Some Aspects of the Properties of Nylon-6, 6/Poly(ethylene naphthalate) Blends

DYLAN D. JUNG, DEBES BHATTACHARYYA, ALLAN J. EASTEAL

Centre for Composites Research, The University of Auckland, New Zealand

ABSTRACT: Blends of Nylon 66(Ny66) and polyethylene naphthalate (PEN) with 30, 50, 70 wt % Ny66, and one blend with 50% Ny66 and 3% compatibilizer, prepared by extrusion and injection molding, were investigated using ^{13}C and ^1H nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) ,and scanning electron microscopy (SEM). A new band in the FTIR spectra of blends, at $1324-1329$ cm^{-1} is interpreted as arising from partial reaction of Ny66 and PEN occurring during melt processing. However, NMR spectra show no evidence of interchange reaction between Ny66 and PEN. SEM indicates that the phase inversion point is close to equal proportions by weight of the two homopolymers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1504–1514, 2001

Key words: nylon-6,6; poly(ethylene naphthalate); blends; interchange reaction

INTRODUCTION

Recent work has been reported on a number of different blends with poly(ethylene naphthalate) (PEN) as one component, including PEN/poly(ethylene terephthalate) (PET),[1] PEN/polycarbonate (PC),[2] PEN/liquid crystal polymers (LCP),[3] PEN/poly(ether imide),[4] and PEN/Nylon-6 (Ny6).[5] The purpose of the present investigation was to extend this work to the PEN/Ny66 system.

Ny66 has low heat resistance (relatively low glass transition temperature, compared to that of PEN) but reasonable mechanical strength and price, whereas PEN has much greater heat resistance (high glass transition temperature) and toughness but a higher price. Since blends combine the properties of the component homopolymers, blending PEN with Ny66 can in principle enhance the engineering properties of Ny66, and

our primary objective was to investigate that possibility, initially through a study of chemical interactions between the homopolymers.

The compatibility of the component homopolymers is an important consideration. Compatibility is enhanced by miscibility of the two (or more, as the case may be) phases, and by the addition of block and graft copolymers or of functional/reactive polymers, and *in situ* graft copolymerization (reactive blending).[6] In addition, interchange reactions occurring in the interphase region can create chemical bonds between the phases. Interchange reactions between amide functional groups of Ny6 or Ny66 and ester functional groups of several polyesters such as PET,[7-9] PC ,[10-17] and poly butylene terephthalate (PBT)[18] are well known. More vigorous interchange reaction is observed in blends with a high proportion of Ny6 in Ny6/PC blends because of the more abundant amino end groups in Ny6 compared with Ny66.[19] In addition, higher proportions of nylon in Ny6 or Ny66/PC blends promote interchange reaction because the more abundant mobile end-amide groups in nylon attack carbonate
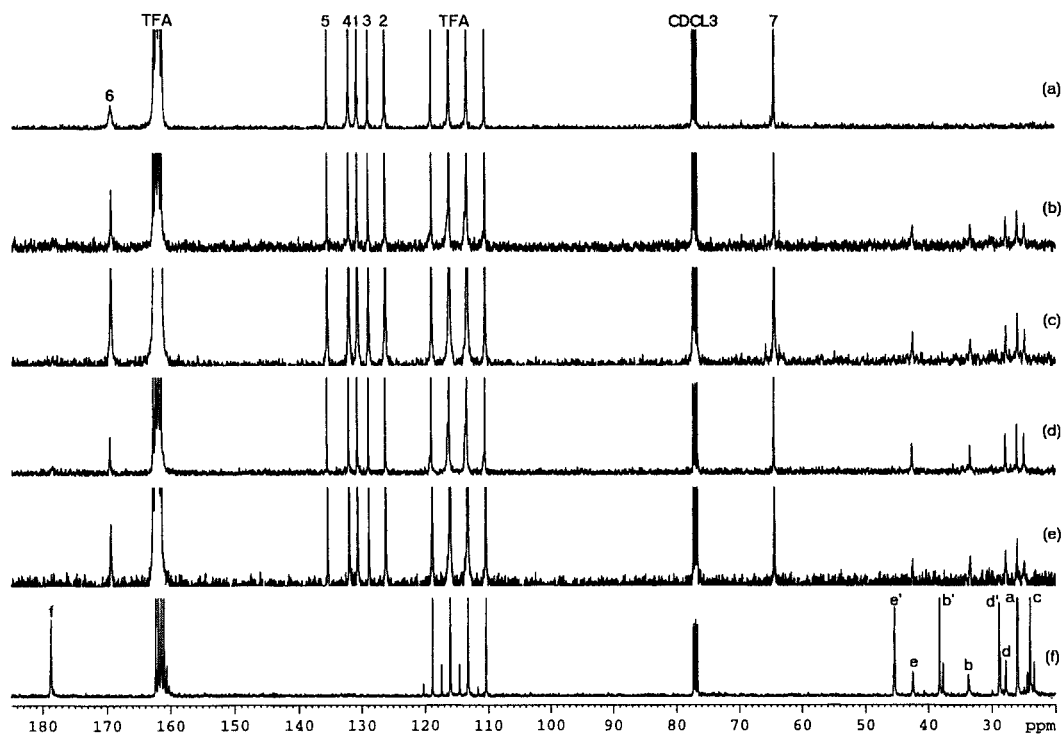
Figure 1 ^{13}C NMR spectra of Ny66/PEN (wt %/wt %) blends, from the first series of experiments: (a) 0/100, (b) 50/50+GMA (3 wt %), (c) 30/70, (d) 50/50, (e) 70/30, and (f) 100/0.

groups in PC vigorously, which results in more interchange reaction in blends with 70–90 wt % of nylon.

