation, in addition to the branched lamellar structure [1]. The n values obtained in the present paper ($n \sim 3$) for $T_c > 428$ K conforms with the development of such a superstructure.

Table 1 shows that, for a fixed value of the n-exponent, the value of G increases with increasing crystallization temperature. Similar results have been reported for PET and PET/PEN blends [9,10]. The G-parameter is known to be proportional to the number of nuclei per unit volume and to the rate at which growth from these nuclei occurs [18]. Thus, our results suggest that, for a certain type of crystallization (constant n-value), the number of nucleating sites and/or the rate of nuclei growth increase with increasing T_c.

4. Conclusions

In conclusion:

- Hardness of amorphous PEN is shown to decrease with increasing temperature as a result of the thermal expansion of the sample. The coefficient of thermal softening β markedly increases above T_g due to the higher free volume available for segmental motions in the liquid-like state.
- The hardness of amorphous PEN is additionally shown to steeply increase with crystallization time during the initial stages of crystallization. The steep H-increase is followed by a final leveling-off. The final H-value seems to be independent of T_c within the range of the crystallization temperatures investigated ($423\ \mathrm{K} \le T_c \le 448\ \mathrm{K}$).
- Avrami analysis of the crystallization curves shows n values around 2 for the lowest crystallization temperatures ($T_c \le 428$ K) while $n \sim 3$ within the range $433\ \mathrm{K} \le T_c \le 448\ \mathrm{K}$. This result is consistent with previous TEM investigations which revealed a dendritic morphology that developed during isothermal crystallization of PEN from the glassy state. The dendritic superstructure is constituted, at high T_c, by bundles of lamellae with radial orientation, in addition to the lamellar structure observed at low T_c [1]. The Avrami G-value is shown to increase with increasing T_c provided the n-value is constant.

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