

Miscibility and Fracture Toughness of Thermoplastic Polyurethane/Poly(vinyl chloride)/Nitrile Rubber Ternary Blends with Special Reference to the Blend Composition

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ABSTRACT: Ternary blends of thermoplastic polyurethane and a poly(vinyl chloride)/nitrile rubber blend were investigated in this work. The blends, with weight ratios of 100/0, 80/20, 40/60, 60/40, 80/20, and 0/100, were prepared via melt blending. Dynamic mechanical analysis showed that the blends with ratios of 20/80 and 80/20 were miscible, whereas the 40/60 and 60/40 blends were partially miscible. IR spectroscopy studies showed shifts in the peaks due to specific interactions in the blends. The blends showed degradation behavior between the blend components. The

fracture toughness was investigated with the *J*-integral by the locus method; the components and the miscible blends had good fracture toughness, whereas the other blends had lower toughness. Similar behavior was observed for the tensile properties. Scanning electron microscopy studies showed the morphological variations in the blends. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1763–1770, 2005

Key words: blends; fracture; miscibility; structure-property relations

INTRODUCTION

Thermoplastic polyurethane (TPU) occupies the upper end of the versatile thermoplastic elastomer (TPE) spectrum because of its high tensile strength, high abrasion resistance, and good resistance to oil, grease, and solvents.^{1,2} This is coupled with the ease of processability of thermoplastics and the functional performance of thermosets. It is characterized by a two-phase morphology: the soft phase consists of polyether or polyester, and the hard phase consists of aromatic diisocyanates extended with a short-chain diol. A large number of polymers, such as acrylonitrile-butadiene-styrene terpolymer (ABS), and poly(vinyl chloride) (PVC), have been blended with TPU to enhance its various properties.^{3–5}

A blend of PVC and nitrile rubber (NBR) was the first example of the commercialization of miscible polymer blends.⁶ Small amounts of NBR in PVC improve the impact strength of rigid PVC compositions, whereas small amounts of PVC can be added to NBR to improve the ozone and flame resistance of the vulcanizates. PVC/NBR blends can even be used as TPEs.⁷

The objective of this work was to study the properties of blends of TPU and a PVC/NBR blend. Various studies have been carried out on blends of PVC and

polyurethane,⁸ PVC and TPU,⁵ plasticized PVC and TPU,⁹ and NBR and TPU.¹⁰ All the blends have been found to be miscible and have interesting properties. Our study was aimed at the characterization of the blends with respect to dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), fracture toughness, and physical properties.

EXPERIMENTAL

Materials and blend preparation

The TPU used was Desmopan 385 from Bayer (India). It was a soft TPU based on polyester and had a hardness of 85 Shore A. A blend of PVC and NBR (50/50 w/w) was obtained from Apar, Ltd. (India). The materials were used as received. The various blends of TPU and PVC/NBR were made in a Brabender Labstation plasticorder (Germany) at 180°C and 80 rpm. First, PVC/NBR was softened for 3 min. Predried TPU was then added, and mixing was continued for another 3 min. The blend was sheeted in a two-roll mill immediately after being taken from the plasticorder and was kept in a desiccator until the molding. The molding was performed in a compression-molding press at 170°C for 2 min at 10 MPa. The blends were coded PN/T-*x*/*y*: PN is the PVC/NBR blend, T is TPU, *x* is the weight percentage of the PVC/NBR blend, and *y* is the weight percentage of TPU. The details are given in Table I.

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TABLE I
Thermal and Thermomechanical Properties of the Blends

Blend	Temperature for $\tan \delta_{\max}$ (°C; from DMA)	TGA temperature (°C)	
		2 wt % loss	50 wt % loss
PN/T-100/0	51	256	397
PN/T-80/20	43	247	403
PN/T-60/40	31, −16	258	396
PN/T-40/60	27, −27	259	400
PN/T-20/80	−25	269	404
PN/T-0/100	−35	298	399

DMA

DMA of the blends was carried out on a Rheometric Scientific PL Mk III dynamic mechanical thermal analyzer (UK). The samples were scanned from −50 to +100°C at a heating rate of 3°C/min. The dynamic stress applied to the samples produced a dynamic (oscillatory) strain amplitude of 32 μm at a fixed frequency of 1 Hz.

