

Influence of the Mixing Time on the Phase Structure and Glass-Transition Behavior of Poly(ethylene terephthalate)/Poly(ethylene-2,6-naphthalate) Blends

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ABSTRACT: Blends of poly(ethylene terephthalate) and poly(ethylene-2,6-naphthalate) (70 : 30 w/w) were prepared via a melt-mixing process at 280°C with various mixing times. The melt-mixed blends were analyzed by magnetic resonance spectroscopy, differential scanning calorimetry, dynamic mechanical measurements, transmission electron microscopy, and tensile tests. The results indicate that the blends mixed for short times had lower extents of transesterification and were miscible to a limited extent. The blends initially show two glass transitions, which approached more closely and merged gradually with increasing mixing time. A mechanical model was used to help understand the glass-transition behavior. With increasing mixing time, the phase structure of the blends improved, and this led to an increase in the tensile strength. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 673–679, 2013

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INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most important polymeric materials, and it is widely used for fiber, film, and packaging applications because of its easy processability, good creep resistance, resistance to chemical attack, and excellent optical clarity. However, its gas-barrier properties and thermal performance are not good enough to meet the requirements for some particular applications, such as the packaging of oxygen-sensitive foods and hot-fill applications. Poly(ethylene-2,6-naphthalate) (PEN) has proven to be a promising candidate to take the place of PET in high-performance applications. The naphthalene ring in PEN leads to an enhancement of the thermal, mechanical, and gas-barrier behaviors. However, PEN is more expensive and, therefore, less attractive for industrial use.^{1,2}

A desirable combination of the economics of PET and the superior properties of PEN can be achieved through the blending of these two polymers. The phase structure, transesterification reactions, crystallization, and physical characteristics of PET/PEN blends have been studied, and different miscibility levels have been reported.^{3–7} When PET and PEN are blended in the molten state, transesterification reactions occur; these result in the formation of block copolymers that become more random as the reactions proceed.^{8,9} The copolymers formed during the transesterification reactions function as compatibilizers

between PET and PEN because PET and PEN are completely incompatible, and their blends show a phase-separation phenomenon.^{10–13}

Transesterification reactions in PET/PEN blends should affect the blend miscibility, phase structure, and ultimately the final properties of the product blends. The extent of transesterification should be closely related to the processing parameters, such as the melt-mixing time.¹⁴ As is known, the melt-mixing technique is commonly used to prepare polymer blends. Thus, from the processing and application points of view, the influence of the melt-mixing time on the structural and morphological characteristics may provide some useful guidance for optimizing the final properties of this blend material.

In this study, we prepared PET/PEN blends with various mixing times by melt processing and then determined the extent of transesterification of these blends with ¹H-NMR. We carried out differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), and tensile measurements of the blends. On the basis of our experimental results, we report the feature of the phase structure and the glass-transition behavior of the prepared PET/PEN blends and discuss the miscibility level in the blend system as a function of the mixing time. A model is also illustrated to illustrate physical insights into the phase structure of the blends.

Therefore, the main objective of this investigation was to perform a detailed analysis of the structures and properties for PET/PEN blends with various mixing times.

EXPERIMENTAL

Materials

The PET homopolymer used in this study was provided by Far Eastern Industry, Ltd. (Shanghai, China), and had an intrinsic viscosity of 0.75 dL/g. The PEN homopolymer used for the blends was supplied by Teijin, Ltd. (Japan), and had an intrinsic viscosity of 0.55 dL/g. This was measured in phenol/tetrachloroethane (60/40 w/w) at 25°C. To reach a minimum level of moisture content, both PET and PEN were dried for 16 h at 120°C before melt mixing.

Preparation of the Samples

The PET/PEN blend samples were prepared via melt processing at 280°C. The equipment used was a Thermo Haake torque rheometer (PolyLab Systems) connected to a Rheomix 600p mixing chamber and equipped with roller rotors. A low rotor speed of 40 rpm was used, and a nitrogen atmosphere was present to prevent degradation. Mixing times of 5, 10, 15, 20, and 25 min were used for the blends. The samples prepared in each run were naturally cooled to room temperature for ¹H-NMR, DSC, and SEM measurements.

