

Notes

Spherulitic Morphologies of Poly(ethylene terephthalate), Poly(ethylene 2,6-naphthalate), and Their Blend

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Abstract: The supermolecular structures of poly(ethylene terephthalate) (PET), poly(ethylene 2,6-naphthalate) (PEN), and their blend were investigated with optical microscopy and small angle light scattering. With increasing the crystallization temperature, incomplete spherulitic texture was developed for the PET samples. At a high crystallization temperature of 220°C, the light scattering pattern represented a random collection of uncorrelated lamellae. The general morphological appearances for the PEN samples were similar to that of the PET. A notable feature was that the spherulites of the PEN formed at 200°C showed regular concentric bands arising from a regular twist in the radiating lamellae. The spherulitic morphology of the PET/PEN blend was largely influenced by the changes of the sequence distribution in polymer chains determined by the level of transesterification. The increased sequential irregularity in the polymer chains via transesterification caused a morphological transition from a regular folded crystallite to a tilted lamellar crystallite.

Keywords : PET, PEN, blend, transesterification, superstructure.

Introduction

Poly(ethylene terephthalate) (PET) is used for many beverage packages because of its low cost, good performance properties and favorable recycling position. However, new packaging opportunities demand performance levels which cannot be reached by PET alone. The packaging engineers now have solution to meet these demanding performance requirements with poly(ethylene 2,6-naphthalate) (PEN).

PEN has 4 times higher oxygen barrier performance compared to that of PET and 5 times higher carbon dioxide barrier performance. PEN, having 43°C higher glass transition temperature than that of PET, can be used where thermal performance is needed. PEN offers mechanical benefits as well. Compared with PET, PEN has a 35% higher tensile strength and a 50% improved modulus. PEN is thus an ideal candidate for many demanding package design. At the same time, the high-performance PEN carries premium price, resulting in a more costly polymer than the PET. Therefore, the blending PET with PEN is a means to satisfy the perfor-

mance requirements of many food and beverage containers and minimize material and processing cost.

PET and PEN are not miscible. When melt-compounded, they inherently form two phases, resulting in a milky-white bottle preform. Clear bottles are obtained only when sufficient transesterification during processing occurs to induce miscibility. The transesterification leads to the formation first of block copolymers and then of random copolymers, which enhance the miscibility of the blend. The transesterification in PET/PEN blends and its effects on miscibility have been reviewed by other researchers.¹⁻⁴ Stewart *et al.*¹ reported that the primary factors controlling the transesterification were the blending time and temperature, whereas the composition of the blend and the residual polyester catalysts had little or no effect on the ester interchange reactions. Lee *et al.*² studied the phase behavior at a high temperature in PET/PEN blends with differential scanning calorimetry (DSC). They found that the phase homogenization induced by transesterification took place during annealing. The blend samples heat-treated for up to 11 min at 280°C showed two glass transitions, which approached closer with the increase of reaction time. After 13 min, a single glass transition was observed and the glass transition range became narrow with

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the lapse of reaction time.

Because of the changes in the phase behavior and the formation of copolymers, it is quite likely that crystalline morphologies will vary as the transesterification reaction proceeds. The crystalline structure and morphological features determine the actual polymer properties. Therefore, to describe and understand the properties of PET/PEN blends, we have to investigate the morphological dependence on the transesterification occurring during the melt-mixing of PET and PEN. In this paper, we concentrated our study on the crystalline structure and morphologies of PET, PEN and their blend at a spherulitic level. The supermolecular structures were examined with optical microscopy (OM) and small angle light scattering (SALS). The key issues addressed here were the chain-folding direction in crystals and the crystal orientations in the spherulites.

Experimental

Materials. Commercial PET and PEN produced by SKC Co. were used. The number average molecular weight, \overline{M}_n , of PET was 2.3×10^4 , and the intrinsic viscosity of PEN in a mixed solvent of *p*-chlorophenol and tetrachloroethane (7/3 v/v) at 30°C was 0.62 dL/g. After being dried in a vacuum oven at 150°C for 24 h, the PET and PEN were melt-mixed at 280°C on a 30 mm co-rotating twin screw extruder (Werner Pfleiderer) at a speed of 200 RPM. The residence time for the melt-mixing was less than 1 min. The extrudate was quickly quenched in ice-water to freeze the structure in the melt and was then pelletized. The composition of the PET/PEN blend was 50/50 by weight.

