

Blends of Poly(vinyl butyral-*co*-vinyl alcohol) and Poly(ethylene terephthalate-*co*-ethylene naphthalate): Thermal, Mechanical, and Morphological Properties

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ABSTRACT: The miscibility behavior and morphology of a series of poly(vinyl butyral-*co*-vinyl alcohol) (PVBA) copolymers containing 29, 52, 76, and 88 mol % of vinyl alcohol units with poly(ethylene terephthalate-*co*-ethylene naphthalate) (PETN) was investigated by DSC and SEM. Blends of the PETN with PVBA were prepared by coprecipitation from a chloroform/*o*-chlorophenol (20/80 wt %) mixture solvent. It was found that PVBA with different vinyl alcohol content will form an immiscible phase with the amorphous PETN in the solution-cast films. Also, PETN and PVBA with 29 mol % vinyl alcohol (PVBA-29) are not miscible within the whole composition range. The glass-transition temperatures of the blends were higher than those of the two-component polymers. The values of the tensile properties of the blend films were also better than those of the original copolymer films. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2746–2751, 2001

Key words: PETN; PVBA; miscibility; tensile property; morphology

INTRODUCTION

Poly(vinyl butyral-*co*-vinyl alcohol) (PVBA), which is a random copolymer of vinyl butyral and vinyl alcohol units, is an amorphous polymer of great technological interest because it is widely used in a variety of commercial products. PVBA is

characterized by transparency, a nonlinear optical property, high bonding force (both polar and hydrogen bonding), and miscibility with both hydrophilic and hydrophobic polymers.^{1–3} PVBA has been used in paper sizings, adhesives, and the plasticized polymer for laminated safety glass. It has been found that PVBA is miscible with nylon 6, poly(methyl methacrylate), and poly(vinyl alcohol) in the range of 70–90 mol % of vinyl alcohol content of PVBA.^{4–9}

Poly(ethylene terephthalate-*co*-ethylene naphthalate) (PETN), which contains an aromatic ring, a naphthalene ring, and flexible aliphatic diol moiety, was shown to have good processability, more applications, and better physical and

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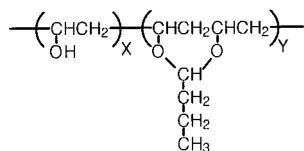
mechanical properties than the widely used homo poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN), respectively.^{10–12} PETN is a thermoplastic polymer. It has exceptional properties: good impact strength, extreme toughness, and transparency.^{13,14}

To obtain some useful new materials based on PVBA, two approaches have been tried. One approach was to prepare blends that were controlled by using a mixture of the two copolymers and then extensively study their thermal properties and miscibilities. We also considered a DSC study of the miscibility of PETN with PVBA with four different vinyl alcohol contents (29, 52, 76, and 88 mol %) and examined the effect of the variation of the vinyl alcohol content in the PVBA copolymer. The second approach was to study the morphology of the blends as a function of the PVBA content in the PETN polymer. We then studied the correlation between the morphology of the blends and the measured mechanical properties.

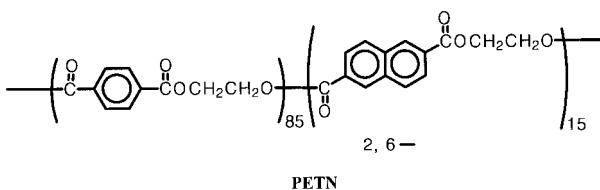
EXPERIMENTAL

Materials

PVBA used in this study was synthesized through a multistep procedure.^{9,15} PVBA contained 29, 52, 76, and 88 mol % vinyl alcohol content, respectively. PETN, composed of 85 mol % of ethylene terephthalate content, was supplied by Kolon Co. (Yongin, South Korea). The composition of the polyblends was PETN/PVBA-*x*, where *x* is the mole percentage of vinyl alcohol in PVBA copolymer:



PVBA (*x*=29, 52, 76, and 88)



PETN

Blending and Film Preparation

The blends were prepared by codissolving PETN and PVBA in a chloroform/*o*-chlorophenol (20/80

wt %) mixture solvent. The solutions were cast onto glass slides and then dried under vacuum at room temperature for 24 h. The films were then cleaned in an ultrasonic cleaner with ethanol for 15 min. These films with the solvent removed were dried again in a vacuum oven for 1 day.

