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POLYURETHANE-NITRILE RUBBER BLENDS

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ABSTRACT

Polyurethane (PU)/nitrile rubber (NBR) blends of different compositions were prepared by a combination of solution blending and mastication process. The thermal, mechanical, dynamic mechanical, and morphological properties indicated synergistic behavior of the two components. Incorporation of NBR in PU showed an increase in the % elongation, thermal stability and solvent resistance of the PU network, while the PU network could attribute improved tensile strength to NBR. The blend rich in PU exhibited optimum tensile strength, whereas the blends rich in NBR exhibited optimum % elongation at break. Morphology revealed that the minor component was dispersed in the major continuous phase. DMA showed the existence of two separate glass transitions. The loss tangent plots showed inward shift of the two peaks with increasing the NBR content indicating increasing miscibility. The increase in carbon black content in blends increased the stress-strain properties up to some extent.

Key Words: Polyurethane; Nitrile rubber; Morphology; Visco-elastic; Mechanical properties.

INTRODUCTION

Blending of polymers offers a means of producing new materials with tailored properties and has been extensively used in plastics, rubbers, composites,

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films, fibers, coatings, and adhesives [1]. The objective of polymer blending is to achieve commercially viable products having desired properties and low cost. Performance of the blends depends on the extent of miscibility of the components. The blends with apparent miscibility but with good adhesion between phases show good performance.

Acrylonitrile butadiene rubber (NBR) is used in gaskets, for lining valves, in expandable shaft, and has many other engineering applications. It has excellent oil and abrasion resistance, but poor ozone resistance and processibility. Fillers are added to improve its mechanical strength. However, the addition of fillers has some limitations and desired properties cannot be achieved. Hence, the blending of NBR with another polymer like PU can overcome these limitations. PUs are important engineering materials used as barrier materials, sealants, foams, and shoe soles. The blend of these two can exhibit a wide spectrum of properties. The compatibilized blends of NBR–PU can exhibit good damping behavior, and serve as vibration and sound dampers. Attempts in this direction are done by various researchers.

Thomas *et al.* have studied the blends of NBR with polypropylene [2] and poly(ethyl-co-vinyl acetate) [3]. They have investigated the effect of the addition of different fillers and their loading on blend properties. They could also correlate the blend morphology with the variation in dielectric properties and blend composition. Bromitz and Kosfield [4] have reported NBR/phenolic resin blends which were used in abrasion resistant gaskets and cables. The adhesive and composite properties of NBR/phenolic resin blends containing silica filler have been studied by Acharya and Ramaswamy [5]. They observed that the silica filler not only acts as a reinforcing agent, but also as a surface compatibilizer. The same authors have further reported NBR-modified epoxy film adhesives whose performance was observed to improve on addition of interfacial agents [6].

However, the blends of PU and nitrile rubber have been studied to a limited extent. Suresh and Tachil [7] have developed the blends of castor oil based PU and nitrile rubber. Dynamically cured polyether based thermoplastic polyurethane (TPU) and nitrile rubber blends were prepared by Tang *et al.* [8]. Dynamic vulcanization was reported to improve the blend properties significantly. The blends rich in TPU had excellent mechanical properties with the tensile strength higher than that of pure TPU; whereas the blends rich in NBR were reported to show good oil and ozone resistance. The superior physical properties, such as oil resistance at 393°K, resistance to ozone aging, and mechanical properties, of these materials were correlated with blend structures and morphologies [9]. The mechanical properties for these TPU/NBR vulcanizates were much better than those for TPU/NBR simple blend systems. The ultimate tensile strength of the vulcanizates was even better than that of pure TPU, indicating synergistic effect. The same author also studied the synergism of tensile strength in binary heterogeneous polymer blends using PU/nitrile rubber blends as one of the systems [10]. Synergistic effect in tensile strength of the blends was reported when both the components were crosslinked and the adhesive strength of interface exceeded a certain critical value.

Specialty polymer blends of polyurethane elastomers and carboxylated nitrile rubber of different compositions were prepared by three different techniques by Roy *et al*. [11]. The properties of the blends were improved when the NBR was vulcanized with sulfur. The extraction of NBR phase in the solvents was also reduced, due to interchain crosslinking. The blends of natural and nitrile rubbers, as well as their vulcanizates with polyurethane ionomers, were also prepared by Dimitrievski and Malavasic [12]. They studied the influence of the polyurethane ionomers on the blend properties, blend miscibility and on the course and kinetics of vulcanization. Some more reports on PU/NBR blends and their uses in the development of adhesives [13], laminates [14], and textile fibers with oil and solvent resistance [15] are available.

We have developed the blends of NBR and PU with different compositions which were thoroughly characterized for the thermo-mechanical and morphological properties. With a view to enhance the interaction between the two components, hydroxy terminated polybutadiene (HTPB) was used as the soft segment in PU. Effect of carbon black filler on blend properties was also examined.

EXPERIMENTAL

The blends of NBR are either prepared on roll mill or by extrusion. When the blending of NBR is carried out on roll mill, the mastication has to be continued for a long time so as to obtain homogeneous blends. The thermal stability of the PU system derived from hydroxy terminated polybutadiene (HTPB) is lower than that of NBR, to achieve good mixing in a shorter mastication period, we have prepared blends in two steps. In the first step, solution blending of PU and NBR in THF was carried out. These blends were further homogenized on a roll mill.

Materials

Sources of the chemicals used for the synthesis of the blends are given in Table 1. TMP was dried to moisture content less than 0.1%. The other materials were used without further purification.

Preparation of Blends

The required quantity of NBR was dissolved in THF with stirring at room temperature to obtain a 25% (w/v) solution. A mixture of sulphur and the accelerators (tetramethyl thiuram disulphide, TMTD and mercaptobenzo thiazyl disulphide, MBTS) (5 phr) was added to NBR solution along with carbon black and the

Table 1. Chemicals Used for the Synthesis of Blends

Materials	Description	Source
1. Hydroxy terminated polybutadiene (HTPB)	Hydroxyl value: 45.8 mg KOH/g Molecular weight: 2600 Yellowish viscous liquid	Vikram Sarabhai Space Center, Thiruvananthapuram, India
2. Toluene diisocyanate (TDI)	80/20 mixture of 2,4 and 2,6 isomers	Fluka AG, Switzerland
3. 1,1,1-trimethylolpropane (TMP)	PU crosslinker	Fluka AG, Switzerland
4. Nitrile Rubber (NBR)	33 % acrylonitrile	Bayer, Germany

stirring was continued. The PU prepolymer containing HTPB (1 mol) and 3.25 mols of toluene diisocyanate (TDI), was added to this mixture followed by the crosslinker 1,1,1-trimethylol propane (TMP) (1.5 mols) and catalyst dibutyl tin dilaurate (DBTDL). The mixture was stirred to make it homogeneous. The excess THF was distilled off from the system and traces of solvent were removed by drying in vacuum oven. The reaction mass was transferred to a two roll mixing mill for further homogenization. The mastication was continued for 15 minutes. The well-blended sheets obtained at the end of this process were compression molded at 150°C for curing**.** A series of blends with varying compositions of PU, NBR and carbon black were prepared.