It has been suggested[18] that inner–inner and outer–inner interchange reaction mechanisms occur in PET/PC and PBT/PC during melt processing. End-group-activated or catalyst-activated interchange may occur in such systems below 300°C, whereas both thermally activated interchange (i.e., without catalysts) and thermal decomposition occur above 300°C.

In the present work we report evidence from Fourier transform infrared (FTIR) spectroscopy for an apparent new bond formed by interchange reaction in Ny66/PEN, and ^{1}H nuclear magnetic resonance (NMR) data that do not support the hypothesis of new bond formation. In addition, we report additional characterization of the blends by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Polymers used in this study were (PEN) supplied by Toyobo Co. Ltd. and Ny66 (Grilon EMS T300)

from EMS—CHEMIE. In addition, Elvaloy PTW (from Du Pont), an ethylene copolymer containing epoxy functionality, was used as a possible compatibilizer.

Pure Ny66, PEN, and Ny66/PEN mixtures in the proportions (wt %), 70/30, 50/50, and 30/70, and Ny66/PEN (50/50) + Elvaloy PTW (3% of weight of blend) were dried at 70°C for 48 h *in vacuo*. Mixtures 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 280–290°C.

NMR spectroscopy was carried out using a Bruker DRX-400 instrument to obtain ^{13}C and ^{1}H spectra, in two series of experiments as follows.

Series A: About 50 mg of each melt-blended sample was dissolved in CHCl$_3$ (5 mL)/TFA (5 mL), plus trifluoroacetic anhydride (TFAA) (1 mL). A 50 mg sample of pure Ny66 was dissolved in CHCl$_3$ (10 mL)/TFAA (2 mL) without TFA. TFAA was used to trifluoroacetylate Ny66 because pure Ny66 was not completely dissolved by CHCl$_3$/TFA solvent.[10] he solutions were ultrasonicated for 30 min then vacuum distilled, and the residues were dissolved in deuterated trifluoroacetic acid (0.4 mL)/CDCl$_3$ (0.4 mL, with 0.03

Table I Assignment of ^{13}C NMR Spectra

Ny66	Chemical Shift (ppm)	PEN	Chemical Shift (ppm)
f	178.85	6	169.46
e′	45.37	5	135.44
e	42.45	4	131.98
b′	38.24	1	130.63
b	33.67	3	128.85
d′	28.89	2	126.18
d	27.83	7	64.38
a	26.07		
c	24.02		

1. PEN Carbon 13C
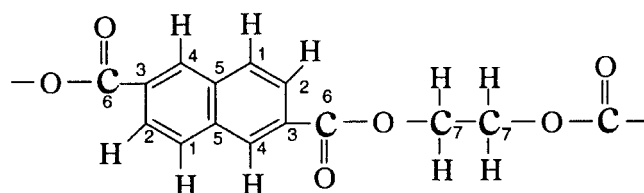
2. Ny66 Carbon 13C
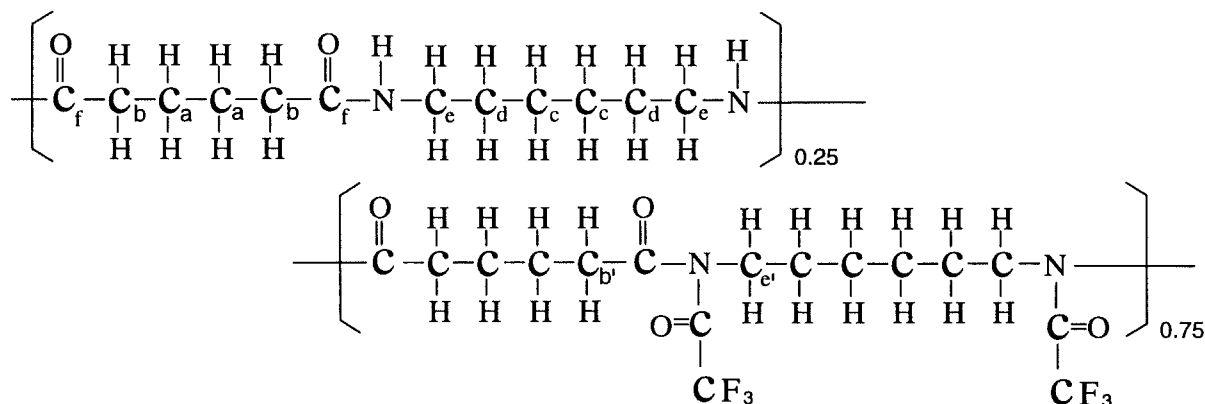
wt % tetramethylsilane). Pure PEN was dissolved in deuterated trifluoroacetic acid (0.4 mL)/CDCl$_3$ (0.4 mL).

