Chapter 3

Polyurethane /Nitrile Rubber Blends

INDEX

Page No.

3.1 Introduction

Blending of polymers offers a means of producing new materials with tailored properties and has been extensively used in plastics, rubbers, composites, 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 good adhesion between phases exhibit good properties.

Acrylonitrile butadiene rubber (NBR) has excellent oil and abrasion resistance but poor ozone resistance. Hence blending of NBR with other polymers is desirable. 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 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 reinforcing agent but also as 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 were reported to have 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 ageing, and mechanical properties, of these materials were correlated with blend structures and morphologies[9]. The mechanical properties of these TPU / NBR vulcanizates were much better than those of TPU / NBR simple blend systems. The ultimate tensile strength of the vulcanizates was reported to be better than that of pure TPU, indicating synergistic effect. The same author also reported the synergism in tensile strength of binary heterogeneous polymer blends composed of PU - nitrile rubber blends as one of the components[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.

Onoue et al[11] have developed rubber containing laminates of polyurethanes with peeling strength 1.5 kg/cm. The peel strength without NBR was found to be 0.3 kg/cm. Yanagusawa et al[12] have reported good flexibility and alkali resistance for the adhesives derived from polyurethane, nitrile rubber, epoxy resins and polyamines. Carboxyl-modified nitrile rubber compositions containing PUs were developed by Saito et al[13], for the treatment of fibers for oil and solvent resistance.

Specialty polymer blends of polyurethane elastomers and carboxylated nitrile rubber of different compositions were prepared by three different techniques by Roy et al[14]. The properties of the blends were reported to be improved when the NBR was vulcanized with sulfur. The extant of extraction of NBR phase in the solvents was also reported to be reduced, due to interchain crosslinking. The blends of natural and nitrile rubbers, as well as their vulcanizates with polyurethane ionomers, were prepared by Dimitrievski and Malavasic[15]. They studied the influence of the polyurethane ionomers on the blend properties, blend miscibility and on the course and kinetics of vulcanization. The same authors have investigated the effect of PU-NBR interactions on dynamic mechanical properties of the blends[16].

Usually, reinforcement in rubber compounds is achieved by the use of carbon black as well as non carbon black fillers. Fillers are used to modify the processing characteristics and mechanical properties and also to reduce the shrinkage and to increase the modulus and hardness. The filler interphase distribution in elastomer blends has been reported by several authors[17-20].

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.

3.2 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 PU system derived from hydroxy terminated polybutadiene (HTPB) being 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.

3.2.1 Materials and purification

The nitrile rubber with 33 % acrylonitrile content, from Bayer, Germany was used as received. Other sources of the chemicals used for the synthesis of the blends are given in section 1.3.1.

3.2.2 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 stirring was continued. The PU prepolymer containing 1 mole HTPB and 3.25 moles of toluene diisocyanate (TDI), was added to this mixture followed by the addition of 1.5 moles of crosslinker 1,1,1-trimethylol propane (TMP) and catalyst dibutyl tin dilaurate (DBTDL). The mixture was stirred to make it homogeneous. Excess of 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.

3.2.3 Characterization

The synthesized blends were tested for tensile mechanical properties, shore A hardness, fractured surface morphology, thermal stability, visco-elastic properties and transport properties in solvents by the procedure described in section 1.3.3.

3.3 Results And Discussion

The NBR / PU blends with 100 / 00, 90 / 10 (N90), 70 / 30 (N70), 50 / 50 (N50), 30 / 70 (N30) and 00 / 100 compositions were prepared as described earlier. 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 the blends were designated as N50 (10), N50 (15), N50 (20) and N50 (25) respectively. The blends developed without adding any filler showed poor dimensional stability. Hence a minimum of 10 phr filler was added to all the blends.

3.3.1 Scanning Electron Microscopy

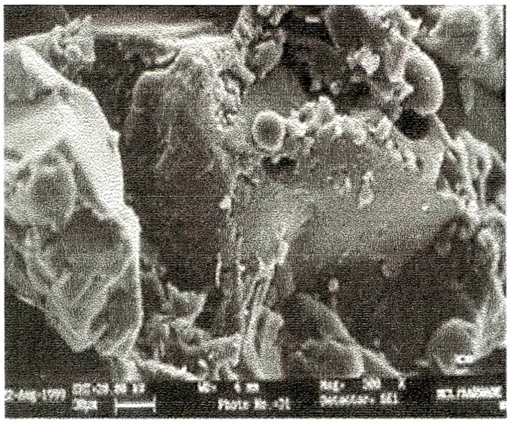
The electron micrographs of the fractured surfaces of homopolymers and the blends are shown in Fig. 3.1 (A-G). In 30/70, NBR/PU blend (N30) (Fig. 3.1A) the minor phase, NBR, is dispersed in the major continuous phase PU, whereas in 50 / 50 NBR / PU blend (N50) (Fig. 3.1B) the two phases are homogeneously distributed leading to a bicontinuous morphology. In N70 (70 / 30 NBR / PU blend) (Fig. 3.1C) 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 (Fig. 3.1D) indicates a ductile fracture. NBR, on the other hand, exhibits relatively smooth fracture surface, (Fig.3.1E) characteristics for rubbers.

