

Spectroscopic Analysis of Poly(Ethylene Naphthalate)–Poly(Butylene Terephthalate) Blends

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ABSTRACT: The characteristics of poly(butylene terephthalate) (PBT), poly(ethylene naphthalate) (PEN), and blends with 30, 40, 50, 60, and 70 wt % PEN prepared by melt-blending were analyzed using Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction, solid-state nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy. The spectroscopic analyses provide no direct evidence for the occurrence of transesterification reactions occurring during melt-processing of the blends under the conditions that were used. The improved

mechanical properties of the PBT/PEN blends are attributed to physical interactions occurring over a large interfacial area. X-ray diffraction and high-resolution solid-state carbon-13 (¹³C) NMR confirmed the formation of the α -PEN phase after annealing samples at 200°C for 19 h. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1860–1868, 2007

Key words: poly(butylene terephthalate) (PBT); poly(ethylene naphthalate) (PEN); spectroscopic analysis

INTRODUCTION

Poly(ethylene-2,6-naphthalene dicarboxylate), also known as poly(ethylenenaphthalate) (PEN),^{1–3} was discovered in 1948 by Whinfield and Dickson. PEN is a thermoplastic polyester that raises the performance of this polymer family to levels not attainable with polyethylene terephthalate (PET). PEN has thermal, mechanical, chemical, and dielectric properties that are generally superior to those of PET. Because of these improved properties, PEN is positioned as a high-performance extension of PET with no significant change in resin preparation chemistry. The high melt viscosity of PEN makes it appropriate for its use in processes requiring good melt strength. Copolymers and blends of PEN and other resins based on dimethyl-2,6-naphthalene dicarboxylate can be prepared for fiber spinning, and extrusion-blow molding and film extrusion, sheet extrusion and injection molding.

Polybutylene terephthalate (PBT),^{4–6} an advanced, semicrystalline resin, is one of the toughest and most versatile of all engineering thermoplastics. Strong and lightweight, this polyester is characterized by low moisture absorption, excellent electrical properties, broad chemical resistance, lubricity, durability, mechanical strength, and heat resistance.

These properties are stable over a broad range of temperature and humidity conditions. PBT is a versatile blending material as well as a component of numerous commercial products. It can be blended with 10 to 30% Nylon to facilitate glass reinforcement. Moisture absorption can be reduced and processibility and mechanical properties boosted simultaneously when PBT is blended with 15–25% low-density polyethylene (LDPE). An enhanced gloss surface can also be achieved when PBT is blended with PET.

To take advantage of the superior properties of PEN and PBT, blending and characterization of these polymer blends have been undertaken by several researchers.^{7–10} Kim and Kang showed evidence of transesterification reaction between PEN and PBT by thermal annealing at 270°C for 30 min, using differential scanning calorimetry (DSC) and NMR. Calcium stearate was added to the blends to lower the viscosity of PEN and as a transesterification catalyst, which reduces the mechanical properties of the blends as consequence.⁷ However, evidence of transesterification reaction was not found in their work without thermal annealing or a catalyst, which agrees with our previous observations.⁸ Guo and Zachmann, in the course of a research program on blending of polyesters,^{9–14} reported the occurrence of a new ¹³C-NMR peak from PET and PEN as direct evidence of transesterification.^{12–14} However, it was noted that the miscibility of PBT and PEN at the molecular level suggested by solid-state ¹³C NMR (CP/

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MAS technique) arose from a kind of physical interaction within a very short distance (2–4 nm),^{9–11} which was further investigated by us.⁸ Additionally, it was after at least 10 min heat treatment at 280°C that a new peak, arising from transesterification reaction between PET and PEN, was detected by solution NMR.¹⁰

In recent research, we have investigated the mechanical and thermal properties, and carried out a solution NMR analysis, of PBT/PEN blends.^{8,15–17} The present study is focused on the possibility of formation of new chemical bonds arising from interchange reactions between PBT and PEN under typical conditions of extrusion and injection molding without further thermal annealing, and assessing the effects of heat treatment on PBT/PEN blends and the two homopolymers through spectroscopic analysis using Raman, FTIR, NMR, X-ray photoelectron spectroscopy, and X-ray diffraction.

EXPERIMENTAL

Material

Polymers used in this study were PEN, purchased from Teijin, and PBT (Arnite T06-202), supplied by DSM Engineering Plastics. Pure PBT, pure PEN, and PBT/PEN mixtures were dried at 70°C for 48 h in vacuum. Blends with 30, 40, 50, 60, and 70 wt % PEN were extruded with an Axon (model BX-18-286) single screw extruder and injection-molded using a BOY (model 50M) automatic injection-molding machine at 250–280°C.^{16,17}

Experimental details

FTIR-photoacoustic spectroscopy (PAS) was carried out using a BIO-RAD FTS-60 spectrometer on small pieces of chopped injection-molded samples, with the photoacoustic cell purged with nitrogen.

A Renishaw (Model 1000) Raman spectrometer was used for Raman spectroscopic analysis using a 488-nm blue laser, which allowed access to the range 4000–100 cm⁻¹ of Raman shifts. Samples were cut into small blocks before analysis.

A Bruker (Model AXS D8 ADVANCE) X-ray powder diffractometer was used to measure intensity (counts) versus diffraction angle (2θ) in the range 5°–40°. Two types of samples were used for XRD analysis: (a) unannealed, (b) annealed at 200°C for 19 h. The X-ray source used was Cu Kα with wavelength of 15.4051 nm.