Characterization

The synthesized blends were tested for various properties.

Tensile Tests

Stress/strain properties of all the blends were measured on a standard Instron testing machine (No. 4204) using test specimen in the form of dumbbells according to ASTM standard and procedure (D 638). The gauge length was 50.0 mm. The crosshead speed was 10mm/min at 25°C and 50% humidity. The data given are the average of five measurements.

Shore hardness was measured on Frank hardness tester with shore A durometer at several points on the surface of the specimen. An average of 8 measurements was taken as the result.

Thermogravimetric Analysis

TG plots of some selected blends were recorded using DT 30 Shimadzu Thermal Analyzer at a heating rate of 10°C/min in air atmosphere.

Swelling Behavior

The diffusion of selected organic solvents through the blend films was investigated using the conventional sorption method [6]. Various parameters such as swelling coefficient, molecular weight between crosslinks, and degree of crosslinking and crosslink density were calculated

Dynamic Mechanical Analysis

DMA measurements of the selected blends were carried out on a Seiko DMS 200 SDM 5600 analyzer. The samples were 30 mm long and had a cross section area of ca. 1.8 mm^2. The rate of scanning was 2°C/min. The range of temperature in which the analysis was carried out was –100°C to 100°C at the frequencies of 1, 2, 5, and 10 Hz. The nitrogen flow rate was 200 ml/min.

Scanning Electron Microscopy

Surface morphology of blends was examined by using Leica Cambridge, U. K. (stereoscan 440) scanning electron microscope (SEM). Polymer specimens were coated with gold (50 µm thick) in an automatic sputter coater (Polaron Equipment Ltd., USA). The accelerating potential 10 kv was used for the analysis of sample. The photographs of representative areas of the samples were taken at different magnifications.

RESULTS AND DISCUSSION

The NBR/PU blends with 100/00, 90/10, 30/70 (N30), 50/50 (N50), 70/30 (N70), and, 00/100 compositions were prepared. The sulphur and accelerators content was kept constant at 5 phr and that of carbon black was at 15 phr. To study the effect of concentration of carbon black as a filler on blend properties, 50/50 NBR/PU blends were prepared by using 10, 15, 20, and 25 phr of carbon black, and were designated as N 50 (10), N 50 (15), N 50 (20), and N 50 (25), respectively. The blends developed without adding any filler showed poor dimensional stability. Hence, a minimum of 10 phr filler was added to the blends.

Scanning Electron Microscopy

The micrographs of the homopolymers and the blends are shown in Figure 1 (A-G). In 30/70, NBR/PU blend (N30) (Figure 1A) the minor phase, NBR, is dispersed in the major continuous phase, PU, whereas in 50/50 NBR/PU blend (N50) (Figure 1B) the two phases are homogeneously distributed leading to a bicontinu-

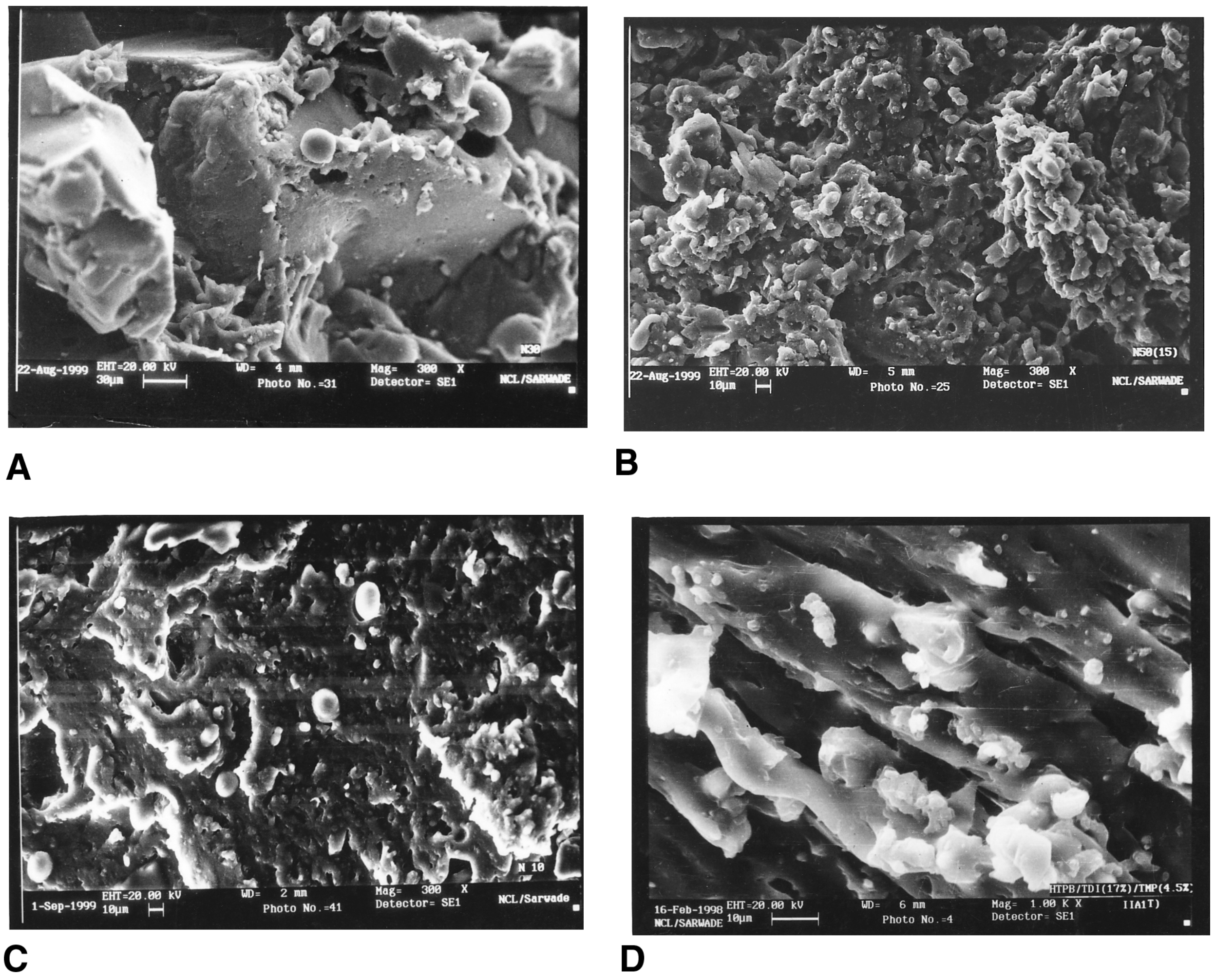

Figure 1. SE micrographs of tensile fractured NBR/PU blends, A: N 30; B: N 50; C: N 70; D: PU; E: NBR; F: N 50 (15); G: N 50 (25).

