

Sequential Interpenetrating Polymer Network Based on Nitrile–Phenolic Blend and Poly(alkyl methacrylate)

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ABSTRACT: Interpenetrating polymer networks (IPNs) based on a nitrile rubber (NBR)–phenolic resin (PH) blend and poly(alkyl methacrylates) were synthesized by a sequential method. The cured blends were swollen in a methacrylate monomer containing a crosslinker and initiator. The swollen rubber sheets were cured at 60°C. From the swelling study of the monomer, it was found that IPN formation in the blend is in between the rubber and poly(alkyl methacrylate) phases only. The IPNs thus formed were characterized for their tensile, dynamic mechanical, and solvent-resistance characteristics. The tensile strength of the IPNs are dependent on the PH content; at a lower content of PH (up to 20 parts), IPNs have a higher strength compared to their corresponding blends, whereas at a higher content of PH (beyond 30 parts), the strength decreases. But for every NBR/PH-fixed composition, the strength of IPNs was found to be increasing in the order of PBUuMA < PEMA < PMMA. The dynamic property results showed that NBR/PH blends are incompatible. The storage modulus of IPNs are always higher than their corresponding blends at all temperatures. The $\tan \delta$ peaks of IPNs are broad, indicating the presence of microphase-separated domains. The IPNs show superior solvent-resistance characteristics compared to the blends. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 255–262, 1998

INTRODUCTION

When a polymer is subjected to cyclic stress, molecular motion sets in which, at the glass transition, converts a substantial amount of mechanical work into heat. Such conversion is of special interest in reducing transmitted noise and vibration.¹ Damping reduces noise and also chances of hysteresis failure in aircraft, automobiles, and machinery. As the acoustic spectrum covers frequencies in the range of 20 Hz to 20 kHz, it is impossible to design a damping material from one type of polymer since a single polymer is able to exhibit damping over a very narrow frequency or temperature range. This is because the mechanical relax-

ation spectrum of a single polymer in a frequency or temperature scale is very sharp. Mechanical blending and grafting are some of the important techniques attempted toward widening the temperature and frequency range of damping.^{2–8} However, interpenetrating polymer networks (IPNs) seem to be superior in designing a broad band vibration damper due to their unique structure.^{9–15}

IPNs have several advantages over blends since the synthesis is done by crosslinking of two or more different polymers individually in the immediate presence of each other so that crosslinked chains are intermingled, resulting in considerable phase mixing through the restriction of domain size.⁹ This causes an appreciable improvement in strength and dynamic mechanical properties of IPNs compared to the simple blends. Studies on IPNs based on various elastomers and vinyl poly-

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mers reported in the literature indicated the enhancement of mechanical strength and broadening of viscoelastic damping over a wide temperature range covering the relaxation peaks of individual polymers.^{16–21} Nitrile rubber (NBR)/phenolic resin (PH) blends are known to have excellent mechanical properties.²² Poly(alkyl methacrylate)s are known to have very a high damping behavior compared to many other polymers.¹⁰ As the phenolics contain hard segments, its introduction into soft NBR may lead to formation of a constrained layer in the matrix. A constrained layer may cause high damping (over a narrow range of frequency or temperature) and, at the same time, may retain high mechanical strength over a wide and useful temperature range. It will, therefore, be interesting to determine the behavior of IPNs based on a NBR–phenolic blend and poly(alkyl methacrylate)s, particularly in respect to the mechanical strength and damping effectiveness over a wide temperature range. The synthesis and characterization of sequential IPNs based on NBR/PH blends and poly(alkyl methacrylate)s are reported here.

EXPERIMENTAL

Materials

Nitrile rubber (NBR, grade N241, acrylonitrile content 29%, Mooney viscosity 56) was from Japan Synthetic Rubber Co. Ltd., Japan, whereas phenolic novolak resin (HR 6521) was obtained from and Bakelite Hylam, India. Dicumyl peroxide (DCP) (Rubochem Industries Ltd., India) was used as received. Methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BuMA) monomers (all from Fluka) were freed from the inhibitor by washing with an aqueous sodium hydroxide (NaOH) solution and finally distilled under reduced pressure before use. Tetraethylene glycol dimethacrylate (TEGDM; Fluka) was used as a crosslinker without further purification. Benzoyl peroxide (BPO; BDH, India) was recrystallized from methanol prior to use as an initiator.