The solid-state ¹³C NMR experiments were carried out at room temperature using a Bruker MSL300 NMR spectrometer operating at 75 MHz, with cross polarization (CP)/magic angle spinning (MAS) and dipolar decoupling (DD), on both unannealed and

annealed samples. The samples were examined in the form of powders to obtain the signal by partial averaging of the chemical-shift anisotropy according to the different orientations of local motions in the bulk below *T_g* (glass transition temperature). For all the samples, the sample spinning rate was 6 kHz, with contact time 1 ms, and the recycle time of the pulse was 1 s. Chemical shifts were referenced to tetramethylsilane via the carbonyl carbon signal of glycine (176.03 ppm).

X-ray photoelectron spectroscopy was carried out with a Kratos XSAM800 instrument using a Mg Kα (1253.6 eV) X-ray source. The samples were outgassed for 3 days in the environmental chamber, then transferred to the analytical chamber whose pressure was below 1 × 10⁻⁹ Torr. Wide, narrow, and valence scans for samples were obtained with 65, 20, and 20 eV pass energies.

RESULTS AND DISCUSSION

FTIR spectroscopy

Figure 1 shows that the labeled major functional groups in the frequency regions are present in pure PEN, PBT, and five different PBT/PEN blends, with relative band intensities varying with the weight proportions of the homopolymers in the blends. Around 3060 cm⁻¹, weak bands associated with an aromatic C–H stretch vibration and at 2960 cm⁻¹ strong bands from an aliphatic C–H stretch vibration appear. Both weak and strong bands are present in PEN, but weak bands are hard to be seen in PBT. The implication is that the bands from long aliphatic segments are more dominant than those from the aromatic segment in PBT, and the bands from the fused aromatic rings (naphthalene) are

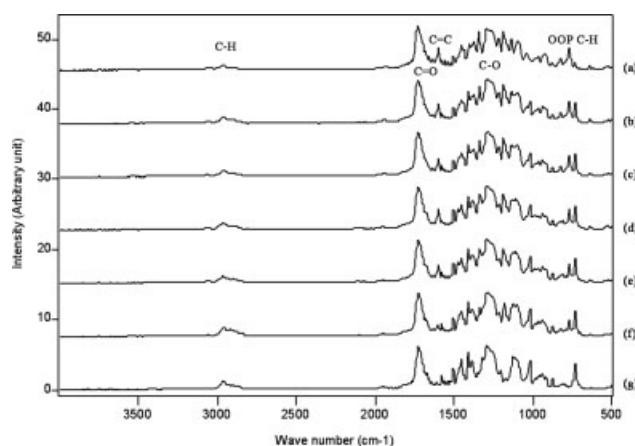


Figure 1 FTIR spectra of PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

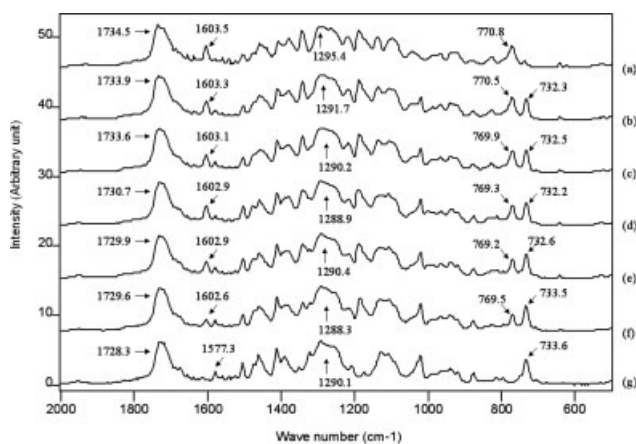


Figure 2 Expanded FTIR spectra of PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

shown by PEN because of the shorter carbon chains of PEN compared to PBT. In the PBT/PEN blend spectra in the vicinity of 3000 cm^{-1} , the bands from the aliphatic segments increase in intensity and those from the aromatic segments decrease in intensity as the proportion of PBT increases. The other major bands are assigned as: C=O $\sim 1730\text{ cm}^{-1}$, aromatic C=C $\sim 1600\text{ cm}^{-1}$, C—O $\sim 1290\text{ cm}^{-1}$, and aromatic out-of-plane bending vibration (OOP—CH) $\sim 730\text{ cm}^{-1}$. Unlabeled bands are from CH₂ groups around 1450 cm^{-1} and from ester groups of phthalate and naphthalate in the range of $1200\text{--}1050\text{ cm}^{-1}$. The additional bands arising from C=C stretch vibrations are not interpretatively useful owing to the large number of bands and the presence of weak overtone, combination and difference bands.¹⁸

Figure 2, which shows expanded scale bands of Figure 1 in the range of $2000\text{--}500\text{ cm}^{-1}$, reveals frequency shifts for several functional groups as the proportions of the blend components vary. The carbonyl group band from the ester groups in PEN and PBT shifts from $1735\text{ to }1728\text{ cm}^{-1}$, two aromatic C=C bands from the naphthalene ring of PEN at 1604 cm^{-1} and from the benzene ring of PBT at 1577 cm^{-1} shift and change in intensity, and the C—O bands from the ester groups shift from $1295\text{ to }1290\text{ cm}^{-1}$ as the proportions of the constituent homopolymers vary.^{18–20}

The frequency shifts and changes in intensity are also in accordance with the change of proportions of the components for two aromatic out-of-plane bending vibrations arising from naphthalene (770 cm^{-1}) and benzene (730 cm^{-1}). These changes of frequency and intensity of major bands, and the absence of new bands arising from chemical reaction, indicate that interchange reaction between