Series B: Samples of about 40 mg, including pure Ny66, were dissolved (only partially in the case of pure Ny66) in CDCl$_3$ (0.4 mL)/deuterated trifluoroacetic acid (0.4 mL) mixtures. The number of scans for ^{13}C spectra was increased from 300 to about 10000 in this series of experiments, to improve the S/N ratio.

X-ray photoelectron spectroscopy was carried out with a Kratos XSAM800 instrument using MgK$_\alpha$ (1253.6 eV). The analytical chamber pressure was about 10^{-9} Torr.

For examination by scanning electron microscopy [using a Philips XL 30S(FGG) instrument],

specimens were cooled in liquid nitrogen then fractured by impact. One fracture surface was gold coated, and the other surface was etched with trifluoroethanol in an ultrasonic bath for 15 minutes, to dissolve Ny66, before gold coating.

Fourier transform infrared–photoacoustic spectroscopy (FTIR-PAS) was carried out using a BIO-RAD FTS-60 instrument on small pieces of injection molded samples, with the photoacoustic cell purged with nitrogen. Spectra were normalized relative to the band at 770 cm^{-1} from the =C—H out-of-plane vibration of pure PEN, and the pure PEN spectrum was subtracted from each normalized spectrum. The PEN-subtracted spectra were normalized again relative to the band at 1652 cm^{-1} (the C=O stretch band) of pure Ny66 and the pure Ny66 spectrum
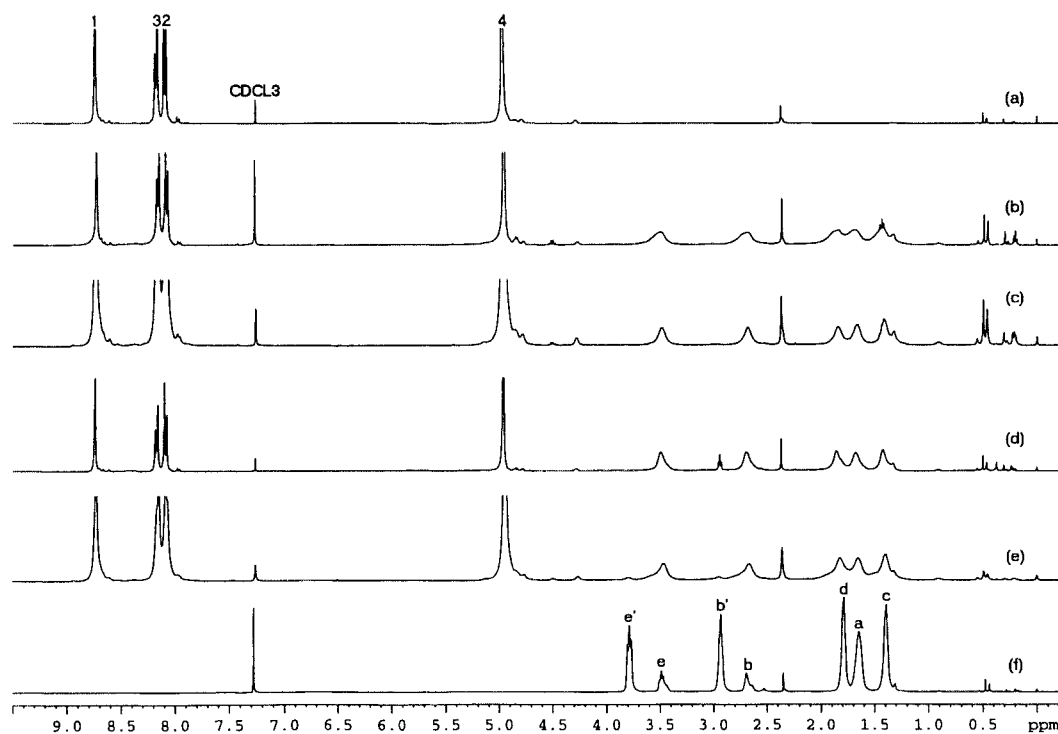
Figure 2 ^{1}H NMR spectra of Ny66, PEN, and Ny66/PEN (wt %/wt %) blends, from the first series of experiments: (a) 0/100, (b) 50/50+GMA (3 wt %), (c) 30/70, (d) 50/50, (e) 70/30, and (f) 100/0.

was subtracted from each of the PEN-subtracted spectra. The reverse order was applied to the Ny66/PEN (50/50 wt %)/GMA (3 wt %) spectrum.

RESULTS AND DISCUSSION

NMR Spectra

Figure 1 shows the first series of ^{13}C NMR spectra of Ny66, PEN, and Ny66/PEN blends. The assignment of the signals (Table I) agrees with reported work[10,20] on partial acetylation of Ny66. For pure Ny66, two groups of signals, at 42.45, 33.67, and 27.83 ppm from normal Ny66, and 45.37, 38.24, and 28.89 ppm from trifluoroacetylated Ny66, are present because TFAA was used to react with and thereby solubilize the Ny66 component. The signals at 37.8, 24.5, and 23.5 ppm are believed to be due to additives in the (commercial grade) Ny66. In the blend spectra signals arising from acetylated Ny66 were not observed because the much smaller proportion of TFAA used in the solvent mixture, and the presence of 25–75% PEN in the blends led to an insignificant extent of trifluoroacety-

lation. The signal at 178.85 ppm, which is from the carbonyl group in Ny66, was weak and broad in the spectra of the blends, because the PEN component in the blends altered the environment of Ny66 and influenced the rate of conformational rotation around the amide group.