SALS and OM. After the sample was held at 280°C for a certain time (t_s), it was rapidly transferred onto a hot stage

set at a desired crystallization temperature in a light scattering photometer equipped with a charged-coupled device camera,⁵ and then the supermolecular structures were examined. A polarized He-Ne gas laser of 632.8 nm wavelength was directed to the film specimen. We used the H_v geometry, in which the optical axis of the analyzer was set perpendicular to that of the polarizer. The spherulitic morphology of the specimens was also observed with OM.

DSC. The melting behavior was investigated by a Perkin-Elmer DSC-7 differential scanning calorimetry (DSC). The extruded sample was first melted at 280°C for t_s and then rapidly cooled to a desired crystallization temperature. After crystallizing isothermally for 1 h, the sample was heated to 300°C at a rate of 10°C/min in nitrogen atmosphere.

Results and Discussion

The spherulitic morphologies of the two pure polymers were examined. Figure 1 shows optical micrographs with crossed polarizers and corresponding H_v scattering patterns for pure PET samples crystallized at various temperatures. At temperatures lower than 200°C, the spherulites display the "Maltese Cross" extinction pattern. Scattering pattern (a), the classical cloverleaf with zero intensity at the center, represents ideal, well-developed spherulites. With increasing the crystallization temperature, a diffuse four-lobe pattern is observed, indicative of the development of small and perhaps incomplete spherulitic texture. At a high crystallization temperature of 220°C, unusual spherulites were observed, and their H_v pattern shows a much diffused pattern. It can represent a random collection of uncorrelated lamellae. A possible explanation for the formation of highly disordered spherulites can be given as follows: at a high temperature of

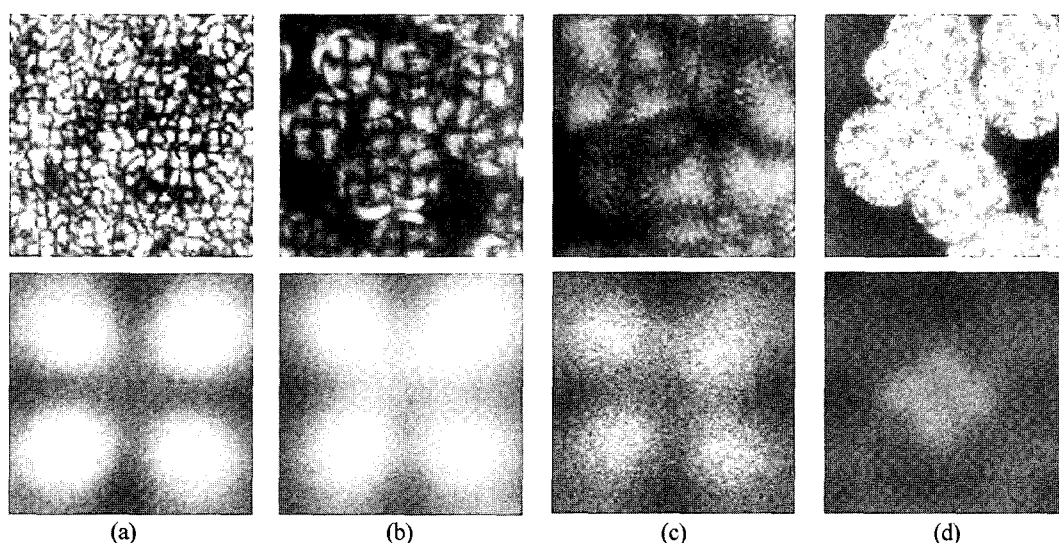


Figure 1. Optical micrographs with crossed polarizers and corresponding H_v scattering patterns for pure PET crystallized at various temperatures : (a) 120°C; (b) 160°C; (c) 200°C; (d) 220°C.