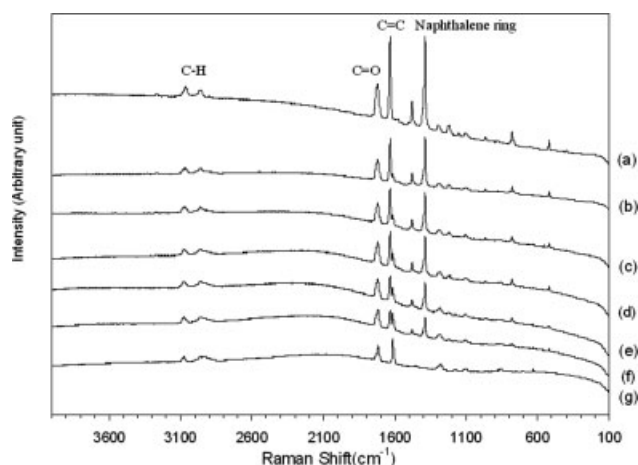


Figure 3 Raman spectra of PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

PEN and PBT did not occur to a significant extent under the blending conditions (a short residence period during extrusion and injection molding) that were used.

Raman spectroscopy

Figure 3 shows Raman spectra of PBT/PEN blends over the whole accessible frequency range. Some of vibrations for PBT/PEN blends are Raman-active, others are IR-active and some are active in both Raman and IR. Around 3060 cm^{-1} , weak bands from an aromatic C—H stretch vibration and around 2960 cm^{-1} strong bands from an aliphatic C—H stretch vibration in IR, appear as medium bands in Raman. The band for C=O around 1720 cm^{-1} and

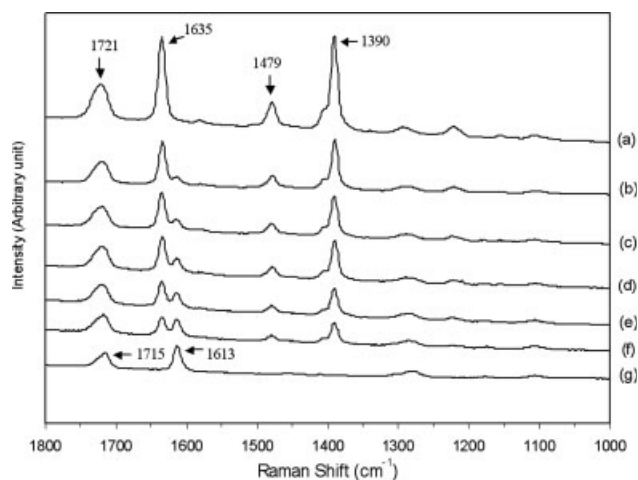


Figure 4 Expanded Raman spectra of PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

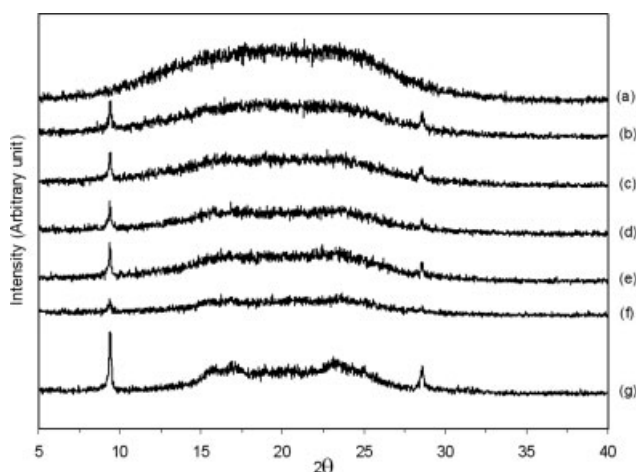


Figure 5 WAXS of unannealed PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

two aromatic C=C bands around $1640\text{--}1610\text{ cm}^{-1}$ appear in the Raman and IR spectra.^{19–24}

The C=C stretch vibration of the aromatic ring is strong for PEN around 1479 cm^{-1} but very weak in PBT around 1457 cm^{-1} . An intense band associated with the disubstituted naphthalene ring of PEN appears at 1390 cm^{-1} .¹⁹

Expanded scale Raman spectra of PBT/PEN blends are shown in Figure 4. The C=O bands from PEN (1721 cm^{-1}) and PBT (1715 cm^{-1}) are superimposed and the Raman shift varies with the proportions of the homopolymers. Two aromatic C=C bands, from the naphthalene ring of PEN (1635 cm^{-1}) and the benzene ring of PBT (1613 cm^{-1}), are also shifted and their intensities change according to the weight fractions of the blend com-

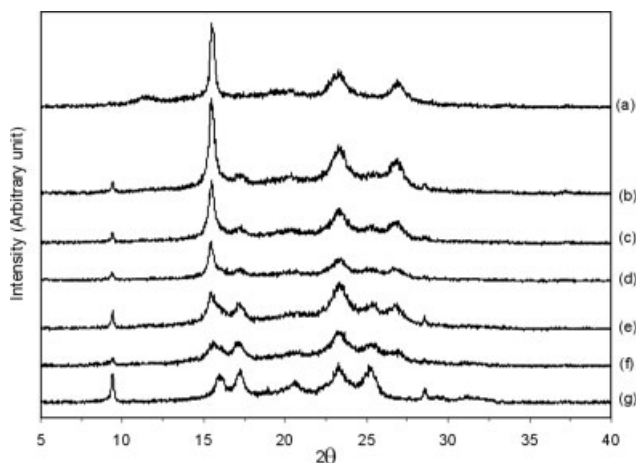


Figure 6 WAXS of annealed PBT/PEN (wt %/wt %) blends at 200°C for 19 h: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