Preparation of NBR–PH Sheet

NBR was masticated in a two-roll mill before mixing with the PH resin. The masticated NBR was mixed with the PH resin at different proportions to obtain various blend compositions. In all the

compositions, 3 phr of DCP was used as a crosslinker. The premixed blends were cured into a sheet under compression at 150°C for 1 h under a pressure of 100 kg/cm².

Synthesis of IPN

Prewighed sheets of the NBR–PH blend were swollen in an excess amount of the alkyl methacrylate monomer containing 2% (w/w) each of BPO and TEGDM. After swelling for specific periods, the swollen sheets were kept in an oven between two plates (to reduce evaporation of the monomer from the surface) at 60°C for the polymerization. After polymerizing for a requisite time, the IPN samples were vacuum-dried at 40°C to a constant weight. Several IPNs were synthesized in this way by varying the NBR–PH blend composition and swelling time in the monomers.

CHARACTERIZATION

Mechanical Properties

The tensile strength and elongation at break of IPNs were measured by employing an Instron testing machine (Model 1123) according to ASTM D 638. Dumbbell-shaped specimens were used and the crosshead speed was maintained at 20 mm/min.

Dynamic Mechanical Properties

The dynamic mechanical spectra were recorded using a dynamic mechanical thermal analyzer (Rheometric Scientific, Model MK III) in the temperature range of –60 to +100°C. The heating rate was maintained at 3°C/min. All the samples were tested in a fixed frequency mode (1 Hz) where the amplitude of oscillation was 0.2 mm (peak to peak).

Solvent-resistance Characteristics

Prewighed blend and IPN samples were dipped into a wide variety of solvents such as carbon tetrachloride, dichloroethane, methyl isobutyl ketone, xylene, engine oil, and a saturated sodium chloride solution for 96 h. The samples were then removed, and the solvent wiped off using tissue paper and weighed.

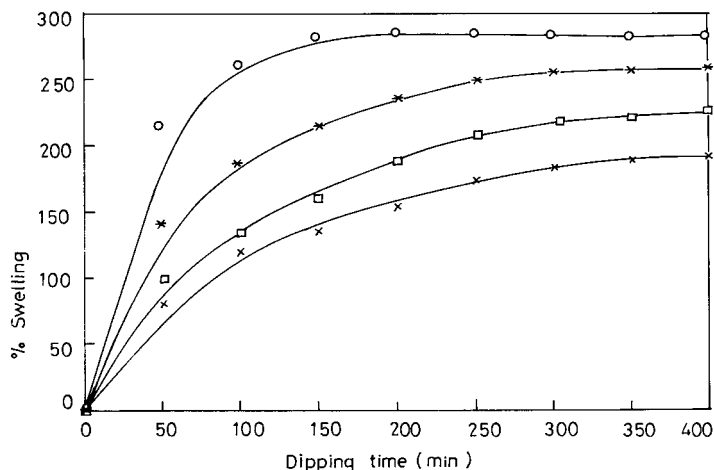


Figure 1 Plots of % swelling versus dipping time of NBR and NBR/PH blends: (○) NBR; (*) 90 NBR/10 PH; (□) 70 NBR/30 PH; (×) 60 NBR/40 PH.

RESULTS AND DISCUSSION

All the IPNs were synthesized by the sequential method. It was observed that the swelling of the NBR–PH blend in the monomer prior to polymerization is only due to the NBR phase. The PH resin was separately checked for swelling in alkyl methacrylate monomers for a long period. However, no swelling was noticed. The swelling time in the monomers was varied for different blends as per their swelling capabilities. Figure 1 shows the swelling behavior of various blends and pure NBR. It can be seen that the swelling of NBR is quite fast, whereas that of blends decreases with PH content. This behavior can be explained on the basis of the negligible interaction of PH with the monomers as has been mentioned above. The presence of PH in the matrix does not allow the penetrant to flow directly. It takes a longer route for diffusion. The phenomenon is akin to permeation through a semicrystalline matrix. Therefore, the time taken for an appreciable uptake of the monomer is relatively high.

