

Characterization of Microfibrillar Reinforced Poly(ethylene naphthalate)/Polypropylene Composites via Polarized Raman and Polarized FTIR Spectroscopy

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ABSTRACT: In polarized Fourier-transformed infrared spectroscopy and polarized Raman spectra of drawn poly(ethylene naphthalate)/polypropylene (PP) blends, the intensities of the orientation-sensitive bands of the blend components increased or decreased with increasing elongation, depending on the orientation of the corresponding vibrations. A significantly larger extent of molecular orientation was induced, when localized heating was applied to the blend during elongation (zone-drawing). Greater degree of

molecular orientation resulted in a higher strength blend. The strengths of the blends after each stage of microfibrillization, namely fibrillization and isotropization, were measured and correlated with spectral changes. After isotropization, the PP chains were randomized as shown by equal band intensities of the parallel and perpendicular spectra. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1442–1449, 2010

Key words: composites; FTIR; Raman spectroscopy

INTRODUCTION

Microfibrillization has emerged in recent years as a new technique for forming efficient *in situ* fiber reinforcement, to achieve high stiffness and strength to weight ratio in composites. Microfibrillar reinforced composites (MFCs) are generated from immiscible binary blends by mechanical drawing (fibrillization) followed by annealing (isotropization). MFCs acquire their strength reinforcement from the alignment of intrinsically strong C—C bonds in the backbone of the dispersed phase polymer. The drawing action deforms the dispersed phase into microfibrils and orients the polymer chains in the drawing direction. The annealing stage is performed between the melting points of the two blend components. Being the higher melting component, the microfibrils retain their fibrillar form and molecular orientation, whereas the lower melting matrix component returns to its isotropic state.

Characterization of the orientation of polymer chains is an important aspect in MFCs, because the strengthening effect provided by the microfibrils depends specifically on molecular orientation. X-ray

scattering techniques have been used in the literature to investigate the chain alignment of MFCs.^{1–4} In this study, polarized Raman and Fourier-transformed infrared spectroscopy (FTIR) spectroscopy were used to follow the change in molecular orientations of poly(ethylene naphthalate) (PEN)/polypropylene (PP) blends at each stage of microfibrillization. Spectroscopic techniques are not as direct as X-ray scattering, but they have the advantage that the polymers need not to be crystalline.

The morphology of the PEN/PP blends characterized in this study has been examined by scanning electron microscopy and reported elsewhere.⁵ PEN was found to disperse in PP matrix in fibrillar form. Polarized Raman and polarized FTIR techniques were correlated with the change in tensile properties of the blends at different stages of microfibrillization.

Spectroscopic information for many thermoplastic polymers has been well documented. The Raman and FTIR bands of PP and PEN in this study were assigned, according to the information available from the literature. Stress-sensitive or orientation-sensitive bands can be used to determine the orientation of blend components, if these bands are not obscured by bands of other blend components.

EXPERIMENTAL

PEN used was Teonex 8065S manufactured by Teijin Chemicals, Japan and PP used was JE6100 manufactured by Montell, Australia. PEN/PP blends of 10, 20, and 30 wt % PEN were extruded using a single screw

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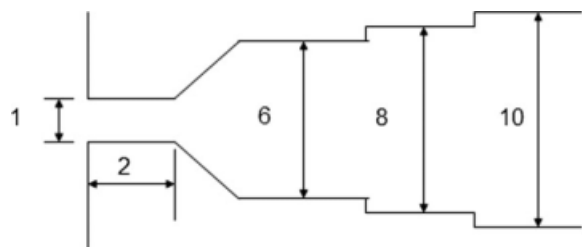


Figure 1 Geometry of the extrusion die (dimensions in millimeter).

extruder (Axon BX-18 with an Axon Gateway[®] venting screw; screw diameter = 18 mm; screw length to diameter ratio = 30; screw center height = 255 mm) equipped with an extrusion die with geometry shown in Figure 1. The extrusion conditions are listed in Table I.

Microfibrillation of the blends

The extruded blends were drawn to maximize the reinforcing effect provided by the microfibrillar phase. A small scale zone-drawing rig was built to fit on a tensile tester. The rig consisted of a set of grips from a tensile tester which held and effected drawing of the specimen with the aid of a band heater. The drawing direction was the same as the extrusion direction. The band heater, which was heated to controlled temperatures (100 and 140°C) and driven by a motor with adjustable speed, was moved downward from the top at 5 mm min⁻¹. Local heating was applied to the sample, while the upper grip of the tensile tester moved upward to stretch the sample. Using the band heater, necking and elongation of the sample followed the movement of the zone-heater. In the case of cold-drawing, no heating was applied.

Drawn blends were annealed at 180°C in a vacuum oven for 10 h to induce isotropization of the PP matrix.

