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Blends of poly(ethylene 2,6-naphthalate) with liquid-crystalline polymers: crystallization behavior and morphology

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Abstract

The isothermal crystallization behavior and morphology of blends of Poly(ethylene 2,6-naphthalate) (PEN) with two types of liquid-crystalline polymers (LCP) (rigid and semiflexible) have been studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and scanning electron microscopy (SEM). The blends posses a two-phase morphology due to immiscibility of the two components. The dispersion of the minor LCP phase is favored at a low LCP concentration (7 wt%). The PEN overall crystallization rate is enhanced strongly by the addition of LCPs. The maximum enhancing effect has been found to occur at a LCP concentration of ca. 7 wt%. The POM observations show that PEN spherulite dimensions decrease in the presence of LCPs. These results have been interpreted on the basis of a heterogeneous nucleation played by the crystallized LCP particles on the molten PEN matrix. The nucleation mechanism and the equilibrium melting temperature of PEN are not changed by the presence of a dispersed LCP phase. The relationship between blend morphology and nucleation phenomena has been discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene 2,6-naphthalate)/liquid-crystalline polymer blends; Crystallization; Morphology

1. Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is produced by polycondensation of 2,6-naphthalene dicarboxylic acid and ethylene glycol [1]. PEN and poly(ethylene terephthalate) (PET) structures differ only in the aromatic moiety in the repeating unit. PEN is a high-performance thermoplastic with superior mechanical properties, lower gas permeability and higher capability of absorbing UV radiation than those of PET [1–3]. The PEN polymer resin has been suited for use in high-performance applications for films, fibers, extrusion-based processes, engineering polymers, medical packaging and color concentrates. Additionally, applications exist for the material in several bottling markets.

However, the PEN homopolymer shows some drawbacks that may limit its use, namely its rather high-melt viscosity makes difficult fiber spinning and injection molding [4]. Therefore, blending PEN with thermotropic liquid-crystalline polymers (LCP) results in an interesting system for application and fundamental studies on the properties of LCP–polymer blends. It is well known that LCP can provide not only improved mechanical properties to the thermoplastic matrix polymer by the formation of fibril in situ, but also improves the processability of the polymer by reducing the melt viscosity [5–7]. For these blends the effect of LCP upon the kinetics and thermodynamics of polymer crystallization has been also investigated with a view to define whether LCP can accelerate the rate of crystallization [8,9]. If LCP causes a reduction in the crystallization rate, the time of manufacturing cycle is increased and, therefore, the productivity is decreased.

The crystallization behavior of the PEN matrix in PEN–LCP blends has not yet been studied. However, the studies carried out on blends of PET with different LCPs led to contradictory results. For example, it has been shown that the wholly aromatic LCP Vectra-A (VA) by Hoechst–Celanese has a nucleating effect upon PET crystallization [10–12]. On the contrary, in other investigations [13–15] no evidence in favor of a nucleating effect of VA has been found. The study on the phase behavior of blends of PET with VA and the semiflexible LCPs Rodrun LC-5000 and Rodrun LC-3000 by Unitica has demonstrated that all LCPs retard the dynamic crystallization of PET [16]. The lower the LCPs degree of aromaticity, the more pronounced was the latter effect [16].

The kinetics of crystallization of pure PEN from melt under isothermal and non-isothermal conditions as well as

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its crystal morphology have been studied [2,17–19]. PEN has been shown to follow the Avrami behavior during isothermal crystallization [17]. The activation energy for isothermal crystallization is higher than that for PET, and results from the rigidity of the naphthalene ring raising the crystallization barrier due to geometrical constraints [17]. The unit cells of the two PEN crystal structures (α-form and β-form) [19] have been determined. The existence of an additional unit cell (γ-form) has been found [19] and recently a mesomorphic form has been described [20]. The PEN equilibrium melting parameters have been also established [21].

In this work, the influence of two types of LCP (rigid and semiflexible) upon the isothermal crystallization of PEN from melt has been studied. The aim has been to establish if the minor LCP phase can accelerate the crystallization rate of the matrix PEN phase. The morphology of the melt crystallized PEN structures in the blends has been also investigated.

2. Experimental section

2.1. Materials

The grade of PEN X61, kindly provided by Du Pont Ohio, was used for the preparation of the blends. The sample had intrinsic viscosity of 1.64 (measured in 60/40 phenol/tetrachloroethane at 25°C). The wholly aromatic LCP VA was purchased from Hoechst–Celanese. The semiflexible LCP, referred to as A8, was a laboratory sample, synthesized by melt polycondensation of poly(ethylene terephthalate) (10 mol%), hydroxybenzoic acid (76.5 mol%), terephthalic acid (6.75 mol%) and 4,4′-dixydroxybiphenyl (6.75 mol%) [22]. The latter compound used in the synthesis was in its acetylated form. This LCP had crystal-nematic transition at 305°C and nematic-crystal transition at 271°C, at a heating/cooling rate of 10°C/min [22]. VA had nematic-crystal transition at 255°C at a cooling rate of 10°C/min [16].