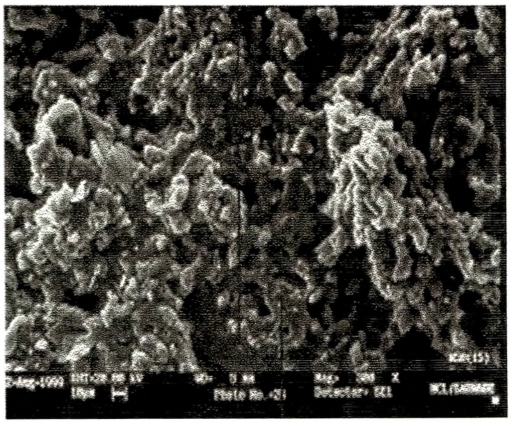
Incorporation of carbon black in N50 blends shows little effect on blend morphology as evident from the micrographs of higher magnification (Fig. 3.1F, G). However, the blends with 15% w / w carbon black showed more homogenous surface with very small domains (Fig. 3.1B).

3.3.2 Mechanical Properties

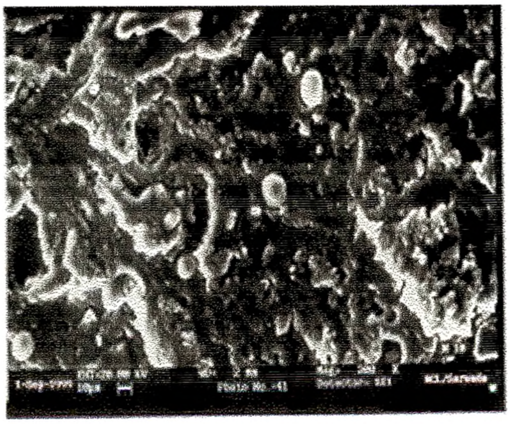
The plots of tensile strength and % elongation at break vs. weight percentage of NBR in the blends are shown in the Fig. 3.2. It is observed that PU has higher tensile strength and lower elongation than pure NBR. Hence tensile strength decreases and elongation increases as more and more NBR is incorporated into PU. The 30/70,



(A) : N30 (300 X)

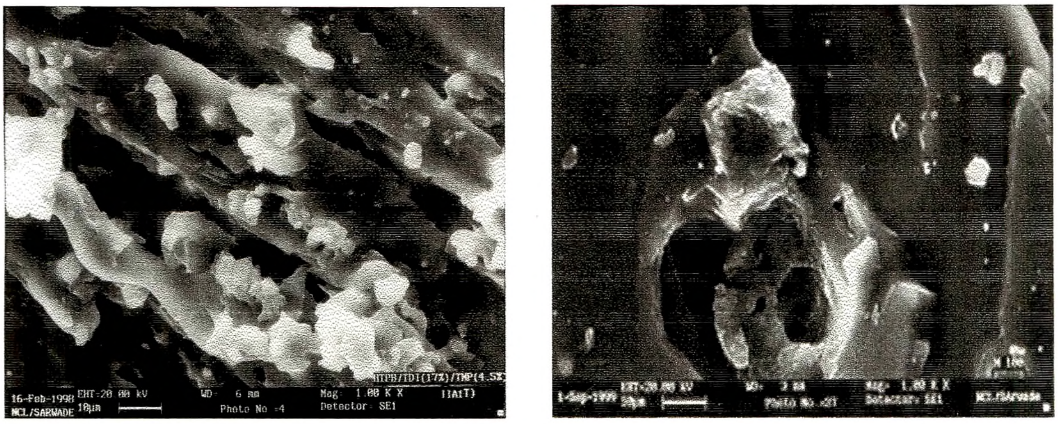


(B) : N50(15) (300 X)



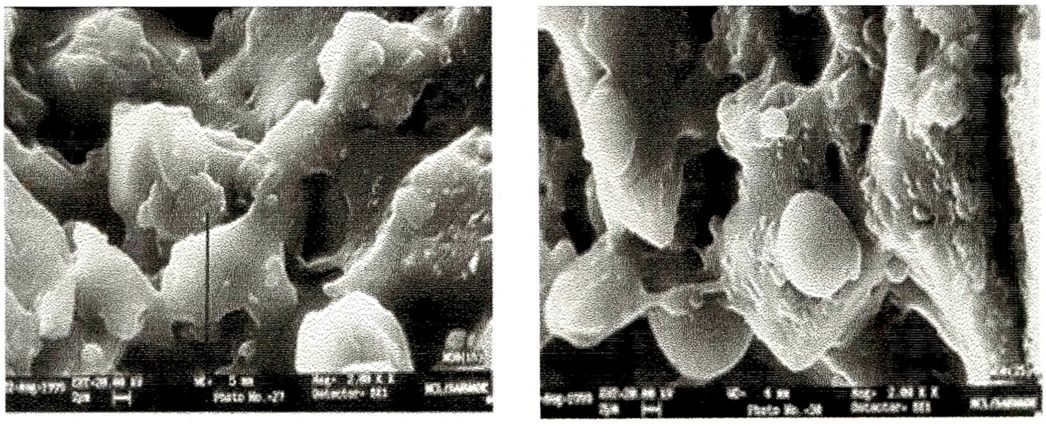
(C) : N70 (300 X)

Fig. 3.1 : SE Micrographs of tensile fractured surfaces



(D) : PU (1K X)

(E) : NBR (1K X)



(F) : N50 (10) (2 K X)

(G) : N50 (25) (2K X)

Fig. 3.1 : SE Micrographs of tensile fractured surfaces

NBR / PU blend (N30) shows highest tensile strength while the 70/30, NBR / PU blend (N70) exhibits highest elongation. This can be explained from the morphology of these blends. As discussed earlier, in 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 respectively may be attributed to the existence of satisfactory rubber-matrix adhesion in these compositions, which prevents interfacial de-cohesion[21] as seen from the SEM (Fig. 3.1A and 3.1C).

Although in 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 increased tensile strength. Thus, synergistic behavior of the two polymers leads to blends with variable stress-strain properties.