Characterization

A DuPont 910 differential scanning calorimeter (DSC; DuPont, Wilmington, DE) was employed to study the glass-transition temperature (T_g) of PETN, PVBA, and their blends (PETN/PVBA). For T_g , the samples were heated from -50 to 150°C (first scan) with a heating rate of $20^\circ\text{C}/\text{min}$ and then maintained at 150°C for 5 min before cooling to -50°C . The samples were then reheated to 150°C (second heating) at $20^\circ\text{C}/\text{min}$. Thermal transitions were determined from second DSC scans. Thermal stability was examined under a N_2 atmosphere on a DuPont 910 thermogravimetric analyzer (TGA) at a heating rate of $20^\circ\text{C}/\text{min}$.

The morphology of the fractured surfaces of the extrusion samples was investigated using a Hitachi S-2400 scanning electron microscope (SEM). The fractured surfaces were sputtered coated with gold using an SPI Sputter Coater for enhanced conductivity.

The mechanical properties of the films were measured at room temperature on an Instron mechanical tester (Model 5564) with a cross-head speed of 5 mm/min. Reported values are the average of eight measurements. The experimental uncertainty in tensile strength and modulus was ± 1 MPa and ± 0.05 GPa, respectively.

RESULTS AND DISCUSSION

Miscibility and Thermal Stability

The inherent viscosities and T_g 's of the two copolymers are recorded in Table I. Because solubilities were good in a single solvent, a concentration of 0.3 g/dL was employed for the solution viscosity measurement. The solution viscosity numbers (Table I) ranged from 0.78 to 1.89. In the case of PETN, inherent viscosity and T_g were 0.78 and 44°C , respectively. PVBA values for inherent viscosities were 1.10–1.89 for each copolymer composition and T_g values rose monotonically with increasing vinyl alcohol content in PVBA from 24°C in 29 mol % to 32°C in 88 mol %.

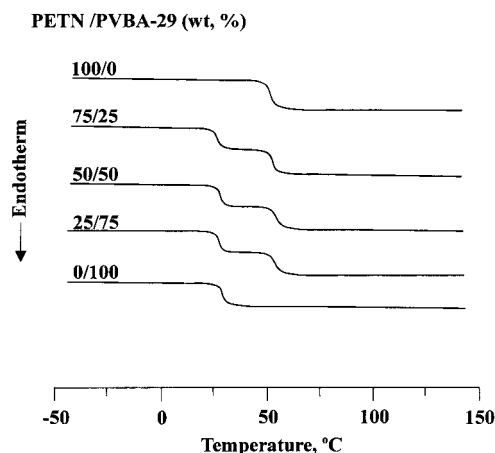
Table I Compositions and General Properties of the Copolymers

Polymer	Vinyl Alcohol Content (mol %)	η_{inh}^a (dL/g)	T_g ($^{\circ}\text{C}$)
PETN	—	0.78	44
PVBA-29	29	1.10	24
PVBA-52	52	1.51	27
PVBA-76	76	1.82	31
PVBA-88	88	1.89	32

^a Inherent viscosities of polymers were at 25 $^{\circ}\text{C}$ at a concentration of 0.3 g/dL in an *o*-chlorophenol.

Generally, thermal characterization of polymer blends is a well-known method used to determine the miscibility of the blends. The miscibility between any two polymers in the amorphous state is detected by the presence of a single T_g intermediate between those of the two-component polymers.¹⁶ It is therefore important to establish the T_g behavior of PETN/PVBA blends.

Blends of PETN and PVBA with four different vinyl alcohol contents (29, 52, 76, and 88 mol %) were studied by DSC, the results of which for 50/50 wt % blended samples are listed in Table II. Regardless of the vinyl alcohol content in PVBA, the transition points of all samples were shown to be between 30 and 36 $^{\circ}\text{C}$ and 49–51 $^{\circ}\text{C}$, separately, and were determined to be the glass-transition temperature of PVBA with different vinyl alcohol contents and the PETN, respectively. The appearance of the two T_g 's suggests that these blends are immiscible. These results also suggest that the blends have a two-phase structure. Immiscibility between the components will be demonstrated later by the two-phase morphology observed through SEM for the fracture surfaces of the blends.

