

Studies on Sequential Interpenetrating Polymer Network (IPN) Based on Nitrile Rubber and Poly(vinyl acetate)

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SYNOPSIS

Several elastomeric sequential interpenetrating polymer networks (IPNs) based on nitrile rubber (NBR) and poly(vinyl acetate) (PVA) have been synthesized. Cross-linked NBR was swollen in vinyl acetate monomer containing benzoyl peroxide (BPO) as initiator and tetraethylene glycol dimethacrylate (TEGDM) as cross-linker and then the swollen mass was polymerized. The composition of the IPNs could be varied by varying the swelling time and concentration of BPO and TEGDM. The properties of these IPNs were investigated by tensile test, differential scanning calorimetry (DSC), dynamic mechanical analysis, and swelling measurement. On increasing the PVA content as well as cross-linking level, the tensile strength increased because of better mixing. DSC showed a single T_g value for all the individual IPNs, the T_g values changing regularly with composition. The $\tan \delta$ peak for IPNs appeared at higher temperature compared to NBR and was found to be dependent on both the composition of IPNs as well as cross-linking level. IPNs having 2 and 5% cross-linker (TEGDM) showed splitting in the $\tan \delta$ peak. On increasing the cross-linker concentration to 9% and beyond, the splitting disappeared. The damping capability of the IPNs has been explained in terms of the magnitude of $\tan \delta$, area under the $\tan \delta$ curve, and $\frac{1}{2}$ peak width. The IPNs also showed better solvent-resistance properties. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Considerable research efforts have been made in various laboratories on the development of polymeric material for damping of vibration covering a wide range of frequencies in the Hz and kHz region. With the acoustic range being broad, i.e., 20 Hz to 20 kHz, there is hardly any polymer that can be singly effective over the entire range and, in general, most of the homopolymers respond to only a narrow range of frequencies at a specified temperature. Blending of two polymers can be of advantage provided that they are miscible, which is not always the case. The interpenetrating polymer network (IPN) is a new class of material with promise in this direction and this subject is presently receiving considerable attention.¹⁻⁶

By virtue of their unique method of synthesis, most of the IPNs exhibit microphase separation and the domain size can be controlled to within 100–1000 Å.⁷ As a consequence, there is possibility of some molecular mixing. Because of the microphase separation or partial miscibility, IPNs generally have broad glass transition. Since damping of mechanical vibration is maximum near the glass transition region, IPNs are expected to damp over a wide range of temperature and/or frequency. Of the various methods reported on the measurement of the damping capability,⁷ the measure of $\tan \delta$ is the most important one as this quantity can be directly correlated to damping capability.

From a study by Sperling et al.,² it has been found that acrylate, nitrile, and acetate groups contribute the maximum toward the damping. Poly(vinyl acetate) (PVA) has a T_g around 28°C and is expected to damp appreciably around ambient temperature. However, it has poor mechanical properties. It can be reasoned that if PVA could be incorporated into the rubber matrix the resulting blend could have

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useful vibration damping properties over a wide temperature range including ambient temperature. The IPN offers a promising route to blend these two polymers, which, otherwise, have poor compatibility.⁸ The present study deals with synthesis and characterization of sequential IPNs based on nitrile rubber (NBR) and PVA.

EXPERIMENTAL

Materials

NBR (AN content 30) was supplied by Rubo Chem (India). Dicumyl peroxide (DCP) (Rubo Chem), a cross-linker for NBR, was used without further purification. Vinyl acetate (Fluka) monomer was freed from inhibitor by the standard method. Benzoyl peroxide (BPO) (BDH) was recrystallized from methanol prior to use. Tetraethylene glycol dimethacrylate (TEGDM) (Fluka) was used as such as cross-linker for PVA during the preparation of the IPN. Laboratory-grade (all from BDH) methyl ethyl ketone (MEK), toluene, carbon tetrachloride (CCl₄), and sulfuric acid were used without further purification.

Preparation of NBR Sheet

NBR was masticated and 5 parts of DCP was mixed in a two roll mill and the rubber was cured into sheet form at 150°C for 20 min under a pressure of 50 kg/cm² using a compression-molding machine.