Fig.3.3 shows the effect of variation in carbon black concentration in 50/50 NBR / PU blend. It was observed that with increasing % of carbon black the tensile strength gradually increases due to the reinforcing effect of the filler. However, elongation increases up to 15 % of carbon black and then decreases. This may be attributed to the homogeneous morphology and decreased particle size as seen in Fig. 3.1 B.

HANSA MEHTA LIBRARY

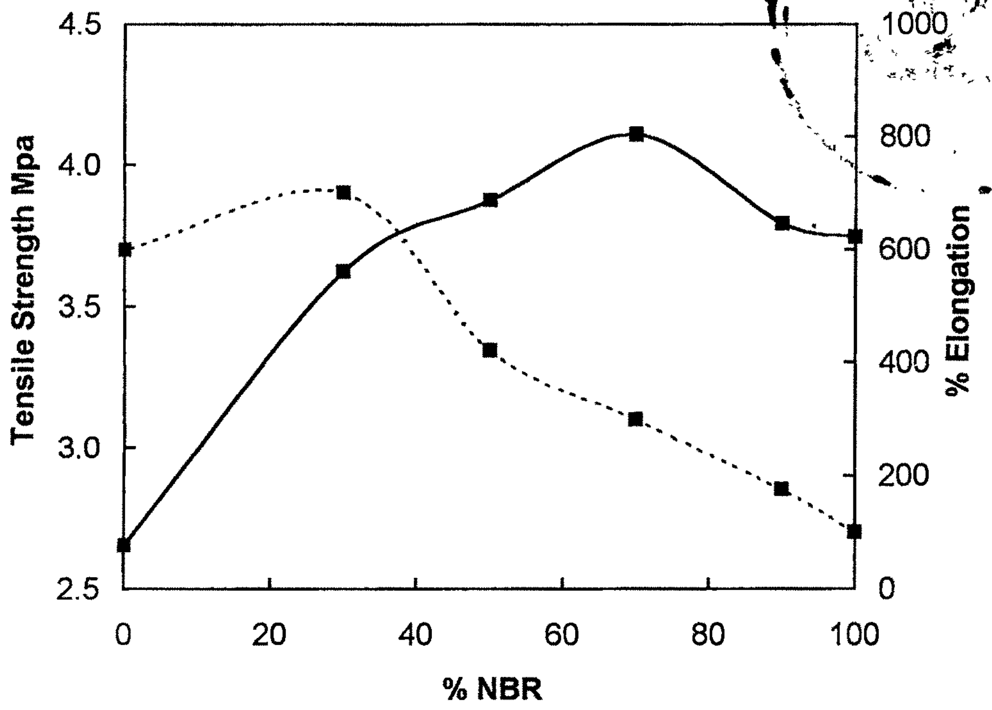


Fig. 3.2 : Effect of weight percentage of NBR on tensile strength (---■---) and % elongation (—■—) of the NBR/PU blends.

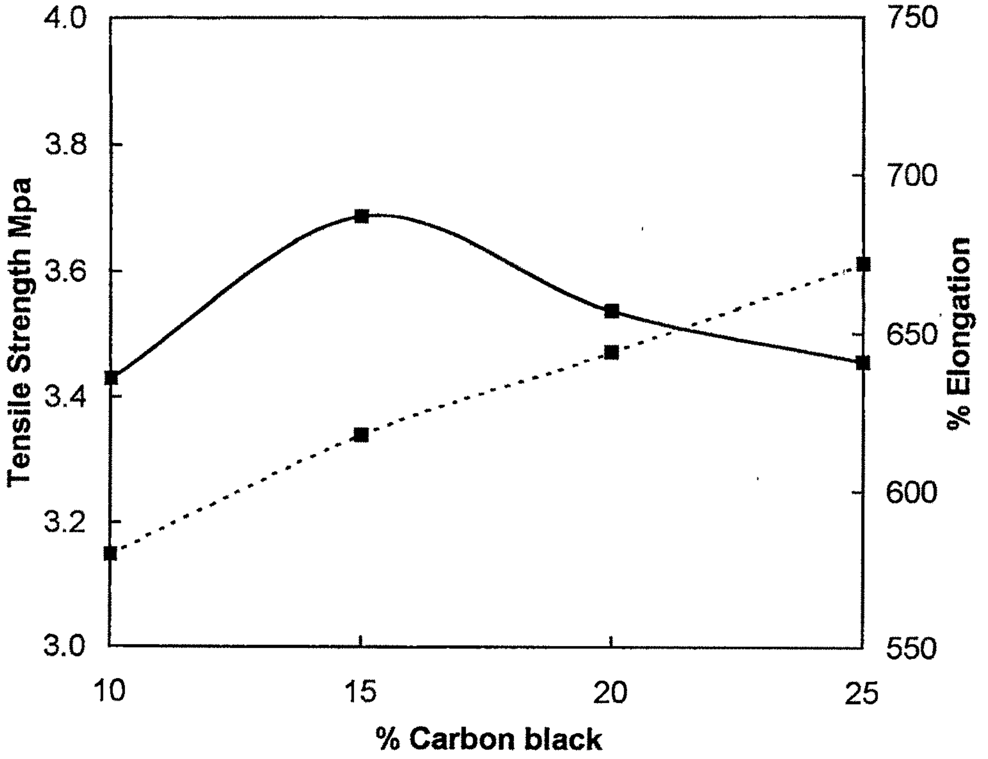


Fig.3.3 : Effect of weight percentage of carbon black on tensile strength (---■---) and % elongation (—■—) of 50 : 50 NBR/ PU blends.

The hardness and the modulus at various % elongations of the blends are given in Table 3.1 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 N50 blend containing 10, 15, 20 and 25 % filler was found to be 80, 82, 86, 90 respectively.

Table 3.1: Mechanical properties of NBR / PU blends.