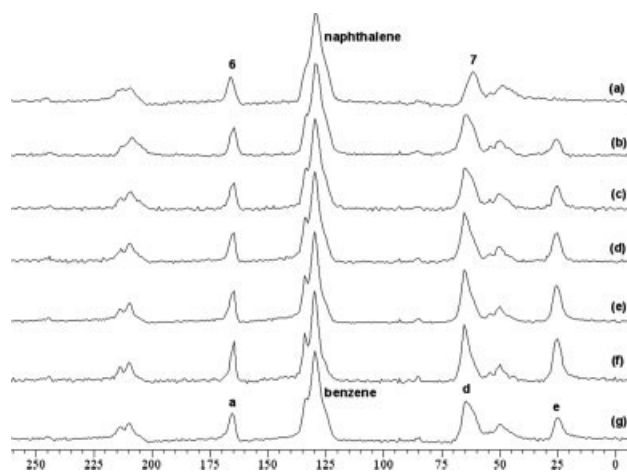


Figure 7 Solid-state ^{13}C NMR of unannealed PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

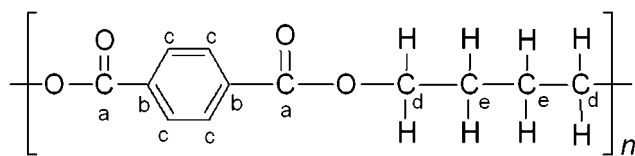
ponents. The C=C stretch from the aromatic ring around 1479 cm^{-1} and the disubstituted naphthalene ring vibration of PEN around 1390 cm^{-1} follow the same trend. However, there are no new bands in the Raman spectra of the blends, confirming that interchange reaction between PEN and PBT occurred to an insignificant extent under the melt-blending and injection-molding conditions used.

X-ray diffraction

Wide-angle X-ray scattering (WAXS) diffraction scans for unannealed and annealed blends are shown in Figures 5 and 6, respectively. Figure 5 shows a broad diffuse signal for amorphous PEN in which crystallization has been suppressed by the rapid quenching that followed injection-molding. PBT shows partial crystallization under the same molding conditions, implying that PBT crystallizes more rapidly than PEN, in accordance with differential scanning calorimeter scans¹⁶ that

TABLE I
Assignment of Solid-State ^{13}C NMR Spectra of the Homopolymers

PBT	Chemical shift (ppm)	PEN	Chemical shift (ppm)
a	164.4	C ⁶	164.4
b	134.0	C ⁵	Not observed
c	129.4	C ⁴	131.9
d	65.3	C ¹	128.7
e	26.7	C ³	Not observed
		C ²	125.0
		C ⁷	60.2



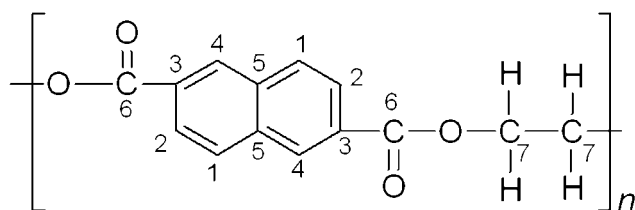
Scheme 1 The structure of PBT.

showed a greater extent of crystallization around 210°C for PEN than for PBT, after cooling injection-molded samples at -50°C for 5 min and heating at 10°C min⁻¹ to 300°C. The blended samples of Figure 5(b-f) appear noncrystalline except for reflections at 9.4° and 28.7° (2θ) that are assigned to PBT.

Figure 6 shows the remarkably different diffraction patterns of the samples after annealing. PEN has strong reflections at 15.5° (α-phase: 010), 23.4° (α-phase: 100), and 27.1° (α-phase: -110), and PBT at 9.4°, 16.2°, 17.3°, 20.8°, 23.4°, 25.4°, and 28.7°.²⁵⁻²⁸ Even though the PEN and PBT reflections partially overlap (around 16° and 23°), all strong reflections change in intensity with the proportions of the components. One notable point is that, under the molding conditions used, PEN was amorphous and was transformed to α-PEN by annealing, in accordance with a previous report.²⁵ The WAXS data also show that the reflections from the components of the blends behave like simple addition of two components, which indicates that there was no significant crystal structure change arising from possible chemical reactions between the two homopolymers.

Solid-state NMR

In polymers in the rubbery state above the glass transition temperature, T_g , and in the liquid state the local motions of bulk polymers are such fast cooperative processes of relatively large amplitude that the main tensorial interactions (chemical-shift anisotropy, homonuclear and heteronuclear dipolar couplings, and quadrupolar couplings in the case of spins higher than [1/2]) are averaged to a large extent by the fast local motions. Consequently, for



Scheme 2 The structure of PEN.

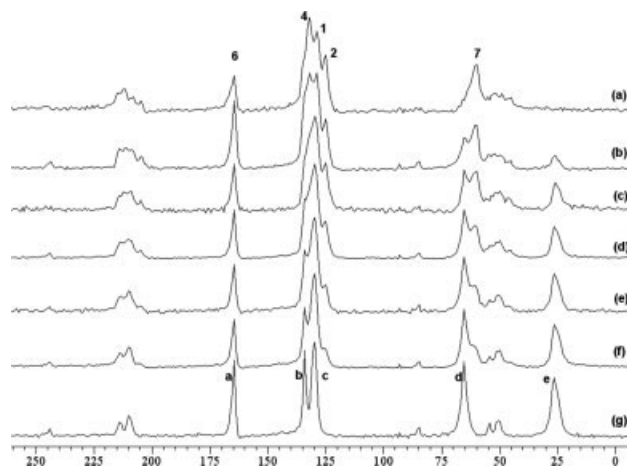


Figure 8 Solid-state ¹³C NMR of PBT/PEN (wt %/wt %) blends annealed at 200°C for 19 h: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

bulk polymers at temperatures well above T_g , high-resolution ¹³C NMR spectra can be obtained by using conventional spectrometers that are used for solution investigations. From an NMR point of view, bulk polymers in this temperature range and polymers in solution share a number of common features. By contrast, motions that may occur in a glassy polymer are much slower than modes observed in the melt, and they are very localized and involve only side groups or short sequences of the main chain.^{29,30} Consequently, the tensorial interactions are only partly averaged, or even not averaged at all when no local modes exist. To obtain high-resolution ¹³C NMR spectra specific line narrowing techniques such as DD, MAS, and CP are used here. One interesting point is that we used