Preparation of the IPN

A preweighed sheet of cured NBR was swollen in vinyl acetate monomer containing known amount of BPO and TEGDM. A liquor ratio of 1:20, i.e., NBR-to-monomer ratio, was maintained for all the experiments. After swelling for a specific period, the NBR sheet was weighed and then kept in an oven in between two plates (to reduce the evaporation of monomer from the surface) at 60°C for polymerization. After polymerizing for the requisite time, the sheet was vacuum-dried at 40°C to constant weight and the compositions were determined gravimetrically. Several IPNs were synthesized in this way by varying the reaction parameters such as concentration of BPO and TEGDM.

Cross-linked PVA was prepared by polymerizing vinyl acetate monomer in benzene solution (30% by weight) containing 0.2 mol % BPO and 2 vol % TEGDM at 60°C.

Measurements of Physical Properties

A. Tensile Measurement

The tensile strength and elongation at break of IPNs were measured by an Instron tester (1123) at room temperature at a crosshead speed of 20 mm/min using dumbbell-shaped specimens according to ASTM D638.

B. Glass Transition Temperature

The glass-transition temperature (T_g) of the IPNs was measured by employing a DuPont 910 differential scanning calorimeter. The operating temperature was -80 to +50°C. A heating rate of 5°C/min was maintained for all the IPNs.

C. Elastic Moduli and Loss Tangent

The dynamic mechanical spectra of the IPNs were obtained by a DuPont 983 dynamic mechanical analyzer. The samples were heated from -80 to +80°C at a heating rate of 5°C/min. The samples were tested in the resonance mode. From the spectra, storage modulus (E') and the loss tangent ($\tan \delta$) were evaluated.

Solvent Resistance

Solvent resistance of the IPNs and NBR was found by dipping a known weight of the sample in different solvents for 7 days. After 7 days, the samples were removed and extent of swelling was noted.

RESULTS AND DISCUSSION

Effect of Reaction Parameters on IPN Synthesis

Figure 1 presents the effect of TEGDM concentration on PVA content in the IPN synthesized by keeping the BPO concentration (2% w/v) and dipping time (5 h) constant. From the results, it can be seen that on increasing the TEGDM concentration the PVA content in the IPN increases. Vinyl acetate is a low boiling liquid (bp 72–74°C at 760 mmHg) and its rate of evaporation is very high. On increasing the TEGDM concentration, the network formation increases because of extensive cross-linking. Moreover, at a higher concentration of TEGDM, the increase in weight after polymerization is not only due to PVA but also to TEGDM. Hence, the concentration of PVA reported for IPNs synthesized at a high concentration of TEGDM is only a nominal one.