[1]H spectra are shown in Figure 2, and the assignments are summarized in Table II. As in the ^{13}C spectrum of pure Ny66 there are two sets of signals, at 3.50 and 2.69 ppm from Ny66, and 3.78 and 2.93 ppm from trifluoroacetylated Ny66. From the signal integration, the ratio of (e′ + b′) protons to (e + b) protons is 2.83, implying that about 74% of the Ny66 homopolymer reacted with TFAA during dissolution. It should be noted that Table II includes a proton signal at 12.40 ppm that was observed in the second, but not the first series of NMR experiments: the signal is attributed to protonation of the Ny66 carbonyl group by TFA.[21] In the first series of experiments, the presence of TFAA in the solvent used to dissolve the blends suppressed protonation of the C=O group in Ny66. The proposed reaction of pure Ny66 with TFAA is

Table II   Assignment of ¹H NMR Spectra

| Ny66	Chemical Shift (ppm)	Area (arbitrary units)	PEN	Chemical Shift (ppm)
f[a]	12.401			
e′	3.784	1.46	1H	8.746
e	3.504	0.50	3H	8.185
b′	2.931	1.45	2H	8.081
b	2.694	0.52	4H	4.955
d	1.788	4.02(d + a)		
a	1.647			
c	1.392	2.09		
g[b]	1.300			

[a] Signal from the protonated oxygen found in the second series of NMR experiments.
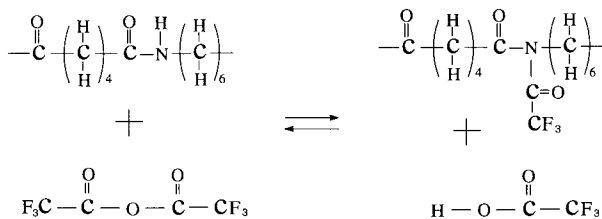[b] This signal is most likely from an aliphatic additive in the commercial grade Ny66.

1. PEN Hydrogen 1
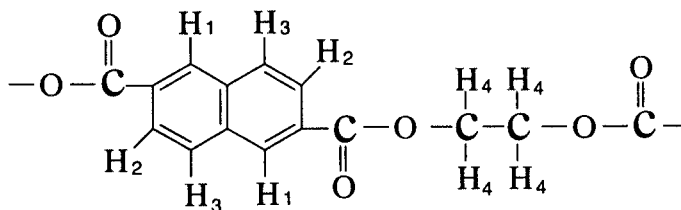
2. Ny66 Carbon 13C
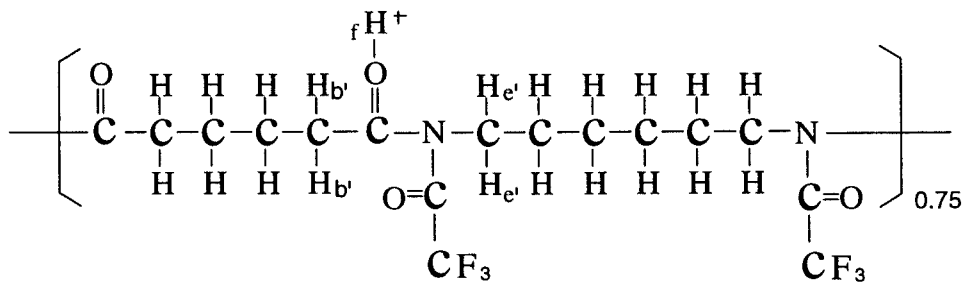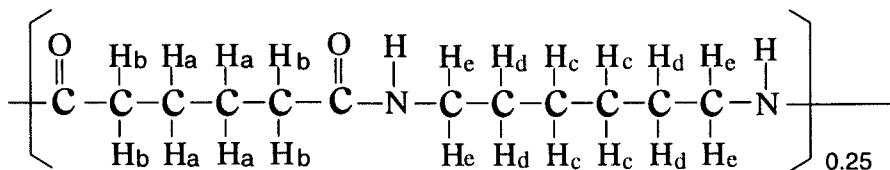
1. *Ny66 and TFAA*

This result was confirmed by the second NMR experiment. In the 20–50 ppm region of the ¹³C spectrum in Figure 3, only the signals correspond-ing to unmodified Ny66 homopolymer appear, when TFAA is not a component of the solvent used to dissolve Ny66. However, expansion of the spectrum (Fig. 4) shows that between 120 and 110 ppm in pure Ny66 there are two quartets of carbon signals assigned to the CF₃ group. The more intense quartet (A) is attributed to TFA, and the less intense (A) set to TFA⁻ anions formed as a result of protonation of the Ny66 C=O group by TFA, as per reaction 2. In addition, around 163 ppm the two quartets of carbon signals arise from the C=O group of TFA (B) and TFA⁻ anions (B). The spectrum of Ny66 treated with TFAA [Fig.