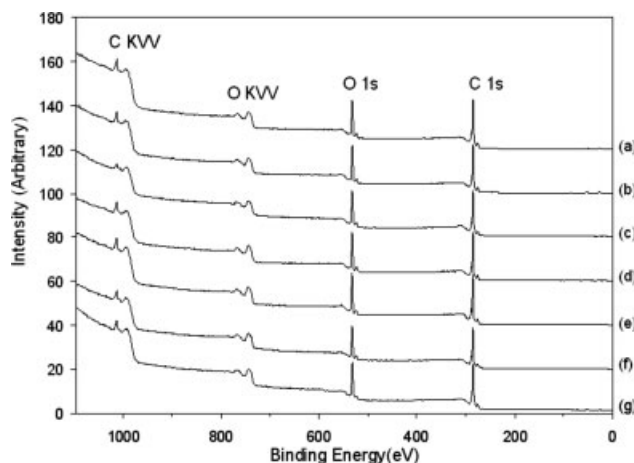


Figure 9 XPS survey spectra of PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

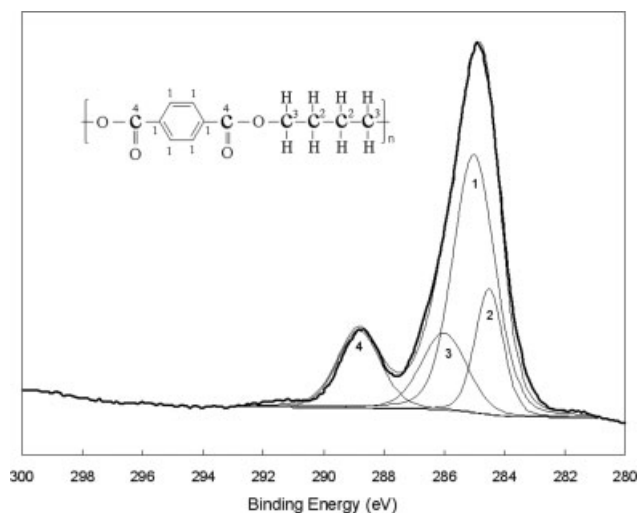


Figure 10 Sub-band analysis of the C1s scans for PBT.

solution NMR for the heat-treated samples to check any change in spectra, but the positions of the signals are exactly the same as those of the samples that had not been heat-treated.⁸ This indicates that the motions of molecules in solution are fast enough to be averaged.

Solid-state ¹³C NMR spectra of unannealed PBT/PEN blends and the two homopolymers are shown in Figure 7. Carbons from carbonyl groups and aliphatic segments of PBT and PEN are very distinctive as shown in Table I and Schemes 1 and 2. Some differences of peak positions from those previously reported^{9,25} seem to be due to different tensorial conditions used in this experiment. Even at the sample spinning rate of 6 kHz, sidebands appear on both sides (at 210 and 50 ppm) of the main PEN signal at 130 ppm. Signals from the naphthalene and benzene rings are not clearly resolved in the unannealed samples, because they

are mostly amorphous. By contrast, Figure 8 shows much better resolved line shapes in the naphthalene and benzene ring areas, confirming that the local rearrangements induced by heat treatment cause a transformation from the amorphous state to an ordered semicrystalline state. The shape of the naphthalene ring signal in PEN matches that from previous work and confirms the formation of α -PEN during annealing.²⁵ Because of the absence of cross polarization between the quaternary carbons (C3 and C5) in PEN and the protons in PBT, the C3 and C5 peaks of the naphthalene ring are not observed in Figure 8.²⁵

Previous work⁹ utilized delay decoupling and no decoupling ¹³C CP/MAS NMR to show that the proton-carbon intermolecular distances are so close that there is molecular scale mixing for the blends. However, ¹³C CP/MAS NMR with dipolar decoupling and the conditions used here does not show molecular scale mixing, but clearly confirms that there are significant changes in molecular arrangement after annealing.

X-ray photoelectron spectroscopy

The XPS survey spectra of the PBT/PEN blends in Figure 9 show O1s and C1s peaks at binding energies around 533 and 285 eV, respectively. Curve fitting of the C1s band for PBT (Fig. 10) enables assignment of sub-bands, where the ratio of the atomic concentrations of C₁, C₂, C₃, and C₄ is roughly 3 : 1 : 1 : 1 (Table II), which matches the relative numbers of C₁, C₂, C₃, and C₄ (6, 2, 2, and 2) in the repeat unit of PBT. Sub-band analysis of the oxygen band for pure PBT is shown in Figure 11. Here, again the numbers of O₁ and O₂ in the repeat unit correspond to 2 and 2, and the area ratio is close to 1 : 1.