Figure 2 shows the microfibrillar morphology of the PEN phase after the extraction of the continuous PP matrix with boiling xylene. The morphology development of microfibrillar PEN in polyolefin matrices by extrusion was reported elsewhere.⁵

For the observation of spectroscopic changes due to different stages of microfibrillation, a 30 wt %

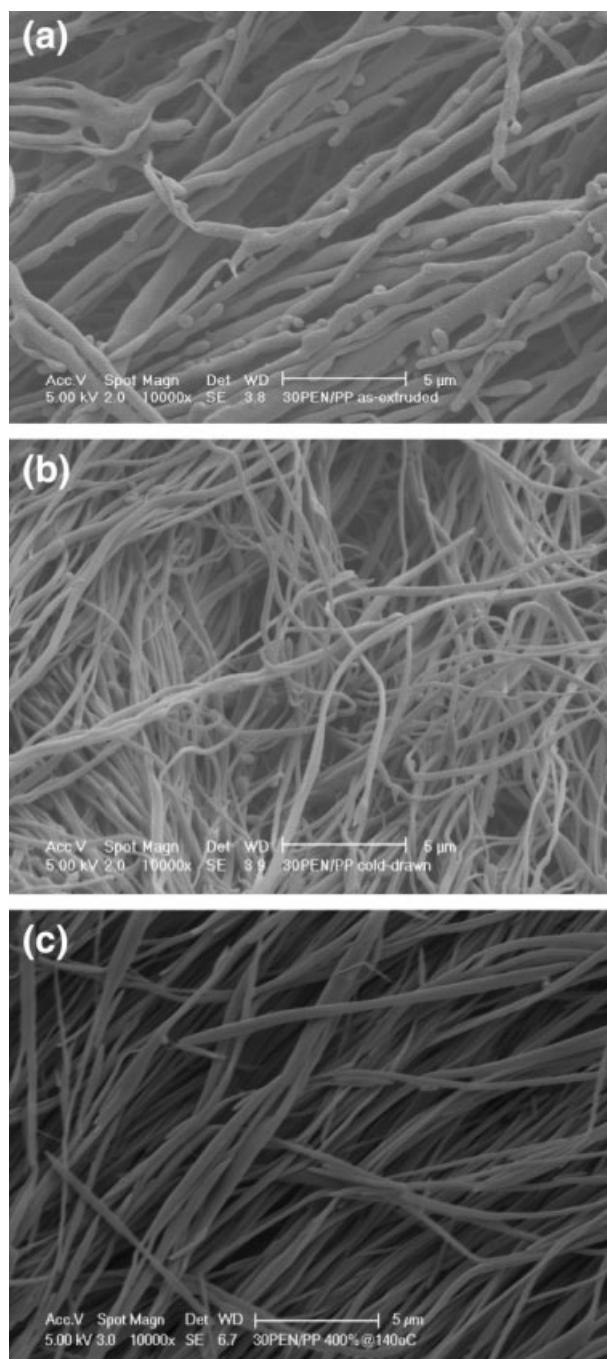


Figure 2 Scanning electron micrographs of PEN microfibrils after extraction of the PP matrix with boiling xylene from (a) an as-extruded sample, (b) a zone-drawn (100°C) sample with 400% elongation, and (c) a zone-drawn (140°C) sample with 400% elongation.

TABLE I
Extrusion Conditions for PEN/PE and PEN/PP Blends

Barrel temperature (°C)				Die temperature (°C)		Screw speed/rpm
Zone 1	Zone 2	Zone 3	Zone 4	Die 1	Die 2	
240	300	300	300	280	280	40

PEN/70 wt % PP blend was used to provide clear and high intensity PEN bands because of its high PEN concentration. The microfibrillar morphology tended to be destroyed at PEN concentration higher than 30 wt % due to the coalescence of PEN microfibrils. It can be seen in Figure 2(a) that coalescence has begun even at 30 wt % to produce microfibrils with branches.

Polarized Raman spectroscopy

Raman spectra were obtained using a Renishaw system 1000 Raman spectrometer equipped with a Leitz microscope. A Renishaw solid-state diode laser with wavelength 785 nm and 26 mW power was used as the excitation source, and the incident laser beam was polarized. Two Raman spectra were collected for each specimen, with the drawing direction of the specimen either parallel or perpendicular to the electric vector of the incident beam in a backscattering geometry (Fig. 3).

The Raman spectra of both PP and PEN contain anisotropic vibrations that could be stimulated to different extent by polarized radiation source. The Raman effect from any molecule is stimulated by the electric field of the incident radiation. The direction of change of polarizability of vibrational modes, which are oriented in the same direction as the electric field vector of the incident radiation will give rise to the higher intensity bands than if they were less oriented with the electric field vector. Therefore, by rotating a drawn PEN/PP blend specimens at 90° (parallel and perpendicular to the drawing direction), intensity changes were observed for the orientation sensitive Raman bands.