IR spectroscopy

Fourier transform infrared (FTIR) spectra of the blends were recorded on a PerkinElmer 1600 FTIR spectrophotometer. Thin films of each blend, approximately 200 μm thick, were prepared via compression molding between two stainless steel plates at 200°C for 2 min at a pressure of 25 MPa. For the spectra, 32 scans with a 4- cm^{-1} resolution were signal-averaged in each case.

Thermogravimetry

The samples were scanned from the ambient temperature to 800°C under a nitrogen atmosphere at a heating rate of 20°C/min in a TA Instruments HiRes TGA 2950 thermogravimetric analyzer.

Determination of the fracture energy

Various methods and specimen configurations are available for the measurement of fracture toughness.^{11,12} Here we used single-edge-notched tensile specimens (2 mm wide and 10 mm thick) with various crack sizes to evaluate the fracture energy in terms of the critical J -integral value (J_c) with the crack-initiation locus-line method.^{13,14} The method determines J_c as follows:

$$J_c = -\frac{1}{B} \frac{\Delta U_c}{\Delta a}$$

where B is the thickness of the specimen, a is the initial crack length, and U_c is the enclosed area between the loading line and the locus line.¹³

Sharp initial cracks of 0.2–0.8 mm (a/w) were made with razor-sharp blades. Tensile tests were performed on a Hounsfield H50KS universal testing machine (UK) at a speed of 50 mm/min. The distance between the grips was kept at 50 mm for all studies. Load–displacement graphs were recorded, and crack-initiation points were marked on each loading line during the test. The crack-initiation points were easily observable as the cracks opened widely before they propagated.

Scanning electron microscopy (SEM)

The morphology of the blends was characterized with a Leo (UK) 1477 scanning electron microscope. The test specimens were tensile-fractured and then coated with a thin layer of gold to avoid charging under the electron beam.

Physical properties

The mechanical properties were measured on a Hounsfield H50KS universal testing machine with dumbbell-shaped specimens cut from compression-molded samples at a speed of 50 mm/min. The hardness was observed on a Shore A or D durometer. The mechanical testing was carried out at 30°C

RESULTS AND DISCUSSION

DMA

Dynamic mechanical testing is a versatile and sensitive tool enabling a complete exploration of relaxation mechanisms in viscoelastic materials, especially polymer blends. The most common use of DMA is the determination of the glass-transition temperature (T_g), at which the molecular chains of a polymer obtain sufficient energy, usually from thermal sources, to overcome the energy barriers for segmental motion.

The dynamic mechanical properties—the storage modulus (E') and loss factor ($\tan \delta$)—of all the samples are illustrated in Figures 1 and 2. The magnitude and nature of the change in the dynamic modulus of elasticity are determined by intermolecular and intramolecular interactions, the latter having greater influence in the different physical states of the polymer.¹⁵ In the glassy state, when the intermolecular interactions are sufficiently great, the dynamic modulus is approximately 10^9 Pa. However, in the rubbery state, when the energy of intermolecular interactions is appreciably lower, the dynamic modulus of the same polymer is approximately 10^6 Pa. Any change in the energy of intermolecular interactions, which will affect molecular motion in polymers, also will have an appreciable influence on the magnitude and nature of the modulus. The PVC/NBR blend shows the maximum E' values and TPU shows the minimum E' values in the glassy region, whereas the behavior is re-