Code	Modulus at % elongation					Shore A Hardness
	50	100	200	300	400	
NBR	0.50	0.80	1.22	1.6	1.94	79
N70	0.49	0.78	1.20	1.52	1.86	79
N50	0.41	0.63	0.92	1.17	1.40	82
N30	0.34	0.53	0.79	0.98	1.14	84
PU	1.31	-	-	-	-	88

3.3.3 Thermal Analysis

The results of the thermo-gravimetric analysis (Fig. 3.4A) show that NBR is thermally more stable than the PU network and the thermal stability of the blends lies in between. All the blends show more or less similar pattern of degradation. The decomposition starts around 375 - 400 °C and about 60 % decomposition takes place at about 650 °C. Thus incorporation of NBR increases the decomposition temperatures and improves the thermal stability of the PU network (Table 3.2). Increase in the content of carbon black also leads to an increase in the thermal stability of the blends (Fig. 3.4B).

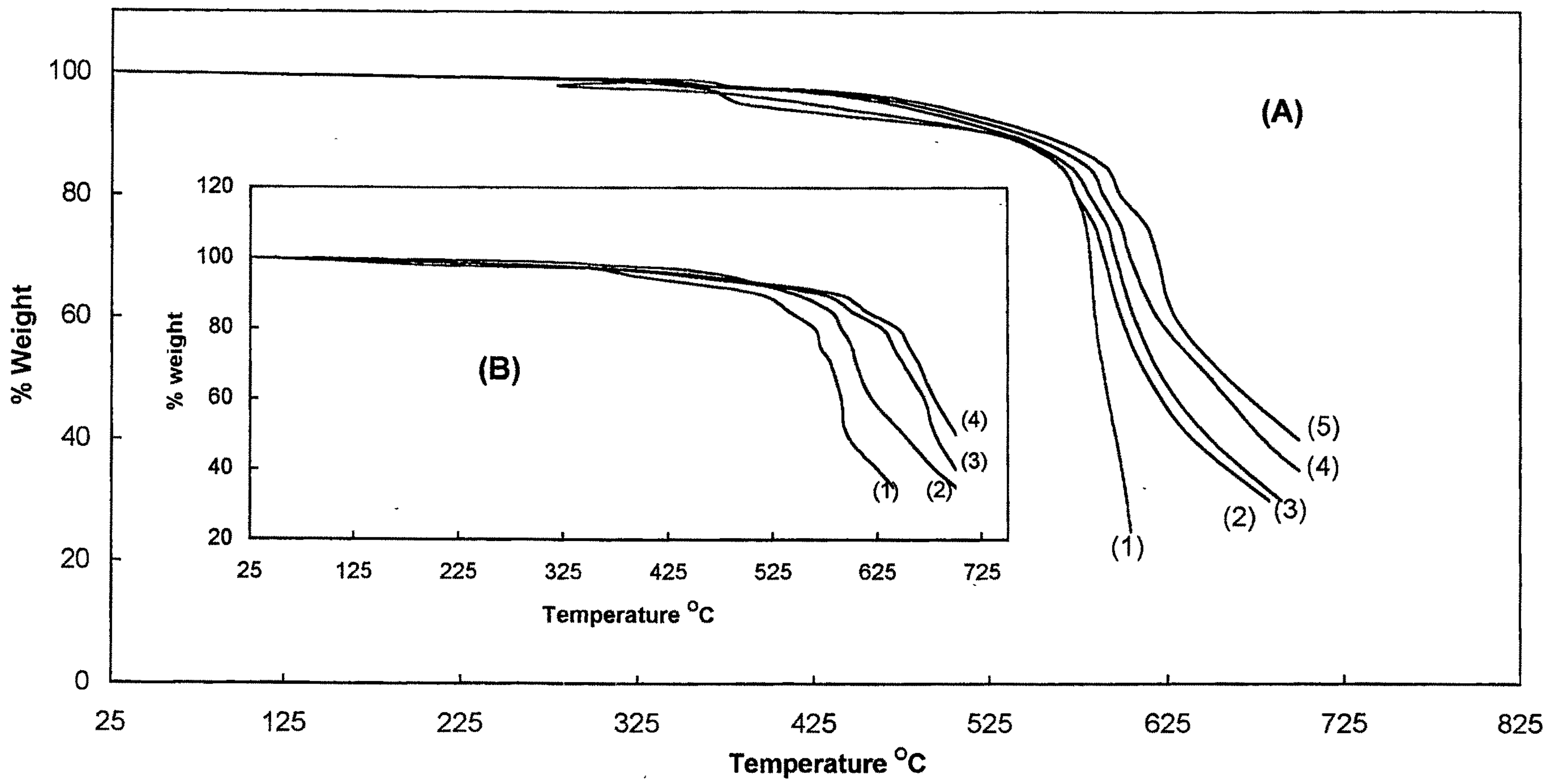


Fig. 3.4 : Thermogravimetric plots for (A) (1) PU, (2) N30, (3) N 50, (4) N70, (5) NBR and (B) N50 blends with (1) 10 , (2) 15 , (3) 20 , (4) 25 weight % of carbon black

Table 3.2 : Decomposition temperatures of blends and homopolymers

% Degradation	Temperature °C				
	NBR	**N70**	**N50**	**N30**	**PU**
1	355	330	325	320	295
5	490	480	470	425	385
25	630	600	600	585	575
50	660	650	625	615	590
60	700	680	650	640	605