The samples after mixing were smashed mechanically with a grinder. From the smashed samples, sheets with dimensions of 120 × 120 × 1 mm³ were obtained by compression molding. In a heated press, the samples were warmed to 290°C and kept for 3 min between the plates without any applied pressure; this allowed for complete melting. After this period, a pressure of 25 MPa was applied at the same temperature for 5 min. The samples were then quenched by being transferred from the heated press to a cold press cooled by the passage of water under a pressure of 15 MPa. After room temperature was reached, the pressure was released, and the sheets were taken out. Samples for DMA and tensile measurements were cut from these sheets with a specimen punching machine.

Tensile Measurements

The tensile strength was measured with a universal testing instrument (SANS CMT4204, Shenzhen, China). The crosshead speed of the apparatus was 50 mm/min. The values of the Young's modulus, yield stress, tensile strength, and elongation at break were determined per ASTM D 638. At least five specimens were tested for each sample, and average values are reported.

¹H-NMR Characterization

¹H-NMR spectra were acquired on a high-resolution Bruker AV500 spectrometer (500 MHz). Tetramethylsilane was used as the internal standard for the chemical shift references. Deuterated trifluoroacetic acid was used as a solvent, and the solution concentration was about 2 wt %.

DSC Measurements

DSC measurements were implemented on a PerkinElmer DSC-7 calorimeter with samples of about 8 mg sealed in aluminum pans under a nitrogen atmosphere. All of the samples were

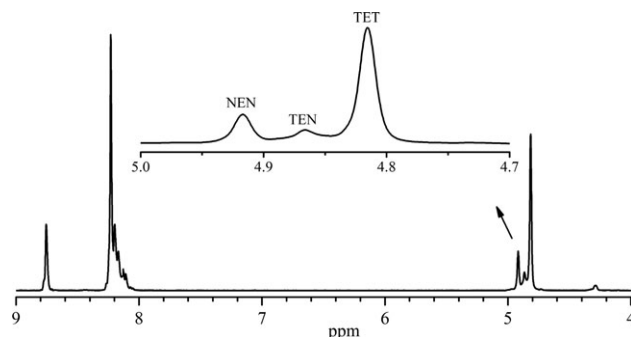


Figure 1. ¹H-NMR spectra of the 70/30 w/w PET/PEN blends with a mixing time of 5 min.

heated at a rate of 10°C/min from 25 to 300°C. The thermal transitions were recorded in the first DSC scan.

DMA Measurements

Dynamic mechanical measurements were performed on cut sheets 1 cm wide and 4 cm long with a TA Instruments DMA Q800 in the tension mode. The isochronal frequency used was 1 Hz. The temperature was scanned within a temperature interval from 25 to 180°C at 2°C/min under a dry nitrogen atmosphere.

SEM

SEM observations were performed at room temperature on a Hitachi S-4800 instrument operated at an accelerating voltage of 15 kV. PET/PEN blend samples prepared in the Haake torque rheometer were immersed in liquid nitrogen and fractured to study their morphology on the fracture surfaces. All of the specimens were coated with a thin gold layer by vapor deposition with vacuum sputter coating before SEM analysis.

RESULTS AND DISCUSSION

Transesterification Reaction

Figure 1 shows the ¹H-NMR spectra of the PET/PEN blends (70/30 w/w) with a mixing time of 5 min. The spectra in the region of 5.0–4.7 ppm corresponded to the ethylene units in the PET/PEN blends. For all of the samples, the peaks observed at 4.82 and 4.92 ppm were attributed to the ethylene units of the PET and PEN homopolymers, respectively. The peak at 4.87 ppm was due to the ethylene unit, which was situated between a terephthalate and a naphthalene group.¹⁵ It was evident that a transesterification reaction had occurred during melt mixing and that copolymers were forming.

