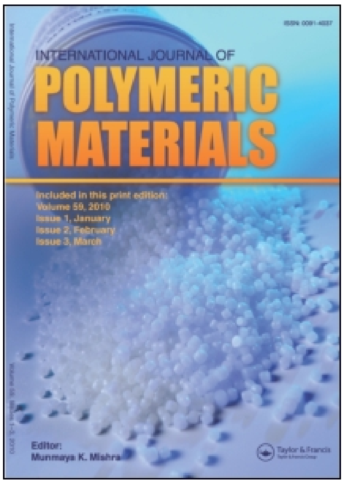

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Crystallization Study of Glassy PET/PEN Blends by Means of Real Time X-ray Scattering*

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The crystallization of several blends of poly(ethylene terephthalate) (PET) and poly(ethylene 2,6 naphthalene dicarboxylate) (PEN) has been investigated by wide angle- (WAXS) and small angle X-ray scattering (SAXS) using synchrotron radiation. The role of transesterification reactions, giving rise to a fully amorphous non-crystallizable material (copolyester) is brought up. For the blends rich in PET, crystallization temperatures (T_c) of 105 and 117°C were used. For blends rich in PEN, crystallization was performed at $T_c = 150$ and 165°C, respectively. The time variation of the degree of crystallinity was fitted into an Avrami equation considering the induction time prior to the beginning of crystallization. The Avrami parameters, the half times of crystallization, as well as the nanostructure development (SAXS invariant and long period) for the blends, are discussed in relation to blend composition and are compared to the parameters observed for the homopolymers PET and PEN.

Keywords: PET; PEN; Blends; Crystallization; X-ray scattering

1. INTRODUCTION

PET and PEN are crystallizable polymers [1–3] having melting temperatures close to each other (268 and 270°C, respectively) though with different T_g values (about 70 and 123°C, respectively), *i.e.*, PET

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* Dedicated to Professor S. Fakirov on the occasion of his 65th birthday.

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having a higher chain mobility in relation to PEN. This is so because the benzene moiety is smaller than the naphthalene one. This chemical difference makes PET and PEN immiscible with one another.

An inherent property of condensation polymers such as PET and polycarbonates, in contrast to polyolefins, is their ability to react with each other undergoing transesterification reactions [4, 5]. These chemical reactions play an important role in the case of PET/PEN blends since both components are crystallizable but not miscible. Zachmann *et al.* [6] studying PET/PEN blends found that for intermediate compositions, processed at 280°C, amorphous, non crystallizable materials (random copolyesters of PET and PEN) were obtained. These authors [6] also found that the extent of transesterification depends on composition and time of melt blending.

In a previous study we investigated the crystallization kinetics of PET/PEN blends by *in situ* microhardness measurements [7]. By means of an analytical model, using the Avrami approach of the hardening curves, we could estimate the amount of non-crystallizable copolyester present in the blends.

The aim of the present work is to complement the above studies, offering additional information concerning the study of the isothermal crystallization of these glassy PET/PEN blends by means of wide angle (WAXS) and small angle X-ray scattering (SAXS), in real time, using synchrotron radiation.

2. EXPERIMENTAL

2.1. Materials

PET and PEN were synthesized from ethylene glycol together with dimethyl terephthalate and dimethyl-2, 6-naphthalene dicarboxylate, respectively, as described elsewhere [1, 3]. Blends containing different concentrations of these starting materials were obtained by coprecipitation from the solution in hexafluoroisopropanol. Thin amorphous films of PET/PEN blends were, then, obtained from the precipitated powder by melt pressing in vacuum at a temperature $T_m = 280°\text{C}$ during a time $t_m = 10\,\text{min}$, followed by quenching in ice water.