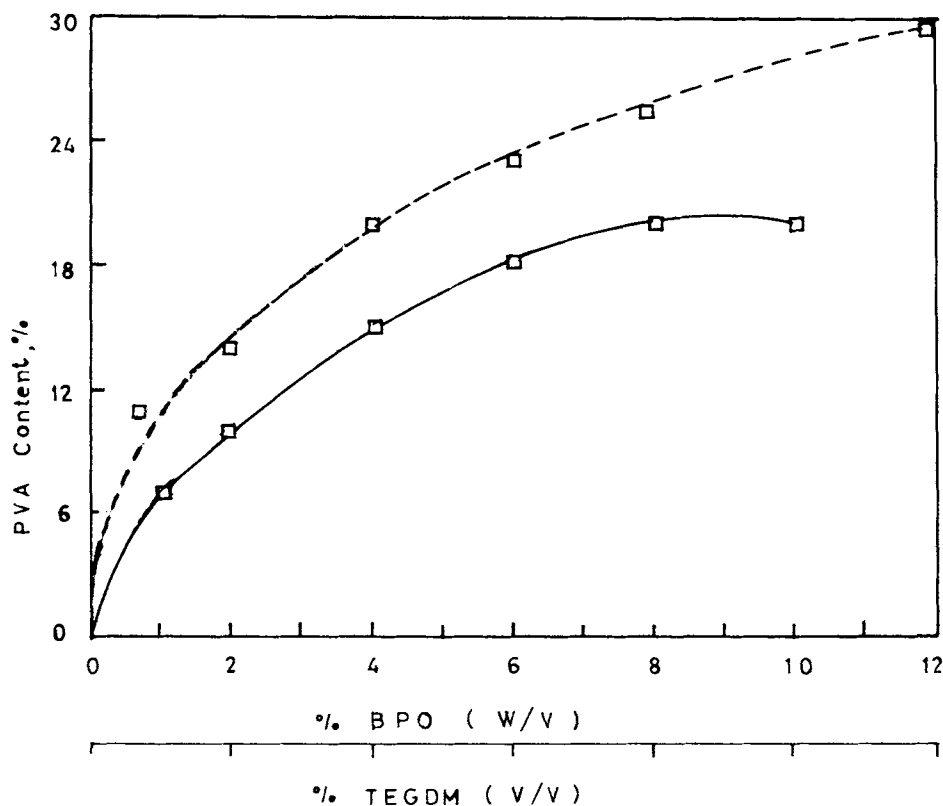


Figure 1 Variation of PVA content (%) in NBR/PVA IPNs with respect to the concentration of (-----) TEGDM and (—) BPO.

IPN synthesis was also carried out by varying the BPO concentration and keeping the dipping time (3 h) as well as TEGDM concentration (2% v/v) constant. The results have been presented in Figure 1. The results show that the PVA content in the IPN increases on increasing the BPO concentration. Increase in rate of polymerization due to an increase in initiator concentration is a known phenomenon and, hence, the PVA content increases with an increase in BPO concentration.

Stress-Strain Behavior

The results of tensile tests of all the IPNs are presented in Table I. From the results, it can be seen that introduction of PVA into the NBR matrix at a constant cross-linker (TEGDM) concentration (2%) increases the tensile strength. This increase continues as the PVA content increases. Additionally, on increasing the cross-linker concentration (although PVA content increases), the tensile

Table I Results of Tensile Measurements

| NBR/PVA Composition | % Cross-linker (TEGDM) in IPN | Tensile Strength (kg/cm ²) | % Elongation at Break |
|---------------------|-------------------------------|--|-----------------------|
| NBR | — | 11.5 | 176 |
| 95/05 | 2 | 13.7 | 171 |
| 90/10 | 2 | 16.8 | 132 |
| 85/15 | 2 | 19.8 | 178 |
| 85/15 | 5 | 20.4 | 129 |
| 80/20 | 9 | 28.5 | 148 |
| 70/30 | 13 | 48.6 | 128 |

strength also increases. A significant increase in strength was noticed when the PVA content increased to 30% and the percent of cross-linker was 13.

Although NBR and PVA do not form highly compatible blends,^{8,9} in case of their IPN there is a possibility of some forced mixing because of the network formation. Moreover, the monomer is expected to polymerize in intimate contact with the base network, as it has been observed that VA monomer is a very good swelling agent for NBR; thus, 300% swelling was observed after dipping for 24 h. Similar phenomenon has been observed by others in the case of PU-PMMA IPN.¹⁰ Grafting of PVA (cross-linked) onto the NBR network during IPN formation is also a distinct possibility. All these factors will contribute toward enhanced mixing and resulting in an increase in tensile strength. The increase in tensile strength with an increase in the cross-linker level is obviously due to an increase in the cross-link density as it reduces the domain size and increases the degree of mixing. Elongation at break, however, did not show any specific trend.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures, T_g , of NBR and IPNs having different contents of PVA synthesized at different cross-linker levels is measured by DSC (only a few scans are presented in Fig. 2) and the values are given in Table II.

All the IPNs gave a single glass transition temperature, indicating that there is no macrophase separation. The T_g value of IPNs increase as the content of PVA increases in the IPN. Thus, NBR (cross-linked) shows a T_g value of about -32°C , whereas for PVA (cross-linked), it is about 30°C , indicating that PVA chains are stiffer than are NBR chains. Hence, on IPN formation, as the PVA content increases, the T_g value increases because of the increase in stiffness. All the IPNs, however, show a T_g value in between the T_g values of NBR and PVA. This coupled with single T_g value for individual IPNs is an indication of greater mixing between the two components. The T_g of all the IPNs was calculated using the Fox equation⁸ and the values are in good agreement with the experimental values (Table II)