Polarized Fourier transformed infrared spectroscopy

Infrared spectra were obtained using a Thermo Electron Nicolet 8700 FTIR spectrometer with Continuum FTIR microscope, fitted with an infrared polarizer at the microscope. Fragments of MFCs were fixed on a specimen holder and polarized spectra were taken by rotating the polarizer such that only radiation with the electric field vector parallel or perpendicular to the drawing direction reached the specimens. Because of nonreflective nature of the blends, the spectra in this study were obtained in transmission mode. To obtain sufficiently thin specimens for the transmission mode, a scalpel was used to cut slices of MFC fragments at a shallow angle to prevent deformation of the fragment. The thickness

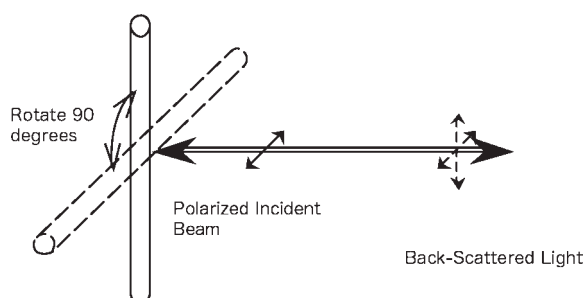


Figure 3 Polarized Raman spectroscopy backscattered geometry.

TABLE II
Crosshead Speeds Used for Tensile Strength Measurements

Sample	Crosshead speed (mm min ⁻¹)	Comments
10–30 wt % PEN/PP	50	Fracture beyond the capability of the Instron
50 wt % PEN/PP	20	Fracture within 0.5–5 min

of the specimens was in the range of 10–20 μm . As for the Raman spectra, it should be noted that absolute intensities of the bands could not be compared between different specimens because specimen thickness was variable.

The magnitude of IR absorption is proportional to the transition dipole moment and the applied electric field vector. The magnitude of absorption depends on the direction of the transition dipole moment relative to the electric field vector of a polarized IR beam. Therefore, absorbance is maximum when the IR beam is polarized such that the electric field vector is parallel to the transition dipole moment. Conversely, when the electric field vector is perpendicular to the transition dipole moment, no absorbance can occur. In an oriented polymer sample, the molecules are oriented to a preferred direction. Therefore, when the excitation IR beam is polarized, by rotating the oriented polymer sample relative to the polarization of the beam, variations in band intensity would be observed.

Tensile properties

Blend specimens in the form of cylindrical cords were tensile tested using an Instron model 5567 tensile tester. The maximum stress before fracture and tensile modulus were determined. A 0.2% secant modulus between 0.05 and 0.25% strain was evaluated from stress–strain curves recorded with crosshead speed 5 mm min⁻¹. The strain for calculating the tensile modulus was estimated by the crosshead extension. The maximum stress during testing was determined with crosshead speed such that the fracture occurred within 0.5–5 min after the test was started (ASTM D-638). Where the blend specimens could not be fractured by the tensile tester under those conditions, 50 mm min⁻¹ was chosen as the crosshead speed. The crosshead speeds used for the blends are summarized in Table II. Five replicates were tested for each sample.

RESULTS AND DISCUSSION

Polarized Raman spectroscopy

As extruded, isotropic blends contain polymer chains that are randomly oriented. Consequently,

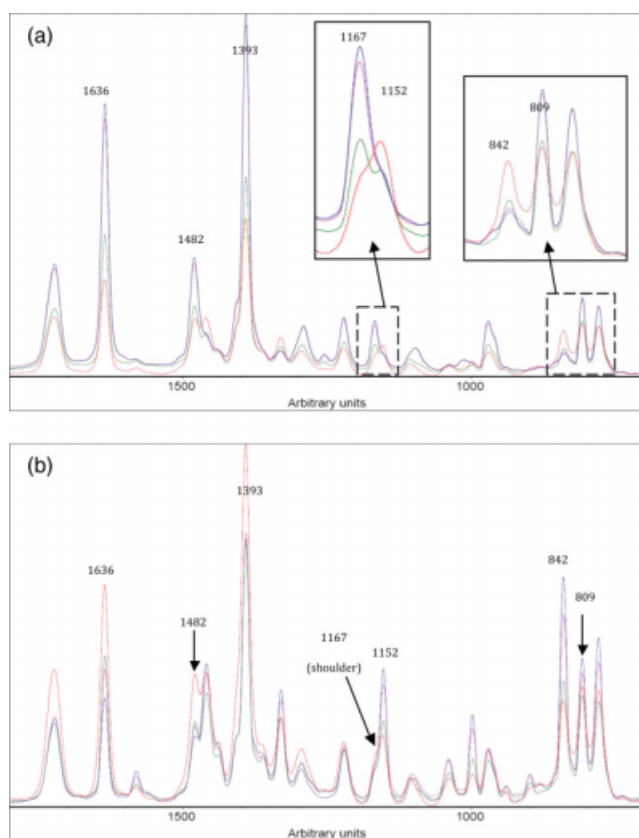


Figure 4 (a) Parallel and (b) perpendicular spectra of 30 wt % PEN/70 wt % PP blend that was drawn to different extents at 120°C; as-extruded (red); 260% elongation (green); 370% elongation (pink); and 510% elongation (blue). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the Raman band intensities of the as-extruded blend were almost identical in the parallel and perpendicular spectra.