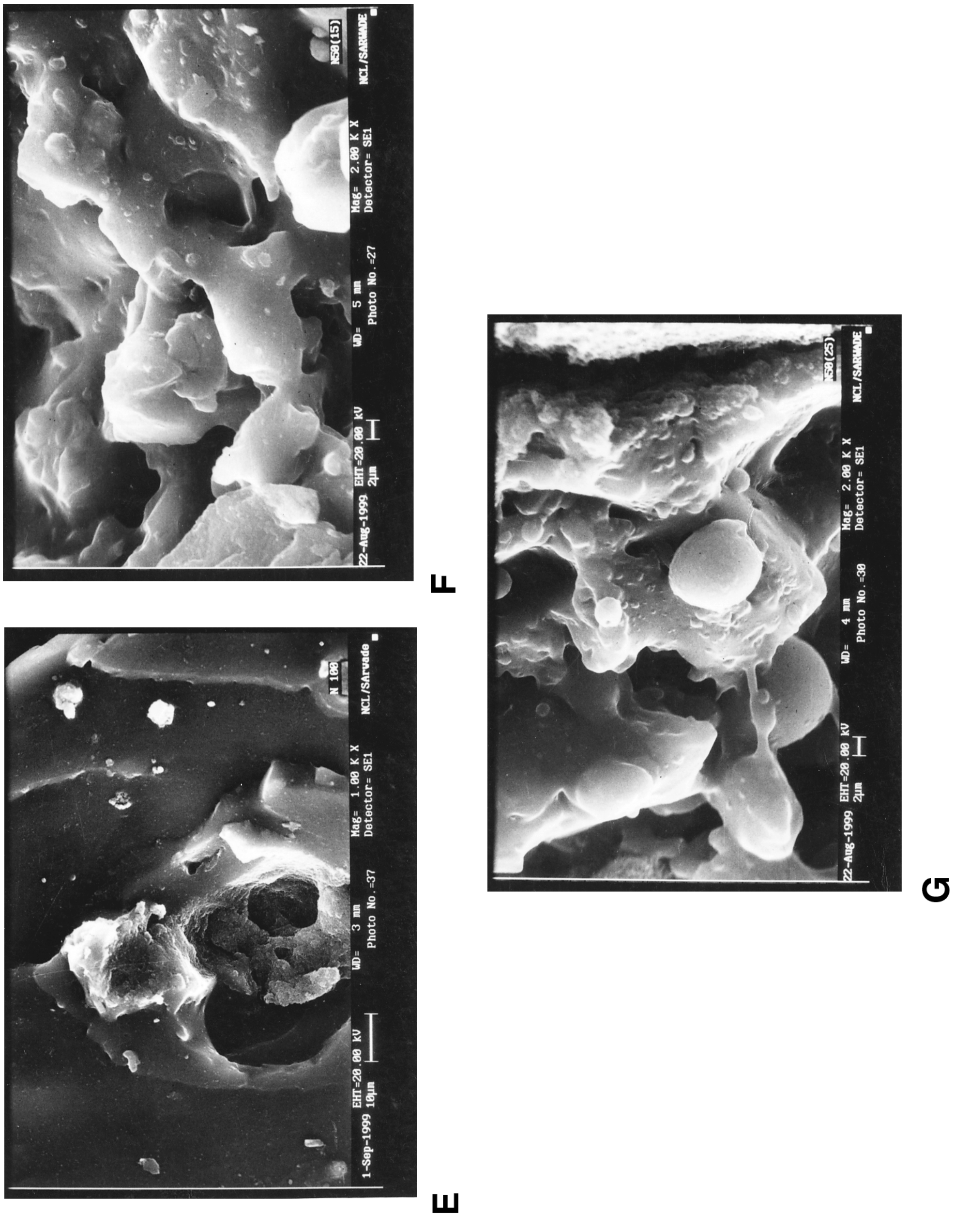

Figure 1. Continued

ous morphology. In N70 (70/30 NBR/PU blend) (Figure 1C), phase inversion takes place and NBR forms the matrix in which the PU is dispersed.

Segmented PU is basically a two-phase system consisting of segregated soft and hard segments. Hence, the tensile fractured rough surface (Figure 1D) indicates a ductile fracture. NBR, on the other hand, exhibits a relatively smooth fracture surface, (Figure 1E) characteristics for rubbers.

Incorporation of carbon black in N50 blends shows little effect on blend morphology as evident from the micrographs of higher magnification (Figure 1 F, G). However, the blends with 15% w/w carbon black showed a more homogenous surface with very small domains (Figure 1B).

Mechanical Properties

The plots of tensile strength and % elongation at break vs. weight percentage of NBR in the blends are shown in the Figure 2. It is observed that the tensile strength of PU is higher than pure NBR but elongation is lower. Hence, tensile strength decreases and elongation increases as more and more NBR is incorporated into PU. The 30/70, NBR/PU blend (N30) shows the highest tensile strength while the 70/30, NBR/PU blend (N70) exhibits highest elongation. This can be correlated with the morphology of this blend. As discussed earlier, in a N30 blend, NBR is dispersed as domains in the continuous PU matrix; while in N50, NBR also begins to form a continuous phase resulting in a co-continuous morphology. In N70, the NBR forms the continuous phase while PU forms the disperse phase. This phase inversion in the morphology of the system from N50 onwards leads to a drastic change in the stress-strain properties of the N30 and N70 blends. Further, the highest tensile strength and elongation at break observed in the case of N30 and N70 blends may be attributed to the existence of satisfactory rubber-matrix adhesion in these compositions, which prevents interfacial de-cohesion [17] as seen from the SEM (Figure 1A & 1C).

Although in the N70 blend, NBR forms the continuous phase, the incorporation of PU leads to a more ductile fracture. Similarly, in N30, incorporation of NBR leads to an increased tensile strength. Thus, synergistic behavior of the two polymers leads to blends with variable stress-strain properties.