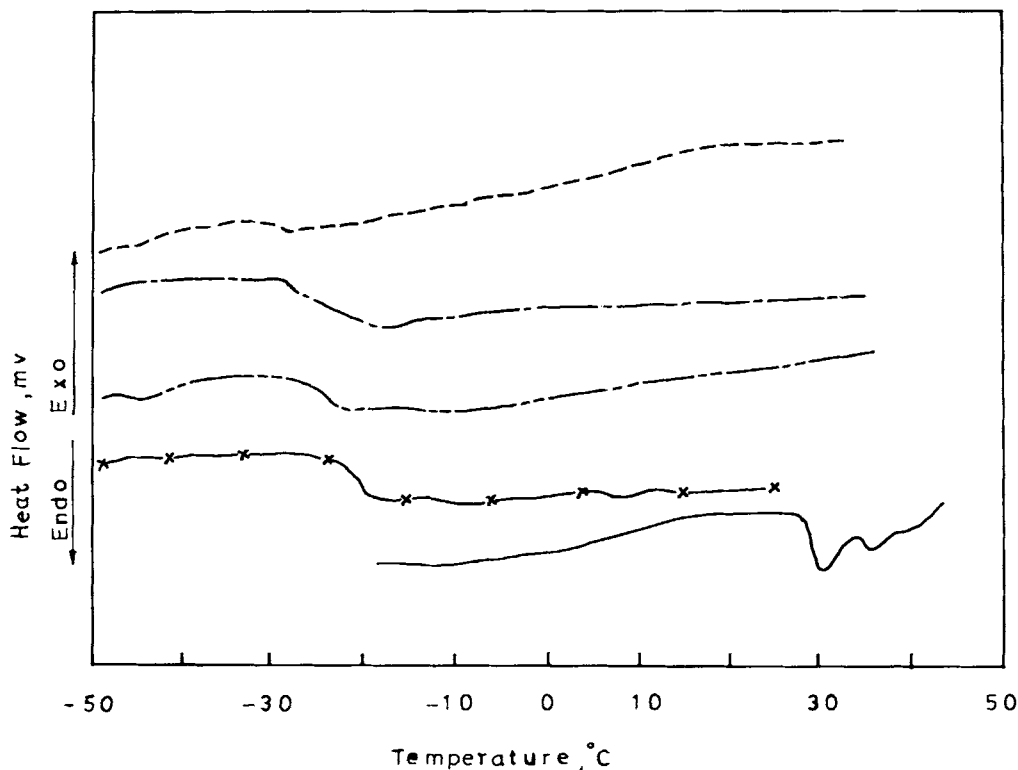


Figure 2 DSC thermograms of NBR, PVA, and NBR/PVA IPNs: (----) NBR; (-·-) 95/5 NBR/PVA (2% TEGDM); (- - -) 85/15 NBR/PVA (5% TEGDM); (- x -) 70/30 NBR/PVA (13% TEGDM); (—) PVA (2% TEGDM).

Table II Results of Glass Transition Temperature Measurement by DSC

| NBR/PVA Composition | % Cross-linker (TEGDM) in IPN | T_g (°C) | |
|------------------------|----------------------------------|--------------|--------------------------------------|
| | | Experimental | Calculated Using the Fox Equation |
| NBR | — | -32 | |
| 95/05 | 2 | -28 | -29.5 |
| 90/10 | 2 | -25 | -26.9 |
| 85/15 | 2 | -24 | -24.4 |
| 85/15 | 5 | -23 | -24.4 |
| 80/20 | 9 | -24 | -21.7 |
| 70/30 | 13 | -21 | -16.2 |
| PVA | — | 30 | |

except for IPNs containing a higher percentage of TEGDM, where the values slightly differ. This is possibly because at a higher concentration of TEGDM the change in T_g is not only due to PVA but also due to TEGDM.

Dynamic Mechanical Analysis

The dynamic mechanical properties of IPNs have been investigated by DMA and the spectra (only

few) have been presented in Figures 3 and 4. From the spectra, $\tan \delta_{\max}$, temperature for E''_{\max} , temperature for $\tan \delta_{\max}$, area under the $\tan \delta$ curve (ta), and half-peak width of the $\tan \delta$ curve are obtained and presented in Tables III and IV.

From Figure 3 it can be seen that NBR has a very low storage modulus-temperature plateau compared to IPN. This plateau increases continuously on increasing the PVA as well as the cross-linker contents.