PP Raman bands at 809, 841, 899, 998, 1167, and 1218 cm^{-1} disappear upon melting and they arise due to highly regular helical sequences, which are associated with crystalline domains.⁶ The 809, 841, 998, and 1167 cm^{-1} bands show varying intensities in Figure 4, reflecting a varying degree of chain orientation after the PEN/PP blend was elongated to different extents. The 899 and 1218 cm^{-1} bands will not be discussed because 899 cm^{-1} band was weak and 1218 cm^{-1} overlaps with a PEN band. Relatively little qualitative information could be obtained from these bands.

The 809 and 841 cm^{-1} bands have been used to estimate the orientation of PP chains.^{6,7} The 809 cm^{-1} band has been related to the helical chains in the crystals. The 841 cm^{-1} band is associated with helical chains where the trans-gauche conformation is disrupted. In other words, 841 cm^{-1} is associated with “kinking”—isomeric defects along the helical chains.⁸ As shown in Figure 4, the intensity of 842 cm^{-1} band was weakest relative to 809 cm^{-1}

band if the chains were parallel to the incident laser polarization, and conversely, the intensity of 842 cm^{-1} band was strongest relative to 809 cm^{-1} band when the chains were perpendicular to the incident beam polarization. In the parallel spectrum [Fig. 4(a)], the intensity at 809 cm^{-1} gradually increased, while 842 cm^{-1} band gradually decreased with increasing elongation. The opposite trend occurred in the perpendicular spectrum [Fig. 4(b)], where the intensity of 842 cm^{-1} band gradually increased relative to 809 cm^{-1} band. These changes in band intensities indicated that the PP crystallites became increasingly oriented with the drawing direction. The fact that 841 cm^{-1} band diminished in the parallel spectrum suggested that the amount of disruption of the trans-gauche conformation in the crystalline helical structure is reduced in the drawing direction, most probably due to stretching action on the helical chain. Although PP crystallites are increasingly oriented with the drawing direction, the growing 841 cm^{-1} band in the perpendicular spectrum suggested that strain-crystallization occurred with the helical “kinking” defects mostly oriented with the perpendicular direction.

Molecular orientation of PP was also indicated by the intensity of 1167 cm^{-1} band relative to 1152 cm^{-1} band.⁹ It is apparent from Figure 4 that 1167 cm^{-1} band became more intense in the parallel spectra but diminished in the perpendicular spectra. The 1167 cm^{-1} band, which has been assigned to contributions from axial stretching of C—C in the polymer backbone, has been suggested to be the most stress-sensitive molecular deformation band. It has also been suggested to correspond to the amorphous phase in isotactic PP. The 1152 cm^{-1} band is not specific for chain conformations that exist in the melt or partially crystalline state.^{8,10} Therefore, the diminishing of the 1152 cm^{-1} band in the parallel spectrum after elongation indicates that less-ordered PP chains were also oriented in the direction of elongation.

The bands that were sensitive to PEN chain orientation were (1) 1636 cm^{-1} , which corresponds to 2,6-disubstituted skeletal symmetric vibration of the naphthalene ring; (2) 1393 and 1483 cm^{-1} , which correspond to naphthalene ring vibrations, but are less sensitive to stretching than the 1636 cm^{-1} band.¹¹ All of these vibrations have their polarizability change closer to the drawing direction. As a result, the increase in intensity of these PEN bands in the parallel spectra is indicative of the alignment of PEN chains in the drawing direction.

These features of the Raman spectra confirmed that the chain orientation of the blend components increased with increasing elongation. It is worth to note that the intensities of the bands showing anisotropy changed dramatically between 260 and 370%

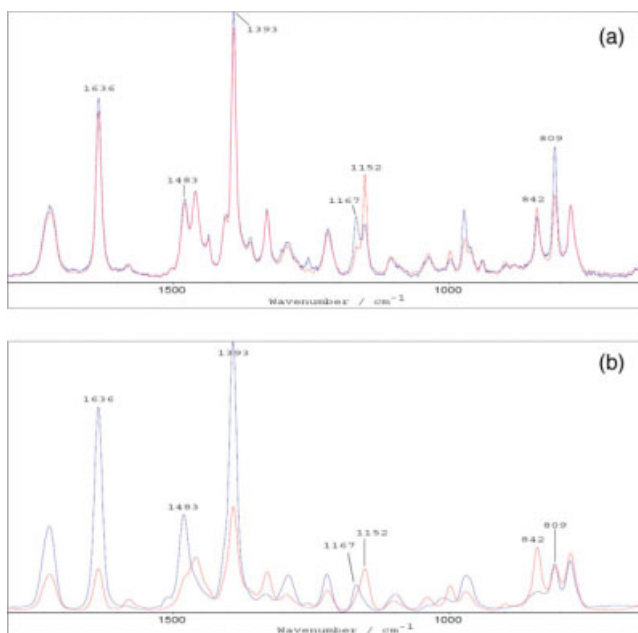


Figure 5 Parallel (blue) and perpendicular (red) Raman spectra of 30 wt % PEN/70 wt % PP blend that was drawn to 400% elongation at (a) room temperature and (b) 140°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

elongation. Further drawing to 510% produced little additional enhancement of chain orientation.