Figure 3 shows the effect of variation in carbon black concentration in 50/50 NBR/PU blend. It was observed that with increasing the % of carbon black the tensile strength gradually increases due to the reinforcing effect of the filler. Elongation increases up to 15% of carbon black, which may be attributed to the homogeneous morphology, and decreased particle size as seen in Figure 1 B. But, it decreases with a further increase in carbon black content due to the increasing hardness and hence, rigidity imparted by the filler.

The hardness and the modulus at various % elongations of the blends are given in Table 2 and show a trend similar to the stress strain properties. The incorporation of carbon black filler increases the hardness of the blends. The hardness of the N50 blend containing 10, 15, 20, and 25% filler was found to be 80, 82, 86, 90, respectively.

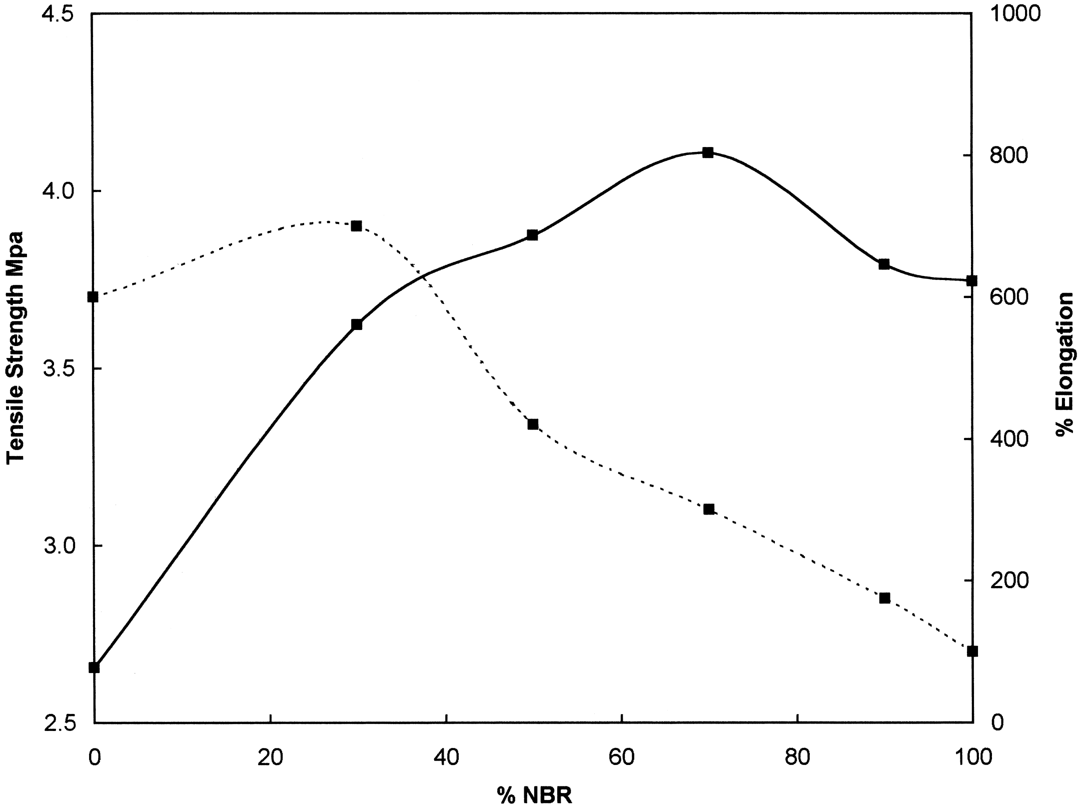

Figure 2. Effect of weight percentage of NBR on tensile strength (---■---) and % elongation (—■—) of the NBR/PU blends.

Thermal Analysis

The results of the thermogravimetric analysis (Figure 4) show that NBR is thermally more stable than the PU network and the thermal stability of the blends lies in between (Figure 4A). All the blends show more or less a similar pattern of degradation. The decomposition starts around 375-400°C and about 75% decomposition takes place at about 700°C. Thus, incorporation of NBR increases the decomposition temperatures and improves the thermal stability of the PU network (Table 3). An increase in the content of carbon black also leads to an increase in the thermal stability of the blends (Figure 4B).

Dynamic Mechanical Analysis

The results of the dynamic mechanical analysis are given in Figures 5-8. The common feature of the linear loss modulus E” or the loss tangent vs. temperature plots is the existence of transition regions between -10 to -75°C, suggesting a rubbery nature of blends above room temperature. The Tg values of the homopoly-