2.2. Techniques

Time-resolved, simultaneous, small and wide-angle X-ray scattering (SAXS and WAXS) measurements were carried out using a double-focussing mirror monochromator camera on the polymer beam line A2 at HASYLAB (Hamburg). Crystallization was performed isothermally bringing up each glassy sample instantly ($\sim 100°\mathrm{C\,min}^{-1}$) up to the crystallization temperature. Scattering patterns were recorded using linear position sensitive detectors, additionally corrected for fluctuations in intensity of the primary beam and background. The data acquisition system is based on CAMAC hardware and modulation software [8]. The accumulation time for each X-ray pattern was 60 s and the elapsed time between consecutive patterns was likewise 60 s. The measurement of the SAXS invariant was carried out in the s range $0.01\,\mathrm{nm}^{-1} < s < 0.18\,\mathrm{nm}^{-1}$ ($s = 2\ \sin\theta/\lambda$ and $\lambda = 0.150\,\mathrm{nm}$). The SAXS patterns were analysed after subtraction of the first SAXS curve recorded at the selected T_c value, after applying the Lorentz correction.

3. RESULTS

3.1. Wide Angle X-ray Scattering (WAXS)

Figure 1 shows the room temperature X-ray scattering patterns for the PET/PEN blends having different compositions after crystallization at two different temperatures. The samples with excess PEN ($x_{\mathrm{PET}} < x_{\mathrm{PEN}}$) (top ones) were crystallized at 165°C for 2 h. Samples with excess PET ($x_{\mathrm{PET}} > x_{\mathrm{PEN}}$) (bottom ones) were crystallized at 117°C for 3 h. While the blends with compositions near 50/50, as well as the blend 70/30, do not crystallize [6], the rest of the blended materials show a crystallization of only the major component. In other words, in the case of the 10/90 blend, only the PEN component crystallizes, whereas in case of the 90/10 blend exclusively the PET partner does crystallize. This behaviour matches well to that observed for the corresponding PET/PEN copolyesters [9]. The amorphous nature of the 70/30 blend suggests the occurrence, in this case, of a transesterification reaction between the PET and the PEN chains [6, 7].

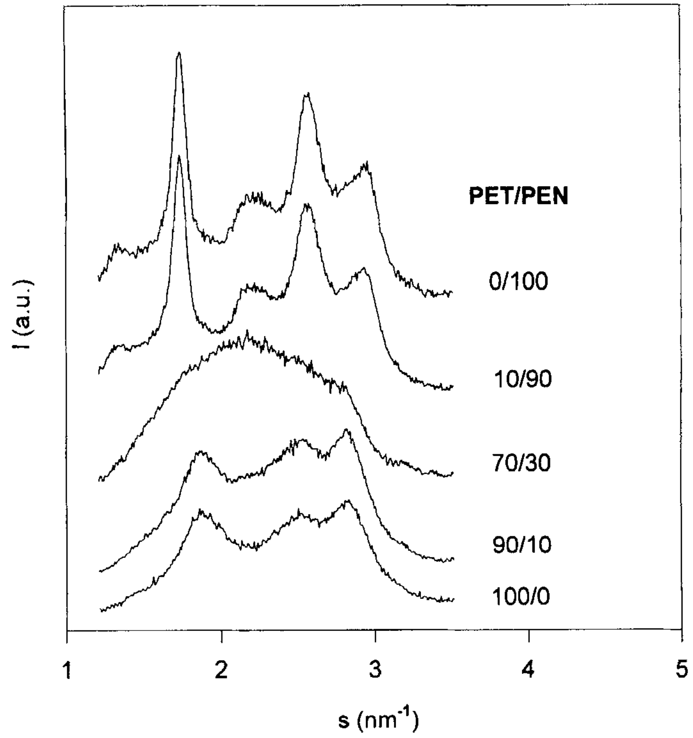

FIGURE 1 X-ray patterns taken at room temperature, for PET/PEN blends after crystallization at 165°C for 2h (2 upper samples) and at 117°C for 2h (3 lower samples).

Simultaneous real time WAXS and SAXS experiments were performed during isothermal crystallization as follows: for the samples with $x_{PET} > x_{PEN}$, crystallization temperatures of $T_c = 105$ and 117°C were used. On the other hand, for the samples with $x_{PET} < x_{PEN}$, T_c values of 150 and 165°C were employed. Figure 2 illustrates the variation of the wide angle X-ray scattering patterns as a function of crystallization time, t_c, for two isothermal experiments carried out at $T_c = 117$ and 165°C, using the blends 90/10 (top) and 10/90 (bottom), respectively. Miller's indexes corresponding to the triclinic unit cells of PET [10] and PEN [11] (α-modification) are given.

