

Effect of shearing on crystallization behavior of poly(ethylene naphthalate)

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Abstract

The effect of shear history on the isothermal crystallization behavior of poly(ethylene naphthalate) (PEN) was investigated by rheological and morphological measurements. Time sweep measurements of storage modulus (G') and dynamic viscosity (η') were carried out on the molten PEN by Advanced Rheometric Expansion System (ARES) in the parallel-plate geometry at several different temperatures and frequencies, followed by structural analysis by differential scanning calorimeter (DSC), X-ray diffractometer, and polarizing microscopy for the shear-induced crystallized PEN specimens in the ARES measurements. The rate of isothermal crystallization of PEN was notably affected by temperature, while the shear rate has an important effect on the structures of the resultant crystals. At a constant shear rate, the rate of crystallization by shear-induced structuring mechanism was increased with lowering temperature over the temperature range 230–250°C. The rate of crystallization was increased with increasing shear rate at a given temperature. An increase in shear rate increased both nucleation and number of crystallites. Further, it increased the content of the α -form crystal in the specimen. On the other hand, lower shear rate offered more favorable conditions for forming the β -form crystal. DSC analysis exhibited that the β -form crystal had higher melting temperature (T_m) than the α -form crystal. The wide angle X-ray diffraction (WAXD) patterns also ascertained that higher content of the α -form crystal was produced in the PEN specimen crystallized at higher frequency. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene naphthalate); Rheology; Shear-induced crystallization

1. Introduction

Shear-induced structural changes in polymeric materials take an increasing interest in the field of polymer processing. In real polymer processing very complex deformation histories are involved, which can influence ultimate properties of plastics. Recent advances in experimental techniques that allow in situ measurements of materials under deformation have escalated research in this subject area. It has been known for a long time that flow stress have accelerating effect on the crystallization of semi-crystalline polymers [1–6]. It is supposed that the application of a shear stress to a polymer melt should lead to formation of orientation and reduce the entropy of the melt, which results in a higher melting temperature and, hence, lead to an increased supercooling [3,7]. Several experiments have been described in the literature where attempts were made to quantify the shear stress-induced crystallization in molten semi-crystalline polymers such as polypropylene [3,8,9], polyethylene oxide [10], polypropylene [11–13], and polybutene-1 [3,14]. Some investigators used rotational viscometers and

measured either the volume change [15] or the number of nuclei formed during shearing [11,14]. The polymers enumerated above are apt to process because of low melting point and viscosity. On the other hand, PEN has good thermal and mechanical properties and is being used as engineering plastics.

PEN is reported to have two different triclinic crystalline structures, α -form and β -form crystals. Of two crystal forms, the β -form crystal is known to be more stable than the α -form. The effect of crystallization temperature on the resultant crystal structure is well recognized; lower temperature favors formation of the α -form crystal. The critical temperature is reported about 230°C. However, the effect of shear history on the crystal structure of PEN has not been reported. In this study, the shear-induced crystallization behavior of PEN was investigated on the rheological basis. The effect of shear history on the crystalline structure was also discussed in terms of thermal and morphological properties.

2. Experimental

2.1. Material

The PEN tested was a commercially available grade

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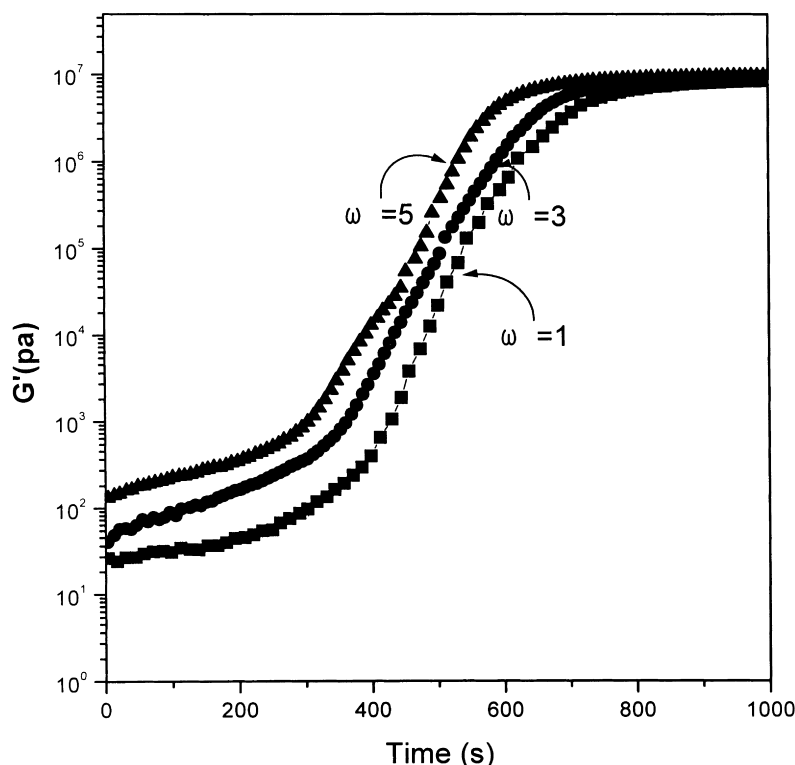


Fig. 1. Variation of G' with time for PEN melt at 240°C at three different frequencies.

supplied by Kolon Group in South Korea. The inherent viscosity, 0.344 dl/g was determined in a mixture of trifluoroacetic acid and chloroform (1/3 v/v%) with an Ubbelohde viscometer at $25 \pm 0.1^\circ\text{C}$. The polymer was dried in a vacuum oven at 120°C for 24 h prior to use.