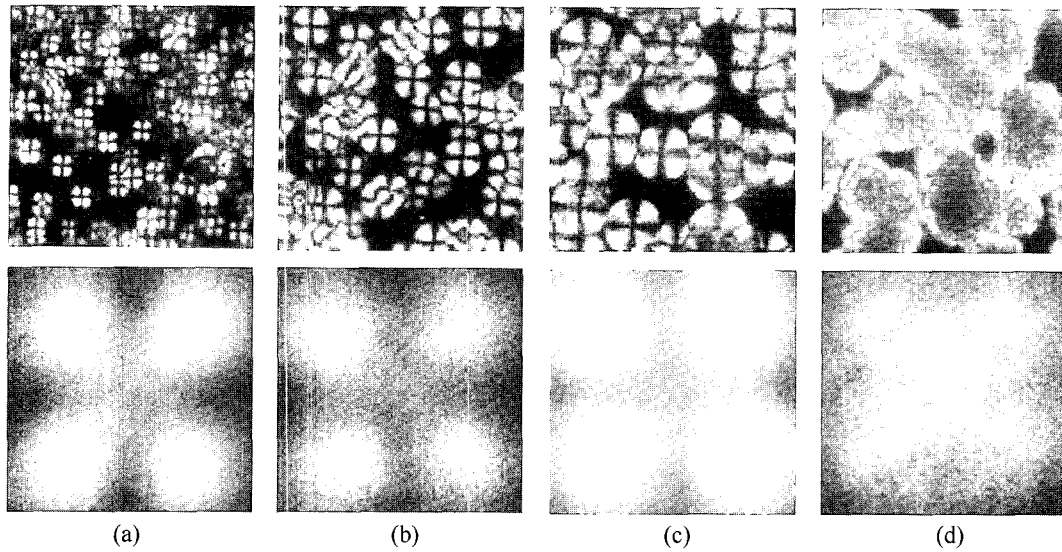


Figure 2. Optical micrographs with crossed polarizers and corresponding H_v scattering patterns for pure PEN crystallized at various temperatures : (a) 160°C; (b) 180°C; (c) 200°C; (d) 220°C.

220°C, the medium composed of noncrystallizable components might be mobile enough to fluctuate the lamellar orientations, leading to the random arrangement of the individual lamellar crystallites. It is worth noting that the unusual spherulites can be observed only at a high crystallization temperature near to the melting point. It seems, therefore, that the unusual spherulites are more stable than the usual spherulites from the viewpoint of thermodynamics, though optically, the unusual spherulites look very coarse. The general morphological appearance of the PEN spherulites is similar to that of PET as shown in Figure 2. One interesting feature is that the spherulites formed at 200°C have regular concentric bands which arise from a regular twist in the radiating lamellae. A question is why the radiating lamellae exhibit such a regular twist. The answer may lie in the nature of screw dislocations present in the crystals.⁶ As more crystals are nucleated and themselves form the screw dislocation, a net twist can be built up. Such a twist in the radiating dominant lamellae will affect the orientation of the secondary, infilling lamellae and may lead to the periodic banding on the spherulites. However, generalization of the detailed evolution of banded spherulites is still uncertain.

While there are some similarities between PET and PEN, remarkable dissimilarities also exist between the two polymers, particularly in the crystallization kinetics. Figure 3 shows a typical plot of the reciprocal of crystallization half-time, $\tau_{1/2}$ versus crystallization temperature for pure PET and PEN. The detailed procedure for determining $\tau_{1/2}$ from isothermal DSC data is described elsewhere.⁷ The plot indicates that the crystallization rate is noticeably influenced by the crystallization temperature, relatively stronger influence being observed for the PET sample. It is expected that various morphologies might be encountered in the PET/PEN blend

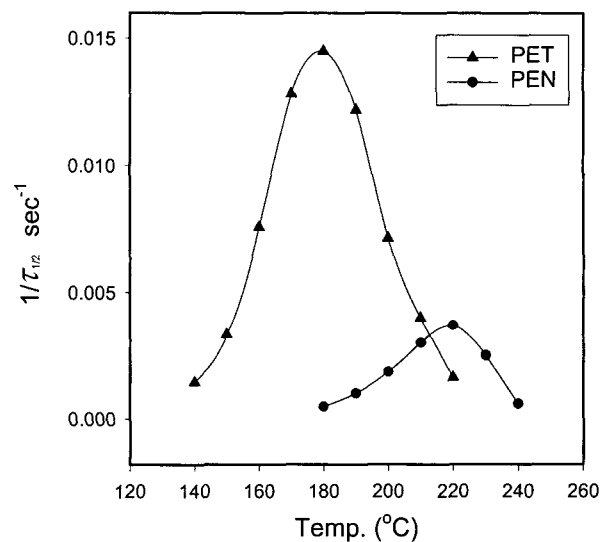


Figure 3. Plot of the reciprocal of the crystallization half-time, $\tau_{1/2}$ of PET and PEN over a temperature range.

when both components of the blend crystallize at the same time. Which type of morphology will be found is undoubtedly related to such factors as melt compatibility, diffusion rate, and crystallization rate. It is, therefore, interesting to investigate the morphology development at a specific crystallization temperature regime. We confine discussion to the representative temperature of 200°C, at which PET and PEN crystallize together with some difference in the crystallization rate.