Figure 3 shows the variation of the crystallinity index, X_c as a function of crystallization time for the isothermal experiments carried

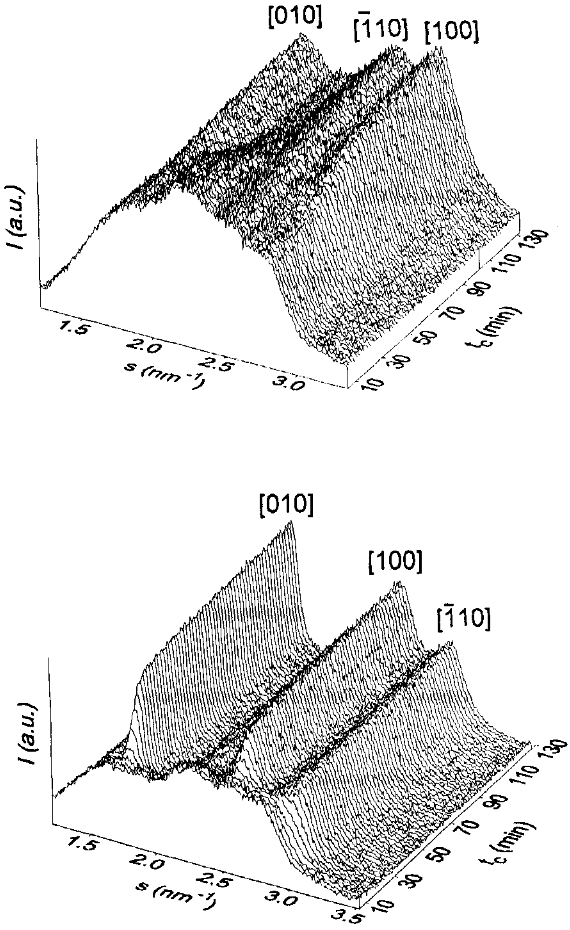

FIGURE 2 Variation of the WAXS patterns during isothermal crystallization at 117°C of the blend 90/10 (top) and at 165°C of the blend 10/90 (bottom).

out at $T_c = 117°C$ ($x_{PET} > x_{PEN}$) and at $T_c = 165°C$ ($x_{PET} < x_{PEN}$), respectively. When crystallization takes place at $T_c = 117°C$ (Fig. 3(a)), after an induction time, t_{ind}, for the homopolymer PET and the blend 90/10 (the blend 70/30 does not crystallize at all), there is an initial fast increase in the X_c values with increasing t_c (primary crystallization) followed by a much slower rate of increase for longer times (secondary crystallization). The induction time, as well as the half crystallization time ($t_{1/2}$) and the crystallinity achieved depend