2.2. Measurement of physical properties

The dynamic rheological properties were measured by ARES (Rheometric Scientifics) in the parallel plate geometry. The plate diameter was 12.5 mm, strain level was 5%, and gap between the plates was 1 mm. The PEN chips were melted at 300°C . The initial gap was set to a value equivalent to final gap plus $50 \mu\text{m}$. The excess sample squeezed out by reducing the gap was carefully trimmed off. The value was reset to the final gap value, 1 mm. To remove the residual stress the newly set PEN specimen was relaxed for about 5 min at the temperature in nitrogen atmosphere, then cooled to the predetermined temperature for rheological measurements. A time-sweep experiment was continued for the specimen till the G' reached the ceiling value of the apparatus. After ARES measurement, the molten PEN sample was detached from the plates for measuring other properties such as thermal and morphological properties by DSC, X-ray diffractometer and polarizing optical microscopy.

Thermal properties were measured by Perkin–Elmer DSC-7 over the temperature 50 – 300°C at the heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen purge. The isothermal

crystallization experiment was performed by two different methods. Firstly, the PEN sample was heated to 300°C at the heating rate of $200^\circ\text{C}/\text{min}$, and held for about 5 min, then they were cooled to the preset temperature to bring about the isothermal crystallization for same time required in ARES experiment. Secondly, the PEN chips were melted at 300°C between two slide glasses for 5 min on the hot stage. They were moved to an oil bath very quickly and isothermally crystallized at 230, 240, and 250°C for 4, 10, and 24 h, respectively.

Wide angle X-ray diffraction patterns of the isothermally crystallized PEN specimen in the oil bath and ARES were obtained by X-ray diffractometer (Rigaku Denki) with Ni-filtered $\text{CuK}\alpha$ radiation at 35 kV and 35 mA. Morphology of quiescent and shear-induced crystallized PEN specimen was observed by polarized microscopy (Nikon HFX-IIA). The spherulite structure was observed by microtoming the specimen.

3. Results and discussion

In the plot of G' and η' versus time at a given frequency for a polymer, the two parameters may give information on the change in physicochemical properties of the polymer. For thermally sensitive polymer melts, an irreversible decrease of viscosity with time at a constant shear rate suggests the possibility of thermal degradation of polymer molecules, whereas an irreversible increase of viscosity

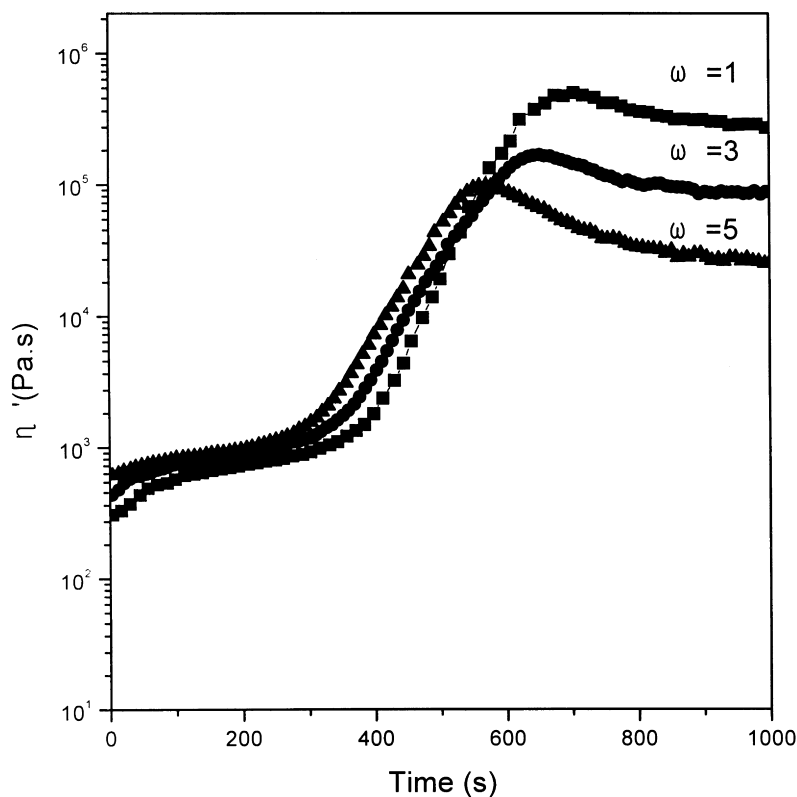


Fig. 2. Variation of η' with time for PEN melt at 240°C at three different frequencies.