2.2. Blend preparation

The blends were prepared in a Brabender Plastograph mixing bowl (30 ml capacity) under nitrogen atmosphere. The mixing temperature was 320°C, the rotation speed 60 rpm and the mixing time 5 min. Blends of PEN with 7 and 13 wt% LCPs were prepared. The pure PEN underwent the same treatment before characterization.

2.3. Methods

The isothermal crystallization kinetics were studied using a Perkin Elmer DSC-7 apparatus, calibrated with indium and tin standards, under nitrogen atmosphere. The specimens were heated to 320°C in order to destroy the PEN crystal nuclei [17], kept at this temperature for 5 min, and cooled to the appropriate crystallization temperature T_c (in the range 170–230°C) at a rate of 200°/min. The heat evolved upon isothermal crystallization was recorded and the fraction X_t of the polymer crystallized at time t was evaluated as the ratio of the area under the curve at time t to that of the whole exotherm. The starting time of crystallization was taken as that at which thermal equilibrium was reached at T_c. The area of the exotherm was measured by back extrapolation of the baseline after complete crystallization.

The melting temperature T_m of the isothermally crystallized samples was determined by heating them, directly from T_c, at a rate of 10°/min.

Optical microscopic observations were made on a Leica DMLP polarizing microscope equipped with a hot stage. Small blocks were cut from the sample, placed onto a clean glass slide and melted at 320°C. The melted polymers were then sheared using a razor blade in order to obtain thin polymer films. The films were transferred quickly on the hot stage of the microscope, preliminarily preset at the temperature of crystallization T_c. The photomicrographs were taken at room temperature.

The scanning electron microscope (SEM) observations were performed on a JEOL 5300 apparatus. The polymer samples were fractured in liquid nitrogen and the fracture surfaces were contrasted with gold.

3. Results and discussion

3.1. Isothermal crystallization behavior of PEN–LCP blends

The isothermal crystallization of PEN, either neat or blended with both LCP was studied in the range of crystallization temperatures between 170 and 230°C. It could be stated that the LCPs remain in the solid crystalline state in the temperature interval of PEN isothermal crystallization. Thus, the recorded isothermal differential scanning calorimetry (DSC) traces consist of single exothermic peaks whose area provides a measure for the extent to which PEN crystallization occurs.

Fig. 1 shows plots of the conversion degree X_t of the PEN component against log time for neat PEN (Fig. 1a) and for a 93/7 PEN–VA blend (Fig. 1b) at various T_c. The plots that have a typical sigmoidal shape are shifted to shorter crystallization times with increasing T_c from 170 to 190°C and are shifted to longer times with increasing T_c from 190 to 230°C for the neat PEN (Fig. 1a) and for the blend (Fig. 1b). That means the maximal rate of crystallization of the samples, crystallized from melt, appears at $T_c = 190$°C. This result for the neat PEN is in perfect agreement with literature data [2]. Evidently, the presence of the LCP component does not influence the temperature of the maximal rate of crystallization of PEN. However, the presence of the LCP causes a drastic shift of the crystallization isotherms of the blends to shorter crystallization times at every T_c (Fig. 1a and b).