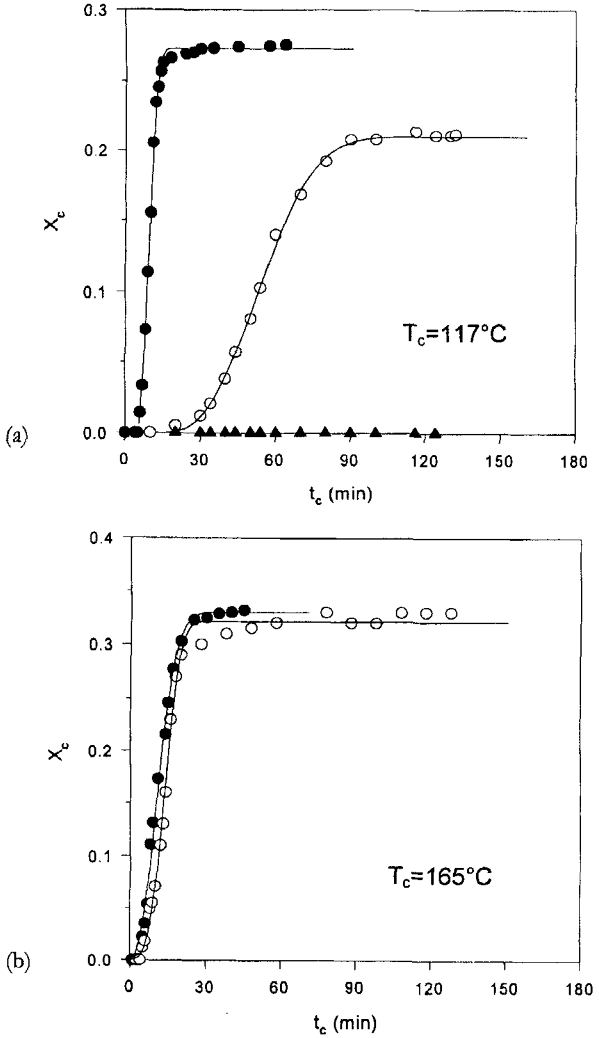

FIGURE 3 Time dependence of the crystallinity index, X_c for isothermal cold crystallization of PET/PEN blends at 117°C (top): (●) 100/0, (○) 90/10, (▲) 70/30, and at 165°C (bottom): (●) 0/100, (○) 10/90.

on the concentration of PET, the lower x_{PET} the longer either t_{ind} and $t_{1/2}$ and the lower X_c. On the other hand, for $T_c = 165°C$ (Fig. 3(b)), the homopolymer PEN as well as the 10/90 blend show a similar crystallization behaviour.

The evolution of X_c with crystallization time (continuous lines in Fig. 3) can be described by the Avrami equation [12–14]:

$$X_c(t) = X_c^{max}\left[1 - \exp\left(-G(t_c)^n\right)\right] \tag{1}$$

where X_c^{max} is the maximum crystallinity, and G and n are the Avrami parameters. If a third parameter, t_{ind}, is introduced into the above expression, Eq. 1 can be expressed in the form:

$$X_c(t) = X_c^{max}\left[1 - \exp\left(-G(t_c - t_{ind})^n\right)\right] \tag{2}$$

In order to determine the n and G values as well as t_{ind}, Eq. 2 has been fitted to the experimental X_c data (continuous line in Figs. 3a and 3b). The calculated parameters are collected in Table I. The half-crystallization times, $t_{1/2}$, derived according to the equation:

$$t_{1/2} = n\sqrt{\frac{\ln 2}{G}} + t_{ind} \tag{3}$$

are also presented in Table I.

3.2. Small Angle X-ray Scattering (SAXS)

Figure 4 shows the variation of the SAXS invariant Q (normalized to 1) and of the long period L, derived from Bragg's law, as a function of crystallization time for the samples rich in PET isothermally treated at $T_c = 117°C$. Comparison of Figures 4(a) and 3(a) leads to the

TABLE I Induction time, t_{ind}, half-crystallization time, $t_{1/2}$, Avrami constant, G, and Avrami exponent, n determined from the crystallinity variation for isothermal crystallization of PET/PEN blends

x_{PET}	0.0		0.1		0.7		0.9		1.0	
$T_c(°C)$	150	165	150	165	105	117	105	117	105	117
$t_{ind}(min)$	8	0	12	0	[a]	[a]	[a]	15	6	4
$t_{1/2}(min)$	35	10	34	14	[a]	[a]	[a]	54	27	10
$G \times 10^4$	18.2	24.6	48.1	1.2	[a]	[a]	[a]	0.4	4.6	83.0
n	1.8	2.5	1.6	3.3	[a]	[a]	[a]	2.6	2.5	2.6

[a] Could not be determined because the sample does not crystallize under the present experimental conditions.