Figure 3 ^{13}C NMR spectra of Ny66/PEN (wt %/wt %) blends, from the second series of experiments: (a) 0/100, (b) 50/50+GMA (3 wt %), (c) 30/70, (d) 50/50, (e) 70/30, (f) 100/0, and (g) CDCl$_3$ + TFA solvent.

1(f)] also shows two sets of quartets. The more intense signals in the 110–120 ppm region are attributed to the —CF$_3$ group of TFA; the weaker signals are from —CF$_3$ associated with trifluoroacetylated Ny66. Similarly, the two quartets in the vicinity of 163 ppm can be ascribed to the C=O group from TFA and the C=O group of the trifluoroacetyl group in trifluoroacetylated Ny66.

2. Ny66 and TFA

The proton spectrum in Figure 5 shows the OH$^+$ signal at 12.4 ppm. In the blends the signals due to TFA$^-$ anions are weaker, and they are absent from the PEN spectrum. In is interesting to note that Ny66/PEN blend samples were soluble in a mixture of 5 mL TFA + 1 mL of TFAA, but were

not dissolved by a mixture of 5 mL TFA + 5 mL of TFAA. The reason for the low solubility in the latter solvent mixture is most likely the reduced polarity of the solvent with equal volumes of TFA and TFAA.

By analogy with the interchange reaction mechanisms that have been proposed to occur in inner–inner and outer–inner groups,[18] the corresponding reactions for Ny66+PEN blends can be represented as follows.

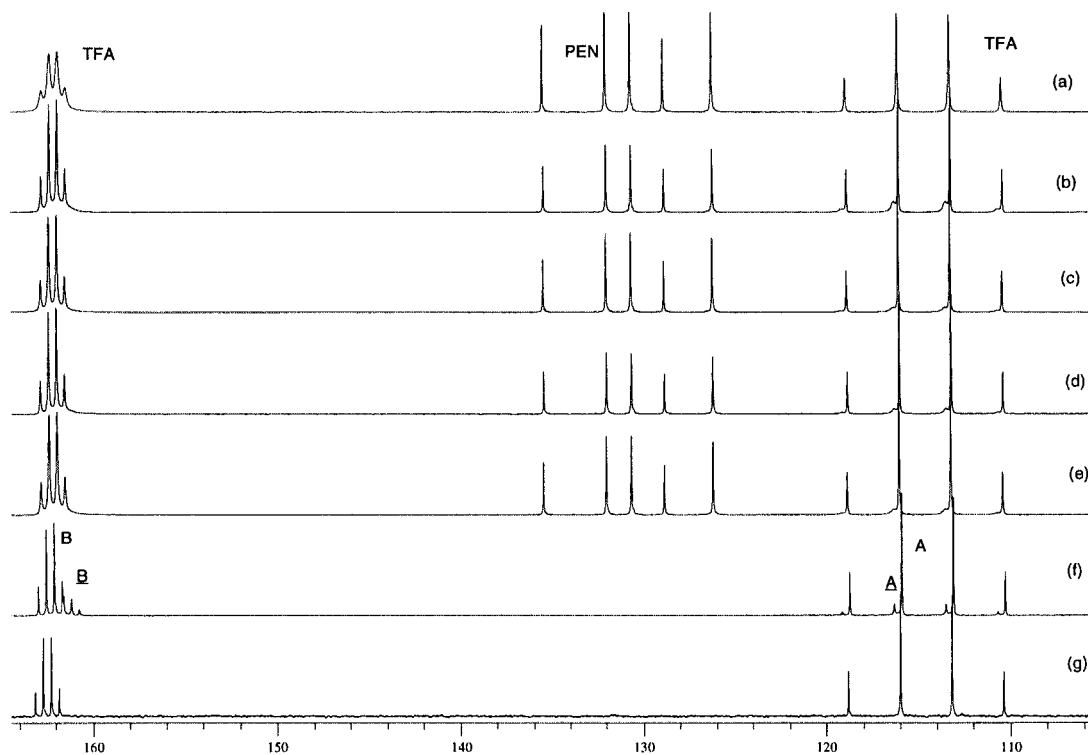*Outer amide/Inner carbonyl interchange:*