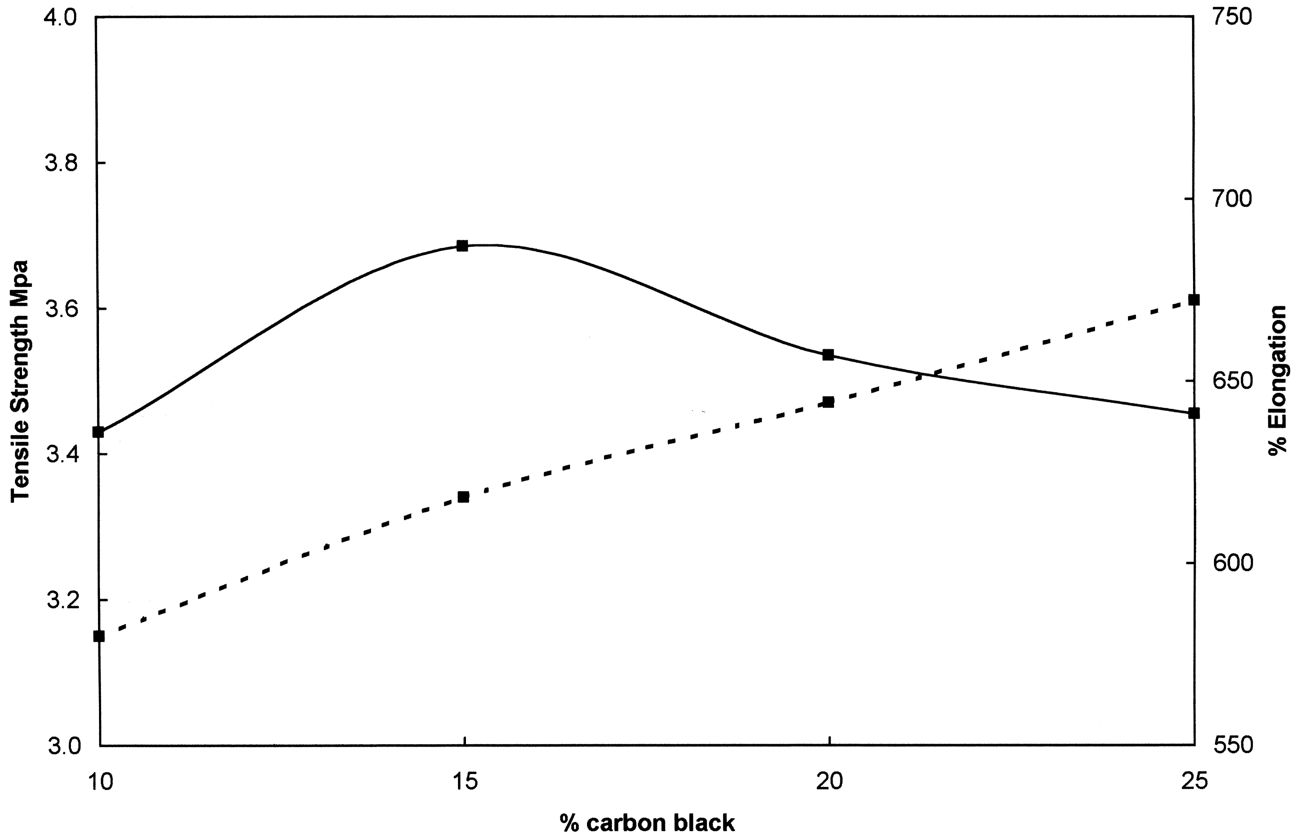

Figure 3. Effect of weight percentage of carbon black tensile strength (---■---) and % elongation (—■—) of the NBR/PU blends.

Table 2. Mechanical Properties of NBR/PU Blends

Code	Modulus at % Elongation 50	100	200	300	400	Shore A Hardness
NBR	0.50	0.80	1.22	1.6	1.94	79
NBR:PU 70:30	0.49	0.78	1.20	1.52	1.86	79
NBR:PU 50:50	0.41	0.63	0.92	1.17	1.40	82
NBR:PU 30:70	0.34	0.53	0.79	0.98	1.14	84
PU	1.31					88

mers and the blends are given in Table 4. Two separate glass transitions were observed for the two components of the blends. However, with an increasing NBR weight percentage, the Tg of the two components shifted higher. This can be attributed to the improved morphology of the N50 and N70 blends. N50 shows a co-continuous morphology with uniformly dispersed phases and very small domains. N70 exhibits the morphology of a ductile fracture. Although a single Tg could not be observed, the shift of the loss peaks to a higher side is an indication of improved compatibility. Figure 6 illustrates the influence of weight percentage of NBR on tan δ_{max}. Not much a variation in tan δ_{max} was observed up to 50% of NBR. However, above 50% of NBR in the blends, the observed sharp increase in tan δ_{max} indicates phase inversion as seen in SEM (Figure 1C). A similar observation was made by Varghese *et al.* [18] for NBR/EVA blends. Thus, the damping behavior of blends increases as the NBR content increases. The glass transition region lies below zero indicating rubbery behavior of these blends above room temperature.

The loss modulus plots (Figure 7) for the blends also showed more or less a similar nature with each phase exhibiting its own separate Tg. The variation of storage modulus of the blends with temperature is shown in Figure 8. This plot also showed the presence of two distinct transitions corresponding to each phase as observed in the case of loss tangent and loss modulus curves. The curves for all the blends have three distinct regions: a glassy region, a transition region, and rub-

Table 3. Decomposition Temperatures of Blends

% Degradation	Temperature °C NBR	NBR:PU 70:30	NBR:PU 50:50	NBR:PU 30:70	PU
1	355	330	325	320	275
5	490	480	470	425	420
25	610	600	600	585	575
50	660	650	625	615	605
60	700	680	650	640	610