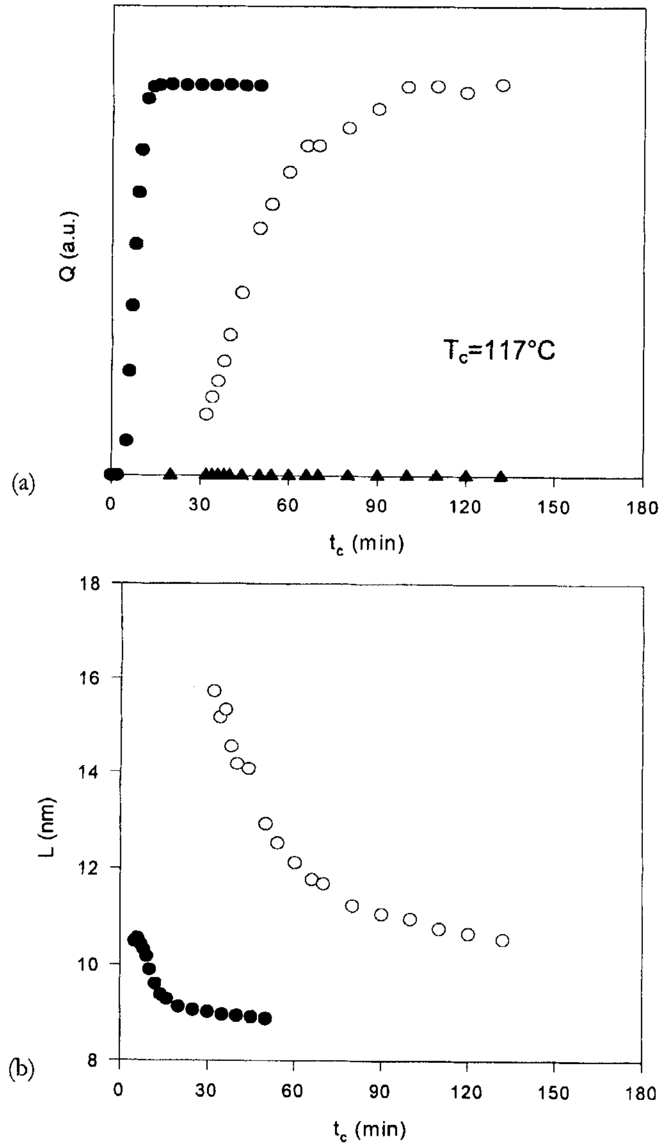

FIGURE 4 Variation of the SAXS invariant, *Q* (a) and the long period, *L* (b) during isothermal crystallization of PET/PEN blends at 117°C (symbols as in Fig. 3 top).

conclusion that the invariant and the crystallinity, X_c present a similar variation with t_c. The time dependence of *L* is represented in Figure 4(b). It is seen that the homopolymer PET develops a long period for shorter t_c values as compared to the blend 90/10. In both two cases, L gradually decreases with crystallization time. However, the L-variation for the blend is larger (from 16 down to 10.5 nm) than that of pure PET (from 10.5 to 9 nm).

Similarly, the Q and L variation for the samples rich in PEN, isothermally crystallized at $T_c = 165°C$, is illustrated in Figures 5(a),