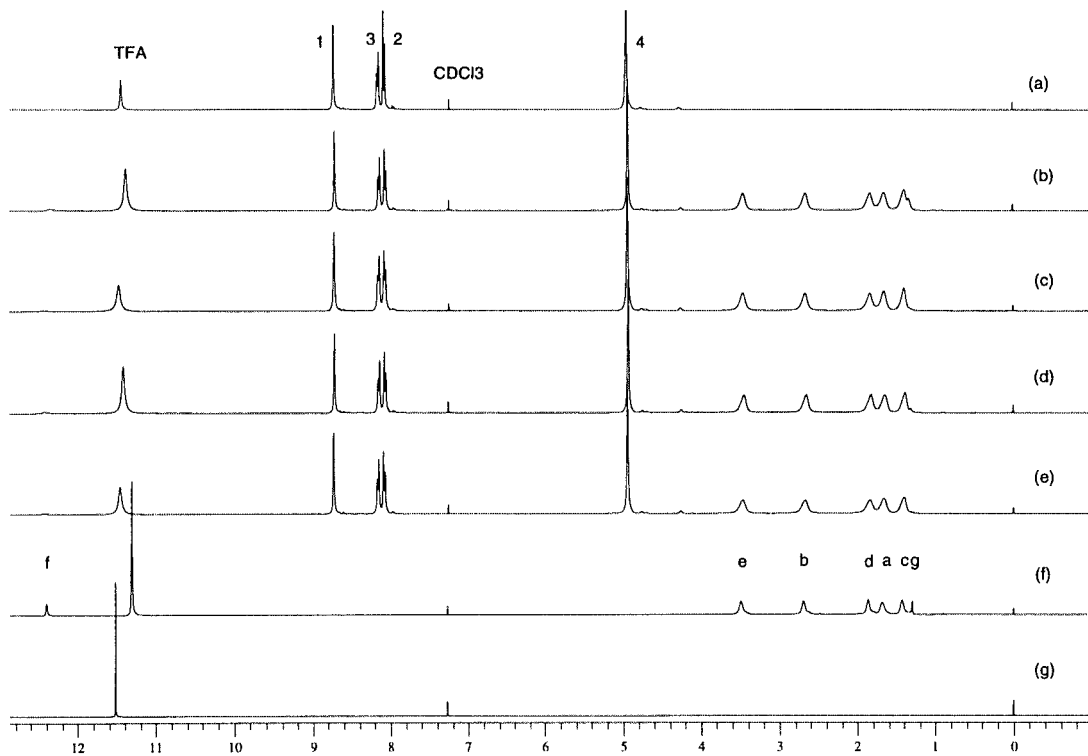**Figure 4**   Magnified spectra of TFA from the second series of experiments.

Figure 5 ^{1}H NMR spectra of Ny66, PEN, and Ny66/PEN (wt %/wt %) blends, from the second series of experiments: (a) 0/100, (b) 50/50+GMA (3 wt %), (c) 30/70, (d) 50/50, (e) 70/30, (f) 100/0, and (g) $CDCl_3$ + TFA solvent.
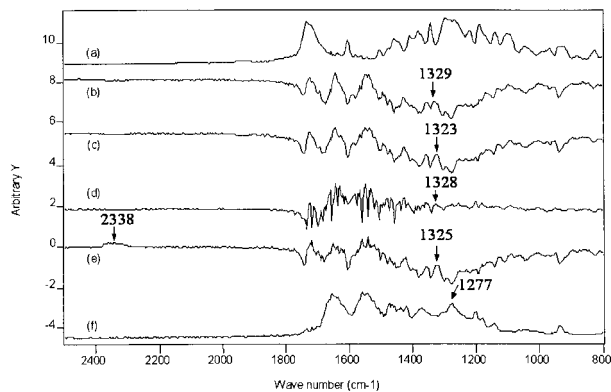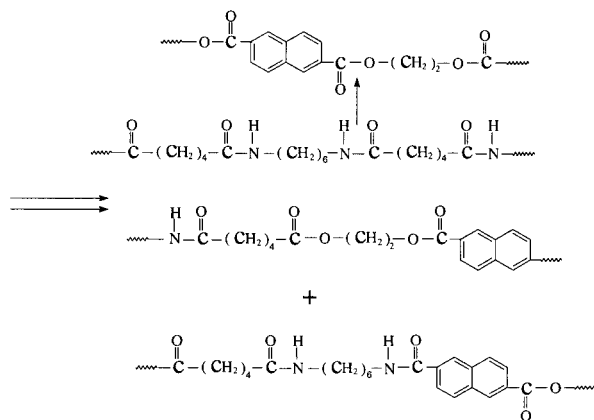
Figure 6 FTIR spectra of Ny66 and PEN, and subtraction spectra of Ny66/PEN (wt %/wt %) blends: (a) PEN, (b) Ny66/PEN (30/70), (c) Ny66/PEN (50/50), (d) Ny66/PEN (50/50) GMA (3 wt %), (e)Ny66/PEN (70/30), and (f) Ny66.

Figure 8 Atomic concentrations in Ny66, PEN, and Ny66/PEN blends. Unshaded symbol refers to the blend with 3% compatibilizer.

Inner amide/Inner carbonyl interchange:

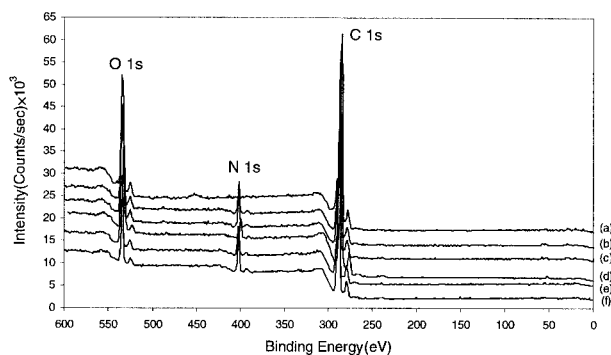Both reactions, if they occur, will produce an amide group that is obviously different from the

amide group in Ny66. If the reactions took place to a significant extent during melt processing, we would expect to see a new C=O signal in the 170–180 ppm region of Figure 3. That no additional signal was detected suggests that the interchange reactions represented above take place to an extent that is too small to be detectable by NMR. However, as noted below there is some evidence from FTIR spectra to suggest that the interchange reactions occur to some extent.