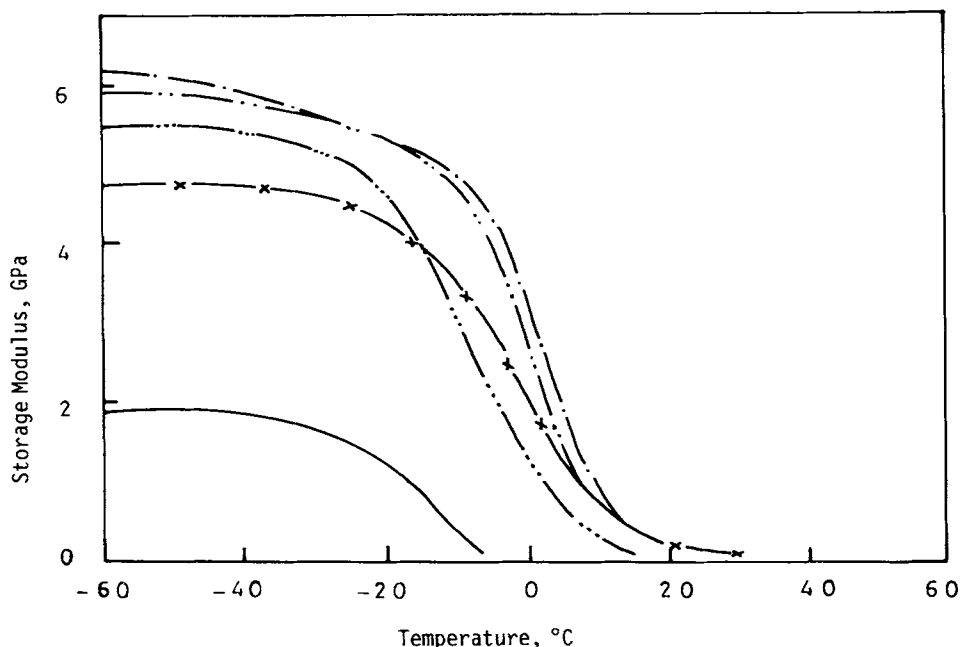


Figure 3 Plots of storage modulus vs. temperature of NBR and NBR/PVA IPNs: (—) NBR; (-·-) 95/5 NBR/PVA (2% TEGDM); (-··-) 85/15 NBR/PVA (5% TEGDM); (-···-) 80/20 NBR/PVA (9% TEGDM); (-x-) 70/30 NBR/PVA (13% TEGDM).

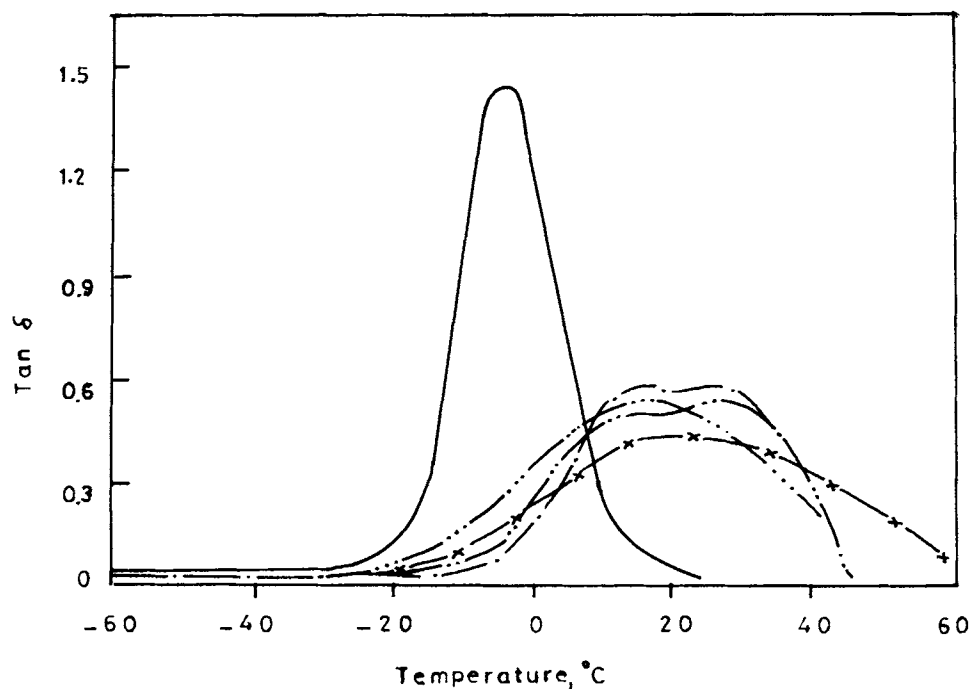


Figure 4 Plots of loss tangent vs. temperature of NBR and NBR/PVA IPNs: (—) NBR; (---) 95/5 NBR/PVA (2% TEGDM); (···) 85/15 NBR/PVA (5% TEGDM); (-·-·-) 80/20 NBR/PVA (9% TEGDM); (-x-) 70/30 NBR/PVA (13% TEGDM).