The extent of transesterification in the PET/PEN blends could be quantified by a method using the peak intensities (I_{TET} , I_{TEN} , and I_{NEN}) of the ¹H-NMR spectra, as proposed by Yamadera and Muano.¹⁵ Three types of ethylene units are: TET (ethylene unit between two terephthalate groups), NEN (ethylene unit between two naphthalate groups), and TEN (ethylene unit between one terephthalate and one naphthalate group). The values of the transesterification level (f_{TEN}), the degree of randomness (B) of the reactive blends, and the average sequence lengths of the PEN and PET blocks (L_{nPET} and L_{nPEN} , respectively) are given by eqs. (1)–(4):

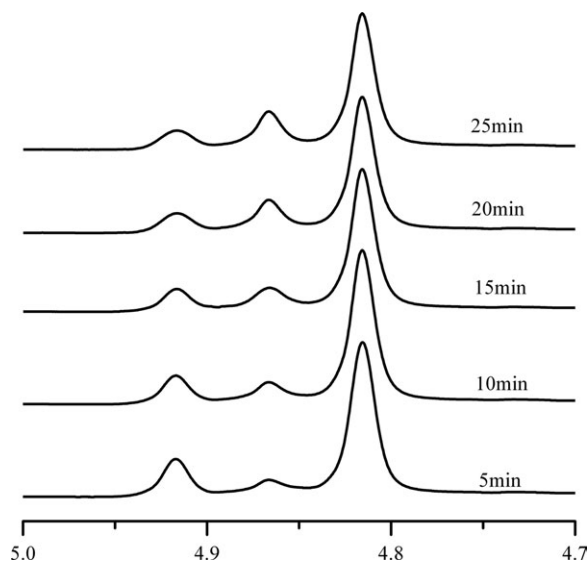


Figure 2. $^1\text{H-NMR}$ spectra of the ethylene region of the 70/30 w/w PET/PEN blends with mixing times of 5, 10, 15, 20, and 25 min.

$$f_{\text{TEN}} = I_{\text{TEN}} / (I_{\text{NEN}} + I_{\text{TEN}} + I_{\text{TET}}) \quad (1)$$

$$L_{n\text{PET}} = 1 + 2I_{\text{TET}} / I_{\text{TEN}} \quad (2)$$

$$L_{n\text{PEN}} = 1 + 2I_{\text{NEN}} / I_{\text{TEN}} \quad (3)$$

$$B = 1 / L_{n\text{PET}} + 1 / L_{n\text{PEN}} \quad (4)$$

Figure 2 presents the $^1\text{H-NMR}$ spectra of the ethylene region of the PET/PEN blends (70/30 w/w) with various mixing times. Table I shows the data obtained from the analysis of the $^1\text{H-NMR}$ spectra. The extent of transesterification was apparently affected by the mixing time. With the progress of transesterification, there was an increase in the amount of copolymer, and the randomness of the blends increased, whereas the $L_{n\text{PET}}$ and $L_{n\text{PEN}}$ values decreased.

Thermal Properties

The miscibility between polymers is often ascertained through measurements of the glass-transition temperatures (T_g): miscible binary polymer blends exhibit a single T_g between the T_g 's of the pure components, whereas immiscible blends show two T_g 's corresponding to the two homopolymers.¹⁶ Therefore, DSC analysis may provide useful knowledge concerning miscibility in polymer blends.

Table I. f_{TEN} , $L_{n\text{PET}}$, $L_{n\text{PEN}}$, and B Values as Revealed by the $^1\text{H-NMR}$ Data of the 70/30 w/w PET–PEN Blends with Mixing Times of 5, 10, 15, 20, and 25 min

Mixing time (min)	f_{TEN} (%)	Block length		B
		$L_{n\text{PET}}$	$L_{n\text{PEN}}$	
5	4.5	33.2	11.2	0.12
10	11.3	13.2	4.5	0.30
15	16.6	9.0	3.0	0.44
20	20.4	7.3	2.5	0.54
25	22.7	6.6	2.2	0.60