TABLE II
Binding Energies, Full Widths at Half Maximum (FWHM), and Atomic Concentration (%) from Narrow Scans of PBT and PEN

		C1s				O1s	
		1	2	3	4	1	2
PBT	BE (eV)	285.00	284.49	286.00	288.80	531.00	532.46
	FWHM (eV)	1.65	1.11	1.80	1.70	1.68	1.64
	Atomic concentration (%)	50.96	16.70	16.61	15.73	49.74	50.26
	Sensitivity factor	0.25	0.25	0.25	0.25	0.66	0.66
	Mixing ratio (GL)	80	80	80	80	80	80
PEN	BE (eV)	285.00	286.76	289.10		531.12	532.76
	FWHM (eV)	1.40	1.46	1.50		1.60	1.60
	Atomic concentration (%)	71.46	14.28	14.26		49.38	50.62
	Sensitivity factor	0.25	0.25	0.25		0.66	0.66
	Mixing ratio (GL)	80	80	80		80	80

GL mixing ratio: Gaussian-Lorentzian.

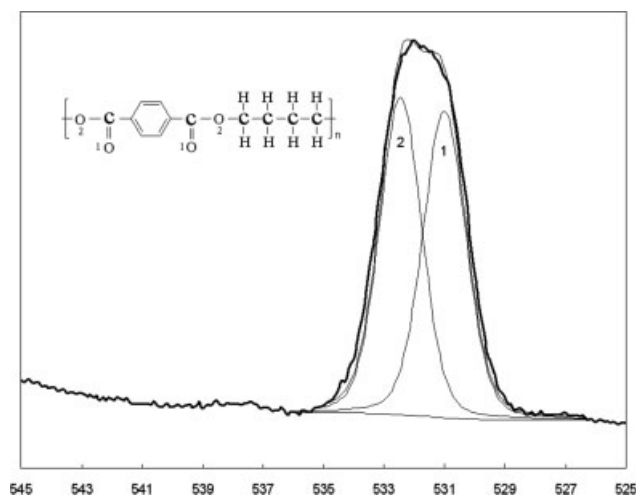


Figure 11 Sub-band analysis of the O1s scans for PBT.

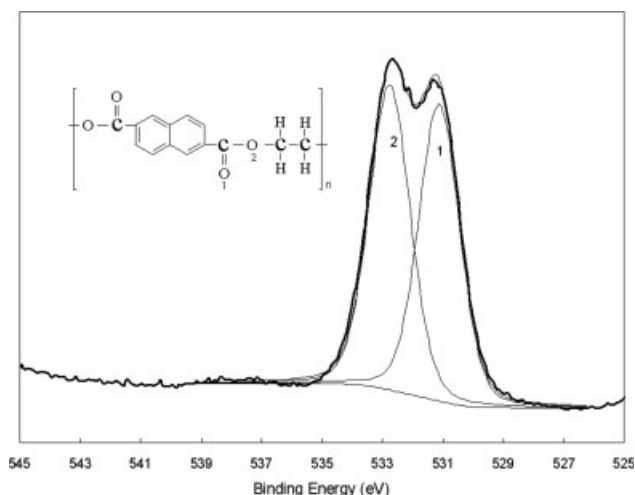


Figure 13 Sub-band analysis of the O1s scans for PEN.

The sub-band analysis of C1s for PEN is shown in Figure 12, in which the proportion of the atomic concentrations of C₁, C₂, and C₃ is close to 5 : 1 : 1 (Table II), which matches the relative numbers of C₁, C₂, and C₃ (10, 2, and 2) in the repeat unit of PEN. The sub-band analysis of O1s for PEN (Fig. 13) shows the ratio of atomic concentration of O₁ and O₂ as 1 : 1, which matches the numbers of O₁ and O₂ (2 : 2) in the repeat unit.

The sub-band analysis of C1s for PBT/PEN (50/50 wt %) blend is shown in Figure 14, where the sub-band analyses for PBT and PEN have in effect been combined, retaining the atomic concentration ratios for the homopolymers. The calculated band profile agrees well with the observed profile with only very minor shifts in the sub-band binding energies. The XPS data provide confirmation that the 50 : 50 (w/

w) blend can be regarded as a physical mixture of the two homopolymers.

The sub-band analysis of the oxygen band for PBT/PEN (50/50 wt %) blend is shown in Figure 15. Here, the atomic concentrations are close to 25% for each oxygen (O₁ and O₃ for PBT, O₂ and O₄ for PEN) corresponding to almost equimolar proportions of the two homopolymers, each of which contributes two oxygen. There is a 0.1 eV shift of binding energies for PBT/PEN (50/50 wt %) blend relative to the two homopolymers. This shift is likely to be attributable to physical interaction of the coexisting homopolymers at close distance rather than chemical reaction. Overall, the sub-band analysis of the carbon and oxygen bands shows that there is little change in chemical struc-

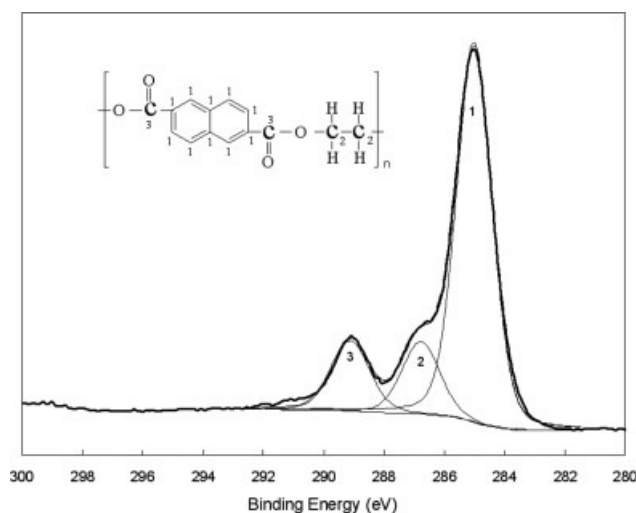


Figure 12 Sub-band analysis of the C1s scans for PEN.