FTIR-PAS spectra of blends, after normalization and subtraction of PEN and Ny66 spectra, are shown in Figure 6. After subtraction the C—N band from Ny66 (1277 cm) moves to higher frequencies: a new band at 1324–1329 cm^{-1}, assigned to C—N, appears in all of the blend spectra. It seems reasonable to attribute the new band to amide produced by interchange reaction. The band at 2338 cm^{-1} in the spectrum of Ny66/

Figure 7 XPS survey spectra of Ny66/PEN blends. (a) PEN, (b) Ny66/PEN (30/70), (c) Ny66/PEN (50/50), (d) Ny66/PEN (50/50) GMA (3 wt %), (e) Ny66/PEN (70/30), and (f) Ny66. Note that the scans have been displaced on the vertical axis for clarity.
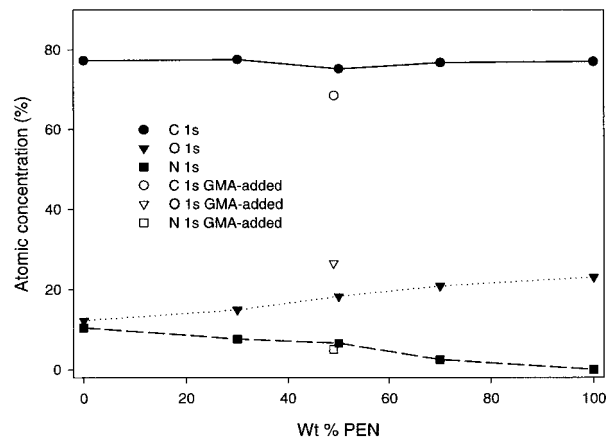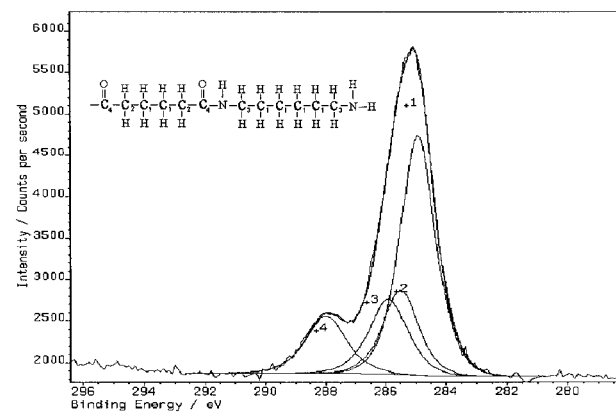

Figure 9 Subband analysis of the C1s scan for Ny66.

Table III   Binding Energies, Full Widths at Half Maximum (FWHM), and Atomic Concentration (%) from Narrow Scans of Pure Ny66 and PEN

		C1s				O1s		N1s, 1
		1	2	3	4	1	2	
Ny66	BE (eV)	284.98	285.54	285.94	288.02	531.57		399.89
	FWHM (eV)	1.36	1.37	1.48	1.58	1.93		1.78
	Atomic concentration (%)	50.8	17.94	17.33	13.93	100		100
	Sensitivity factor	0.25	0.25	0.25	0.25	0.66		0.42
	Mixing ratio (GL)	70	70	70	70	100		100
PEN	BE (eV)	285	286.76	289.13		532.78	531.12	
	FWHM (eV)	1.24	1.46	1.32		1.56	1.39	
	Atomic concentration (%)	71.94	14.33	13.73		55.12	44.88	
	Sensitivity factor	0.25	0.25	0.25		0.66	0.66	
	Mixing ratio (GL)	80	80	80		80	80	

PEN(70/30) is most likely due to carbon dioxide that may have been produced by partial decomposition occurring during melt blending or injection molding.

XPS survey spectra typified by Figure 7 show that the atomic concentrations of the blends (Fig. 8) were in accordance with the blended proportions of homopolymers. The blend containing the glycidyl methacrylate-based compatibilizer shows a corresponding decrease in the atomic proportion of carbon and increase in oxygen content.

Curve fitting of the narrow scans (a typical scan is shown in Fig. 9) enabled assignment of subpeaks to pure Ny66, where the ratio of area of C_1, C_2, C_3, and C_4 is 3:1:1:1 from the atomic concentrations found by curve fitting the C1s peak of Ny66 (Table III). This matches the numbers of C_1, C_2, C_3, and C_4 (6, 2, 2, and 2) in Ny66,

and agrees with the atomic composition of carbon in the assigned positions.[22]

Subband analyses, based on the literature,[22, 23] of carbon and oxygen narrow scans for pure PEN are shown in Figures 10 and 11. Here again the numbers of C_1, C_2, and C_3 in PEN correspond to 10, 2, and 2 and the area ratio is roughly 5:1:1. There are shifts in binding energies for the blends, but it is difficult to show unequivocally from the XPS scans that the shifts are the result of interchange reactions that have taken place during blending and injection molding.