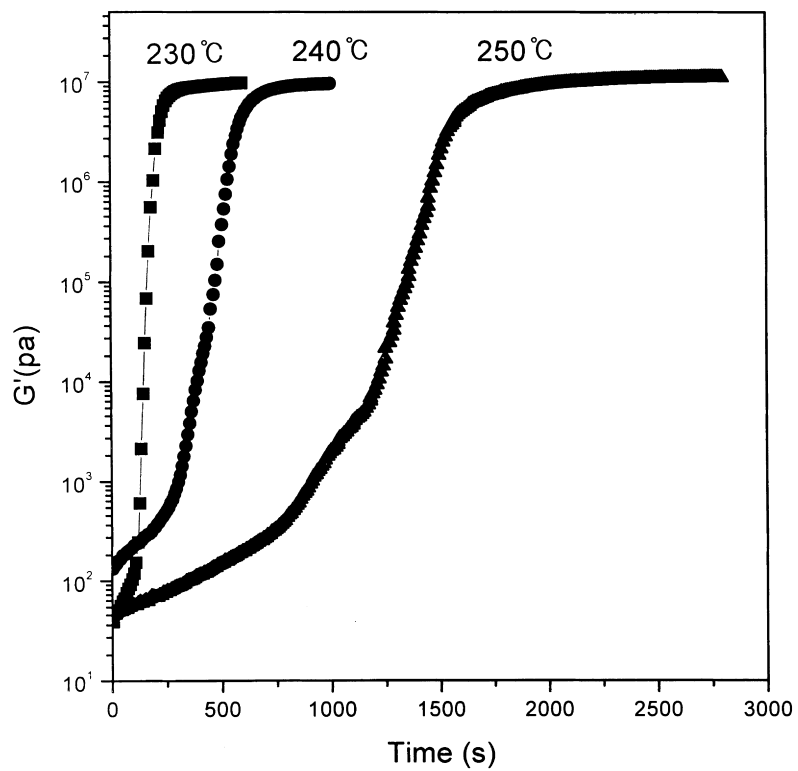
with time indicates the possibility of chemical crosslinking between polymer molecules. Both thermal degradation and chemical crosslinking show irreversibility in the rheological responses. On the other hand, a reversible change in G' and η' with time at a constant frequency may be caused by changing in the physical state of the polymer melts. A typical example of the physical change is the isothermal crystallization. As the crystallites grow to larger sized spherulites within the PEN melt through nucleation and growth, the homogeneous melt system changes to the heterogeneous system. Thus the G' and η' increase with the crystallization time.

Figs. 1 and 2 show the variation of the G' and η' of PEN melt with time at 240°C at three different shear rates (1, 3, and 5 rad/s). At the early stage of experiment, both G' and η' are increased slowly, indicating an induction time for crystallization. The induction period is the stage when randomly entangled polymer chains transform to the regular aligned lattice. Because of topological obstruction of such entanglements, the polymer crystallization is extremely slow [16]. However, an abrupt increase of both parameters follows in some minutes. This phenomenon can be ascribed to the formation of tiny crystals so-called crystallites probably due to shear-induced crystallization. It can be easily imagined that the homogeneous PEN melt changes to a suspension system with proceeding crystallization, in which numerous crystallites are dispersed in the homogeneous molten polymer matrix. The viscosity increases

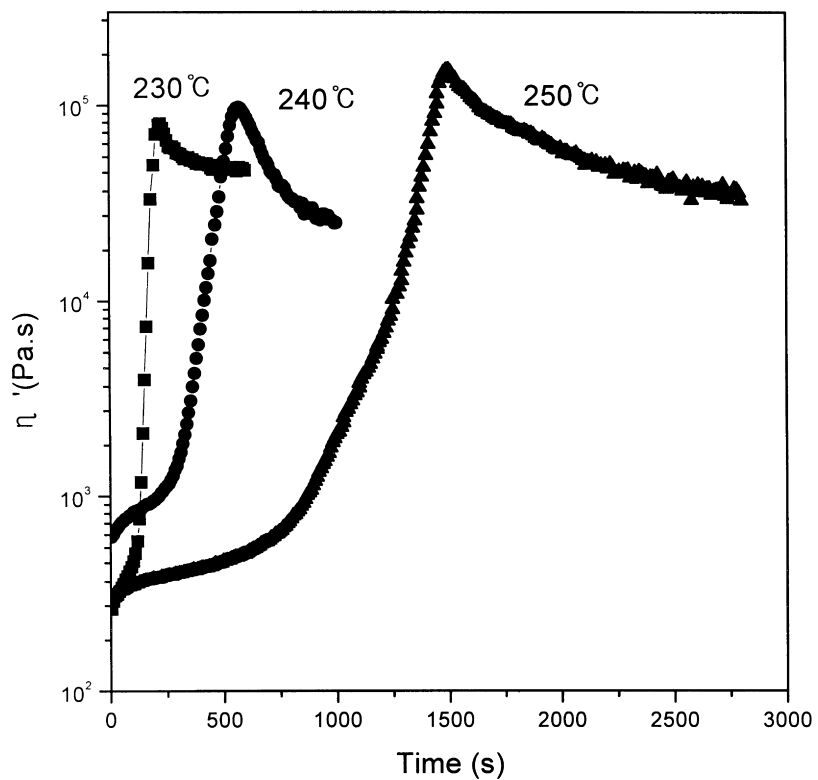
due to increasing the volume fraction of dispersed crystallites with progressing crystallization, which is also reported by others [7,9,11,14,17].