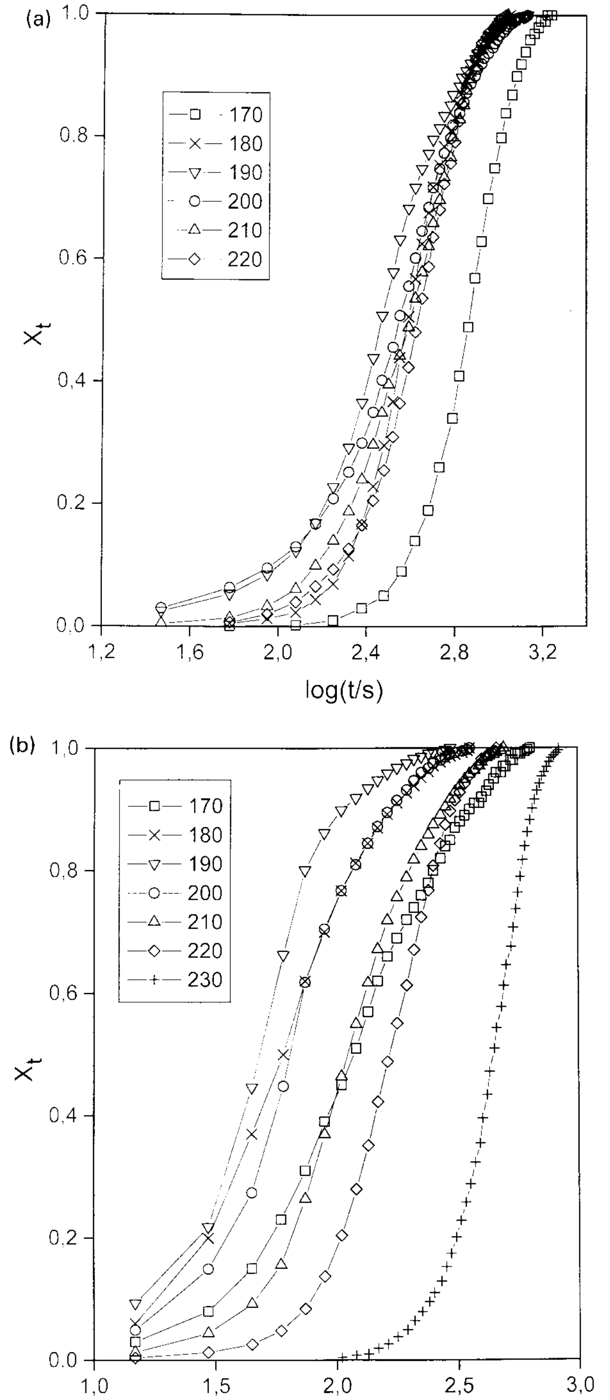

Fig. 1. Plots of PEN component degree of conversion X_t against log t at different T_c: (a) neat PEN; and (b) 93/7 PEN–VA blend.

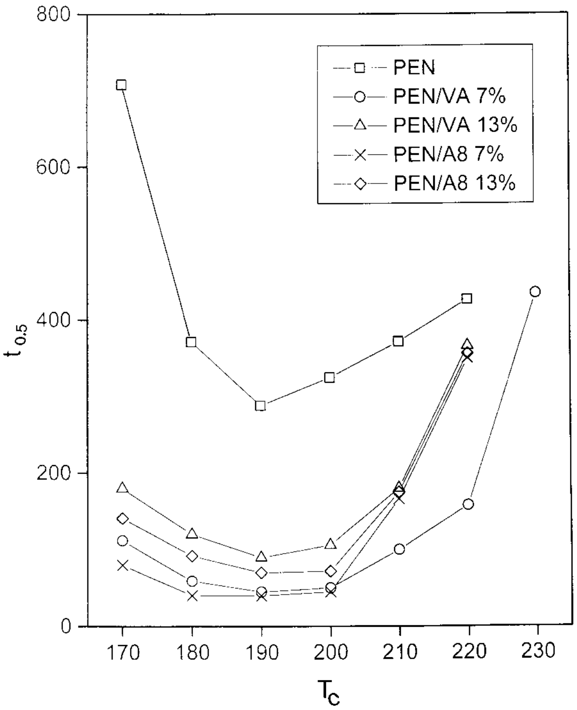

Fig. 2. Dependence of the half-time of crystallization $t_{0.5}$ on T_c for neat PEN and the blends.

Fig. 2 shows the dependence of the half-time of crystallization $t_{0.5}$ on the crystallization temperature T_c for the neat PEN and PEN–LCP blends. The half-times of the neat PEN are lower than those of PENs with lower molar masses, as reported in the literature [2,17]. That means a higher molecular weight PEN crystallizes slowly due to the slower diffusion motion in the melt [17]. It is apparent (Figs. 1 and 2) that the addition of LCPs into PEN decreases the half-crystallization times, particularly for the 7 wt% LCP blends. Evidently, the dispersed LCP phase plays a nucleating role, whose efficiency is greater for the blends with 7 wt% LCP, probably because of the larger interfacial surface obtained for these compositions.

The crystallization kinetics of all samples at each T_c were analyzed by means of an Avrami equation [17]

$$X_t = 1 - \exp(-K_n t^n),$$

where X_t is the fraction crystallized at time t, K_n the kinetic constant and n the Avrami exponent, depending on the nucleation type and growth geometry of the crystals. The values of K_n were determined with the equation [23]

$$K_n = \frac{\ln 2}{t_{0.5}^n},$$

where $t_{0.5}$ is the half-time of crystallization. The Avrami exponent, n, were calculated from the slopes of the linear plots of $\log[-\ln(1 - X_t)]$ versus log (t). Examples of these plots are shown in Fig. 3a for neat PEN and in Fig. 3b for 93/7 PEN–VA blend, isothermally crystallized at various T_c. With increasing T_c the plots shift toward shorter times up to $T_c = 190$°C and then shift toward longer times. This reveals that the crystallization rate increases until the maximal rate of crystallization is reached and then it decreases with the crystallization temperature. This is an evidence that the crystallization takes place by a nucleation-controlled mechanism. It is clearly observed that the slope of the