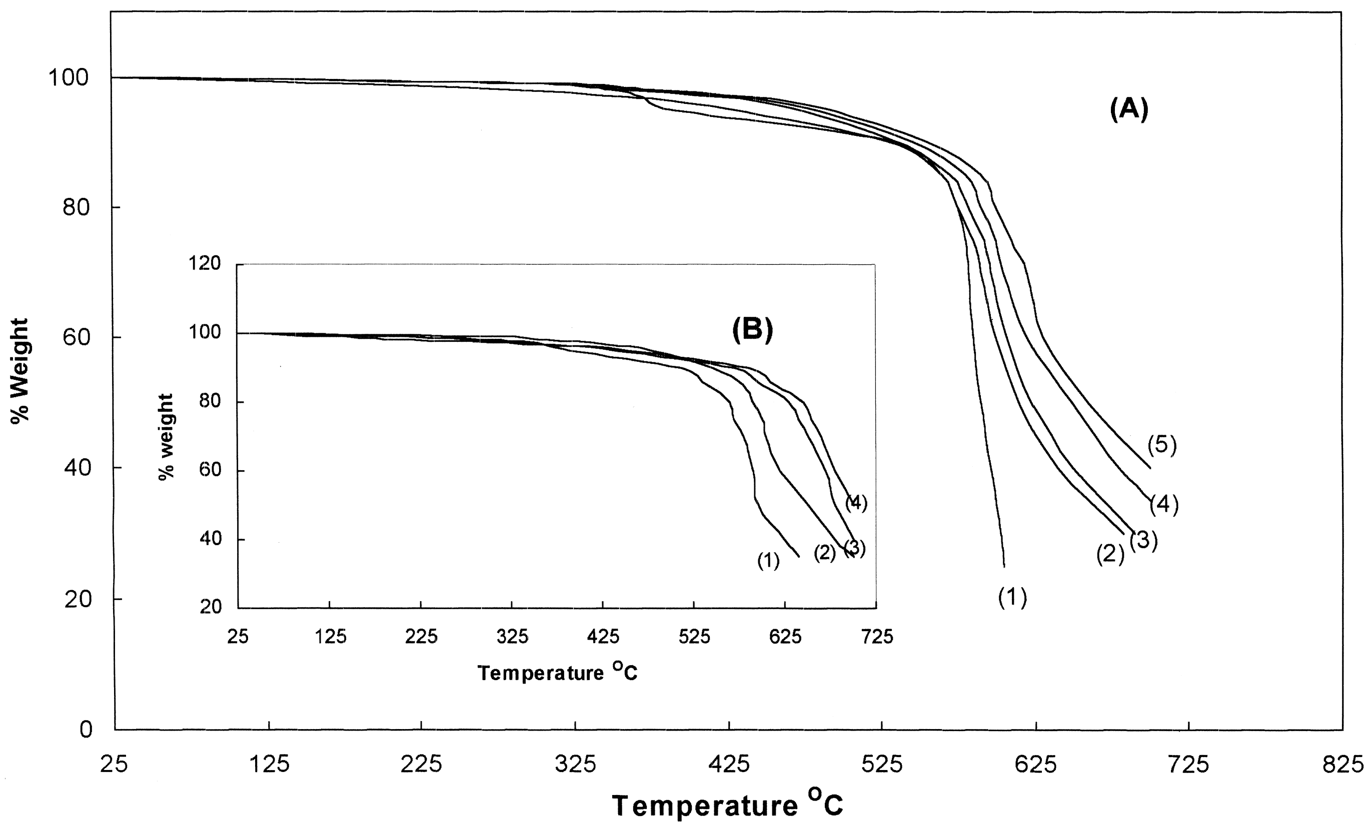

Figure 4. Thermogravimetric curves for: **(A)** Pure polymers and the blends, 1: PU, 2 : N 30; 3 : N 50; 4 : N 70; 5 : NBR. (**B**) 50/50 NBR/PU blends with 10-25% carbon black 1: N 50 (10), 2 : N 50 (15); 3 : N 50 (20); 4 : N 50 (25). the NBR/PU blends.

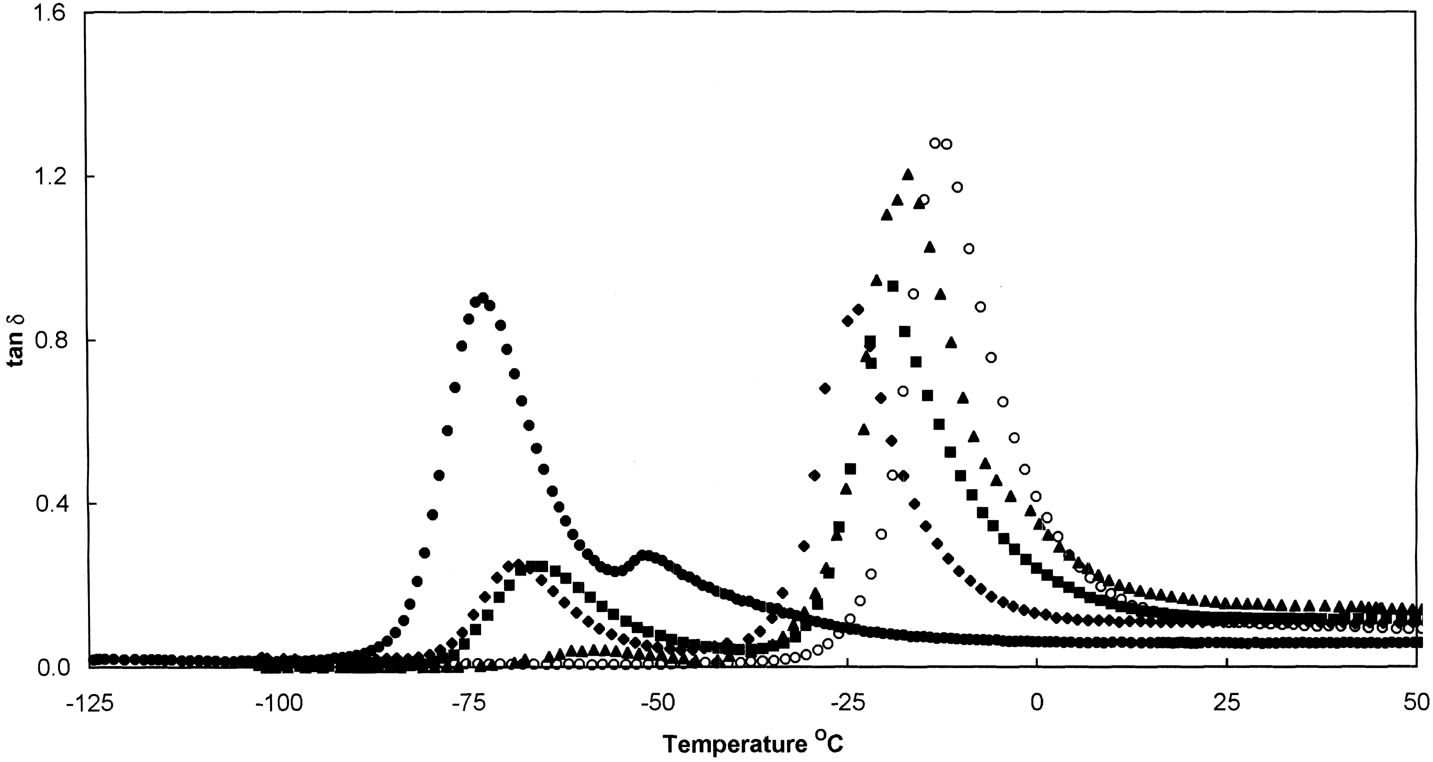

Figure 5. Variation of tan δ with temperature for the NBR/PU blends at 1 Hz. ◆: N 30, ■: N 50, ▲: N 70, ●: PU, ○: NBR.