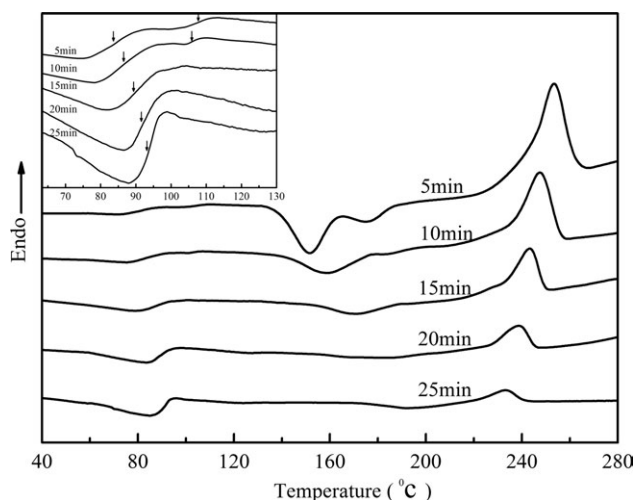


Figure 3. DSC curves of the 70/30 w/w PET/PEN blends with mixing times of 5, 10, 15, 20, and 25 min.

Figure 3 presents the DSC melting curves of PET/PEN blends prepared with various mixing times. Table II shows DSC measurement results. The cold crystallization exotherm split into two peaks with mixing times of 5 and 10 min; but as the mixing time increased, the cold crystallization exotherm and melting endotherm were suppressed, and the melting temperature (T_m) of the blends decreased monotonically. This was attributed to the action of the copolymers formed during the mixing process as a result of transesterification, which hindered the crystallization process.

The insert in Figure 3 presents DSC curves in the glass-transition region with a different scale. Although the curves were not smooth enough due to the enlarged scale, a systematic change in the glass transition behavior was present. For blends with mixing times of 5 and 10 min, two glass transitions were clearly observed corresponding to those of pure PET (81°C) and PEN (125°C), respectively. With increasing mixing time, the $T_{g,\text{PET}}$ and $T_{g,\text{PEN}}$ related to the PET and PEN components approached each other. After 15 min, a single T_g was almost observed, and the glass-transition range became narrower with increasing mixing time. This behavior could be explained by transesterification reactions and the incorporation of some units of each component throughout the polymer chains of the other; this led to homogeneity within the blend system. Similar results have also

Table II. DSC Measurement Results of the PET/PEN Blends (70/30 w/w)

Mixing time (min)	$T_{g,\text{PET}}$ (°C)	$T_{g,\text{PEN}}$ (°C)	T_{c1} (°C)	T_{c2} (°C)	T_m (°C)
5	83.4	108.1	154.9	178.5	256.5
10	87.7	105.8	163.1	193.0	251.7
15	91.8	—	174.7	—	246.5
20	92.5	—	182.9	—	242.2
25	93.2	—	197.8	—	236.4

T_{c1} , first cold crystallization temperature; T_{c2} , second cold crystallization temperature.

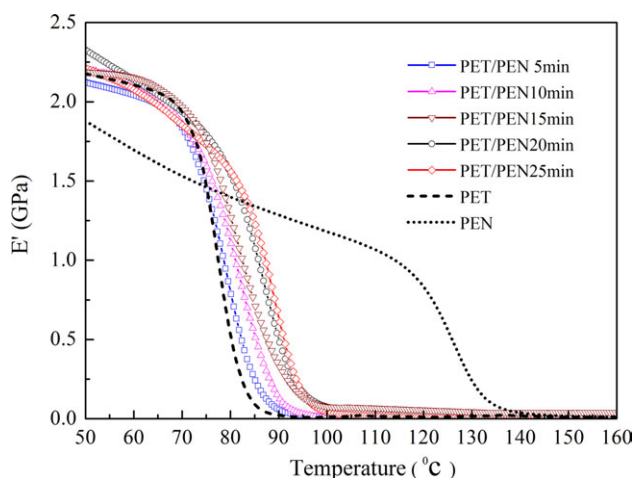


Figure 4. E' as a function of the temperature of the PET, PEN, and 70/30 w/w PET/PEN blends with different mixing times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

been reported for different blend systems composed of PEN/PTT poly(trimethylene terephthalate)¹⁷ and PET/PC (bisphenol A polycarbonate),¹⁸ and we double-checked the results in the later DMA testing.