NBR shows a sharp peak both for loss modulus as well as for $\tan \delta$ compared to IPNs. Thus, the E''_{\max} and $\tan \delta_{\max}$ peaks for NBR appeared at -12 and -4°C , respectively. But the range of relaxation is very narrow, which is evident from the $\frac{1}{2}$ peak width. The relaxation peak for all the IPNs shifts inwardly to a temperature between the two transition peaks of NBR and PVA. But there is splitting in the relaxation peak even when the cross-linker concentration is 5%. This is indicative of some phase separation. However, the splitting disappears as the cross-linker level increases to 9% and beyond. It has been reported that blends of NBR and PVA are not compatible.⁸ In the present case, because of the IPN

formation, there is possibility of some mixing^{4,11} as the first $\tan \delta_{\max}$ in all the IPNs appeared at a much higher temperature than that of NBR. The appearance of second $\tan \delta_{\max}$ may be associated to PVA component. But as the cross-linker level increases to 9% and beyond, there seems to be more cross-linking, resulting in more mixing³ and formation of finer phase domains.⁴ As a consequence, only a single $\tan \delta$ peak is observed.

Normally, $\tan \delta_{\max}$ appears at a higher temperature than does E''_{\max} ,¹² which is true in the present case also (Table III). The temperature for E''_{\max} is also an indication of T_g . On comparing the T_g values obtained from DSC measurement with those ob-

Table III Dynamic Mechanical Properties of NBR/PVA IPN

| NBR/PVA Composition | % Cross-linker (TEGDM) in IPN | Temp ($^\circ\text{C}$) for E''_{\max} | Temp ($^\circ\text{C}$) for $\tan \delta_{\max}$ |
|---------------------|-------------------------------|--|--|
| NBR | — | -10.0 | -5.0 |
| 95/05 | 2 | 4.7 | 12.5, 28.6 |
| 90/10 | 2 | 2.4 | 11.2, 25.9 |
| 85/15 | 2 | 3.2 | 11.1, 27.1 |
| 85/15 | 5 | 1.7 | 11.2, 27.5 |
| 80/20 | 9 | -4.5 | 15.6 |
| 70/15 | 13 | 0.0 | 20.5 |

Table IV Damping Characteristics of IPNs

| NBR/PVA Composition | % Cross-linker (TEGDM) in IPN | $\tan \delta_{\max}$ | Area of $\tan \delta$ Curve ($^{\circ}\text{C}$) | $\frac{1}{2}$ Peak Width of $\tan \delta$ Curve ($^{\circ}\text{C}$) |
|---------------------|-------------------------------|----------------------|--|--|
| NBR | — | 1.41 | 24.7 | 15.0 |
| 95/05 | 2 | 0.57 | 19.0 | 34.6 |
| 90/10 | 2 | 0.51 | 19.2 | 36.0 |
| 85/15 | 2 | 0.49 | 19.2 | 36.0 |
| 85/15 | 5 | 0.52 | 19.3 | 39.0 |
| 80/20 | 9 | 0.51 | 19.0 | 42.6 |
| 70/30 | 13 | 0.41 | 17.8 | 51.0 |

tained from DMA, it can be seen that E''_{\max} appeared at higher temperature than the T_g observed in DSC. This is probably due to the high resonance frequency for the loss maxima, because the observed increase in loss peak temperature may be due to fact that increasing the temperature facilitates the mobility and thereby reduces the relaxation time (or increases the relaxation frequency).¹³