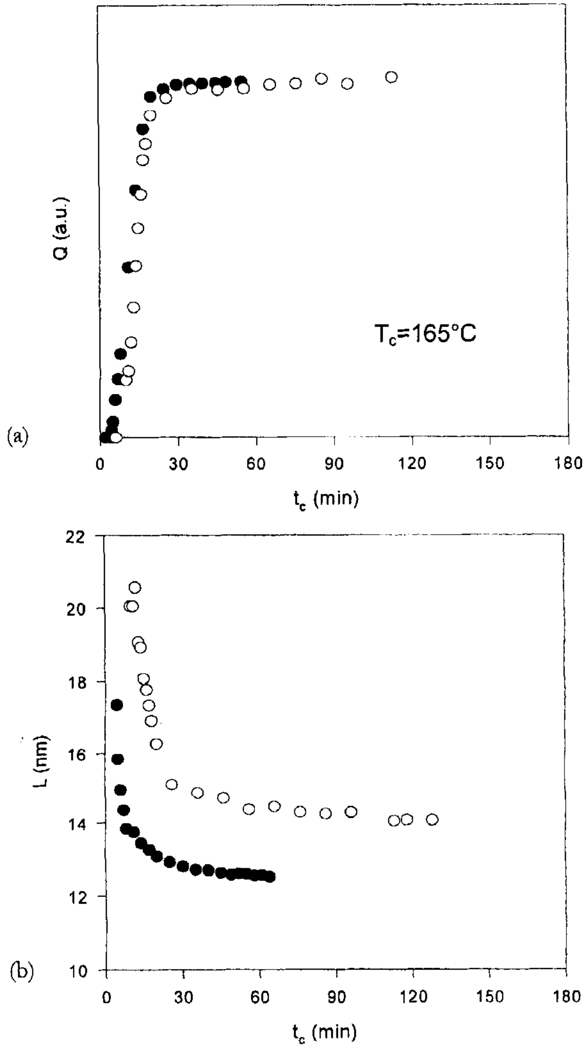

FIGURE 5 Variation of the SAXS invariant, Q (a) and the long period, L (b) during isothermal crystallization of PET/PEN blends at 165°C (symbols as in Fig. 3 bottom).

(b) respectively. Figure 5(a) shows that the homopolymer PEN and the 10/90 blend presents an indistinguishable Q-variation from each other, with t_c. It is noteworthy that both samples also showed a similar X_c behaviour (see Fig. 3(b)). On the other hand, Figure 5(b) illustrates the decreasing variation of L with t_c. Again, the starting L-value observed for pure PEN is lower than that for the blend sample. This tendency persists for the isothermal crystallization time investigated. It is to be noted that for higher t_c values (secondary crystallization) L continues to decrease while X_c slightly increases (Fig. 3) and a levelling-off for Q is observed (Figs. 4 and 5). According to the lamellar insertion model [15, 16], the observed decrease in L, while X_c slightly increases, could be due to the formation of thinner laminar crystals between the preexisting ones.

4. DISCUSSION

4.1. Transreactions

It is well known that chemical transreactions during blending of condensation polymers occur [5]. Here, the fraction of transesterified copolyester depends only on the blending conditions. Preceding studies indicate [6] that owing to the transesterification reactions, miscibility of PET and PEN is achieved giving rise to a single phase material (PET/PEN copolyester). According to these studies [6], after heat treatment of the blends (around 50/50) for 2 min at 280°C, miscibility of the PET and PEN phases was completed to give an amorphous, non-crystallizable PEN/PET copolyester. Based on microhardness measurements, we found that the degree of transesterification is maximum for blends with an intermediate composition, being larger in the case of blends rich in PET ($x_{PET} > x_{PEN}$) [7]. In accordance to this mechanism the blend 70/30 appears to be essentially amorphous (see Fig. 1).

4.2. Influence of Composition and T_c on the Crystallization Kinetics

From the t_{ind} and $t_{1/2}$ values listed in Table I, the influence is evident of the crystallization temperature, T_c on the induction time and crystallization time values. Furthermore, while for blends rich in PET (90/10) these parameters are 4–5 times larger than for the homopolymer PET, for blends rich in PEN (10/90), the t_{ind} and $t_{1/2}$ values are similar to those observed for PEN. On the other hand, by comparison of Figures 3(a) and 3(b) it is seen that for blends rich in PET X_c^{max} largely decreases with an small increase of x_{PEN}, while for blends rich in PEN the X_c^{max} value is indistinguishable from that of pure PEN. These results can be explained in the light of the T_c values used in relation to the T_g of the single components. Thus in case of the crystallization temperatures $T_c = 105$ and 117°C, used for isothermal crystallization of blends rich in PET, the PEN component ($T_g =$ 123°C) remains in the glassy state. This means that the PEN phase is frozen, thus causing a restriction in the mobility of the liquid-like PET component. Consequently, the crystallization of the PET phase is delayed. Indeed, the t_{ind} and $t_{1/2}$ values increase with increasing concentration x_{PEN} within the blend. On the other hand, for the temperatures of $T_c = 150$ and 165°C used during isothermal crystallization of the blends rich in PEN, both PET and PEN components are in the liquid state. As a result, the PET phase of the 10/90 system does not influence so markedly the crystallization kinetics of the blend as in the case of the homopolymer PEN (Fig 3(b)).