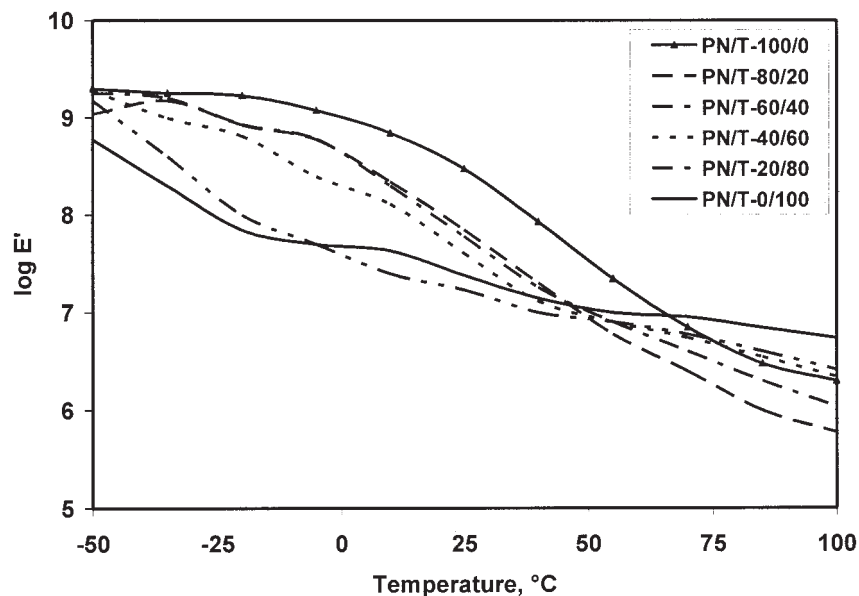


Figure 1 E' versus the temperature for the blends.

versed in the rubbery region. The blends show a progressive decrease in E' as the TPU content increased.

In polymer blends, DMA shows a single transition lying between the individual T_g 's if the two components are fully miscible and only one phase exists. On the other hand, if the two polymers are immiscible and exist as two distinct phases, then the blends will show two distinct peaks. If the polymer blends exist between these two conditions, that is, they are partially compatible, there will be a shift in T_g 's toward each other.¹⁶ Figure 2 shows the $\tan \delta$

δ /temperature plots of the blends and individual polymers. The pure PVC/NBR blend and TPU have T_g 's of 51 and -35°C , respectively. The PN/T-80/20 and PN/T-20/80 blends show single transitions at 43 and -25°C , respectively, which indicate the miscibility of the two components with these blend ratios. The other two blends, however, show two peaks corresponding to the components. The main peak is due to the PVC/NBR blend, and the shoulder is due to TPU. Both peaks, however, are shifted to each other with respect to the individual T_g 's, and

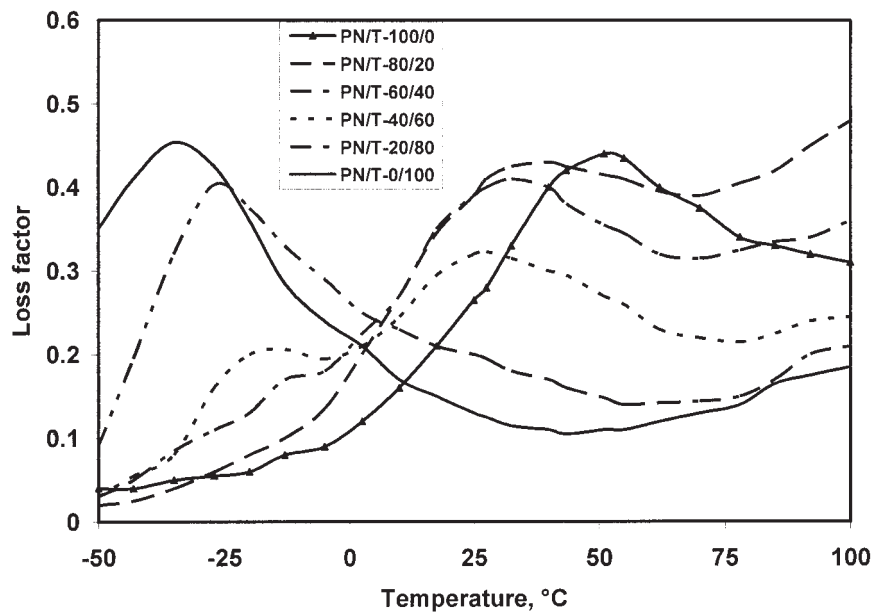


Figure 2 $\tan \delta$ versus the temperature for the blends.