**Figure 1** DSC thermograms of PETN/PVBA-29 blends.

In the blends of PETN/PVBA-29 (see Table II), two glass transitions were observed in the 75/25, 50/50, and 25/75 PETN/PVBA-29 blends. These two distinct T_g 's indicate that the cast films of PETN/PVBA blends are also immiscible. For example, the samples with PETN/PVBA-29 blends showed two T_g 's: one at 28–30 $^{\circ}\text{C}$ and the other at 49–51 $^{\circ}\text{C}$, which correspond to the glass-transition temperatures of PETN and PVBA, respectively. Figure 1 shows second-heating DSC thermograms for the pure copolymers and their blends as a function of copolymer composition.

Regardless of the vinyl alcohol contents in PVBA, the T_g 's of all blends are higher than predicted according to the additivity principle. These results indicate the occurrence of intermolecular interaction between the polymeric chains of the two components.

The thermal stability of the pure copolymers and their blends under a nitrogen atmosphere was studied by TGA. Table III summarizes the experimental results of thermogravimetric anal-

Table II Glass-Transition Temperatures of the Copolymers and Their Blends

Polyblend 50/50 (wt %)	T_g ($^{\circ}\text{C}$)		PETN/PVBA-29 (wt %)	T_g ($^{\circ}\text{C}$)	
	Copolymer	Blend		Copolymer	Blend
PETN/PVBA-29	30	49	100/0		44
PETN/PVBA-52	30	50	75/25	28	50
PETN/PVBA-76	34	51	50/50	30	49
PETN/PVBA-88	36	50	25/75	30	51
			0/100	24	

Table III Thermogravimetric Analyses of the Copolymers and Their Blends

PETN/PVBA-29 (wt %)	T_D^i ^a (°C)	T_D^{\max} ^b (°C)	T_D^{\max} ^c (°C)	wt_R^{600} ^d (%)
100/0	406	—	464	22
75/25	384	421	459	15
50/50	377	419	457	9
25/75	370	419	457	2
0/100	348	426	—	2

^a Initial weight loss temperature.

^b Maximum weight loss temperature for PVBA.

^c Maximum weight loss temperature for PETN.

^d Weight percentage of residue at 600°C.

yses. Initial weight loss (T_D^i) was observed at 348–406°C, depending on the PETN weight percentage in the blends. With decreasing PETN content, T_D^i values decreased. Maximum rates of weight loss (T_D^{\max}) were observed in the temperature ranges of 419–426 and 457–464°C, which were T_D^{\max} for PVBA and for PETN, respectively. Figure 2 shows the TGA thermogram of 25/75 PETN/PVBA-29 (wt %). There are two peaks for maximum weight loss, occurring around 420 and 460°C. The weight residues at 600°C, wt_R^{600} , were decreased from 22 to 2% with decreasing PETN contents in blends. A comparison of T_D^i , T_D^{\max} (for PETN), and wt_R^{600} in Table III leads to the conclusion that a higher PETN content blend is more thermally stable, although all of the polymers show fairly good thermal stability.

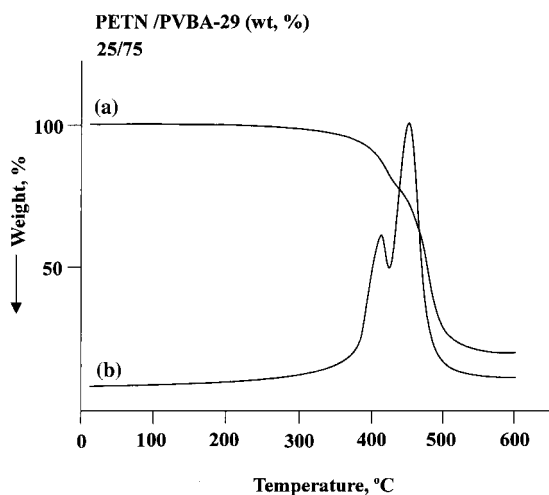


Figure 2 Thermogravimetric analysis (a) and differential thermogravimetry (b) thermograms of 25/75 PETN/PVBA-29 (wt %) blends.