Figure 4 shows DSC thermograms of the blend samples crystallized isothermally at 200°C after annealing at 280°C for t_s . The area of melting endotherms reduces with the

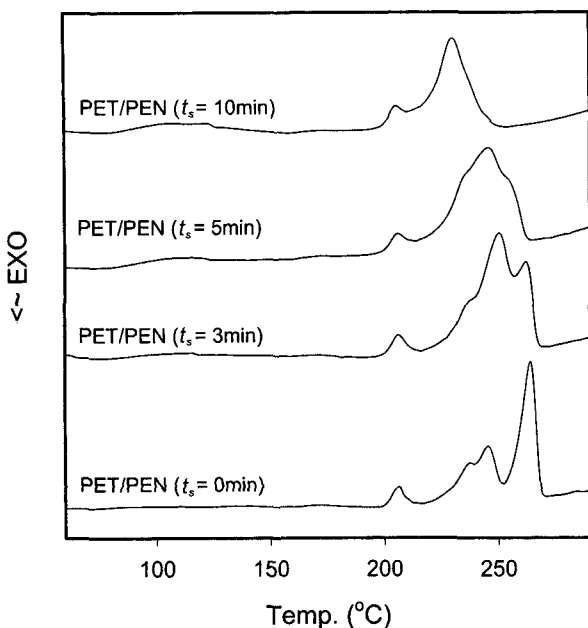


Figure 4. DSC thermograms of the PET/PEN blend crystallized isothermally at 200°C for 1 h after annealing at 280°C for t_s .

increase of t_s , indicating that the crystallization of the polymers is significantly hindered by the disruption of chain periodicity as a consequence of transesterification. Another interesting feature in the figure is the change in the melting temperatures. For a sample with $t_s = 0$ min, a conspicuous melting peak at 265°C is clearly observed, which is nearly coincident with the melting peak for pure PEN. As t_s increases, this high melting peak shrinks and finally disappears. When the crystallization of PEN precedes that of

PET, a distinct crystalline morphology for PEN may be preserved in the blend. However, when the crystallization rate of PET is faster than that of PEN, PET crystallizes first, forming a spherulite morphology. PEN crystallizes later in an infilling fashion within the PET spherulites. In that case, the crystallization of PEN is somehow restrained by the presence of the PET crystal, resulting in the development of coarse crystalline structures with a low melting point for PEN. Because the phase homogenization induced by the transesterification between the two polymers causes an increasing amount of PET in the PEN-rich phase, it is likely that the morphological effect of the PET crystals formed previously on the crystallization of PEN becomes important with longer t_s . From the viewpoint presented above, we can interpret the fact that the high melting peak of PEN is rapidly merged into lower melting peaks with t_s .

The supermolecular structures of the PET/PEN blend were observed with SALS. Figure 5 shows a series of H_v patterns obtained from the blend samples crystallized at 200°C. Typical four-leaf clover patterns are obtained for the samples of $t_s < 3$ min. The pattern with lobes at 45° to the polarization direction (45° pattern) has been interpreted as arising from optic axes oriented parallel or perpendicular to the spherulite radius.⁸ With increasing t_s , the patterns become more diffuse and less azimuthally dependent, which is representative of a greater degree of spherulite disorder⁹ or the presence of randomly oriented material within the spherulites.¹⁰ The influence of the chain constitution on the supermolecular structure is important. The incorporation of copolymer units or other irregularities into the chain alters the major characteristics of the spherulitic morphology. Thus, the increase of the sequence distribution in polymer chains via transesterification restricts the formation of well-