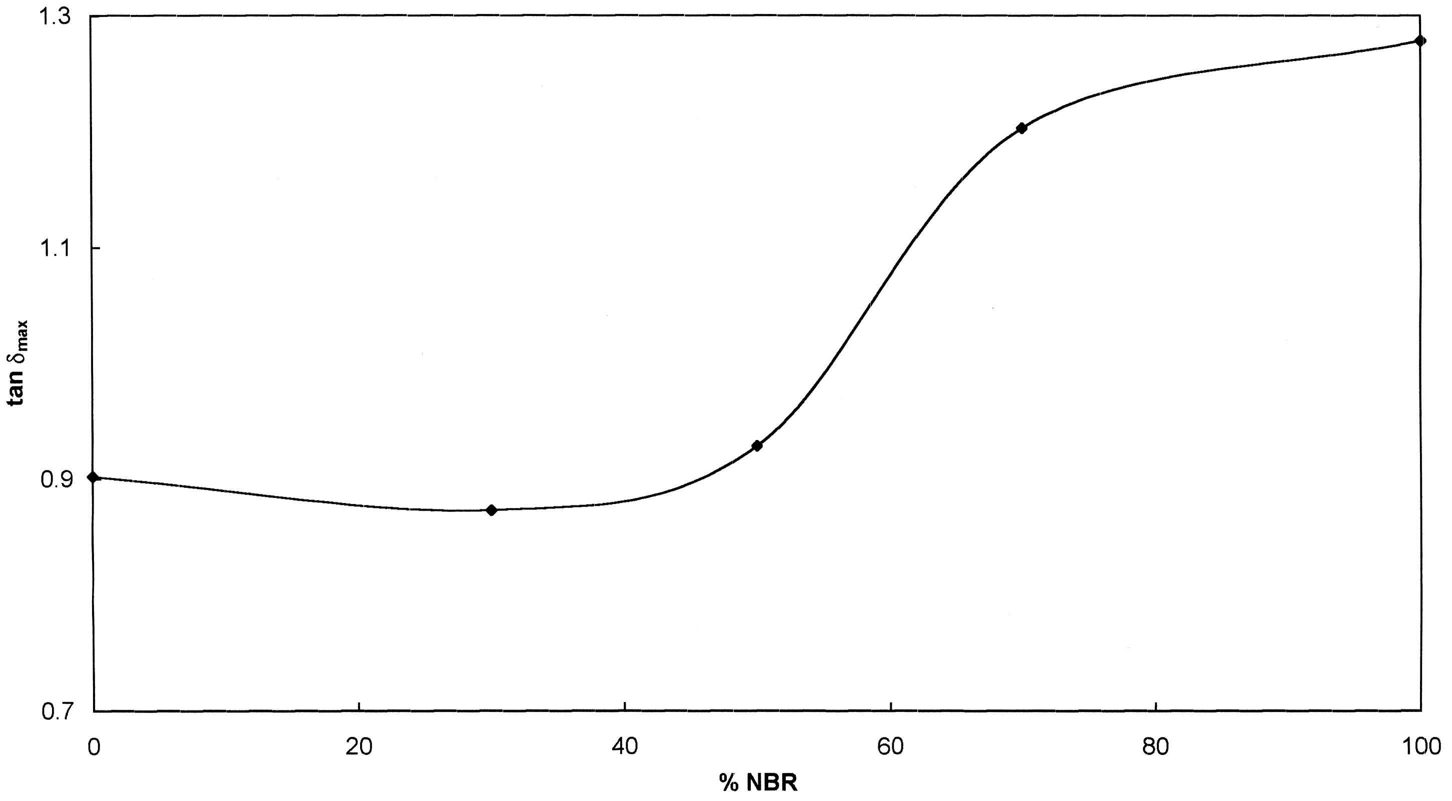

Figure 6. Dependence of tan δ_{max} on the NBR content of the blends.

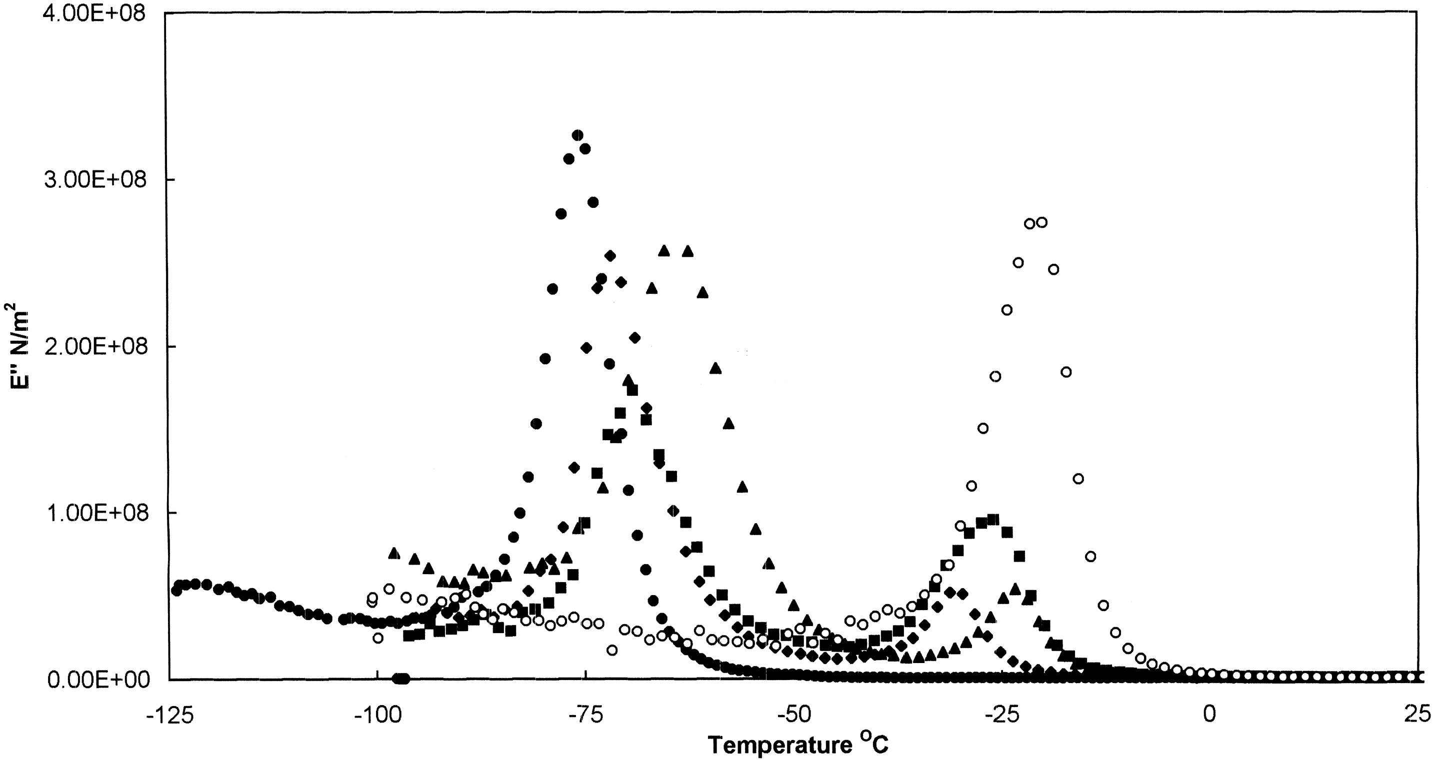

Figure 7. Variation of loss modulus (E”) with temperature for the NBR/PU blends at 1 Hz. ◆: N 30, ■: N 50, ▲: N 70, ●: PU, ○: NBR.