Table IV Tensile Properties of the Copolymers and Their Blends

PETN/PVBA-29 (wt %)	Ultimate Strength (MPa)	Initial Modulus (GPa)	E.B. ^a (%)
100/0	48	1.34	160
75/25	50	1.38	110
50/50	73	2.80	62
25/75	88	3.56	62
0/100	52	3.13	373

^a Elongation percentage at break.

Tensile Properties

The pure copolymers and their blends were cast into films with varying composition ratios, and the films were examined for tensile strength (δ), modulus (E_0), and elongation at break. As shown in Table IV, the values of the tensile properties of the blend films were better than those of the pure copolymer films. Also, strength and modulus values increased up to 75 wt % content of PVBA-29, and thereafter decreased with increasing PVBA-29 percentage. It thus appears that the blended films resulted in an increase in tensile properties compared with those of pure copolymers. In this blend system, the reinforcing effect did not follow the rule-of-mixtures. Similar trends were previously observed in investigations of other polymer blends.^{17–19}

For example, the strength values increased from 48 to 88 MPa, with increases up to 75 wt % level of PVBA-29 in polyblends, and then decreased to 52 MPa at pure PVBA-29. Similar to the trend of ultimate strength, the values of initial modulus increased from 1.34 to 3.56 GPa at PVBA-29 content from 0 to 75 wt % and then decreased to 3.13 GPa at pure PVBA-29. The mechanical properties of the blends were not greatly enhanced in low PVBA-29 content, but a high PVBA-29 content caused an increase in strength and modulus. The improved tensile properties of the blend systems may be explained by assuming intermolecular interactions of the two copolymers in the blend, although adhesion between them was weak. This poor adhesion was confirmed by morphological studies by SEM as shown in Figures 3 and 4. The presence of the –OH and alkyl side group along the chain in PVBA-29 may also contribute to better intermolecular interaction between PETN and PVBA-29.