Tensile Properties

The results of tensile tests of the IPNs are presented in Table I. The crosslinker (TEGDM) concentration for all the samples has been kept constant at 2%. The tensile strengths of IPNs increase as the alkyl methacrylate is varied from PBuMA to PMMA. This may be attributed to decrease in the bulkiness of the pendant alkyl group or increase in the glass transition temperature (T_g) of the methacrylate phase.^{23,24} As expected,

the elongation at break increases with the bulkiness of the pendant alkyl group or decrease in T_g . Similar results were observed in our earlier work on NBR/poly(alkyl methacrylate) IPN.²⁵ The tensile strength is also dependent on the content of PH in the IPN. Thus, introduction of polyalkylmethacrylate into the NBR–PH blend increases the tensile strength for lower PH content. How-

Table I Mechanical Properties of IPNs Prepared Using 2% TEGDM

Composition	Tensile Strength (MPa)	% Elongation at Break
95 NBR/5 PH	2.44	135
51 NBR/3 PH/46 PMMA	13.42	92
53 NBR/3 PH/44 PEMA	9.97	124
46 NBR/3 PH/51 PBuMA	4.42	196
90 NBR/10 PH	2.88	177
53 NBR/6 PH/41 PMMA	11.51	48
48 NBR/5 PH/47 PEMA	9.41	94
43 NBR/5 PH/52 PBuMA	4.90	236
80 NBR/20 PH	4.62	224
40 NBR/10 PH/50 PMMA	14.45	88
50 NBR/12 PH/38 PEMA	9.86	80
45 NBR/11 PH/34 PBuMA	6.60	176
70 NBR/30 PH	5.87	90
51 NBR/22 PH/27 PMMA	3.88	236
50 NBR/20 PH/30 PEMA	3.88	332
54 NBR/23 PH/23 PBuMA	3.77	324
60 NBR/40 PH	6.55	50
35 NBR/24 PH/41 PMMA	5.34	100
43 NBR/28 PH/29 PEMA	5.21	96
47 NBR/31 PH/23 PBuMA	4.50	84

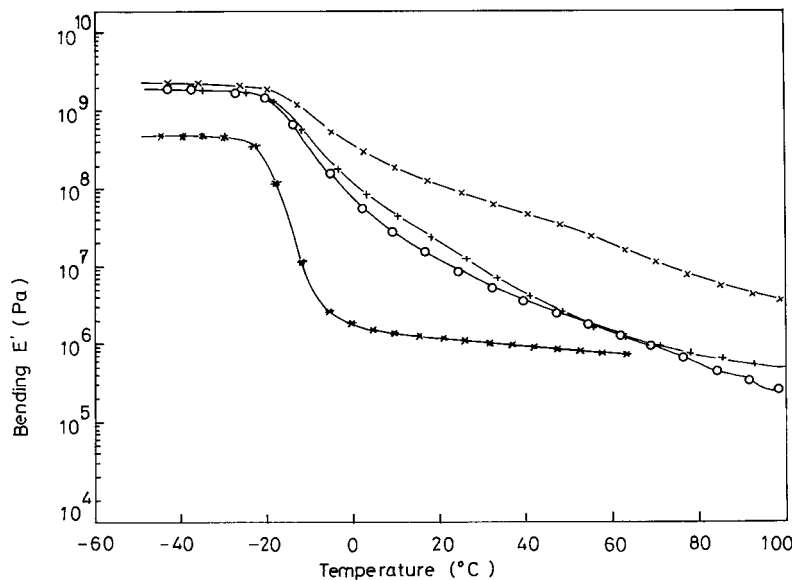


Figure 2 Plots of storage modulus versus temperature of NBR-PH blend and IPNs: (*) NBR-PH; (+) 54 NBR/3 PH/43 P BuMA; (O) 65 NBR/4 PH/31 PEMA; (X) 55 NBR/3 PH/42 PMMA.

ever, beyond 30 parts of PH, a decrease in tensile strength was observed. The NBR matrix consists of soft segments, whereas the PH matrix contains hard segments. The compatibility seems to be very low. However, the mechanical strengths of the blends are much higher than those of pure NBR. This is partly attributed to the participation of PH in the crosslinking during vulcanization.²² IPN formation between NBR and polyalkylmethacrylate was reported earlier.²⁵ Therefore, the increase in strength at a lower loading of PH can be attributed to IPN formation between the NBR phase and poly(alkyl methacrylate) by forced mixing due to network formation. However, beyond 30 parts of PH, the proportion of the hard segment reaches a level where forced mixing is hindered, resulting in a low reinforcing effect. The strength beyond 30 phr becomes predominantly dependent on the hard segment. The introduction of comparatively low strength polyalkylmethacrylate reduces the strength.