The effect of drawing temperature on chain orientation is shown in Figure 5. In the case of cold drawing, PEN showed very limited molecular orientation [Fig. 5(a)]. In the zone-drawn blend [Fig. 5(b)], the large difference in the intensities at 1636, 1483, and 1393 bands shows that PEN was highly oriented.

PP also showed a smaller degree of molecular orientation in the cold-drawn specimen than in the zone-drawn specimen. The band at 1152 cm^{-1} is still observable for the cold-drawn blend but is reduced to much lower intensity for the zone-drawn blend.

After annealing of the PEN/PP blend at 180°C, preferred orientation was retained in PEN but PP became isotropic. Figure 6 shows that PEN remained highly oriented as shown by the bands at 1393, 1483, and 1636 cm^{-1} . For PP, although the 1167 cm^{-1} band intensity was still slightly more intense in the parallel spectrum (than in the perpendicular spectrum), a significant drop in its intensity after annealing indicated that PP was close to its completely isotropic state. Similarly, the intensities of the 1152, 842, and 809 cm^{-1} bands became almost identical in the parallel and perpendicular spectra after annealing.

FTIR spectroscopy

Similar to the conclusions made in the Raman spectroscopy section, the polarized FTIR spectra showed that PEN and PP molecules were increasingly

aligned to the drawing direction with increasing elongation. The infrared band assignments of the PP and PEN bands are based on the work by Andreasen⁹ and Ouchi et al.¹² unless otherwise stated. The infrared spectra of the drawn blends and annealed blends are shown in Figures 7 and 8, respectively. The dichroic ratio of some important bands that indicate PEN and PE molecular orientation are shown in Table III.

Figure 7 shows polarized infrared spectra for the PEN/PP blend drawn to different extents. The aromatic ring vibrations of PEN at 1600 cm^{-1} , 1500 cm^{-1} , and 1405 cm^{-1} show parallel polarization on stretching [(Fig. 7(a–d)]. The increasing dichroic ratios of these bands indicate that the aromatic segments of PEN became increasingly oriented to the drawing direction with increasing elongation. A zone-drawn blend showed significantly greater dichroic ratio than a cold-drawn blend which was drawn to a similar elongation. This indicated that zone-drawing at above the glass transition temperature of PEN promoted the molecular orientation of PEN chains. In the case of cold-drawing, by contrast, the PEN molecules had insufficient mobility to be aligned by mechanical stretching.

It has been reported that the trans-CH₂ bending of PEN at 1477 cm^{-1} intensifies after heat treatment or mechanical drawing. This observation indicates the tendency of PEN to take the most extended, trans-conformation during heat treatment or mechanical drawing. In this study, 1477 cm^{-1} band emerged in 400% zone-drawn spectra as a shoulder at the band between 1450 and 1470 cm^{-1} [Fig. 7(c)]. When the blend was drawn at room temperature, the shoulder at 1477 cm^{-1} was not observed [Fig. 7(d)], implying that zone-drawing facilitated the transformation of PEN chains into the more extended trans-conformation but cold-drawing could not. This reinforces the observation in the previous paragraph that the aromatic vibrations show greater orientation by zone-drawing than cold-drawing. The band at 1436 cm^{-1}

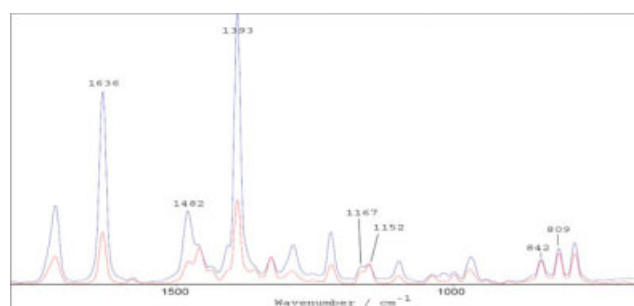


Figure 6 Parallel (blue) and perpendicular (red) Raman spectra of 30 wt % PEN/70 wt % PE blend that was drawn to 400% elongation at 140°C followed by annealing at 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