3.3.4 Dynamic Mechanical Analysis

The results of the dynamic mechanical analysis are given in Fig. 3.5 - 3.8. The common feature of the linear loss modulus E” or the loss tangent vs. temperature plots is the existence of glass transition regions between - 10 to - 75 °C, suggesting rubbery nature of blends above room temperature. The Tg values of the homopolymers and the blends are given in the Table 3.4. Two separate glass transitions were observed for the two components of the blends. However, with increasing NBR weight percentage, the Tg of the two components shifted inwards. This can be attributed to the improved miscibility of the N50 and N70 blends. N50 shows a co-continuous morphology with uniformly dispersed very small domains. N70 exhibits the morphology of a ductile fracture. Although a single Tg could not be observed, the inward shift of the loss peaks is an indication of improved compatibility. Fig. 3.6 illustrates the influence of weight percentage of NBR on tan δ_{max}. Up to 50 % of NBR not much variation in tan δ_{max} was observed. However, above 50 % of

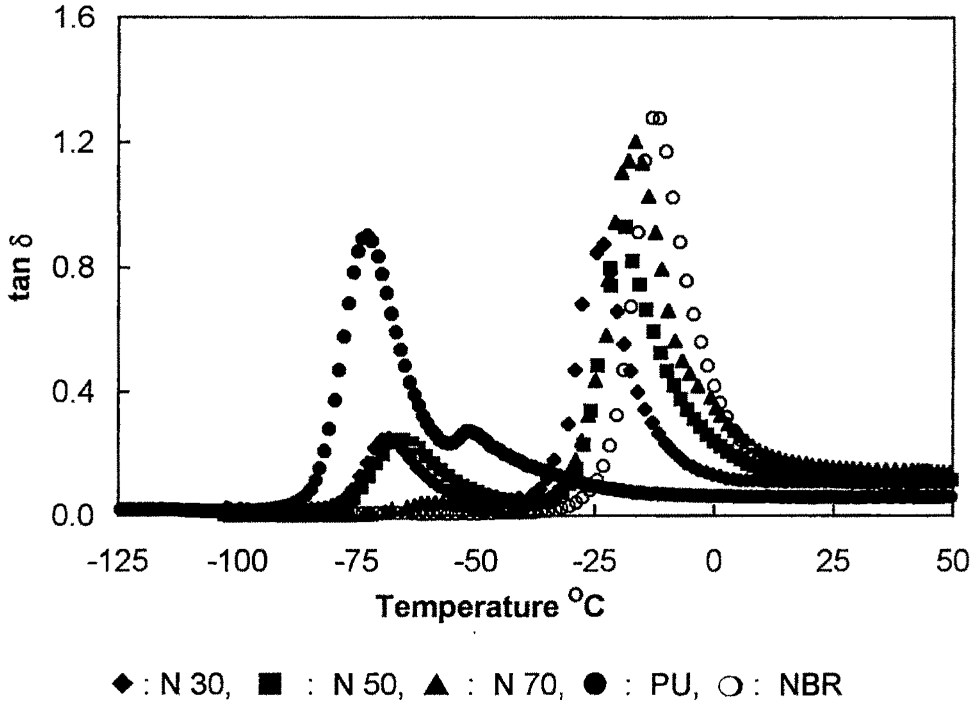


Fig. 3.5 . Variation of tan δ with temperature for the NBR / PU blends at 1 Hz.

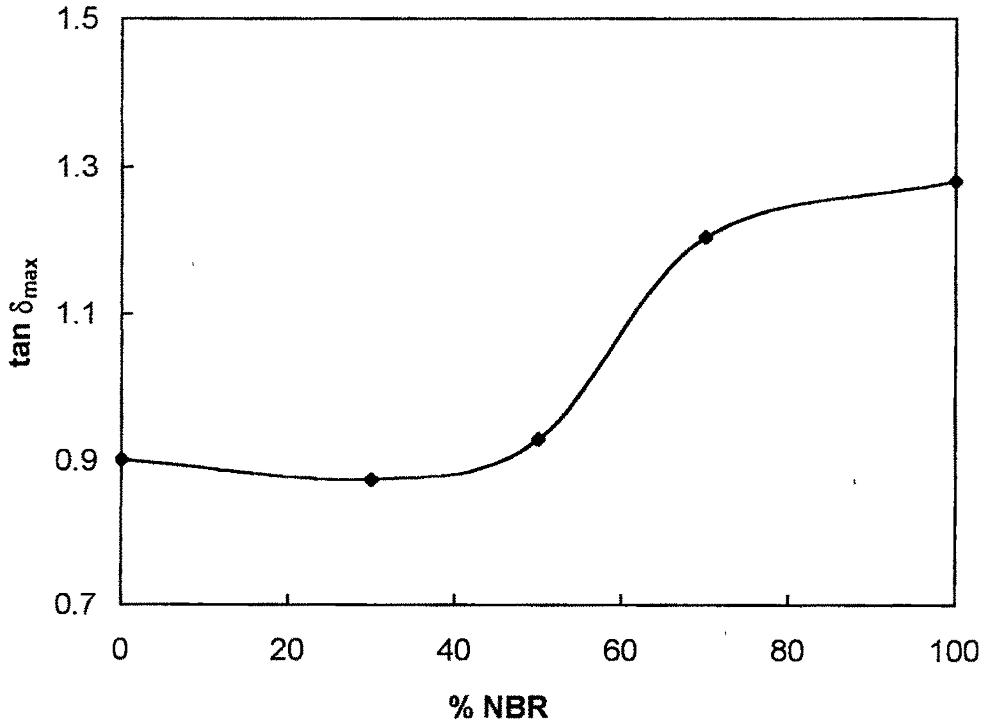


Fig. 3.6 : Dependence of tan δmax on the NBR content of the blends.

NBR in the blends, the observed sharp increase in tan δ_{max} indicates phase inversion as seen in SEM (Fig. 3.1C). Similar observation was made by Varghese et al[22] 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.