SEM images of the etched surfaces were used to identify the dispersed and matrix phases. Figure 12 shows the surface that was etched to remove Ny66, leaving dispersed globules of PEN. It is difficult to identify the matrix and dispersed phases in Figure 13, suggesting that the 50/50 wt % blend composition is close to the phase inver-
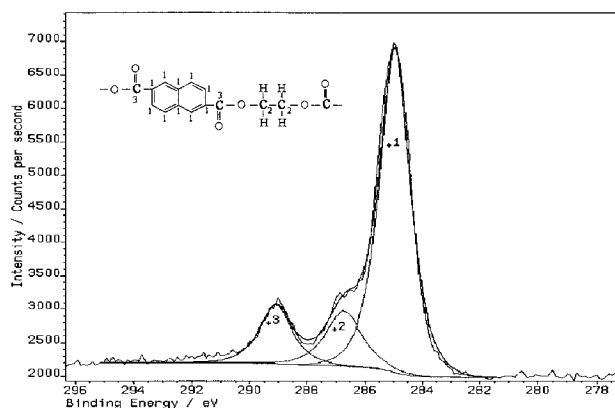
Figure 10   Subband analysis of the C1s scan for PEN.
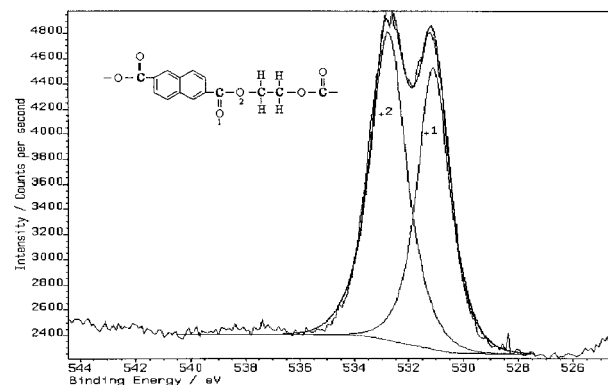
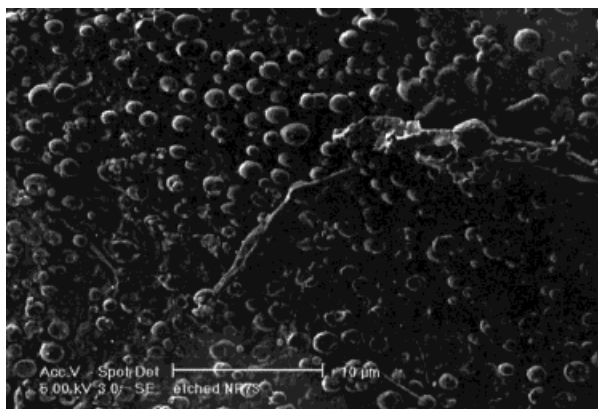**Figure 11**   Subband analysis of the O1s scan for PEN.

Figure 12 SEM image of the fracture surface of Ny66/PEN (70/30) etched with trifluoroethanol.
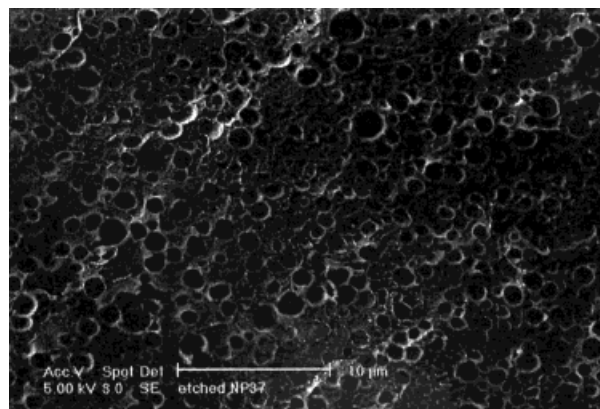

Figure 14 SEM image of the fracture surface of Ny66/PEN (30/70) etched with trifluoroethanol.

sion point. The cavities in the etched surface shown in Figure 14 confirm that the matrix in this blend is PEN.

CONCLUSIONS

From NMR spectra there is no evidence to indicate that interchange reaction between Ny66 and PEN occurs, whereas FTIR spectra seem to show that there is some reaction taking place between ester groups from PEN and NH_2 or NH groups of Ny66 during melt processing. The extent to which such reactions take place is very limited under the melt processing conditions that were used. While more extensive heat treatment may enhance interchange reactions, it seems unlikely that the extent of thermally induced reaction

would be sufficient to produce significant miscibility between the homopolymer phases.

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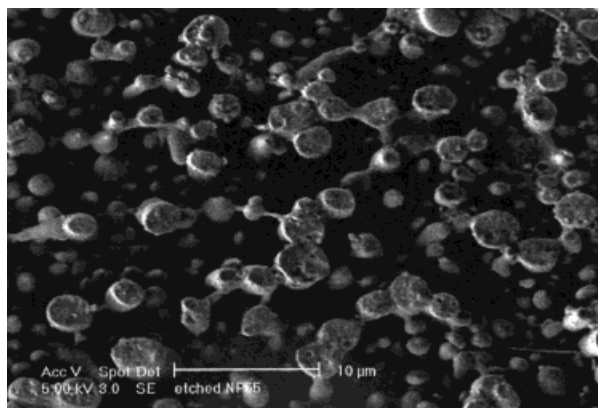14. Gattiglia, E.; Turturo, A.; Pedemonte, E. J Appl Polym Sci 1989,138, 1807.

Figure 13 SEM image of the fracture surface of Ny66/PEN (50/50) etched with trifluoroethanol.

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