Dynamic Mechanical Properties

Wagner, with coworkers from our laboratory,¹⁴ reported that PET/PEN blends in which the PEN concentration was equal to or less than 30 wt % showed a phase-separation phenomenon, which was investigated by dynamic rheology experiments. In this study, DMA was used to measure the physical properties of the glass-transition region.

Figure 4 represents the storage modulus (E') as a function of the temperature of the PET, PEN, and PET/PEN blends (70/30 w/w) obtained by melt processing at 280°C with different mixing times. In the glass-transition region, the materials' E' values in all cases decreased very sharply, and in all of the prepared blends, E' was higher than that of the pure PET. The naphthalene units in PEN provided stiffness to the PET/PEN blend. Furthermore, the PET/PEN blend with a longer mixing time had a higher E' in the glass-transition region. This was an indication that perhaps there was improved adhesion between the PET and PEN phases after longer mixing times and, for this reason, the blends became stiffer.

Figure 5(a) represents the loss factor ($\tan \delta$) as a function of the temperature of the PET, PEN, and PET/PEN blends (70/30 w/w) obtained by melt processing at 280°C with different mixing times. As shown in Figure 5(a), the maxima of the temperature dependence of $\tan \delta$ for the PET and PEN homopolymers and PET/PEN blends were slightly different from the corresponding T_g 's obtained by DSC. For example, the maximum $\tan \delta$ peak for the PET/PEN blend with a mixing time of 25 min was 95°C, about 2°C higher than the corresponding T_g calculated with DSC. Such a difference is very common between the two methods. In DMA, the exact position of T_g depends mainly on the studied frequency, whereas in DSC, T_g depends on the heating rate used. Above the glass-transition region, the $\tan \delta$ curves of the PET and PEN homopolymers did not show a continuous decrease down to the initial baseline; this was attributed to the particular viscoelastic features of these systems.^{19–21}

Figure 5(a) also shows a systematic change in the $\tan \delta$ curves of the PET/PEN blends. It was possible to observe two different