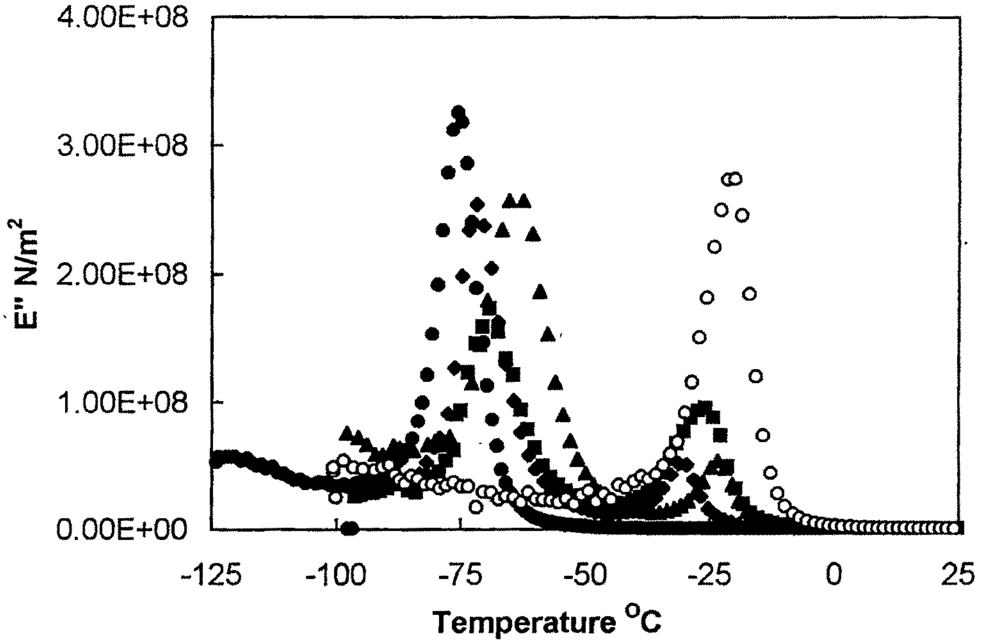
The loss modulus plots (Fig. 3.7) for the blends also showed more or less similar nature with each phase exhibiting its own separate Tg. The variation of storage modulus of the blends with temperature is shown in Fig. 3.8. This plot also showed presence of two distinct transitions corresponding to each 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 rubbery 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 the transition regions, the storage modulus of NBR was observed to be higher than that of PU and those of blends lie in between.

The results of the activation energy for glass transition calculated from the equation mentioned in section 1.4.6 are given in Table 3.3.

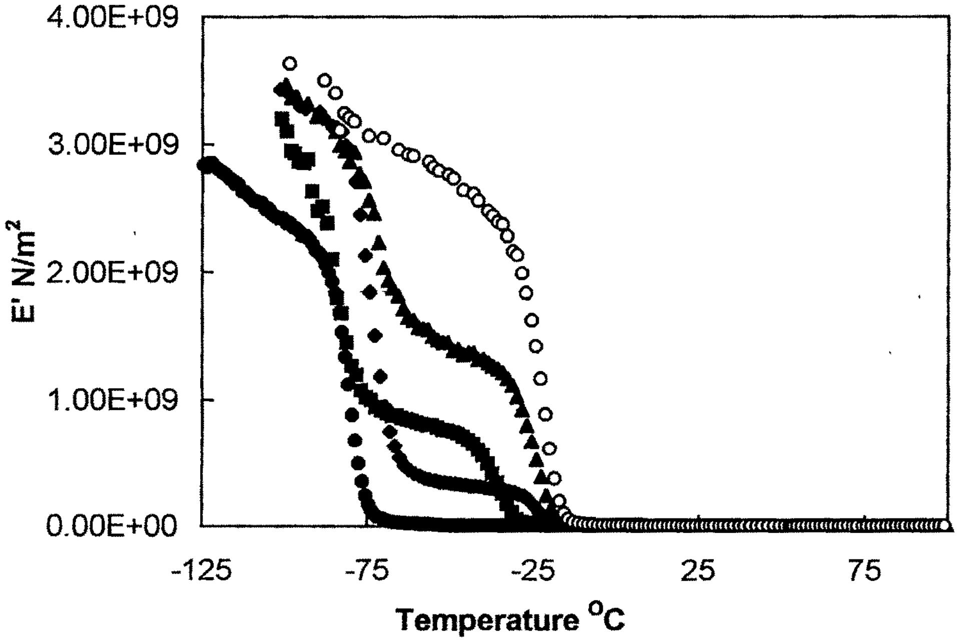
Composite models for DMA

Several mathematical relations represent the variations in dynamic mechanical modulus with composition in polyblends, one of the simplest being the logarithmic additivity rule of mixtures[23,24] i.e.



◆ : N 30, ■ : N 50, ▲ : N 70, ● : PU, ○ : NBR

Fig. 3.7 : Variation of loss modulus (E") with temperature for the NBR/PU blends at 1 Hz.



◆ : N 30, ■ : N 50, ▲ : N 70, ● : PU, ○ : NBR

Fig. 3.8 : Variation of storage modulus (E') with temperature for the NBR/PU blends at 1 Hz.

$$E' = [(1 - \phi_2) / E'_1 + \phi_2 / E'_2]^{-1} \quad (1)$$

Where ϕ_1 and ϕ_2 are the volume fractions of component 1 and 2 respectively and E'_1 and E'_2 are the storage modulus of each component.