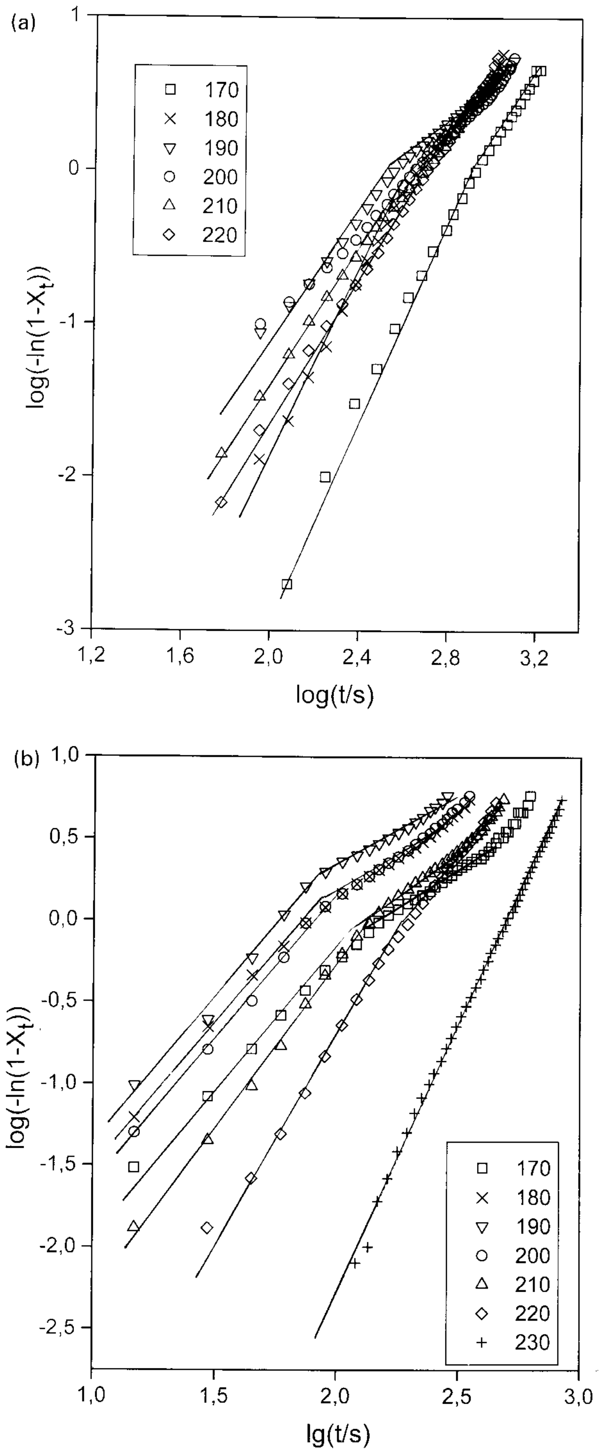

Fig. 3. The Avrami plots for PEN and PEN–LCP blends crystallized at various T_c: (a) neat PEN; and (b) 93/7 PEN–VA blend.

plots tends to become smaller at high X_t, thus showing that secondary crystallization processes take place.

Table 1
Isothermal crystallization parameters

Sample	T_c (°C)	$t_{0.5}$ (s)	n	K_n (s^{-n})
PEN	220	427	2.5	1.8×10^{-7}
	210	372	2.5	2.5×10^{-7}
	200	325	2.4	6.5×10^{-7}
	190	289	2.4	8.6×10^{-7}
	180	372	2.9	2.4×10^{-8}
	170	708	2.9	3.7×10^{-9}
PEN–VA 7%	230	435	2.8	2.8×10^{-8}
	220	158	2.5	2.2×10^{-6}
	210	100	2.4	1.1×10^{-5}
	200	50	2.0	2.8×10^{-4}
	190	45	2.0	3.4×10^{-4}
	180	59	2.0	2.0×10^{-4}
	170	112	2.1	3.4×10^{-5}
PEN–VA 13%	220	366	2.4	4.8×10^{-7}
	210	180	2.5	1.6×10^{-6}
	200	106	2.1	3.8×10^{-5}
	190	90	2.0	8.5×10^{-5}
	180	120	2.0	4.8×10^{-5}
	170	180	2.1	1.3×10^{-5}
PEN–A8 7%	220	350	2.3	9.7×10^{-7}
	210	166	2.3	5.4×10^{-6}
	200	45	2.1	2.3×10^{-4}
	190	40	2.1	2.9×10^{-4}
	180	50	2.1	1.9×10^{-4}
	170	80	2.1	6.9×10^{-5}
PEN–A8 13%	220	356	2.4	5.2×10^{-7}
	210	175	2.4	2.8×10^{-6}
	200	72	2.3	3.7×10^{-5}
	190	70	2.1	9.2×10^{-5}
	180	92	2.1	5.2×10^{-5}
	170	141	2.1	2.1×10^{-5}