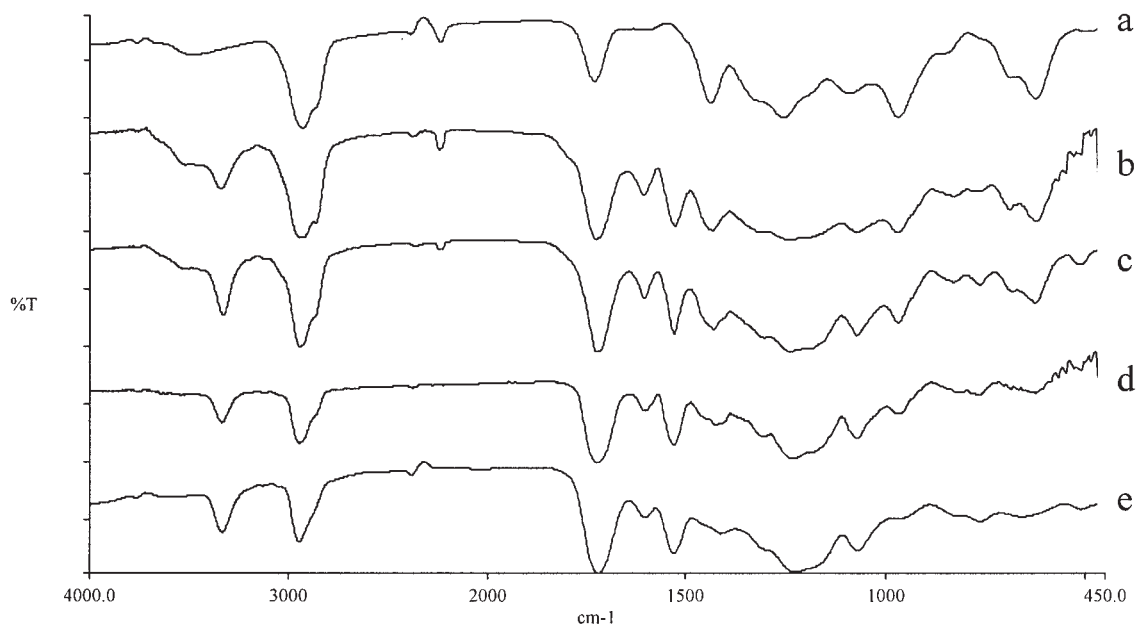


Figure 3 FTIR spectra of the PN/T blends: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, and (e) 0/100.

this indicates partial miscibility for the PN/T-60/40 and PN/T-40/60 blends. The peak temperature values are listed in Table I. Thus, the miscibility of the PN/T blends depends on the blend ratios.

FTIR analysis

FTIR has become a powerful tool for studying polymer blend miscibility. If a blend is miscible or partially

miscible, a specific interaction in the blend disrupts the bonding between the atoms, and a difference can be seen in the absorption spectrum. On the other hand, if a blend is immiscible, the absorption spectrum of the blend will be the sum of the individual components.^{16,17} FTIR spectra of the pure polymers and the blends are given in Figure 3. Pure TPU shows absorption peaks at 3332 ($\gamma_{\text{N-H}}$), 1720 ($\gamma_{\text{C=O}}$), 1530 ($\delta_{\text{N-H}}$), and 1230 cm^{-1} (δ_{CH_3}). For the PVC/NBR