The ceiling value of G' is the same regardless of frequencies and temperatures when finishing crystallization as shown in Fig. 1. On the other hand, the ceiling value of η' is gradually decreased with increasing the applied frequency as shown in Fig. 2. This is attributable to pseudoplasticity. That is, the heterogeneous system is expected to show yield behavior [18]. At low shear rates the heterogeneous systems exhibit very high viscosity, and almost unbounded viscosity at zero shear rate. The viscosity, however, is rapidly decreased if the shear rate exceeds a critical value. Consequently, the ceiling viscosity at 1 rad/s is greater than at 5 rad/s. In addition, the ceiling value of η' shows a gradual decrease with time after having reached maximum as shown in Fig. 2, which is more noticeable at the higher frequency. The gradual decrease of η' seems to result from the restructuring of the heterogeneous systems. That is, the viscosity is decreased with shearing on account of destruction of the ordered filler particle structure. The destruction of the pseudostructure of filler particles is increased as shear rate is increased. Fig. 2 reflects this.

It is also noted in Figs. 1 and 2 that the induction time for crystallization is decreased as frequency is increased. An application of shear stress to a polymer melt would give rise to two characteristic responses, orientation and slippage of polymer molecules. They are associated with the

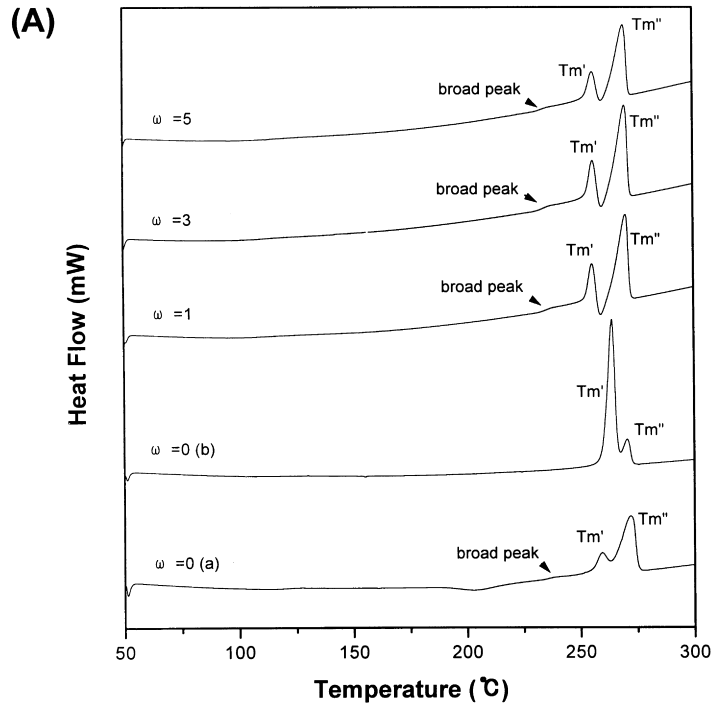


(A)



(B)

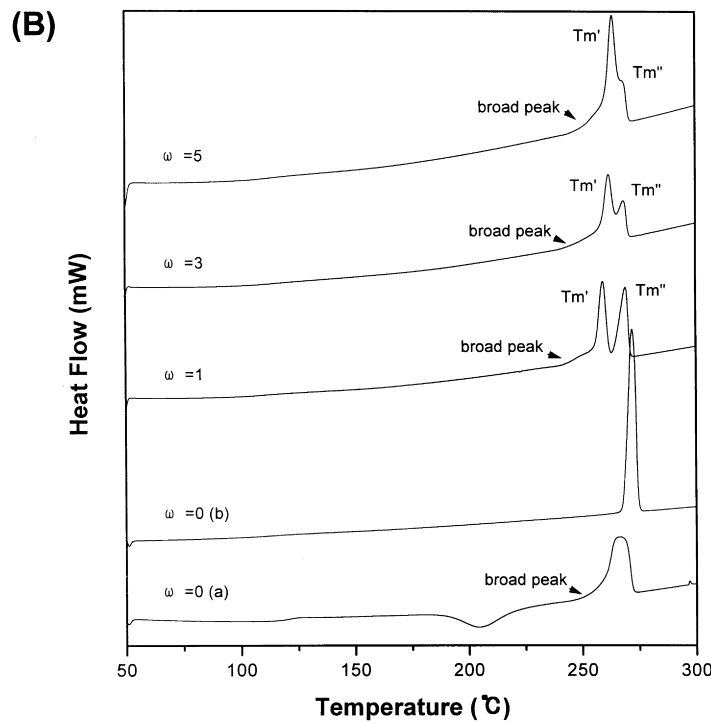
Fig. 3. Variation of G' (A) and η' (B) for PEN melt at 3 rad/s at three different temperatures.