Table : 3.3 DMA data for NBR / PU blends at 1 Hz

Code	PU transition			NBR transition		
	T_g °C	tan δ_{max}	E_{act} kJ /mol	T_g °C	tan δ_{max}	E_{act} kJ /mol
NBR	_	_	_	-13.2	1.279	254
N70	-58.5	0.042	147	-16.8	1.203	237
N50	-65.1	0.2449	155	-18.8	0.9285	249
N30	-68.3	0.2501	150	-23.4	0.873	368
PU	-72.8	0.902	n. d.	_	_	_

n. d. - Not determined

As per Takayanagi's parallel model[26], if the glassy component is the continuous phase, a plot of storage modulus (E') vs. volume fraction (ϕ) at a fixed temperature shows positive deviation from the logarithmic additivity rule, as per the equation

$$E' = (1 - \phi_2) E'_1 + \phi_2 E'_2 \quad (2)$$

As per Takayanagi's series model,[26] if the elastomeric component, polyurethane is the continuous phase, a similar plot would show a negative deviation from the logarithmic additivity rule according to the equation

$$E' = [(1 - \phi_2) / E'_1 + \phi_2 / E'_2]^{-1} \qquad (3)$$

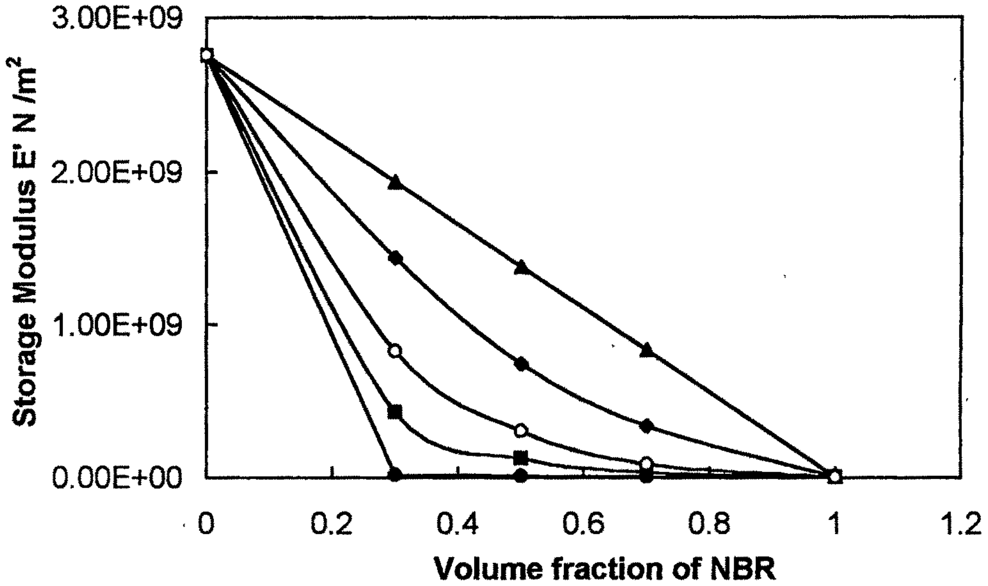
When both the components form co-continuous phase Davie's model is used to calculate storage modulus as a function of volume fraction[26] i.e.

$$E'^{1/5} = (1 - \phi_2) E'^{1/5}_1 + \phi_2 E'^{1/5}_2 \qquad (4)$$

Fig. 3.9 and 3.10 show storage modulus vs. volume fraction plots for the PU / NBR blends at –30 °C and –60 °C. it was observed that at this temperature, NBR behaves as the glassy component and PU behaves as the rubbery component. It was observed that at –60 °C, the experimental points show positive deviation from the logarithmic additivity rule of mixtures and are located between the line corresponding to the Davie's model and the Takayanagi's Series model. At –30 °C, the experimental points lie more close to the Davie's model, At 50:50 composition the experimental point coincides with the logarithmic additivity point. This indicates that the components in the blends are extensively mixed. Thus these models support the synergistic behaviour of the blend components although a direct agreement with the DMA and SEM results is not observed.

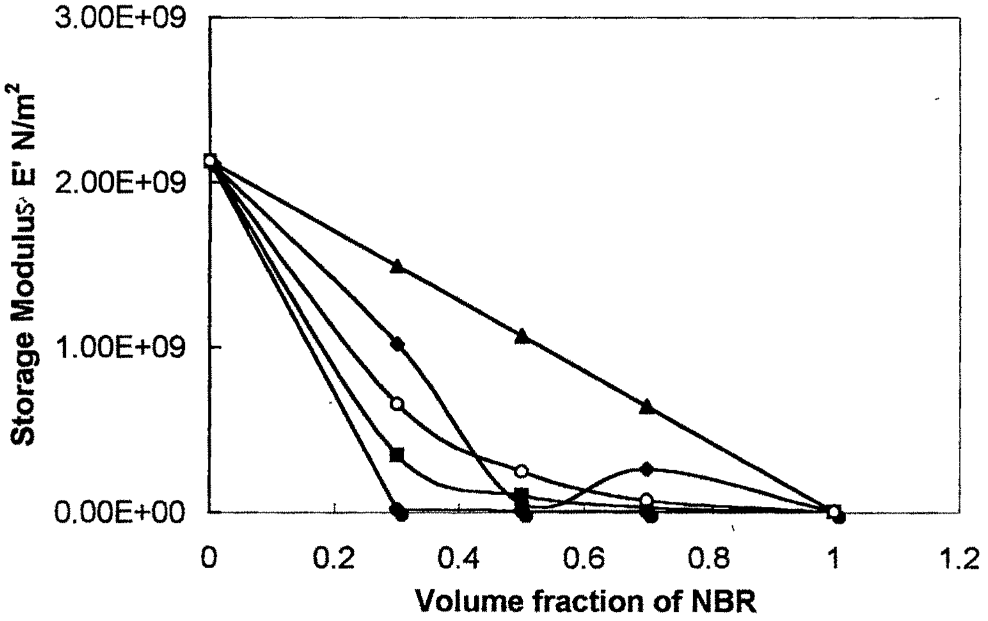
3.3.5 Swelling behavior

Utility of blends or interpenetrating networks depends upon the transport properties for various solvents. 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