The isothermal crystallization parameters are collected in Table 1. The Avrami exponent, n, for the neat PEN is in the range 2.4–2.9, indicating heterogeneous nucleation and three-dimensional growth in good agreement with literature data [17]. The Avrami exponents for the PEN–LCP blends are in the range 2.0–2.8, thus showing that the crystallization mechanism of PEN does not change in the presence of LCP. As seen for both pure and blended PEN, the Avrami exponents n have smaller values in the temperature range $T_c = 190$–200°C where the crystallization proceeds at a higher rate, while in the temperature range 210–230°C, n increases. It could be assumed that an increase of PEN nucleation and crystallization rate at $T_c = 190$–200°C leads to the formation of sheaf-like superstructures not fully developed into spherulites and to impingement of PEN spherulites occurring even during the primary crystallization [24]. The values of n drop to about 1.5 during secondary crystallization of PEN and PEN–LCP blends, which are attributed to heterogeneous nucleation and monodimensional crystal growth. The change in the crystallization mechanism at higher conversion is normally attributed to the effect of impingement and truncation of the spherulites.

The values of the kinetic constants K_n for the PEN–LCP blends are higher than that established for neat PEN at each T_c (Table 1). The kinetic constant K_n as a function of

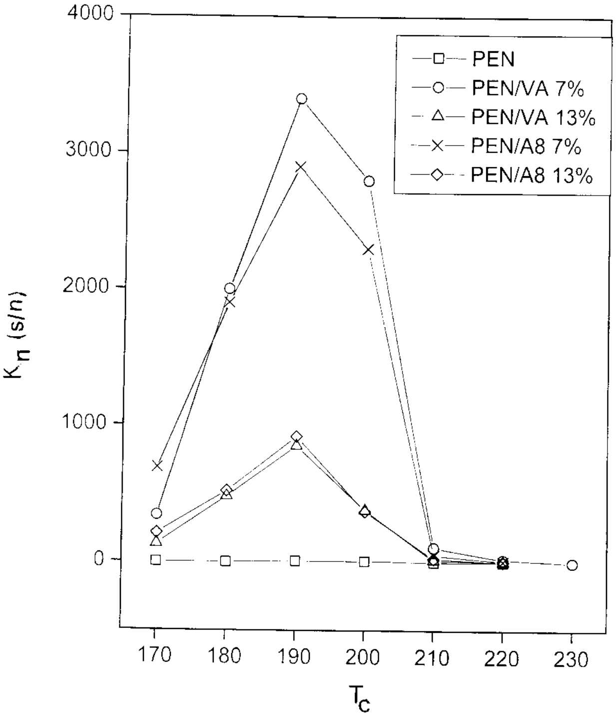

Fig. 4. Dependence of the kinetic constant K_n on T_c for the samples.

crystallization temperature for PEN and PEN–LCP blends is shown in Fig. 4. The data from Table 1 and Fig. 4 show the maximum value around 190°C, at which the half-time of crystallization is a minimum. As seen (Table 1, Fig. 4), there is a drastic increase in K_n (three to four orders of magnitude) for the blends with 7 wt% LCP, while this increase for the blends with 13 wt% LCP is two to three orders of magnitude. The influence of the LCP on the value of K_n tends to decrease at higher T_c. These results show that the overall crystallization rate of bulk PEN increases markedly in the presence of the LCP dispersed phase and this increase is more significant for the blends with 7 wt% LCP. This is due to the nucleation effect of the LCP on the crystallization of PEN matrix, which is more pronounced for the blends with lower LCP content. This result supposes finer dispersion of the LCP phase in the blends with 7 wt% LCP and consequently larger interfacial surface, than that in the blends with 13 wt% LCP. The results from electron microscopic observation on the morphology of the blends confirm the above conclusion.