$\omega = 1,3,5$: sample shear-induced crystallized at 230 °C for 10 min by ARES

$\omega = 0$ (a) : sample crystallized at 230 °C for 10 min in DSC

$\omega = 0$ (b) : sample crystallized at 230 °C for 4 hrs. in oil bath

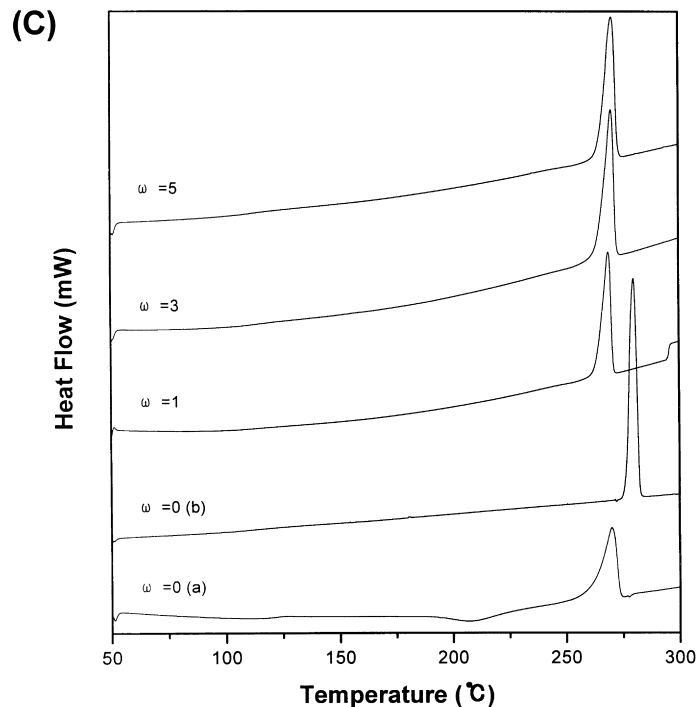


$\omega = 1,3,5$: sample shear-induced crystallized at 240 °C for 17 min by ARES

$\omega = 0$ (a) : sample crystallized at 240 °C for 17 min in DSC

$\omega = 0$ (b) : sample crystallized at 240 °C for 10 hrs. in oil bath

Fig. 4. DSC thermograms of PEN isothermally crystallized at (A) 230°C, (B) 240°C and (C) 250°C at various frequencies.



$\omega = 1, 3, 5$: sample shear-induced crystallized at 250 °C for 47 min by ARES
 $\omega = 0$ (a) : sample crystallized at 250 °C for 47 min in DSC
 $\omega = 0$ (b) : sample crystallized at 250 °C for 24 hrs. in oil bath

Fig. 4. (continued)

macroscopic phenomena of elasticity and flow, respectively. That is, the oriented polymer molecule has fewer possible conformations than the unoriented one, which results in lower entropy. At the melting temperature, the free energy of the crystal equals the free energy of the melt as written by [3]

$$T_m = \frac{\Delta H_f}{\Delta S_f} = \frac{H_m - H_c}{S_m - S_c} \quad (1)$$

Hence, for an oriented melt, the ensuing reduction in entropy raises T_m . Further, it increases the degree of supercooling, accelerating the rate of crystallization. In general, higher shear rate gives better chance for orientation. Consequently, the induction time for crystallization is decreased with increasing shear rate.

In Fig. 3(A) and (B) shows that the annealing temperature

has a profound effect on the nucleation and crystallization mechanism of PEN melts. The increase of G' and η' with annealing time represents the extent of crystallization of the melts with annealing time. Fig. 3 suggests that the number and growth rate of the nucleated crystallites is greater at 230 °C than at 250 °C. That is, both nucleation density and growth rate of crystallites are diminished with raising the annealing temperature. This stands to reason because the maximum rate of the homogeneous crystallization of PEN melts is observed in the vicinity of 215 °C.