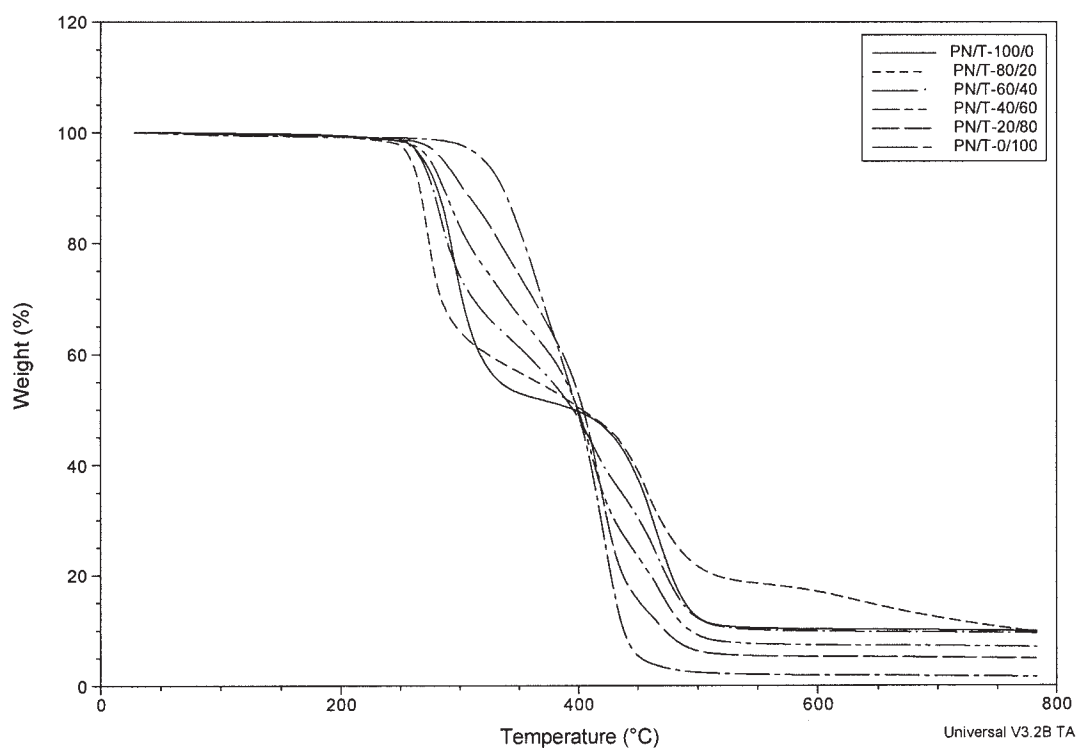


Figure 4 TGA thermograms of the blends.

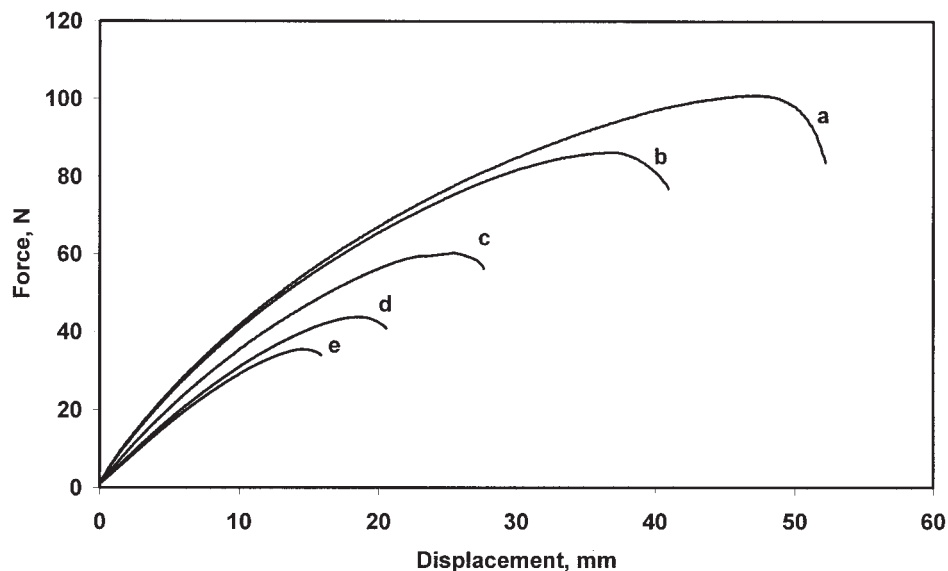


Figure 5 Load-displacement curves of PN/T-60/40 blends with different crack lengths: (a) 2, (b) 3.5, (c) 5, (d) 6.5, and (e) 8 mm.

blend, the major peaks appear at, for example, 2940 ($\gamma_{\text{C-H}}$), 2238 ($\gamma_{\text{C}\equiv\text{N}}$), 1730 (residual $\gamma_{\text{C=O}}$), and 1436 cm^{-1} ($\delta_{\text{C}\equiv\text{N}}$, δ_{CH_2}). The peaks in the blends slightly shift because of the specific interaction between the individual components. The peak at 1720 cm^{-1} for TPU and the peak at 1730 for PVC/NBR shift to 1725 cm^{-1} in the blends. Similarly, the peak at 1436 cm^{-1} for PVC/NBR shifts to a lower value in the blends. The intensity of the absorptions also varies according to the compositional changes. This corroborates the DMA results, in which two blends (20/80 and 80/20) show broad peaks because of the miscibility of the

blends, whereas the other two blends (40/60 and 60/40) show partial miscibility (a shift in the loss tangent peaks toward each other).