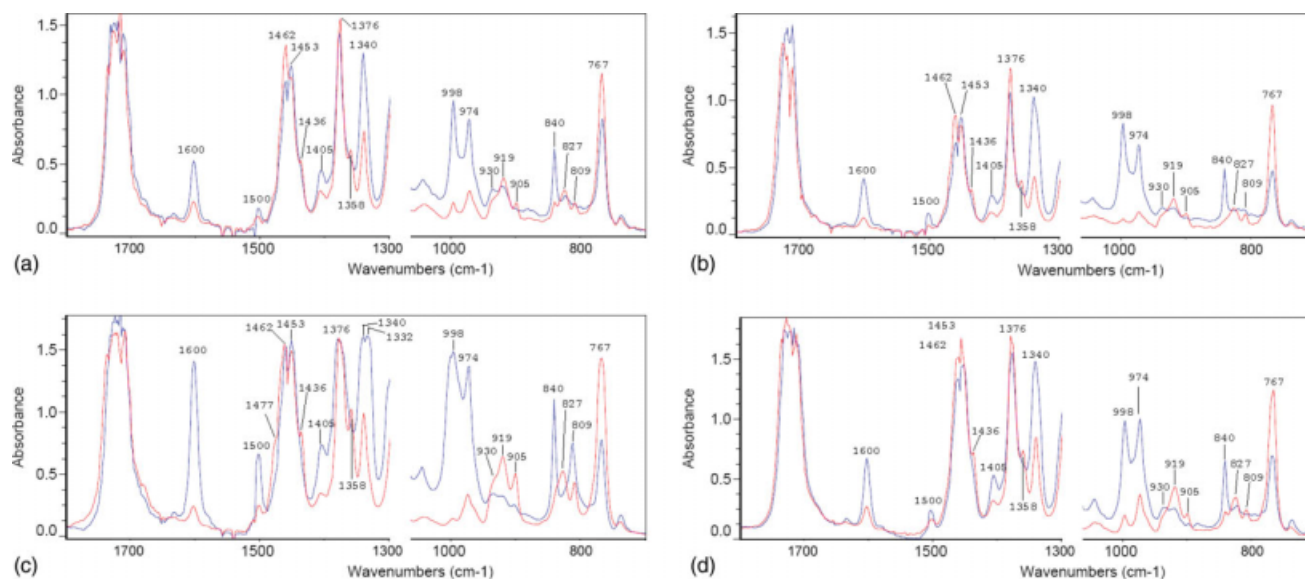


Figure 7 Parallel (blue) and perpendicular (red) infrared spectra of 30 wt % PEN/70 wt % PP blends that were zone-drawn to (a) 230%, (b) 320%, (c) 390% elongation at 140°C, and (d) cold drawn to 400% elongation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that corresponds to CH₂ bending of the gauche conformation of PEN is expected to diminish with drawing or heat treatment. However, this behavior cannot be observed in the blend spectra because the band overlaps with the asymmetric CH₃ bending of PP.

Regardless of the drawing temperature, the dichroism attained by drawing at 1600 cm⁻¹, 1500 cm⁻¹, 1477 cm⁻¹, and 1405 cm⁻¹ was retained after

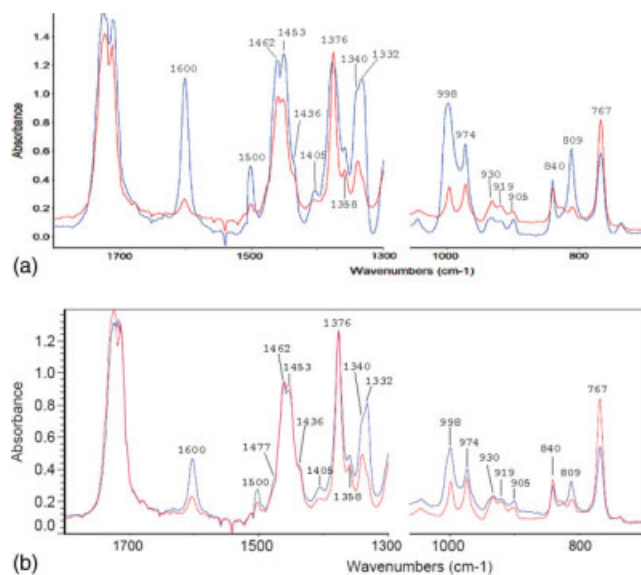


Figure 8 Parallel (blue) and perpendicular (red) infrared spectra of 30 wt % PEN/70 wt % PP blend that was drawn to 400% elongation at (a) 140°C or (b) at room temperature followed by annealing at 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

annealing [Fig. 8(a)]. The dichroic ratio values of the zone-drawn and annealed blends decreased slightly. As annealing was carried out at a temperature above the glass transition temperature of PEN, the slight decrease in the values of the dichroic ratio in 1600 cm⁻¹ and 1500 cm⁻¹ bands after annealing was possibly a result of molecular motion of PEN chains during annealing.