The viscosity behavior of the PEN melt with crystallization in Fig. 3 may be accounted for by adopting the Mooney equation in a qualitative manner [19].

$$\ln(\eta/\eta_1) = \frac{K_E \Phi_2}{1 - \Phi_2/\Phi_m} \quad (2)$$

Table 1

The values of T_m' and T_m'' of PEN with frequency (230, 240 and 250 indicate temperature. (a) and (b) indicate $\omega = 0$ (a) and $\omega = 0$ (b), respectively (see Fig. 6). 1, 3 and 5 indicate frequency

	T_m'	T_m''		T_m'	T_m''		T_m'	T_m''
PEN230(a)	259.2	272.1	PEN240(a)		266.7	PEN250(a)		270.1
PEN230(b)	264.1	270.9	PEN240(b)		272.1	PEN250(b)		280.1
PEN2301	255.6	270.3	PEN2401	259.3	269.3	PEN2501	269.1	
PEN2303	256.0	270.0	PEN2403	261.9	268.7	PEN2503	270.4	
PEN2305	256.2	269.7	PEN2405	263.6	268.0	PEN2505	270.7	

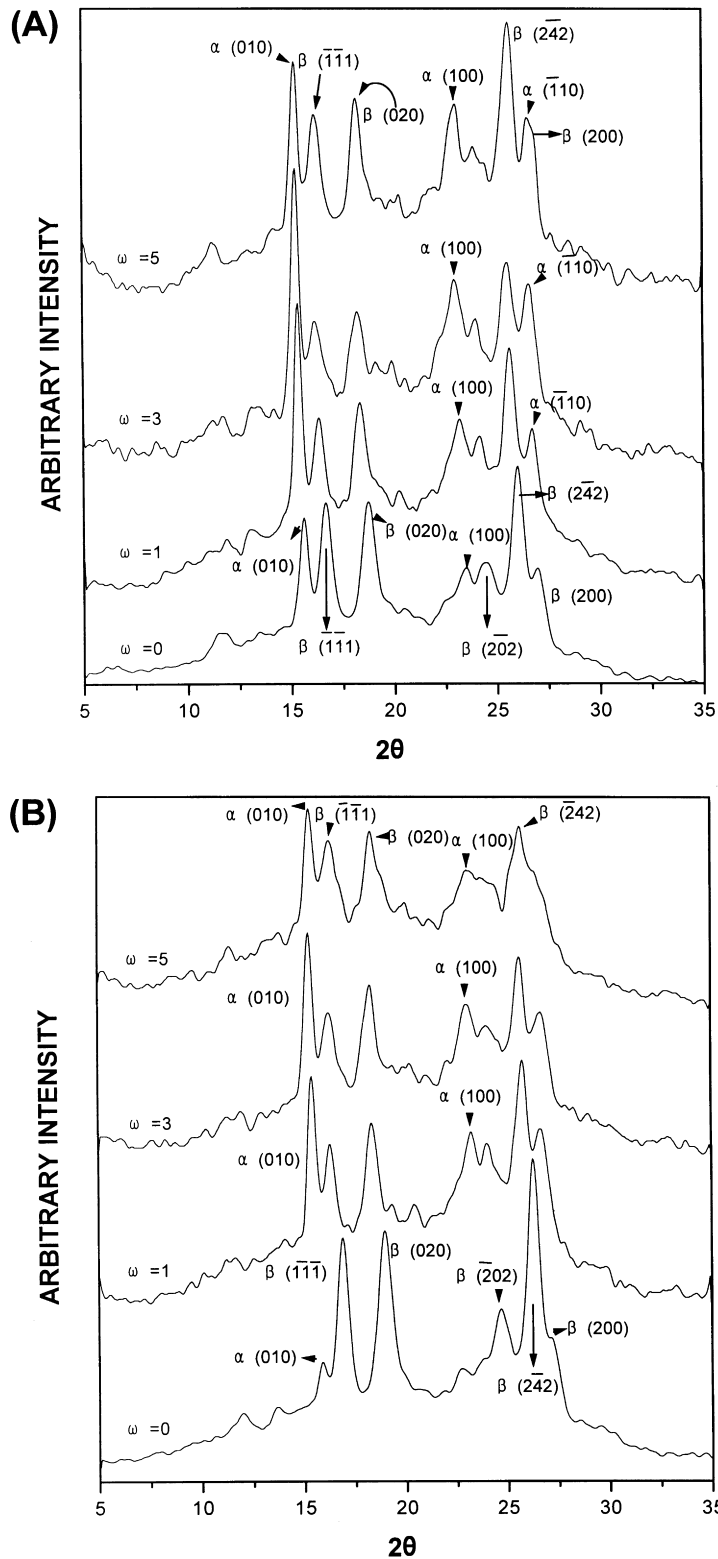


Fig. 5. WAXD patterns of PEN isothermally crystallized at (A) 230°C, (B) 240°C and (C) 250°C at various frequencies.

$$\Phi_m = \frac{\text{true volume of filler}}{\text{apparent volume occupied by the filler}} \quad (3)$$

in which η is the viscosity of the suspension, η_1 is the

viscosity of the suspending medium, ϕ_2 is the volume fraction of the filler, ϕ_m is the maximum volume fraction that the filler can have, and K_E is the Einstein coefficient, whose value is known to be 2.5 for the dispersed spherical filler.