Table I shows n values around 3 for pure PET and blends rich in PET which is consistent with the concept of a three-dimensional growth with a fixed number of nuclei born at $t = 0$ [12–14]. It is known that PET crystallization from the glassy state gives rise to spherulitic materials [17, 18]. However, for PEN and blends rich in PEN, values of $n \approx 2$ for the lowest crystallization temperature ($T_c = 150$°C) and of $n \approx 3$ for $T_c = 165$°C are found (see Tab. I). This finding is in agreement with previous results obtained for PEN [19]. Preceding morphological studies using transmission electron microscopy on the early stages of crystallization of PEN revealed an emerging lamellar structure within a dendritic morphology for $T_c \leq 155$°C [20]. This morphology is consistent with the low n values obtained in the present paper for blends rich in PEN crystallized at $T_c = 150$°C. On the other hand, the TEM electron micrographs from PEN crystallized at higher T_c values show morphologies of bundles of lamellae with radial orientation in addition to the branched lamellar structure [20]. The n values near to 3, obtained for blends rich in PEN, crystallized at $T_c = 165°C$, are in agreement with the development of such a morphology.

It is to be noted, that while the Avrami analysis of WAXS data presented here reveals a unique crystallization regime, the Avrami analysis performed earlier on the microhardness data of PET/PEN blends [7] revealed the occurrence of two different hardening regimes characterized by two different n-values. The same discrepancy is observed when comparing the hardness and X-ray crystallinity values, measured at room temperature, after consecutive thermal treatments of PET at 95°C [21]. This suggests that structural changes in the amorphous state, as revealed by microhardness but not by WAXS, are taking place during the induction period [21–23].

Regarding the G values (Tab. I), it is clear that for both homopolymers PET and PEN the G parameter increases with increasing crystallization temperature, in agreement with preceding results [19, 24]. The G parameter is known to be proportional to the number of nuclei per unit volume and to the growth rate of these nuclei [12]. Thus, the very small G value for the blend 90/10 in relation to pure PET could be due to the fact that PEN and the fraction of copolyester that does not crystallize restrict the mobility of PET. This would decrease the rate of nuclei growth. On the other hand, the G value of the 10/90 blend, particularly for the lower T_c value (150°C) is larger than that of the homopolymer PEN. This could be attributed to the higher mobility of the PEN phase in the blends because of the presence of the more mobile PET component.

4.3. Dependence of Composition on Structure Development

The simultaneous detection of the SAXS and WAXS patterns recorded during isothermal cold crystallization of the PET/PEN blends, reveals a parallel time evolution of the structural parameters. In other words, no delay in the appearance of WAXS crystalline reflections in relation to the development of the SAXS intensity is observed., In contrast to previous findings on the PET [22, 25] and PEN [26] homopolymers, the present results, thus suggest the absence of precrystallization phenomena during the crystallization of the blended samples.

The absence of L values (well below the instrumental resolution of SAXS, ~40 nm) for short crystallization times seems to indicate the non-existence of electron density fluctuations responsible for a SAXS maximum at these early stages of structure development. From the above results, one might expect the emerging crystallizable nuclei to be firstly randomly distributed (no SAXS maximum) and, thereafter, to become better correlated giving rise to the appearance of the observed SAXS maximum. Furthermore, the initial L values observed are larger for the blended samples than for the homopolymers (see Figs. 4(b) and 5(b)). From this observation one may speculate that in the former case of the blends the emerging electron density fluctuation from the growing nuclei might be further separated from each other, owing to the presence of the non-crystallizable material (copolyester and the rest of the minor component) which is located between the growing fronts of the crystallizing phase.

5. CONCLUSIONS

In conclusion, the induction and half crystallization times in PET/PEN blends mainly depend on the crystallization temperature. These times also depend on blend composition, particularly in the case of blends rich in PET for which crystallization is carried out in presence of the glassy PEN component. For most of samples (Tab. I), Avrami analysis of the WAXS crystallinity curves reveals a unique crystallization regime, that is generally characterized by $n \sim 3$. However, for pure PEN and blends rich in PEN crystallized at the low temperature, $T_c = 150°\mathrm{C}$ one obtains a regime characterized by $n \sim 2$.

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