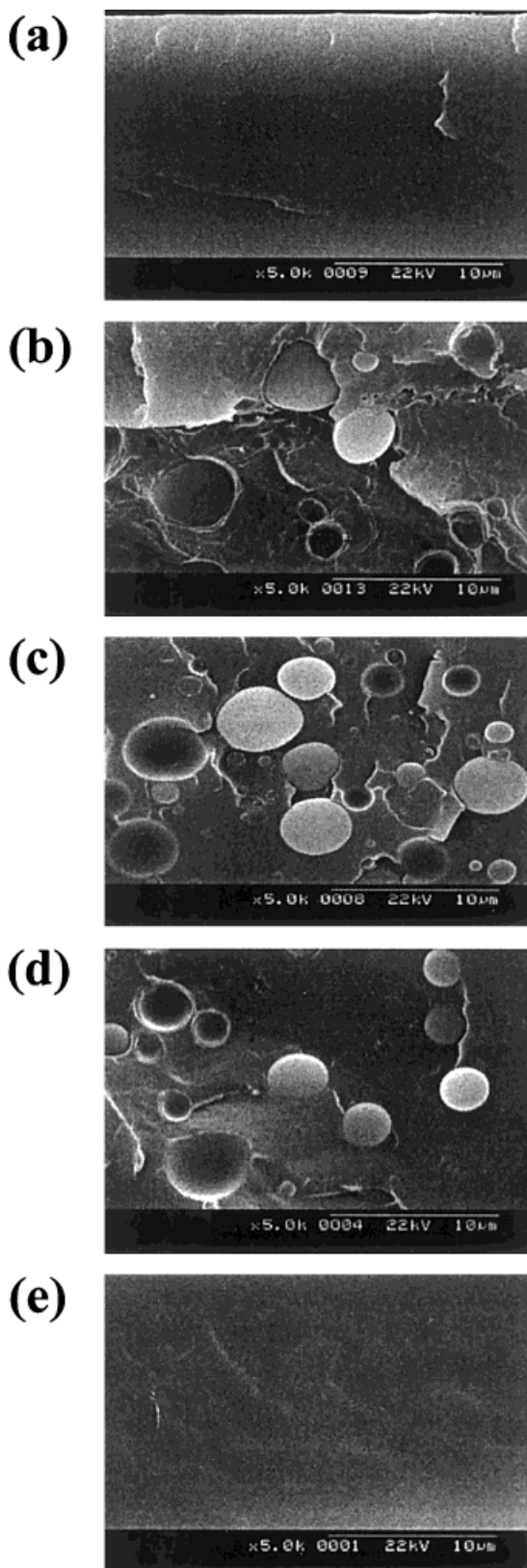


Figure 3 SEM micrographs of PETN/PVBA-29 (wt %) blends ($\times 5000$): (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, and (e) 0/100 PETN/PVBA-29.

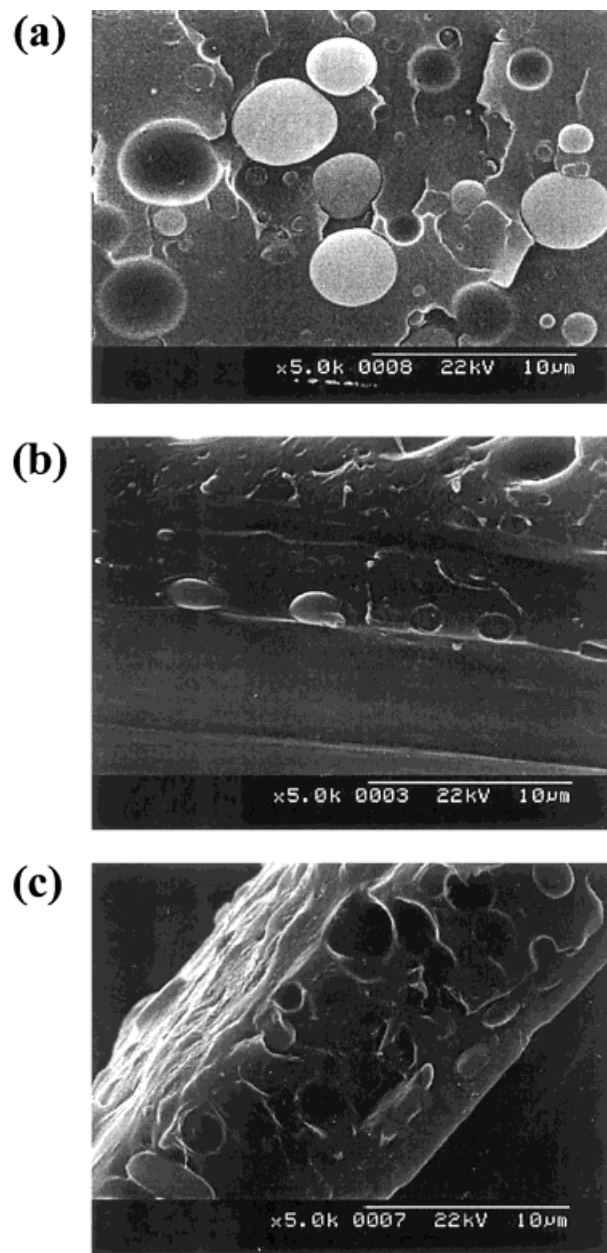


Figure 4 SEM micrographs of 50/50 wt % (a) PETN/PVBA-29, (b) PETN/PVBA-52, and (c) PETN/PVBA-88 blends ($\times 5000$).

This improvement was generally at the expense of reductions in elongation-to-break values. In essence, this led to an improvement in the behavior of two already tough copolymers. As shown in Table IV, the values of elongation percentage at break decreased significantly from 160 to 110% and then remained constantly at 62% with increasing PVBA-29 content from 0 to 75 wt %. The elongation percentage at break of pure PVBA-29 was 373%.

Morphology

The SEM micrographs of the PETN/PVBA-29 blend fracture surfaces exhibit the typical morphology of an immiscible blend, as seen in Figure 3. Pure PETN and PVBA-29 copolymers are shown as typically amorphous (pictureless) [Fig. 3(a), (e)]. The surface shows well-segregated domains of PVBA-29 in the PETN-rich phase [Fig. 3(b)]. On the contrary, PETN domains were segregated in the PVBA-29-rich phase [Fig. 3(d)]. The PVBA-29 and PETN domains have a defined spherical shape with diameter ranges of 130 to 420 nm [see Fig. 3(b)–(d)]. The hole remains where particles have been pulled out of the PVBA-rich phase, illustrating a weak adhesion between the two phases. The domain of PVBA in the PETN-rich phase also showed similar results.