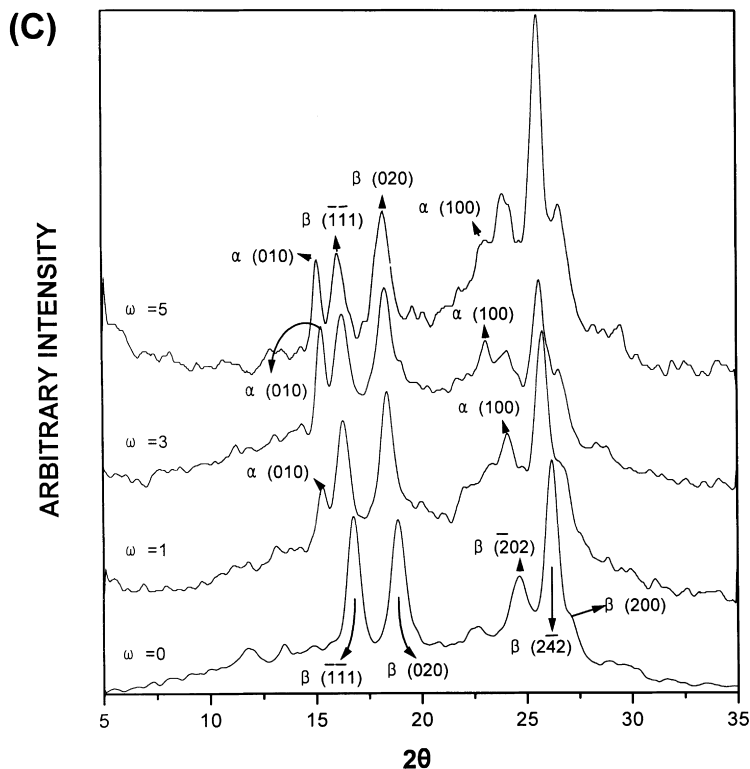


Fig. 5. (continued)

Referring to the Mooney equation, the crystallization patterns of PEN melts at 230°C and at 250°C are distinctively different from each other. The Mooney equation predicts that the degree of increasing the suspension viscosity with increasing ϕ_2 is greatly increased if the spheres form aggregates because the aggregation of spheres (spherulitic crystallites or crystals in this study) increases the apparent filler volume fraction. That is, the immobile portions (homogeneous molten PEN matrix in this study) caged by aggregated spheres also act as filler portion. On this assumption, it may be suggested that an application of higher shear rate during isothermal crystallization tends to increase the heterogeneous crystallization characteristics. Hence, the higher nucleation density and higher growth rate of the nucleated crystallites is obtained at higher frequency, and the resultant is more abundant with less stable α -form crystals (this will be discussed later in detail).

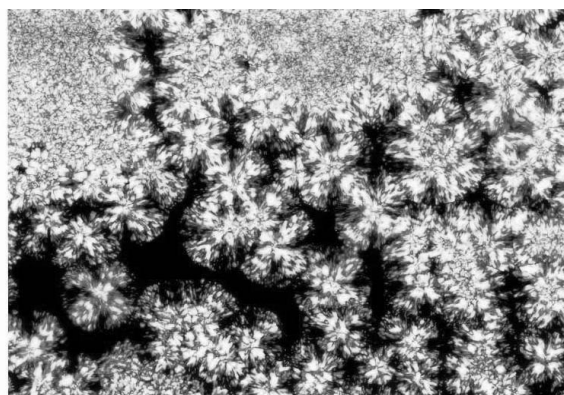
The melt endotherms of quiescently and shear-induced crystallized PEN were shown in Fig. 4 and the corresponding peak temperatures are listed in Table 1. The double melting endotherm behavior is displayed during heating the PEN sample in the DSC cell. In the melting process of the shear-induced crystallized PEN sample, three endothermic peaks are identified; a broad endotherm, a low endotherm (T_m'), and a high endotherm (T_m'') as shown in Fig. 4. The broad endotherm might be due to the thermal history during cooling and reheating, and both low and high endotherms are due to the melting of original lamella and recrystallized one, respectively. These results well coincide

with the results of Zachman et al. [20]: (1) no change of crystal modification is observed during DSC scanning; (2) the double melting behavior of PEN is due to the mechanism based on melting and recrystallization; (3) the β -form crystal has the T_m higher than the α -form crystal by 2°C; and (4) the peaks of two forms of crystal are not separated in DSC thermograms

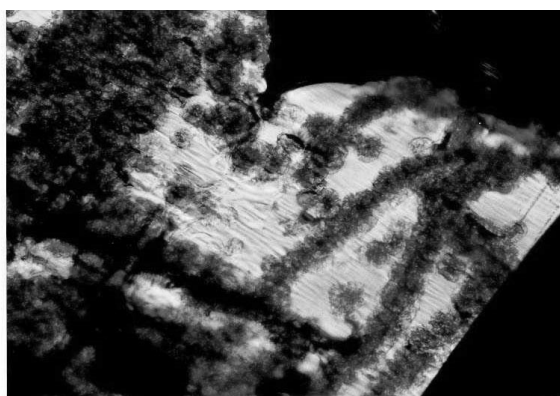
In Fig. 4(A)–(C) $\omega = 0$ rad/s indicates quiescent crystallization. (A) indicates that the PEN sample was crystallized at 230, 240, and 250°C for the same time that required in the ARES experiments, and (B) expresses the PEN sample crystallized in an oil bath at the same temperature as in (A) for the time long enough to fully crystallize. Since the crystallization time in (A) is much shorter than in (B), an exothermic peak is observed in the thermogram (A) at around 205°C.