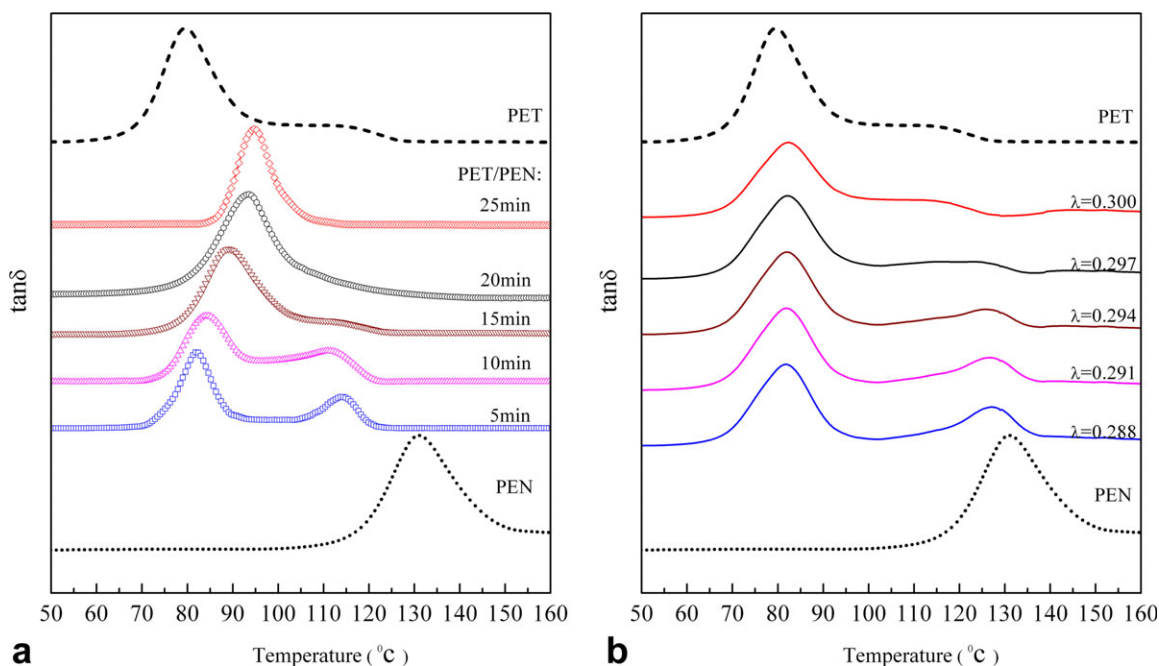


Figure 5. $\tan \delta$ as a function of the temperature of the PET, PEN, and 70/30 w/w PET/PEN blends with different mixing times: (a) experimental and (b) modeling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$\tan \delta$ peaks under shorter mixing times; these corresponded to the pure PET and PEN, respectively. The $\tan \delta$ peak varied as a function of the mixing time; the one related to PET moved toward a higher temperature, and the one related to PEN moved toward a lower temperature until a single $\tan \delta$ peak was formed. As the mixing time increased, the single peak became narrower. This was in agreement with the T_g results determined with DSC. We concluded that during the mixing process, some *in situ* formed copolymers containing the PEN unit as a major component may have penetrated into the PET phase. Similarly, other copolymers with the PET unit as a major component can diffuse into the PEN phase, promoting interfacial interactions between phases. Thus, the miscibility of the PET/PEN blends was improved.

To better describe the glass-transition behavior of the PET/PEN blends (70/30 w/w), a mechanical model was used. For two-phase polymer blends, the most distributed is the Takayanagi series-parallel model, which is originally derived from solid-particle-reinforced material,²² although it has since been used most for polymer blends.^{23,24}

The Takayanagi model performs all arrangements of the two phases in series (which undergo the same strain) or parallel (which are subjected to the same stress), assuming that there are perfect interactions between the phases and that the sample is macroscopically homogeneous and microscopically heterogeneous. In this study, a mixture of series and parallel was used: a fraction of PEN that formed the disperse phase was linked in series to an arrangement that consisted of the rest of PEN and PET linked in parallel. The corresponding expressions related to the complex modulus (E^*) and $\tan \delta$ values of the blends for the model were as follows:

$$\frac{1}{E^*} = \frac{\lambda}{E_{\text{PEN}}^*} + \frac{1 - \lambda}{\phi E_{\text{PEN}}^* + (1 - \phi)E_{\text{PET}}^*} \quad (5)$$

$$E^* = E' + iE'' \quad (6)$$

$$\tan \delta = \frac{E'}{E''} \quad (7)$$

where E'' is the loss modulus of the blends, respectively; λ and ϕ are parameters that correspond to the mixing state and the phase proportions, respectively; and the product $(1 - \lambda)(1 - \phi)$ is equivalent to the volume fraction of PET [with the assumption that the two homopolymers have similar densities; thus, $(1 - \lambda)(1 - \phi) = 0.70$]. The higher ϕ is, the closer the model is to ordinary parallel coupling of the elements, and the higher λ is, the closer it is to series. To perform the modeling, different λ values (from 0.288 to 0.300) were introduced, and the experimental data of pure PET and PEN were assigned to E_{PET}^* and E_{PEN}^* . Equations (5)–(7) were then used to calculate $\tan \delta$ for the corresponding mixing times at which the experimental results were obtained.

The predicted curves, as shown in Figure 5(b), were compared to experimental curves to evaluate the validity of the model. The predicted $\tan \delta$ curves followed the experimental curves in peak numbers and peak tendency to merge. The higher λ corresponded to the longer mixing time, and this means that the

model was closer to series and that the system was heading toward being homogeneous. However, after the initial two $\tan \delta$ peaks merged into one, the real peaks became narrower and shifted to higher temperatures with increasing mixing time, whereas the predictions scarcely moved. The first point to be considered is that the physical behavior of the blends was critically dependent on the two component homopolymers and on the interfacial adhesion to transmit the applied stress effectively. The copolymers formed during melt processing and diffused into corresponding phases; this improved the stress-transfer process. Therefore, the two $\tan \delta$ peaks, as predicted in the model, merged gradually. The second point is that these copolymers in the system reduced the mobility of the macromolecular chains and thus made the experimental $\tan \delta$ peak move to higher temperatures.