The crystalline region of PEN was also oriented by elongation. The band at 1332 cm⁻¹ which emerges as a shoulder at 1340 cm⁻¹ band is related to the CH₂ wagging of the trans-conformation in crystalline PEN. Although a PP band also exists in this region, the intensity of this PP band is weak. Consequently, the vibration due to crystalline PEN can be regarded as the only contribution to the infrared dichroism of this band. As the zone-drawing elongation increased, 1332 cm⁻¹ band showed an increase in intensity and stronger parallel dichroism [Fig. 7(a-c)]. The 1332 cm⁻¹ band became equally

TABLE III
Dichroic Ratio of Selected Infrared Bands

Treatment	Draw ratio	Infrared bands (cm ⁻¹)				
		1600 (PEN)	1500 (PEN)	840 (Overlap)	809 (Overlap)	767 (PEN)
Zone drawn	2.3	3.0	2.7	3.4	0.8	0.7
	3.2	4.9	4.2	8.5	1.1	0.4
	3.9	9.4	5.3	7.2	2.0	0.5
Zone-drawn; annealed	4.0	8.9	4.9	1.6	4.7	0.7
Cold drawn	4.0	3.3	2.5	3.5	0.7	0.5
Cold-drawn; annealed	4.0	3.7	2.5	2.6	1.3	0.7

intense as 1340 cm^{-1} band in the parallel spectrum for 400% zone-drawn specimen. The increase in band intensity at 1332 cm^{-1} indicated that zone-drawing induced cold-crystallization of PEN. The increase in the degree of dichroism in 1332 cm^{-1} band in the zone-drawn specimens indicated that heat assisted the orientation of crystalline PEN. After annealing of the zone-drawn blend, 1332 cm^{-1} band retained its presence and dichroism [Fig. 8(a)]. Although 1332 cm^{-1} band was not observed in the cold-drawn specimen [Fig. 7(d)], it emerged after annealing [Fig. 8(b)]. During annealing at above the glass transition of PEN, the amorphous PEN chains in the cold-drawn blend were able to rearrange and crystallize along the drawing direction. Evidence of partial isotropization of PEN can be found in 767 cm^{-1} band which represents the aromatic CH out-of-plane bending of amorphous PEN.¹³ The 767 cm^{-1} band shows perpendicular dichroism and therefore the dichroic ratios are <1 . The dichroic ratio shifted toward the value of 1 after annealing. This indicated that the amorphous region of PEN became less oriented to the drawing direction.

The 930 cm^{-1} , 919 cm^{-1} , and 905 cm^{-1} bands overlap in the proximity of each other. These three bands correspond mainly to PEN vibrations. The 930 and 919 bands have been assigned to CH_2 wagging of PEN in the gauche conformation and aromatic CH out-of-plane vibration of PEN, respectively. The 905 cm^{-1} is related to the crystalline state of PEN. All three bands grew in intensity with perpendicular polarization upon cold-drawing or zone-drawing [Fig. 7(a–d)]. Stronger dichroism was observed in the case of zone-drawing due to higher degree of molecular orientation. The 919 cm^{-1} band diminished and lost dichroism after annealing (Fig. 8). The loss of dichroism is possibly due to partial isotropization of amorphous PEN. The determination of the dichroic pattern of the 930 cm^{-1} and 905 cm^{-1} bands with elongation was interfered by PP bands in the same region. These PP bands show similar intensities as the PEN bands and also show perpendicular dichroism.

Similar to the analysis by Raman spectroscopy, the intensity ratio between 840 cm^{-1} and 809 cm^{-1} infrared bands is an indication of PP molecular orientation. Although PP and PEN bands overlap in this region, the changes in molecular orientation in PP and PEN can be inferred qualitatively from the infrared dichroism of these bands. The PEN and PP bands showed opposite infrared dichroism for these two bands. At low elongation, parallel polarization at 840 cm^{-1} was mainly contributed by oriented PP molecules [Fig. 7(a)]. The perpendicular dichroism of the PEN 840 cm^{-1} band was overwhelmed by the strong parallel dichroism of the PP band. At high elongation, 840 cm^{-1} band dichroic ratio increased

due to intense parallel dichroism of the PP band [Fig. 7(b,c)]. After annealing, the decrease in the degree of parallel dichroism, as shown by the significant decrease in dichroic ratio of 840 cm^{-1} band is an indication of isotropization of PP (Fig. 8). For instance, the dichroic ratio of 840 cm^{-1} band of the zone-drawn blend decreases from 7.2 to 1.6 due to annealing.

The 809 cm^{-1} band shows little dichroism at low elongation [Fig. 7(a)]. At high elongation, the parallel dichroism due to the oriented crystalline PEN was strong enough to cancel out the perpendicular dichroism of the weak PP band [Fig. 7(c)]. The dichroic ratio of 809 cm^{-1} band increased with the amount of elongation. After annealing, the dichroic ratio increased further indicating increase in parallel dichroism. For instance, dichroic ratio for 809 cm^{-1} band of the zone-drawn blend increased from 2.0 to 4.7 due to annealing. Since the 809 cm^{-1} band is related to PEN crystallinity, the fact that its dichroism became stronger after annealing was possibly due to reorganization of the drawing PEN chains into crystallites during annealing.