TGA

Figure 4 shows thermograms of the individual polymers and blends. The PVC/NBR blend shows typical two-stage degradation due to the dehydrochlorination of PVC and subsequent chain cleavage.¹⁸ The PN/T-80/20 and PN/T-60/40 blends retain the two-stage degradation behavior of the PVC/NBR blend,

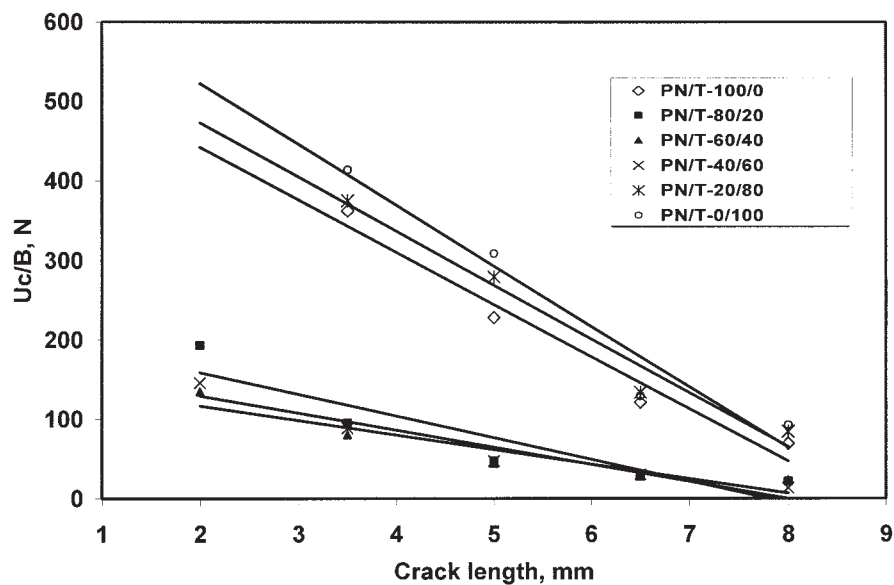


Figure 6 Variation of U_c/B with a for the blends. The lines are least-squared values.

TABLE II
Mechanical Properties of the Blends

Blend	Shore D hardness	Tensile strength (MPa)	Elongation at break (%)	J_c (N mm)
PN/T-100/0	40	13.1	364	65.8
PN/T-80/20	25	11.1	361	27.3
PN/T-60/40	23	9.5	362	18.3
PN/T-40/60	27	15.1	598	21.6
PN/T-20/80	30	16.3	707	67.9
PN/T-0/100	30	22.8	780	76.3

whereas the PN/T-40/60 and PN/T-20/80 blends show single-stage degradation similar to that of TPU. TPU is more stable than the blends, and the degradation starts only at 298°C. The temperatures for 2 and 50% weight losses are summarized in Table I. The degradation is initiated earlier in the PN/T-80/20 blend than in the PVC/NBR blend. This behavior can be seen in many miscible blends in which one of the components is more prone to degradation.¹⁶ All the

other blends show degradation behavior between that of the PVC/NBR blend and TPU, as expected. The temperatures for 50% weight loss are more or less the same for all the blends and individual components. It is evident that the presence of PVC degrades the stability of TPU, as can be seen from the lowering of the initial decomposition from 298 to 269°C with the addition of 20 wt % PVC/NBR blend to TPU. This may be attributed to the release of hydrogen chloride during the degradation of PVC, which is known to catalyze the depolymerization of polyurethanes.¹⁹

Fracture energy and morphology

Figure 5 shows a typical record of load–displacement curves for PN/T-60/40 blends at different crack lengths. The shape of the locus is dependent on the specimen length because the total deformation energy in the specimens before crack initiation is also dependent on the specimen length.¹³ Because the locus method determines J_c by partitioning the essential en-