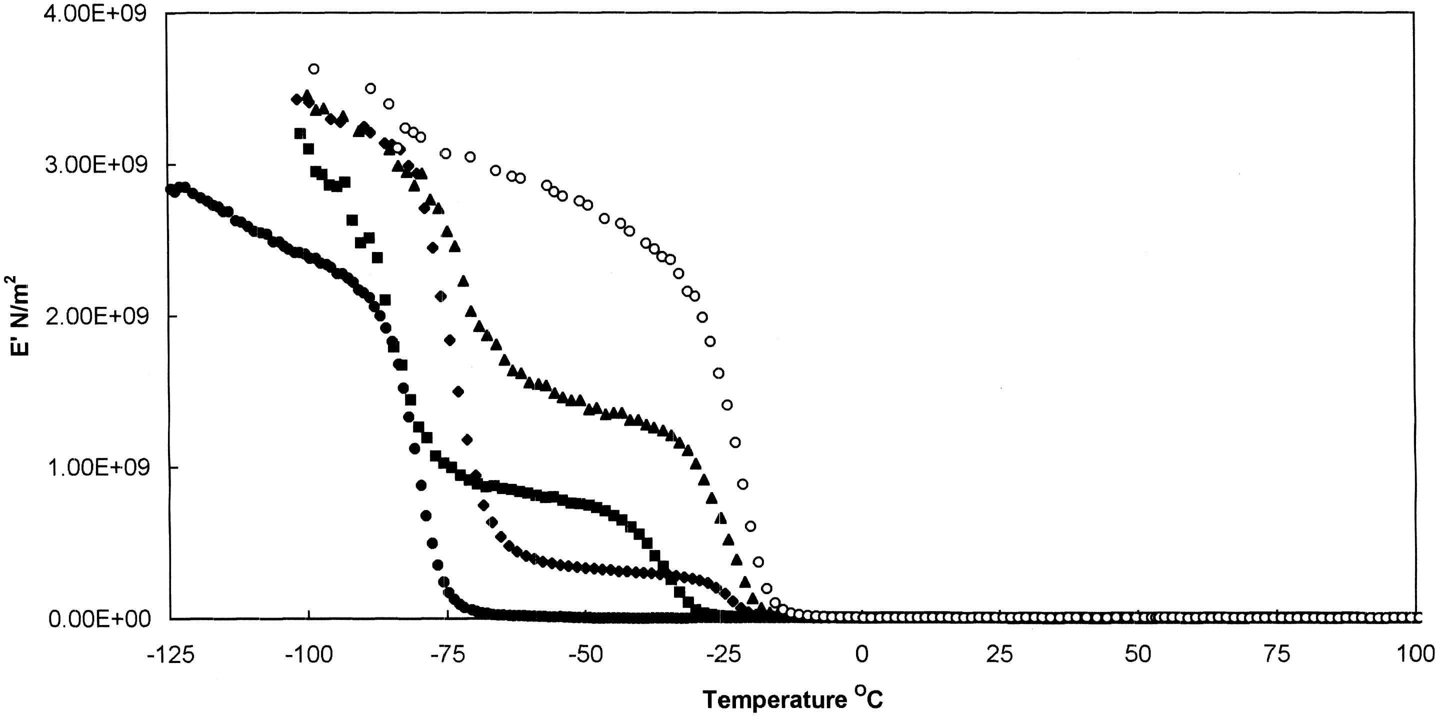

Figure 8. Variation of storage modulus (E') with temperature for the NBR/PU blends at 1 Hz. ◆: N 30, ■: N 50, ▲: N 70, ●: PU, ○: NBR.

Table 4. DMA Data for NBR/PU Blends at 1 Hz

	PU transition			NBR transition		
Code	T_g °C	Tan d_{max}	E_{act} kJ/mol	T_g °C	Tan d_{max}	E_{act} kJ/mol
NBR	_	_	_	−13.2	1.279	254
NBR:PU 70:30	−58.5	0.042	147	−16.8	1.203	237
NBR:PU 50:50	−65.1	0.2449	155	−18.8	0.9285	249
NBR:PU 30:70	−68.3	0.2501	150	−23.4	0.873	368
PU	−72.8	0.902	n. d.	_	_	_

n. d. = Not determined.

bery region. The storage modulus of all the blends showed comparable values in the rubbery region throughout the range of composition because of the amorphous nature of both the materials.

However, in the glassy and transition regions, the storage modulus of NBR was observed to be higher than that of PU, and the blends lie in between.

The activation energy for glass transition was calculated from Equation 1 [19]:

$$\ln \omega_1/\omega_2 = E_A/R\ (\ 1/T_2 - 1/T_1) \tag{1}$$

where ω_1 and ω_2 are the frequencies, and T_1 and T_2 are the T_gs obtained at ω_1 and ω_2, respectively. The results are given in Table 4. It was observed that the energy of activation of NBR transition increases with an increasing PU content in blends, whereas that of the PU transition remained almost constant.

Swelling Behavior

The utility of blends or interpenetrating networks depends upon the transport properties for various solvents. Hence, the sorption of various solvents in the blends showed that nitrile rubber and PU exhibited maximum swelling in carbon tetrachloride and chlorobenzene, respectively. Hence, their solubility parameters were assumed to be 8.6 and 9.5 $(\text{cal/cm}^3)^{1/2}$. However, on account of the oil resistant nature of NBR, its degree of swelling was found to be much lower than PU. Hence, the degree of swelling of the blends was also observed to be lower than that of PU. The molecular weight between crosslinks $\mathbf{M}_C$ was determined from the Flory-Rehner equation [19]. Using values of $\mathbf{M}_C$, the crosslink density $\upsilon_{\mathbf{e}}$ and the degree of crosslinking υ were calculated from the following Equations 2 and 3 [21-23].

$$\upsilon_e = \rho\ /\ \mathbf{M}_C \tag{2}$$

$$\upsilon = 1\ /\ 2\ \mathbf{M}_C \tag{3}$$

Table 5. Swelling Data for NBR/PU Blends in Toluene

Code	Mc	$\nu \times 10^4$	$\nu_e \times 10^4$
NBR	1016	4.90	9.74
NBR:PU 70:30	1296	3.85	7.51
NBR:PU 50:50	1944	2.57	5.01
NBR:PU 30:70	2026	2.46	4.73
PU	2851	1.75	3.23

The swelling data for the blends (Table 5) show that with an increasing NBR content, $\mathbf{M}_C$ decreases and crosslink density increases considerably. The increase in crosslink density indicates an enhanced mixing of the blend components.

However, the presence of the fillers in NBR may not permit the proper swelling of the network for $\mathbf{M}_C$ determination.

CONCLUSION

The studies on PU/NBR blends showed that the two polymers behave synergistically where the incorporation of NBR increases the elongation and incorporation of PU increases the tensile strength. The blends exhibited better mechanical properties than the individual polymers. NBR also improved the thermal stability and solvent resistance of the PU network. The Tgs of the two components also shifted inwards indicating increasing miscibility. Incorporation of the carbon black filler led to an increase in the tensile strength and hardness due to its reinforcing effect. The morphology of the 50/50, NBR/PU blend containing 15% carbon black showed bicontinuous morphology with very small domain size.

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