Tensile properties

The as-extruded blends exhibited relatively low tensile strength which appeared to increase somewhat, approximately linearly with increasing PEN content. Figure 9 shows the tensile strength of the drawn blends compared with the as-extruded blends. After drawing to 400% elongation at room temperature, there was a remarkable increase in strength. Within the level of uncertainty, the tensile strengths of the samples that were drawn at the same temperature did not change with PEN content. The strength varied with drawing temperature from ~ 160 MPa

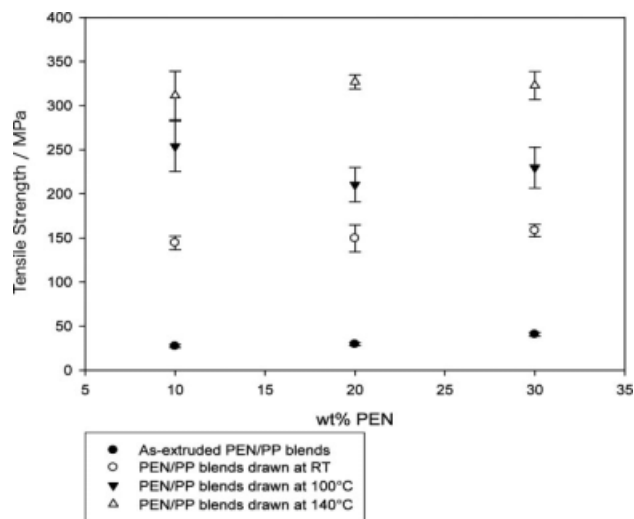


Figure 9 Tensile strength of drawn PEN/PP blends.

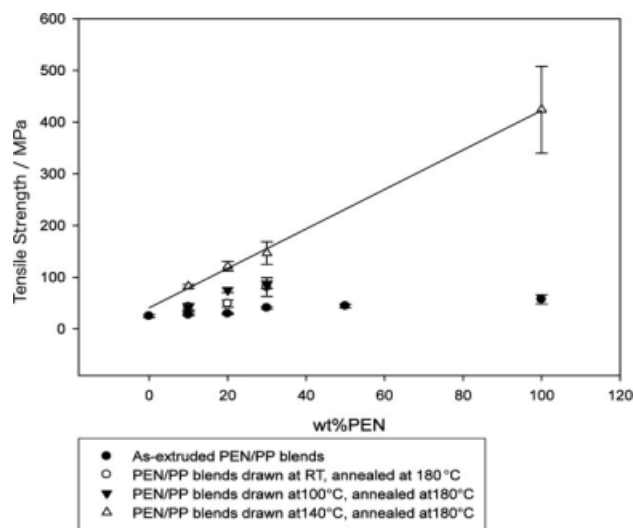


Figure 10 Tensile strength of drawn and annealed PEN/PP blends.

(drawn at room temperature), to ~ 220 MPa (drawn at 100°C), to ~ 320 MPa (drawn at 140°C).

The fact that the strength was relatively insensitive to PEN content is consistent with the PP matrix, the major component of the blends, being oriented and contributing to the strength as well as PEN. The Raman and FTIR spectra indicate that the PEN fibrils and the PP matrix were simultaneously aligned by the stretching action as the tensile strength increased with increasing drawing temperature because the degree of chain alignment was higher if drawing was performed at a higher temperature. The increase in strength was contributed particularly by the molecular orientation of the PEN fibrils. From the polarized FTIR and polarized Raman observations, it is concluded that at room temperature only orientation of the PP matrix contributed to the increase in strength after drawing. As the drawing temperature increased, the PEN fibrils became molecularly oriented to provide further strength improvement.

After annealing, all blends had strength values lower than those of the drawn blends but greater than those of the as-extruded blends (Fig. 10). The blends that were drawn at room temperature and at 100°C were almost identical in terms of the tensile strength after annealing. The annealed blends that were drawn at 140°C had strengths, which were almost twice those of the samples that were drawn at lower temperatures (room temperature and 100°C). Having converted the oriented PP matrix to the isotropic state (as shown by polarized spectroscopic results), the increase in strength compared with the as-extruded specimens must be due to the reinforcing effect of PEN microfibrils. The difference

in strength between the annealed specimens is attributed to the amount and strength of the PEN fibrils after microfibrillation.

Unlike the drawn blends, the strength of the annealed blends increased with increasing PEN content. As a result of greater degree of molecular orientation induced by heat in the drawing stage, after annealing the strength of the blends that were stretched at 140°C increased linearly and more rapidly with PEN content. Extrapolation of the strength of 140°C series in Figure 10 to 100 wt % PEN gives a value for the tensile strength of PEN that coincides with the mean measured value for PEN. Extrapolation of the other two series that were drawn at lower temperatures gives lower strengths for 100 wt % PEN.

It is evident that zone-drawing at a higher temperature, which was close to the glass transition temperature of the PEN, generated stronger microfibrils and greater reinforcement of the PP matrix.

CONCLUSION

The change in molecular alignment due to mechanical and thermal treatment of the PEN/PP blends is reflected in the change in band intensities in polarized Raman and polarized FTIR spectra. Significant increase in molecular alignment was observed at the arbitrarily chosen elongation (400%). The increase in the degree of molecular arrangement in the blend components resulted in enhancement of the overall strength of the blend.

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