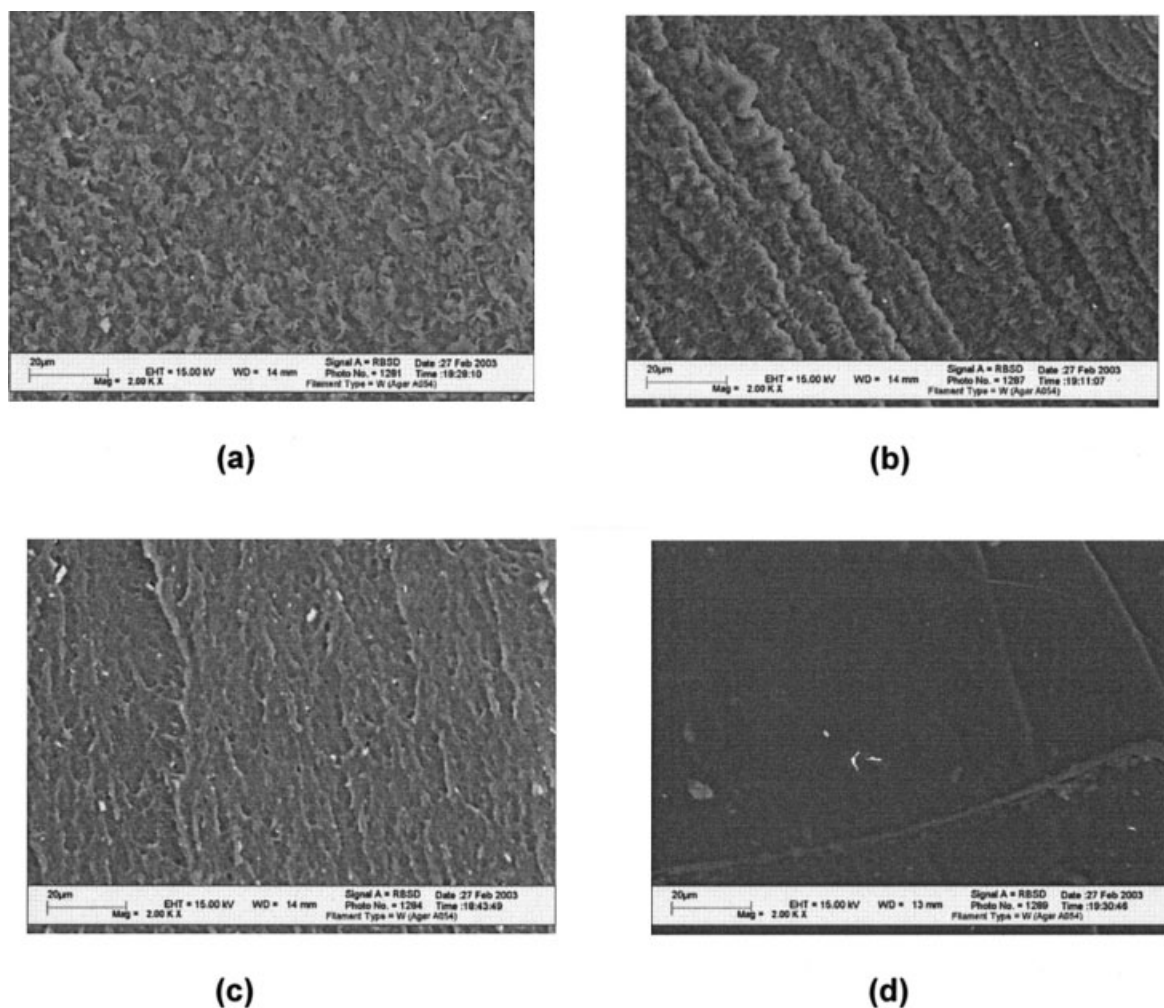


Figure 7 SEM micrographs of (a) PN/T-100/0, (b) PN/T-60/40, (c) PN/T-20/80, and (d) PN/T-0/100.