The melting behavior of the isothermally crystallized samples has been studied by heating them, directly from T_c, at a rate of 10°/min. Fig. 5 shows the DSC melting traces of PEN crystallized isothermally at different temperatures. For PEN and PEN–LCP blends only one melting peak can be seen for $T_c = 170$ and 180°C. Two melting peaks can be observed at T_c in the range 190–220°C for all samples. The high-temperature large melting peak appears around 260–265°C with very little change. The low-temperature small melting peak increases with T_c from 242 to 260°C. At $T_c =$ 230°C, there is only one melting peak left. These results are in perfect agreement with those obtained by Cheng and Wunderlich [21]. Fig. 6 shows the dependence of melting temperatures of the two melting transitions on T_c; the data from Ref. [21] are also incorporated in Fig. 6. Obviously, the melting temperatures of the low-temperature peaks coincide almost completely with those from Ref. [21] in the range of investigated (190–230°C) T_c. The melting temperatures of the high-temperature peaks also present dependence on T_c similar to that in Ref. [21]. Unfortunately, the range of T_c investigated ($T_c = 170$–230°C) does not permit the determination of the equilibrium melting temperature of PEN. As reported in Ref. [21], the extrapolation of the melting temperatures with respect to T_c ($T_c = 227$–247°C), reaches the $T_m = T_c$ line at about 337°C, which is the equilibrium melting temperature of PEN (Fig. 6). However, as the melting parameters of PEN do not change in the presence of LCP in the range of T_c investigated, it could be assumed that the addition of LCP does not change the equilibrium melting temperature of PEN.

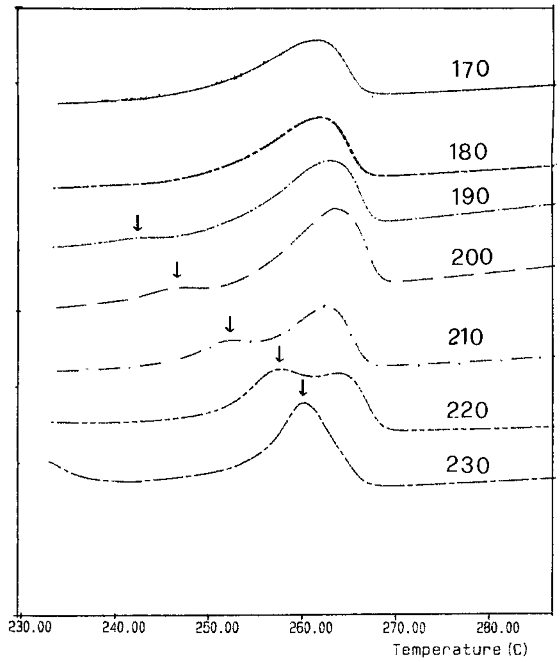

Fig. 5. DCS melting peaks of the neat PEN crystallized at various T_c. The arrows indicate the low-temperature melting peaks.

It should also be noted that the almost horizontal line representing the melting temperatures of high-temperature peaks of all samples suggests that crystal perfection has taken place during heating [21,25].

3.2. Morphology of PEN–LCP blends

The SEM micrographs of 93/7 and 87/13 PEN–VA blends, fractured under liquid nitrogen, are shown in Fig. 7. A two-phase morphology with scarce adhesion was always observed for all blends. The LCP forms the

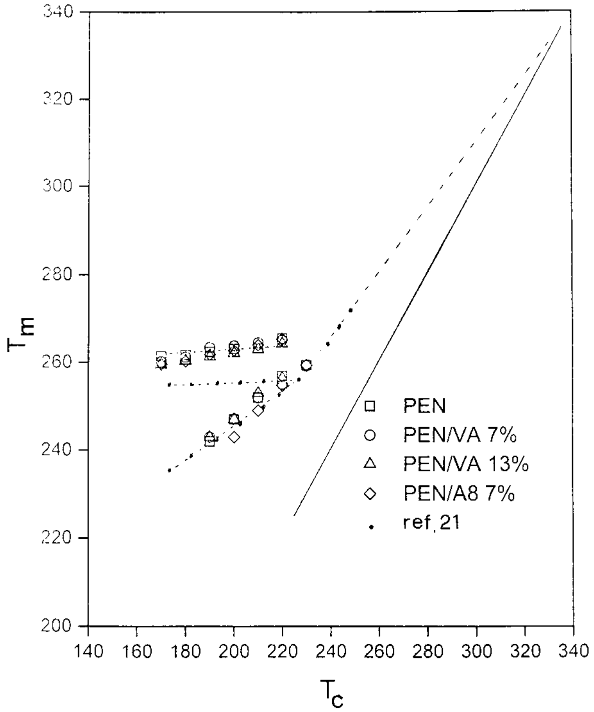

Fig. 6. Melting temperatures of the low-temperature and high-temperature melting peaks of isothermally crystallized PEN phase in PEN–LCP blends versus crystallization temperature. The data from Ref. [21] are also included.

dispersed phase with droplets dimensions depending on the blend composition. At 7 wt% concentration of LCP, the droplets are rather small (0.2–0.5 μm) and uniformly dispersed. At 13 wt% concentration of LCP, the dimensions of the droplets are approximately 4–5 times greater (1–2μm). The interphase adhesion appears worse in the latter blends, and this might be attributed to the fact that, when the LCP concentration grows, the dispersed droplets show an enhanced tendency to coalesce and give rise to large particles, which in turn are pulled out more easily from the matrix when the blend specimen is fractured. The coalescence of the dispersed droplets at an LCP concentration exceeding 7 wt% leads to a reduction of the interphase area and to a decrease in the concentration of heterogeneous nuclei; therefore the nucleation rate of PEN also decreases.