Morphology

Figure 6(a–c) shows the morphology of PET/PEN blends prepared with various mixing times, where the blend ratio of PET to PEN was 70/30. Therefore, PEN was the dispersed phase, and PET was the dispersing medium.

Increasing the time of mixing from 5 to 25 min led to a drastic improvement in morphology. The large dispersed PEN particles with different dimensions could be easily identified from the PET/PEN blends reported in Figure 6(a). However, under a longer processing time, as shown in Figure 6(b), smaller PEN particles were obtained because of the reduction in the extent of pure PET and PEN components as a consequence of transesterification or an increase in the extent of the copolymers, which acted as compatibilizers between the PET and PEN. As the transesterification proceeded, the pure PET and PEN phases continued to decrease. The micrograph of the PET/PEN blends reported in Figure 6(c) shows more uniform dispersed PEN particles of even smaller dimensions, less than 1 μm . This clear difference in the morphology was mainly attributed to longer melting and mixing times and to the greater extent of copolymers formed because of transesterification. The copolymers resulted in less obvious phase separation and a smaller domain size of the dispersed-phase particles.

As shown in the micrographs, in all of the blends, the dispersed PEN phase was very distinct. The observation in the PET/PEN blends with an initial mixing time of 5 min was in line with the well-detected glass transitions by the DSC and DMA methods. However, the visual two-phase appearance of the blends melt-mixed for 25 min was in contradiction with the observation of a single T_g . This fact could be explained by either the small size of the dispersed PEN phase or the high extent of copolymers, which could bring the T_g 's of the two phases closer and thus make them invisible for DSC and DMA.

Mechanical Tensile Properties

The Young's modulus and the yield stress of the PET/PEN (70/30 w/w) blends scarcely changed with the mixing time and were maintained at 2.36 ± 0.07 GPa and 56.8 ± 0.6 MPa, respectively. These values were higher than those of the pure PET (2.15 ± 0.06 GPa and 52.0 ± 0.5 MPa, respectively) because of the stiffness contribution of PEN. The lack of effect of the mixing time was probably observed because the tensile properties in

the small strain range were insensitive to the adhesion between the phases and the compatibility level.

Figure 7 shows the dependence of the tensile strength and elongation at break of the blends on the mixing time. The tensile strength for the 70/30 blend increased from 51.6 ± 0.7 to 54.0 ± 0.8 MPa when the mixing time increased from 5 to 10 min and maintained a range of 53.0–56.0 MPa under