The $\omega = 0$ rad/s (b) curves in Fig. 4 (B) show a single melting peak. The T_m shifts to higher temperature and peak width gets narrower as the crystallization time and temperature are increased. This is attributable to the increased perfectness of the resultant crystal structure, which is observed more clearly when the sample is crystallized at higher temperature as can be seen in Fig. 4(C). Only the β -form crystal exists when the sample is isothermally crystallized at 250°C after having melted at 300°C. This result matches well with the X-ray data. As mentioned the T_m of the β -form crystal is higher than the α -form crystal by 2–4°C.

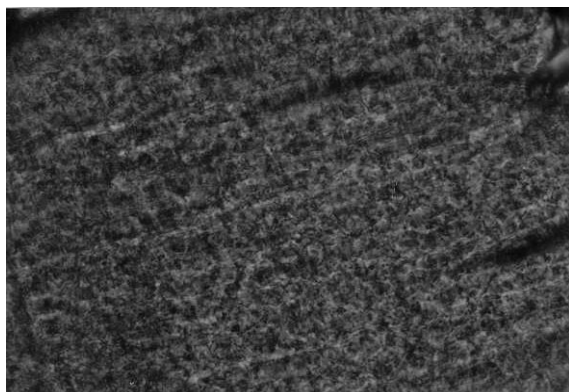
It has been known that PEN has two different triclinic crystal structures. Buchner et al. reported that crystal



(A)



(B)



(C)

Fig. 6. Polarizing optical micrographs of PEN crystallized at 240°C (A) $\omega = 0$, (B) $\omega = 1$, and (C) $\omega = 5$.

structures are influenced by both melting and isothermal crystallization temperature. They observed that the β -form crystal appeared mainly when PEN was isothermally crystallized above 230°C quiescently and the α -form crystal did below 230°C after having melted at 300°C [20]. Fig. 5 presents WAXD patterns of PEN specimens shear-induced

crystallized at (A) 230°C, (B) 240°C, (C) 250°C at several frequencies. In Fig. 5(A) the WAXD patterns for $\omega = 0$ rad/s shows diffraction peaks at 15.6 and 23.3° which correspond to (0 1 0) and (1 0 0) plane of the α -form crystal, respectively. The intensity of these peaks has a tendency to increase with increasing frequency. It means that the application of shear promotes the formation of the α -form crystal and the increase of frequency increases the content of the α -form crystal. In Fig. 5(B) the (0 1 0) plane peak of the α -form crystal is smaller than that of the sample crystallized at 230°C in Fig. 5(A) for $\omega = 0$ rad/s. However, the plane peak is increased with increasing frequency. In the case of the (1 0 0) plane peak, a shoulder appears at $\omega = 0$ rad/s. As frequency increases, the intensity of the plane peak standing for the α -form crystal shows tendency to increase. Particularly, for $\omega = 0$ rad/s in Fig. 5(C) any plane peak of the α -form crystal is not observed, which is consistent with the results reported by Buchner et al. [20]. The (0 1 0) and (1 0 0) plane peaks appear simultaneously, and keep on growing with increasing frequency. In addition, all diffraction peaks of Fig. 5 shift to lower angle when frequency is increased. This suggests that there is deformation in the crystal structures as well. Thus, this X-ray trace of the sample is similar to those of Fig. 5(A) and (B), suggesting similarity in the crystallization behavior at 230–250°C.

In general, the β -form crystal is thermodynamically more stable but more difficult to nucleate than the α -form crystal and the form of the crystal is largely determined by kinetic factors during crystallization such as the rate of nucleation and spherulite growth [21]. In the case of the α -form crystal, one chain passes through the unit cell and the chains in the crystal are extended. In the case of the β -form crystal, however, four chains pass through the unit cell and the chains in the crystal are not completely extended. When the polymer is sheared, the number of crystallites increases with shear rate, representing faster nucleation. Wolkowicz [14] mentioned that the number of crystallites increased exponentially with time at all shear rates. Also, this can be confirmed in Fig. 6, which indicates that nucleation becomes increasingly profuse with increasing frequency until the crystalline structure formed is no longer distinguishable with a microscope [3,22]. Hence, the content of the α -form crystal in the specimen increases with frequency because the α -form crystal is apt to nucleate due to fast nucleation. Consequently, the resultant α -form crystal is thermodynamically less stable than the β -form crystal because of much reduced entropy by molecular orientation under high shear force.

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