PEN morphology, isothermally crystallized from melt, has been studied recently [17,19]. It has been shown that when PEN crystallizes at a high temperature (245–265°C), hedrite-like crystals are mainly formed [17,19], although spherulites could be also observed [17,19]. At lower crystallization temperatures, the formation of spherulitic structures and sheaf-like structures become predominant [17]. The spherulites do not show concentric extinction rings as in banded spherulites [17]. So, the formation of spherulites could be expected in the crystallization temperature range 170–230°C. Moreover, the dimensions of the spherulites should decrease with the increase in the crystallization rate in the T_c range 230–190°C. That is why the morphology of the samples has been examined at $T_c = 230°C$, when the formation of relatively big spherulites should be expected and when the spherulite dimensions decrease in the presence of the LCP should be better observed.

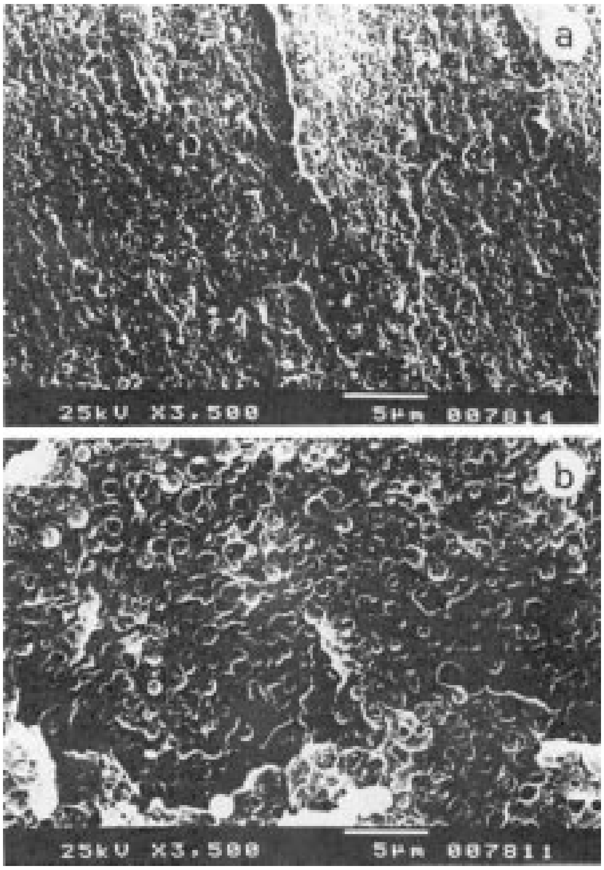

Fig. 7. SEM micrographs of the fractured surfaces of: (a) 93/7 PEN–A8 blend; and (b) 87/13 PEN–A8 blend.

PEN spherulites isothermally crystallized at $T_c = 230°C$ are shown in Fig. 8a. The Maltese cross of the spherulites is weakly developed and they resemble sheaf-like structures, similar to those observed in Ref. [17]. The average dimension of the spherulites vary from 5 to 8 μm. On the contrary, the crystallization of molten films of the blends leads to much smaller spherulites (Fig. 8b), whose dimensions seem to be practically independent of the blend composition. This demonstrates that both LCP act as nucleating agents for PEN crystallization [26].

4. Conclusions

It is well known that PEN has high nucleation density [17]. In spite of this, the results from the study show that the addition of 7–13 wt% of both LCPs (rigid and semi-flexible) leads to a strong increase in the crystallization and nucleation rates of the PEN matrix under isothermal conditions. That means LCP dispersed phase plays a nucleation role in the PEN matrix crystallization. The nucleation