The fractured surfaces of the 50/50 PETN/PVBA-52 and PVBA-88 blends, as shown in the SEM micrographs in Figure 4(b) and (c), do not differ much from those of the 50/50 PETN/PVBA-29 blend [Fig. 4(a)] previously described, and showed immiscible morphologies.

CONCLUSIONS

There have been ongoing concerted efforts to investigate the miscibilities and to improve the mechanical properties of aromatic thermoplastic copolymers (PETN) by blending them with amorphous copolymers with flexible side group (PVBA). In this investigation, we set out to clarify the structural effect of PVBA with various vinyl alcohol contents by reinforcement in a PETN matrix in the form of films. Therefore, the blends of different vinyl alcohol contents in PVBA were studied for miscibility, thermal stability, mechanical property, and morphology. Based on the two distinct glass transitions, PETN copolymers were not miscible with PVBA in any of the blend compositions studied. Even though poor adhesion between the two phases in SEM was observed, however, the glass-transition temperatures are higher than predicted according to the additivity principle. Also, the values of the strength and modulus increased up to 75 wt % content of PVBA-29 and thereafter decreased with increasing PVBA-29 percentage in the blends. These results indicate the occurrence of intermolecular

interaction between the polymeric chains of the two components.

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REFERENCES

1. Zhou, Z. M.; David, D. J.; MacKnight, W. J.; Karasz, F. E. *Turkish J Chem* 1997, 1, 326.
2. Hall, W.; Krusem, R.; Mendelson, R. A.; Tremontozzi, Q. A. in *The Effects of Hostile Environments on Coatings and Plastics*; Garner, D. P.; Stahl, G. A., Eds.; ACS Symposium Series 229; American Chemical Society: Washington, DC, 1983; p. 49.
3. Ide, F.; Hawegawa, A. *J Appl Polym Sci* 1974, 18, 963.
4. Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA, 1991.
5. Joesten, M. D.; Nettekville, J. T.; Wood, J. L. *World of Chemistry*; Saunders: Philadelphia, 1993.
6. Zimmerman, J. in *Polyamides*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; *Encyclopedia of Polymer Science and Engineering*, Vol. 11; Wiley-Interscience: New York, 1988.
7. Ha, C. S.; Lee, W. K.; Roe, T. W.; Cho, W. J. *Polym Bull* 1993, 31, 359.
8. Sincock, T. F.; David, D. J. *Polymer* 1992, 33, 4515.
9. Jeong, H. K.; Rooney, M.; David, D. J.; MacKnight, W. J.; Karasz, F. E.; Kajiyama, T. *Polymer to appear*.
10. Hoffman, D. C.; Caldwell, J. K. *Proc Specialty Polyesters* 1995, 223.
11. Lu, X.; Windle, A. H. *Polymer* 1995, 36, 451.
12. Light, R. R.; Seymour, R. W. *Polym Eng Sci* 1987, 22, 857.
13. Park, J. Y.; Paul, D. R.; Haider, I.; Jaffe, M. J. *Polym Sci Part B Polym Phys* 1996, 34, 741.
14. McDowell, C. C.; Freeman, B. D.; Mcneely, G. W.; Haider, M. I.; Hill, A. J. *J Polym Sci Part B Polym Phys* 1998, 36, 2981.
15. Raghavendrachar, P.; Chanda, M. *Eur Polym J* 1983, 19, 391.
16. Olibisi, O.; Roberson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: San Diego, 1979.
17. Jackson, W. J., Jr.; Kuhfuss, H. F. *J Polym Sci Part A Polym Chem* 1976, 14, 2043.
18. Sukhadia, A. M.; Done, D.; Baird, D. G. *Polym Eng Sci* 1980, 30, 519.
19. Baird, D. G.; Bafna, S. S.; Souza, J. P.; Sun, T. *Polym Compos* 1993, 14, 214.