NBR shows a very high $\tan \delta_{\max}$ value such as 1.41 at -4°C . The magnitude of $\tan \delta_{\max}$ decreases as the PVA content increases in the IPNs. The decrease in the magnitude of $\tan \delta_{\max}$ becomes significant as the cross-linker concentration increases. Thus, IPN having 30% PVA at the 13% TEGDM level shows a minimum $\tan \delta$ value (0.41). Similar types of results have been observed by others also in different systems.^{3,4,11,14} But from the results presented in Table IV for the area under the $\tan \delta$ temperature curve (ta), which gives an indication about the extent of damping,¹⁵ it can be seen that NBR shows the highest ta value of 24.7°C . But on IPN formation, the value reduces to 19 and thereafter remains constant irrespective of the composition. The observed trend of the ta is probably because $\tan \delta$ is dependent on two quantities, E' and E'' , both of which are different for different IPNs. From the loss area study, it has been found by Sperling et al.² that the magnitude of the damping factor and/or loss factor depends on the chemical structure of the polymer. On analyzing the contribution due to various groups, they found that the nitrile group contributes the maximum toward damping and, hence, NBR shows the maximum $\tan \delta$ value. But as the PVA content, which contributes less than nitrile group, increases, there results a decrease in $\tan \delta$ value.

In a recent study,¹⁵ it was reported that whereas the group contribution analysis provides a first approximation to the loss area for the single-phase materials, significant deviation may be obtained for

multiphase polymeric material because of the effect of cross-linking, phase continuity, and miscibility. However, the temperature range of damping, as measured in terms of $\frac{1}{2}$ peak width, is higher in the case of IPNs compared to NBR (Table IV). Thus, the $\frac{1}{2}$ peak width of the $\tan \delta$ curve of NBR is 15°C . But on IPN formation, the value doubles and keeps on increasing as the cross-linker content increases. The IPN having 13% cross-linker (maximum cross-link density) shows the highest $\frac{1}{2}$ peak width, viz., 51°C . This is an indication of microheterogeneous phase morphology of IPNs. This study also indicates that the IPNs can damp over a wide range of temperature compared to the homopolymers, as has also been observed by others.¹⁶

Solvent Resistance

The solvent-resistance characteristics of NBR and IPNs have been studied in different solvents and the results have been presented in Table V. On comparing the swelling values of NBR with those of IPNs, it can be seen that the introduction of 5% PVA (cross-linked) into the NBR matrix results in a sharp decrease in the swelling values. This value further decreases on increasing the PVA content to 30% at a cross-linker level (TEGDM) of 13%, indicating better solvent-resistance characteristics of the IPNs compared to NBR.

CONCLUSION

A series of sequential IPNs based on NBR and PVA has been prepared in the form of sheet by varying the reaction parameters such as concentration of BPO as well as TEGDM. The IPNs have been characterized for their tensile properties, glass transition temperature, dynamic mechanical properties, and swelling behavior.

Table V Results of Swelling Values of IPNs in Different Medium

| Samples NBR/PVA | MEK | Toluene | CCl ₄ | Heptane | Engine Oil C-104 | H ₂ SO ₄ 25% Soln | NaCl 5% Soln |
|--------------------|-----|---------|------------------|---------|---------------------|--|-----------------|
| NBR | 504 | 364 | 117 | 29 | 0 | 0 | 0 |
| 95/05 | 297 | 256 | 98 | 15 | 0 | 0 | 0 |
| 70/30 | 220 | 150 | 32 | 10 | 0 | 0 | 0 |

The tensile strength increases on increasing the PVA content as well as the cross-linker level because of better mixing between the two components. The glass transition temperature of the IPNs is higher than that of NBR because of the increase in stiffness.

Dynamic mechanical analyses of IPNs show that the IPNs have a much higher storage moduli-temperature plateau than does NBR. The temperature for maximum loss due to the relaxation of IPNs, as measured from the temperature for $\tan \delta_{\max}$, appears at higher temperature than that for NBR. IPNs having 2 and 5% cross-linker levels show splitting in the $\tan \delta$ curve, probably because of phase separation. But at higher cross-linker levels (9% and beyond), the splitting disappeared owing to the increase in cross-linking density and better mixing. Although the magnitude of $\tan \delta$ decreases on IPN formation, the area under the loss tangent curve (ta) remains constant irrespective of the IPN composition. The range of damping by IPNs, in terms of $\frac{1}{2}$ peak width, increases on increasing the PVA content as well as the cross-linker concentration. The solvent-resistance properties of the IPNs are better than those of NBR.

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