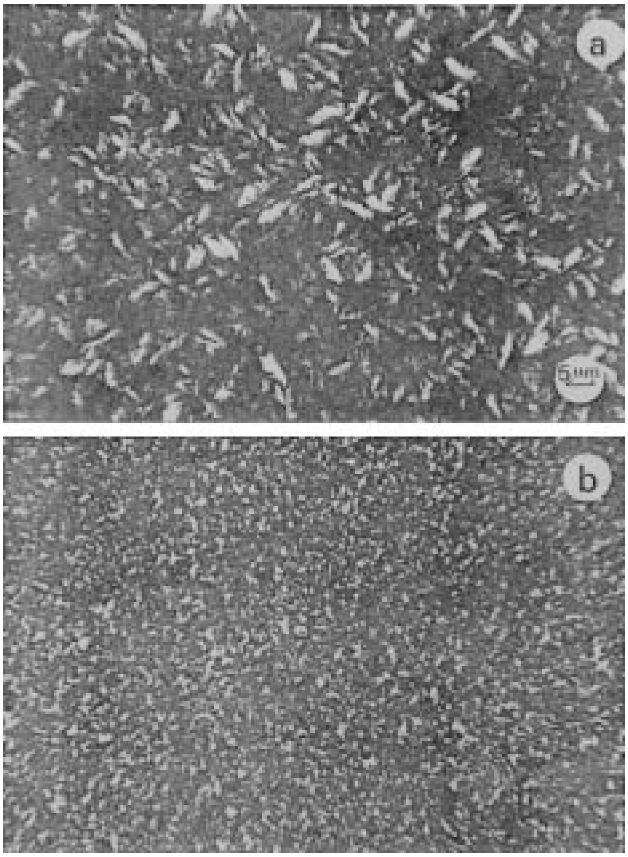

Fig. 8. Optical micrographs of: (a) neat PEN; and (b) 93/7 PEN–VA blend. The samples are crystallized isothermally at $T_c = 230$°C.

efficiency of both LCPs depends on their concentration in the blends; the effect is more pronounced at 7 wt% LCP content in the blend than at 13 wt% LCP concentration. This is interpreted by the larger interphase area between the two phases and consequently by the higher concentration of heterogeneous nuclei in the blends with 7 wt% LCP. This is due to the extremely fine dispersion of LCP in PEN matrix for 93/7 PEN–LCP blends. The decrease in the dimensions of PEN spherulites in the presence of both LCPs confirms the nucleation ability of the LCPs on the PEN matrix crystallization. Moreover, the mechanism of the crystallization and the equilibrium melting temperature of PEN do not change by the addition of an LCP dispersed phase.

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References

[1] Cakmak M, Wang YD, Simhambhatla M. Polym Eng Sci 1990;30(2):721.
[2] Buchner S, Wiswe D, Zachmann HG. Polymer 1989;30:480.
[3] Light RR, Seymour RW. Polym Eng Sci 1982;22:857.
[4] Ulcer Y, Cakmak M. Polymer 1994;35:5651.
[5] Lee W, DiBenedetto AT. Polymer 1993;34:684.
[6] Bafna SS, Sun T, Baird DG. Polymer 1993;34:708.
[7] Datta A, Baird DG. Polymer 1995;36:505.
[8] Dutta D, Fruitwala H, Kohli A, Weiss RA. Polym Eng Sci 1990; 30:1005.
[9] La Mantia FP, editor. Thermotropic liquid crystal polymer blends. Lancaster, PA: Technomic Publ Co, 1993.
[10] Seppälä J, Heino M, Kapanen C. J Appl Polym Sci 1992;44:1051.
[11] Sharma SK, Tendolkar A, Misra A. Mol Cryst Liq Cryst 1988; 157:597.
[12] Melot D, MacKnight WJ. Polym Adv Technol 1992;3:383.
[13] Silverstein MS, Hiltner A, Baer E. J Appl Polym Sci 1991;43:157.
[14] Chang-Chien GP, Denn MM. Polym Adv Technol 1996;7:168.
[15] Kim WN, Denn MM. J Rheol 1992;36:1477.
[16] Magagnini PL, Tonti MS, Masseti M, Paci M, Minkova LI, Miteva TS. Polym Engng Sci 1998;38:1572.
[17] Lee SW, Cakmak M. J Macromol Sci Phys 1998;B37(4):501.
[18] Balta Calleja FJ, Rueda D, Michler GH, Naumann I. J Macromol Sci Phys B 1998;37(4):411.
[19] Liu J, Sidoti G, Hommema A, Geil PH, Kim JC, Cakmak M. J Macromol Sci Phys B 1998;37(4):567.
[20] Carr PL, Nicholson TM, Ward IM. Polym Adv Technol 1997;8:592.
[21] Cheng SZ, Wunderlich B. Macromolecules 1989;21:789.
[22] Valtriani A, Filippi S, Polacco G, Magagnini PL, Incarnato L, Acierno D. Macromol Chem Phys 2001 (in press).
[23] Bodor G. Structural investigation of polymers. Chichester: Ellis Horwood, 1991.
[24] Lopez LC, Wilkes GL. Polymer 1989;30:882.
[25] Wunderlich B. Macromolecular physics, vol. 3. Moscow: Mir, 1984. p. 53.
[26] Wunderlich B. Macromolecular physics, vol. 2. Moscow: Mir, 1979. p. 77.