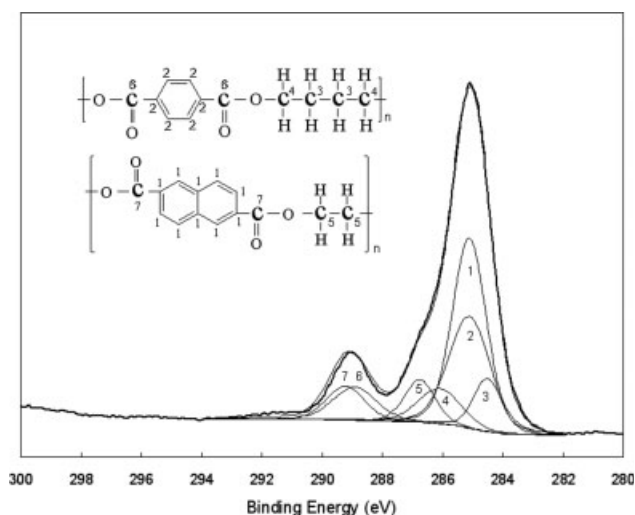


Figure 14 Sub-band analysis of the C1s scans for PBT/PEN (50/50 wt %).

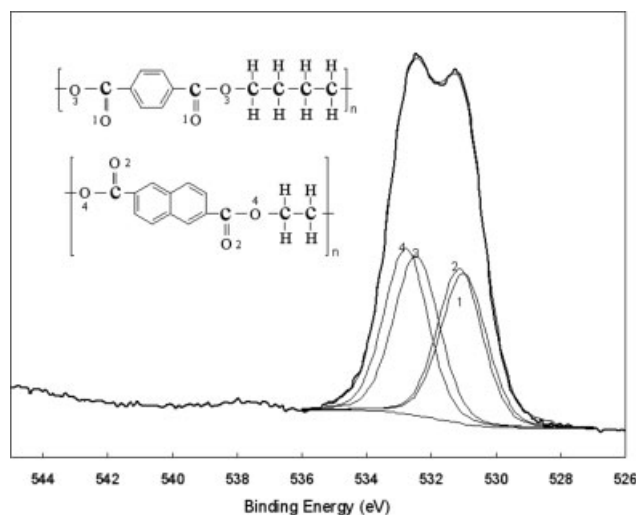


Figure 15 Sub-band analysis of the O1s scans for PBT/PEN (50/50 wt %).

ture of the blend relative to the homopolymer components.

The detailed XPS data including binding energies, full widths at half maximum (FWHM), and atomic concentration (%) from narrow scans of pure PBT, PEN, and PBT/PEN (50/50 wt %) blend are listed in Table III. All assignments are based on the literature.^{31,32}

At the binding energy of 0 eV, there is the Fermi level, which is the highest occupied molecular orbital from which electrons can escape without any required energy, and the valence band shows the spectrum in the vicinity of the Fermi level. Figure 16 shows valence spectra of blends, which are more sensitive to molecular structure than the core lines, since the core lines only indirectly reflect changes in the valence electron distribution. The O2s peaks span 28–34 eV for pure PEN, PBT, and PBT/PEN blends. The shapes of the valence spectra reveal very small changes with blend composition and are characteristic of each material. Hence, valence band spectra may be used to distinguish between blends where the core level XPS photo-

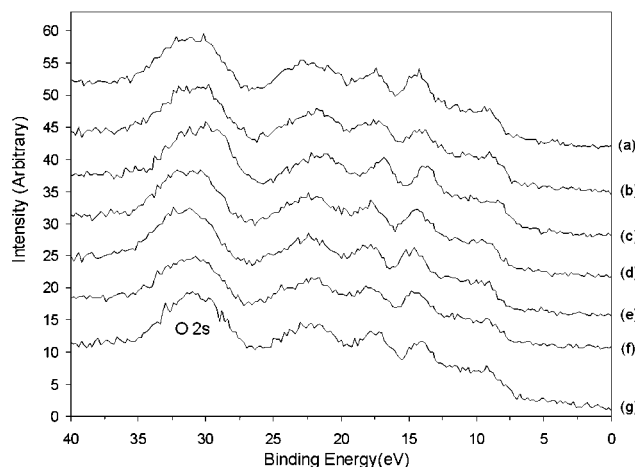


Figure 16 Valence spectra of PBT/PEN (wt %/wt %) blends: (a) 0/100; (b) 30/70; (c) 40/60; (d) 50/50; (e) 60/40; (f) 70/30; (g) 100/0.

electron lines are quite similar in shape and position.

CONCLUSIONS

FTIR spectra revealed distinct major functional group bands, from which the structures of pure PEN and PBT can be deduced without difficulty, but new bands arising from interchange reactions were not found.

The Raman spectra of the blends are consistent with the structures of PEN and PBT, and there is no evidence of new bands resulting from interchange reactions.

The wide-angle X-ray scattering scans showed that in the unannealed samples PEN was amorphous and PBT partially crystalline, indicating that under the molding conditions of rapid quenching after injection, PBT crystallizes more rapidly than PEN. After annealing, the samples show much greater crystallinity, and formation of the α -PEN phase.

Solid-state ¹³C NMR spectra show the effect of heat-treatment on the structural arrangement and confirms the formation of the α -PEN phase.