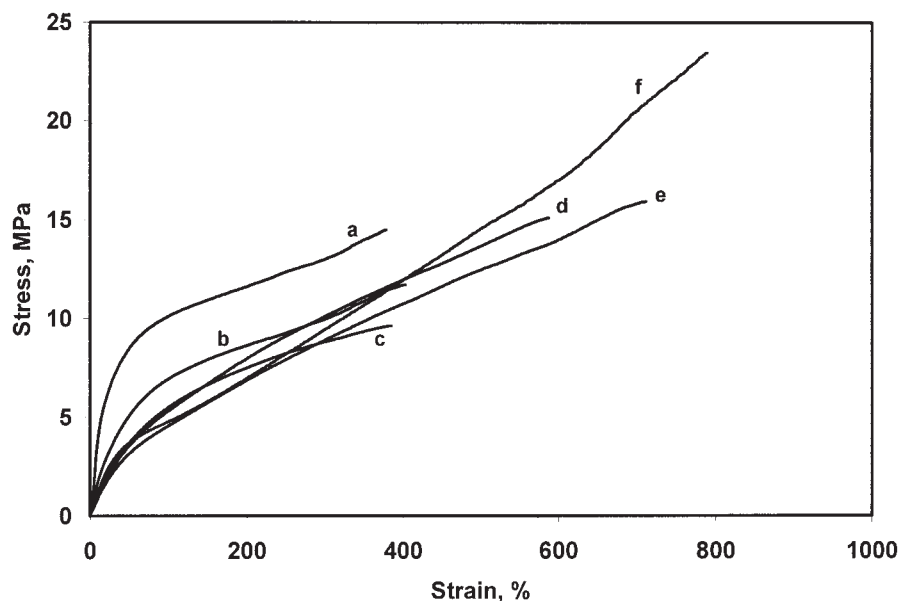


Figure 8 Stress-strain plots of the PN/T blends: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100.

ergy needed for crack propagation, consistent J_c values are obtained, regardless of the specimen length.¹³ Figure 6 shows the variation of the essential energy needed for crack initiation per unit of thickness (U_c/B) for all the blends and individual polymers. The order of increasing fracture toughness is as follows: PN/T-60/40, PN/T-40/60, PN/T-80/20, PN/T-100/0, PN/T-20/80, and PN/T-0/100. TPU shows the highest fracture toughness, and the PN/T-20/80 blend also shows excellent fracture toughness. The elastomeric phase of NBR in PVC gives the PVC/NBR blend good toughness. The PN/T-60/40 and PN/T-40/60 blends, being only partially miscible, show lower toughness. Similar behavior was observed during the tensile testing also. The slopes of the least-square-fitted values yield J_c and are summarized in Table II.

Figure 7 shows SEM images of tensile-fractured PN/T-100/0, PN/T-40/60, PN/T-20/80, and PN/T-0/100 blends. Pure TPU displays only a few smooth lines, and a large area of the fracture surface is smooth and featureless. In comparison, the fracture surface of the PVC/NBR blend is no longer smooth but shows the typical morphology of a plastic rubber blend with small interfacial tension and good adhesion between the phases. The transition in the morphology of the blends from miscible to partially miscible is evident from the two micrographs of the 40/60 and 20/80 blends. The PN/T-20/80 blend shows clear single-phase morphology, whereas the PN/T-60/40 blend shows some evidence of interfacial tension that leads to partial miscibility. It is probable that upon the cooling of the mixture after blending, two separate phases are formed along with microheterogeneous regions of one phase in the other, which leads to some compati-

bilization.²⁰ Such cases of partial miscibility also produce a shift in T_g 's, as seen earlier.¹⁶

Physical properties

The properties of the blends are summarized in Table II, and the stress-strain curves are shown in Figure 8. The hardness of the PVC/NBR blend decreases from 40 Shore D as TPU is incorporated up to 40 wt % and then increases to the hardness of TPU, that is, 30 Shore D. All the blends and individual polymers show typical elastomeric behavior, as shown by the stress-strain curves. The tensile strength of the PVC/NBR blend decreased with the addition of up to 40 wt % TPU and then increased. The reduction in the tensile strength is thought to be the result of the partial miscibility of the system with higher blend ratios. The elongation at break of the blends remains constant up to 40 wt % TPU and then increases. TPU, being inherently elastomeric, possesses a large elongation of 700%. The addition of the comparatively rigid PVC/NBR blend decreases the elongation of the blends.

CONCLUSIONS

In this work, blends of TPU and a PVC/NBR blend with weight ratios of 100/0, 80/20, 40/60, 60/40, 80/20, and 0/100 were prepared via melt blending. The PN/T-40/60 and PN/T-60/40 blends were partially miscible, whereas miscibility existed in the PN/T-20/80 and PN/T-80/20 blends, as observed by DMA. IR spectra showed interactions between the blends, and the results corroborated the DMA analysis. Thermogravimetry of the blends showed that degradation

occurred between the decomposition of TPU and the PVC/NBR blend. The determination of the fracture toughness by the *J*-integral method indicated that the partially miscible blends had lower fracture toughness, and this was also observed in tensile testing. The morphology of the blends was interpreted with SEM photomicrographs.

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