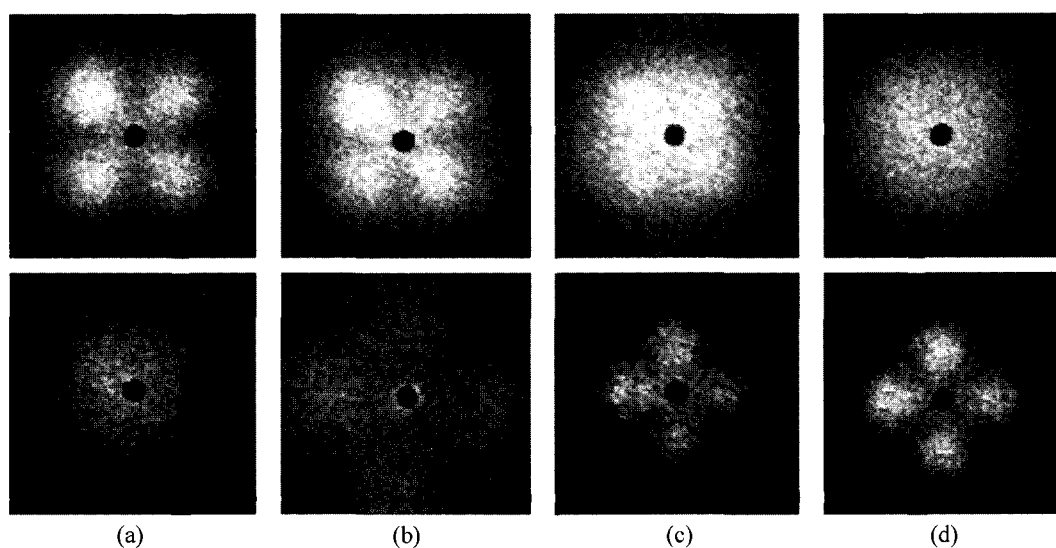


Figure 5. H_v scattering patterns of the PET/PEN blend crystallized at 200°C for 1 h after annealing at 280°C for (a) $t_s = 0$ min, (b) $t_s = 1$ min, (c) $t_s = 3$ min, (d) $t_s = 5$ min, (e) $t_s = 7$ min, (f) $t_s = 10$ min, (g) $t_s = 12$ min, and (h) $t_s = 15$ min.

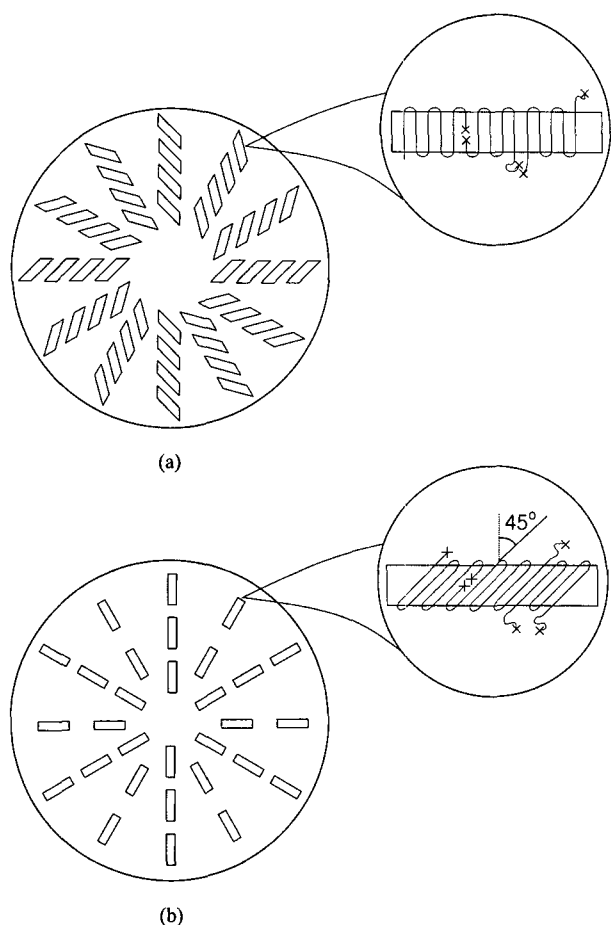


Figure 6. Schematic drawing of spherulite models for the 0-90° pattern : (a) Lamellar crystals are oriented at 45° with respect to the spherulite radius ; (b) Chain-folding is tilted at 45° to the lamellar surface.

developed spherulites and favors randomly arranged lamellae. With longer t_s , a different type pattern is clearly observed, in which the lobes occur along the polarization directions (0-90° pattern), which may be interpreted as arising from optic axes at about 45° to the spherulite radius. The schematic spherulite models for the 0-90° pattern, proposed by Lilaonitkul *et al.*,¹¹ suggest two different arrangements of crystals within the spherulites (Figure 6): the orientation of lamellae is at 45° with respect to the spherulite radius; or the chain-folding direction in crystals is tilted at 45° to the lamellar surface. A possible reason for the chain tilt is that a certain type of regular chain fold may require a small vertical displacement of the chain in the adjacent position giving rise to large surface stresses. The surface stresses are gradu-

ally accumulated with increasing sequential irregularities in polymer chains. As a result, it seems that a morphological transition from the regular folded crystallites to the tilted lamellar crystallites occurs for the samples with longer t_s .

Conclusion

The supermolecular structures of PET, PEN, and their 50/50 (wt/wt) blend were examined. At a high crystallization temperature of 220 °C, the PET sample showed unusual spherulites resulting from a random collection of uncorrelated lamellae. At 200 °C, the band structure appeared for the PEN sample. Banded spherulites were caused by lamellar twisting along the a-axis, which was parallel to the radial direction of the spherulite growth. It was surprising to find that the morphological transition from the regular folded crystallite to the tilted lamellar crystallites occurred in the PET/PEN blend. This implied that the spherulitic morphology of the PET/PEN blend might be largely affected by the changes of the sequence distribution in polymer chains determined by the level of transesterification between the two polymers.

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