TABLE III
Binding Energies, Full Widths at Half Maximum (FWHM), and Atomic Concentration (%) from Narrow Scans of PEN/PBT(50/50 wt %)

	C1s							O1s			
	1	2	3	4	5	6	7	1	2	3	4
BE (eV)	285.10	285.10	284.49	286.10	286.76	288.90	289.20	531.10	531.22	532.56	532.88
FWHM (eV)	1.34	1.65	1.11	1.70	1.20	1.70	1.50	1.68	1.64	1.65	1.60
Atomic concentration (%)	35.49	25.72	8.24	8.32	7.15	7.96	7.12	24.36	24.49	25.55	25.60
Sensitivity factor	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.66	0.66	0.66	0.66
Mixing ratio (GL)	80	80	80	80	80	80	80	80	80	80	80

GL mixing ratio: Gaussian–Lorentzian.

XPS showed that there are minor shifts in binding energies for the PBT/PEN blends that are most likely attributable to physical rather than chemical interaction of the homopolymers.

The data from the five spectroscopic techniques we employed are consistent with the PBT/PEN blends produced by melt-blending and injection-molding being composed of PEN and PBT homopolymers. While the homopolymers may be partially miscible, there is no direct evidence for ester interchange reactions having taken place during melt-processing. Hence, we attribute the improved mechanical properties of the PBT/PEN blends to physical interactions occurring over interfacial areas that are very large due to the very small domain size of the dispersed phase.¹⁶ In addition, annealing at a temperature about 40°C below the melting temperature of PBT allows partial crystallization of the homopolymers to occur, but gives rise only to reflections that are attributable to PBT and PEN.

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References

- Nunes, E. d. C. D.; Agnelli, J. A. M.; Rossi, R. A. *Polimeros: Ciencia e Tecnologia* 1998, 8, 55.
- Frank, M.; *Modern Plastics* 1995, p B51.
- Bradily, G. S.; Clauser, H. R.; Vaccari, J. A. *Materials Handbook*; McGraw-Hill: New York, 1997; p 691.
- Utracki, L. A. *Commercial Polymer Blends*; London Chapman & Hall: London, 1998; p 337.
- Brinson, H. F.; Reinhart, T. J.; Schneider, S. J. *Engineered Materials Handbook*, Vol. 1; ASM International: Metals Park, Ohio, 1987; p 226.
- Bradily, G. S.; Clauser, H. R.; Vaccari, J. A. *Materials Handbook*; McGraw-Hill: New York, 1997; p 690.
- Kim, H. K.; Kang, H. J. *Polymer (Korea)* 2006, 30, 22.
- Jung, D. D.; Bhattacharyya, D.; Easteal, A. *J Mater Res Innov* 2003, 7, 269.
- Guo, M.; Zachmann, H. G. *Macromolecules* 1997, 30, 2746.
- Guo, M.; Zachmann, H. G. *Polym Prepr* 1996, 37, 829.
- Guo, M.; Zachmann, H. G. *Polym Prepr* 1996, 37, 227.
- Guo, M.; Zachmann, H. G. *Polym Prepr* 1997, 38, 884.
- Guo, M.; Zachmann, H. G. *Polym Prepr* 1998, 39, 385.
- Guo, M.; Zachmann, H. G. *Polymer* 1993, 34, 2503.
- Jung, D. D.; Bhattacharyya, D.; Easteal, A. J. *J Appl Polym Sci* 2001, 82, 1504.
- Jung, D. D.; Easteal, A. J.; Bhattacharyya, D. *J Mater Sci* 2003, 38, 2597.
- Jung, D. D.; Bhattacharyya, D.; Easteal, A. J. *J Mater Sci* 2005, 40, 4775.
- Pavia, D. L.; Lampman, G. M.; George, S. K. J. *Introduction to Spectroscopy*; W.B. Saunders Company: Philadelphia; 1979; Chapter 2.
- Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*; Wiley: Chichester, 2001; Chapter 1.
- Hendra, P.; Jones, C.; Warnes, G. *Fourier Transform Raman spectroscopy*; Ellis Horwood Limited: New York, 1991; Chapters 1 and 2.
- Ferraro, J. R.; Nakamoto, K. *Introductory Raman Spectroscopy*; Academic Press: Boston, 1994; Chapter 1, pp 162–166.
- Grasselli, J. G.; Snavely, M. K.; Bulkin, B. J. *Chemical Applications of Raman spectroscopy*; Wiley: New York, 1981; Chapters 1–3.
- Grasselli, G.; Bulkin, B. J. *Analytical Raman Spectroscopy*; Wiley: New York, 1991; Chapter 1.
- Lewis, I. R.; Edwards, H. G. M.; *Handbook of Raman spectroscopy*; Marcel Dekker: New York, 2001; Chapter 1.
- Guo, M.; Zachmann, H. G. *Macromol Chem Phys* 1998, 199, 1185.
- Cakmak, M.; Kim, J. C. *J Appl Polym Sci* 1997, 64, 729.
- Cakmak, M.; Kim, J. C. *J Appl Polym Sci* 1997, 65, 2059.
- Buchner, S.; Wiswe, D.; Zachmann, H. G. *Polymer* 1989, 30, 480.
- Fyfe, C. A. *Solid State NMR for Chemists*; C.F.C. Press: Guelph, ON, 1983.
- Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, 1994; Chapters 1 and 2.
- Briggs, D.; Beamson, G. *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*; Wiley: Chichester, 1992.
- Moulder, J.; Stickle, W.; Sobel, P.; Bomben, K. *Handbook of X-ray Photoelectron Spectroscopy*; Physical Electronics Division, Perkin-Elmer Corp.: Eden Prairie, 1992.