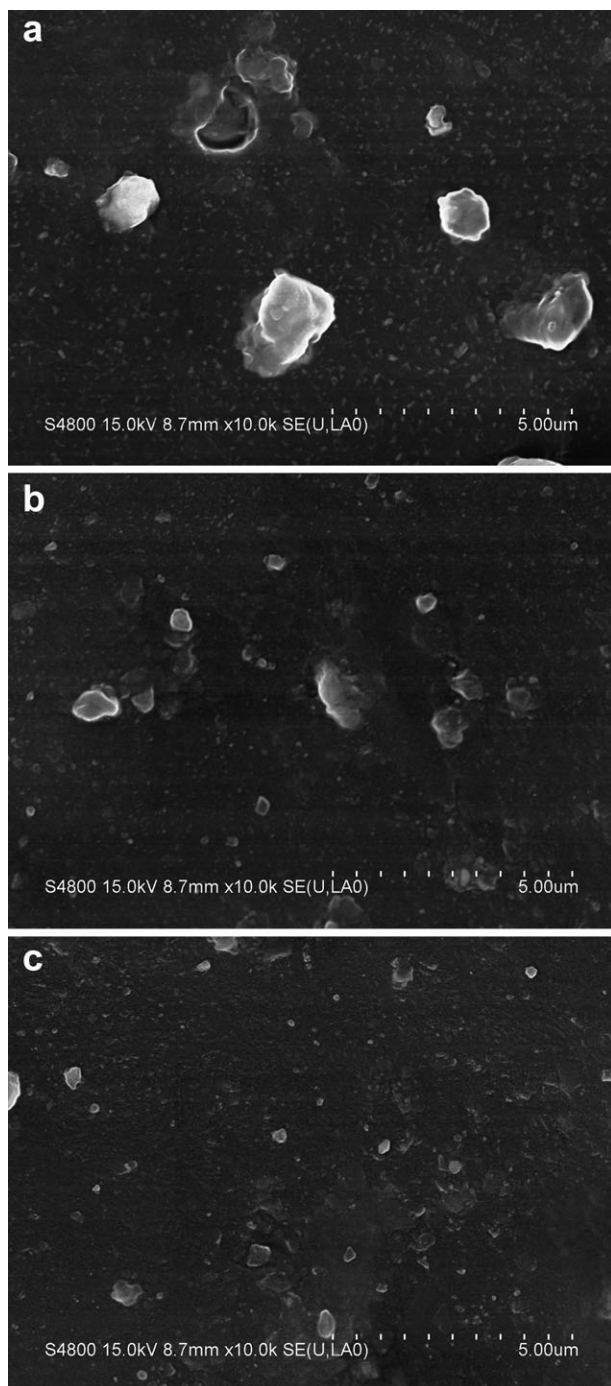


Figure 6. SEM micrographs of the fracture surfaces of the PET/PEN blends with mixing times of (a) 5, (b) 15, and (c) 25 min.

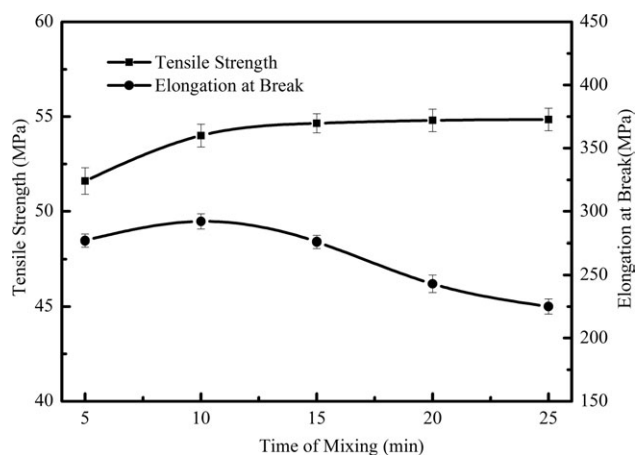


Figure 7. Influence of the mixing time on the tensile strength and elongation at break of the PET/PEN blends.

longer mixing times. The elongation at break at a mixing time of 5 min was $277 \pm 5\%$ and then changed to 292 ± 6 and $225 \pm 6\%$ when the mixing time changed to 10 and 25 min, respectively. These values were lower than that of pure PET ($386 \pm 4\%$). The slight increase in the tensile strength and the initial increase in the elongation at break were probably due to improved adhesion between the PET and PEN phases. However, the elongation at break decreased when the mixing time was longer than 10 min, probably because the copolymers formed during the mixing process resulted in a decrease in the ductility of the blend. These copolymers induced miscibility in the system, and the blends became less ductile because the copolymers reduced the mobility of the macromolecular chains. The possible degradation due to long mixing times may have been another cause for the decrease in the elongation at break.

CONCLUSIONS

In this study, we examined the influence of the mixing time on the phase structure and glass-transition behavior of 70/30 w/w PET/PEN blends, which were prepared via a melt-mixing process at 280°C .

We observed that with an increase in mixing time, B in the blend system increased, whereas the $L_{n\text{PET}}$ and $L_{n\text{PEN}}$ values decreased. By changing the mixing time in the 5–25-min range, we could control the phase structure through the randomness of the copolymers formed by transesterification. The results indicate that the blends mixed for a short time were miscible to a limited extent, showing two glass transitions, which approached more closely with increasing mixing time. When the mixing time reached 15 min, enough transesterification occurred to effectively improve the miscibility of the PET/PEN blends; this resulted in a single T_g . With increasing mixing time, there was an initial increase in the tensile strength. These results are significant in that they show the importance of the mixing time in the generation of the final phase structure and properties of the PET/PEN blends during processing.

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