◆ : Experimental., ■ : Logarithmic additivity rule,
▲ : Takayanagi's parallel model, ● : Takayanagi's series model,,
○ : Davie's model

Fig. 3.9 :Data Fitting in various models for storage modulus at - 50 °C



◆ : Experimental., ■ : Logarithmic additivity rule,
▲ : Takayanagi's parallel model, ● : Takayanagi's series model,,
○ : Davie's model

Fig. 3.10 : Data Fitting in various models for storage modulus at - 30 °C

8.6 and 9.5 (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. As a result the degree of swelling of the blends was also observed to be lower than that of PU. The molecular weight between crosslinks M_C was determined from the Flory - Rehner equation (section 1.4.5). Using values of M_C, the crosslink density υ_e and the degree of crosslinking υ were calculated[27].

The swelling data for the blends (Table 3.4) show that with increasing NBR content, M_C decreases and crosslink density increases considerably. However, the presence of the fillers in NBR may not permit the proper swelling of the network for M_C determination.

Table : 3.4 Swelling data for NBR /PU blends in Toluene

Code	Mc	ν X 10^4	ν_e X 10^4
NBR	1016	4.90	9.74
N70	1296	3.85	7.51
N50	1944	2.57	5.01
N30	2026	2.46	4.73
PU	2851	1.75	3.23

3.4 Conclusion

The studies on PU / NBR blends showed that the two polymers show synergistic effect on their properties. The incorporation of NBR increases the elongation and incorporation of PU increases the tensile strength. The blends exhibited better mechanical properties than the individual polymer. 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.

Though PUs and their IPNs have wide spectrum of applications, which has made them technologically and industrially important products, non-biodegradability is restricting their utility in commodity applications. Hence the possibility of converting them into partially biodegradable products is investigated in the next chapter.

References

1. Paul D. R. and Barlow J. W., in Multiphase Polymers, Cooper S. L. and Estes G. M., Eds., *Advances in Chemistry Series* 176, American Chemical Society, Washington, DC, 315,1979.
2. George S., Varughese K. T. and Thomas S., *J. Appl. Polym. Sci.*, **73**, 255, 1999.
3. Varghese H., Bhagwan S. S. and Thomas, S., *J. Appl. Polym. Sci.*, **71**, 2335, 1999.
4. Borowitz J., and Kosfeld L., *Angew. Macromol. Chem.,* **23**, 100,1981.
5. Acharya P. S. and Ramaswamy R., *J. Appl. Polym. Sci.,* **69**, 1187, 1998.
6. Acharya P. S. and Ramaswamy R., *Macromol. New Front. IUPAC Intern. Symp.,* **2**, 1122, 1998.
7. Suresh K. I. and Tachil E.T. *Angew. Macromol. Chem.,* **55,** 224, 1995.
8. Tang T., Ying S. and Zhang Y., Xiangjiao Gongye, **39**, 743 and 739, 1992.
9. Tang T., Cheng J., Zhao H., Chen H. and Huang B., *Gaofenzi Cailiao Kexue Yu Gongcheng,* **11**, 97, 1995.
10. Tang T., Hu C. P., Ying S. K. and Zhang Y. X., *Adv. Polym. Blends Alloys Technol.,* **4**, 1, 1993.
11. Onoue T., Sawaki M. and Yonemochi S., JP, 02125735 A2, 1990.
12. Yanagusawa S., Shin N. and Takasugi S., JP, 02178382 A2 1990.
13. Saito T., Kawasaki T. and Higashide Y., JP, 09087972 A2, 1997.
14. Roy S.K. Singh A.and Das C.K., *Polym. Polym. Compos.,* **3**, 403, 1995.
15. Dimitrievski I. and Malavasic T., *Kovine Zlitine Tehnol.,* **28**, 311, 1994.

16. Dimitrievski I.; Susteric Z. and Marinovic T., *Prog. Trends Rheol. V, Proc. Eur. Rheol. Conf.*, 5th, 73. Edited by: Emri, I. Steinkopff: Darmstadt, Germany, 1998.

17. Callan J. E., Hess W. M. and Scott C. E., *Rubber Chem Technol* **44**, 814 1971.

18. Chappuis M. M., Polley M. H. and Schulz R. A., *Rubber Chem Technol.*, **28**, 253, 1955.

19. Hess W. M., Vegvari P. C. and Swor R. A. *Rubber Chem Technol.*, **58**, 350,1985.

20. Hess W. M., Swor R. A. and Vegvari P. C., *Kautsch Gummi Kunstst*, **38**, 1114,1985.

21. Varghese T. L. and V. N. Krishnamurthy, *J Polym Mater*, **13**, 2451, 1996.

22. Varghese H., Bhagwan S., and Thomas S., *Macromol. New Front. IUPAC Intern. Symp.*, **2**, 894, 1998.

23. Nielsen L. E., *J. Compos. Mater.*, **1**, 100, 1967.

24. Nielsen L. E., *Mechanical properties of polymers and composites*, Marcel Dekker, NY, 2, 1974.

25. Takayanagi M., Vermura S. and Minami S., *J. Polym. Sci.*, **C5**, 113, 1964.

26. Davies W.E.A., *J. Phys.*, **D4**, 1176, 1971

27. Desai S., Thakore I. M., and Devi S., *J. Appl. Polym. Sci.*, (communicated).