Dynamic Mechanical Analysis

The dynamic mechanical analysis of the IPNs was investigated in the temperature range of -60 to $+100^{\circ}\text{C}$. Representative plots of the storage modulus (E') versus temperature for the NBR-PH blend and IPNs are given in Figure 2. E' values for the IPNs are higher than for the blend. The highest values are obtained for PMMA-based

IPN. This can be attributed to the maximum stiffness of the PMMA chains. Table II gives the E' values in the rubbery plateau (at 20°C) for the blends and corresponding IPNs. The modulus plot in Figure 2 shows that the rubbery plateau for both blends as well as for the IPNs starts around -10°C . However, the modulus of the IPNs in the rubbery region is higher.

Figure 3 shows the $\tan \delta$ versus temperature plot of NBR-PH blends. It was observed that the blends have a sharp $\tan \delta$ peak around -12°C . However, no separate peak due to the PH phase was observed. The $\tan \delta$ peak at -12°C is purely due to NBR.¹⁷ As there is no inward shifting of the $\tan \delta$ peak of NBR, the blend seems to be incompatible. However, the $\tan \delta$ value decreases gradually from 1.4 (for NBR) to 0.59 for NBR-PH containing 40 phr PH. This may be attributed to the presence of hard PH segments restricting the movement of the soft NBR segments.

Figure 4 shows plot of E'' versus temperature of a few representative NBR-PH blends and IPNs. There is shift in the temperature for E''_{max} in the case of a few IPNs. The curve is broader for IPNs compared to the blend. Maximum broadness is observed for IPNs from the NBR/PH (95/5) blend. It is obviously due to more interpenetration between NBR and the polyalkylmethacrylates. However, as the PH content increases, the NBR content decreases, thereby reducing the content of interpenetration and resulting in less damping.

**Table II Dynamic Mechanical Properties of NBR/PH Blends/
Poly(alkyl methacrylate)s IPNs (2% TEGDM)**

Composition	E' at 20°C (MPa)	$\tan \delta_{1\max}$	$\tan \delta_{2\max}$	$T_{1\max}$ (°C)	$T_{2\max}$ (°C)
95 NBR/5 PH	1.20	1.22	—	-12	—
55 NBR/3 PH/42 PMMA	100.00	0.32	0.26	-3	75
65 NBR/4 PH/31 PEMA	14.00	0.57	0.45	-5	50
54 NBR/3 PH/43 PBuMA	25.00	0.52	0.61	1	38
90 NBR/10 PH	1.10	1.05	—	-12	—
75 NBR/8 PH/17 PMMA	5.00	0.98	0.62	-6	73
63 NBR/7 PH/30 PEMA	23.00	0.44	0.33	-4	46
59 NBR/6 PH/35 PBuMA	22.00	0.54	0.63	-12	42
80 NBR/20 PH	1.80	1.00	—	-12	—
59 NBR/15 PH/26 PMMA	3.00	0.83	0.24	-14	76
74 NBR/6 PH/20 PEMA	12.00	0.76	0.30	-12	45
48 NBR/12 PH/40 PBuMA	21.00	0.45	0.55	-11	38
70 NBR/30 PH	5.00	0.78	—	-8	—
55 NBR/24 PH/21 PMMA	30.00	0.53	0.21	-5	90
50 NBR/20 PH/30 PEMA	30.00	0.47	0.32	-12	54
53 NBR/23 PH/24 PBuMA	20.00	0.62	0.25	5	46
60 NBR/40 PH	10.00	0.59	—	-9	—
48 NBR/32 PH/20 PMMA	23.00	0.67	0.23	-10	60
40 NBR/30 PH/30 PEMA	35.00	0.44	0.34	-14	61
47 NBR/31 PH/22 PBuMA	18.00	0.66	0.31	-6	52

Figure 5 shows the $\tan \delta$ versus temperature plot of a few representative IPNs (NBR/PH/PBuMA) where the PH content is varied. It can be seen that the peak due to the NBR phase is shifted marginally. The magnitude of the $\tan \delta$

peak for NBR is very high when the PH content is < 30 parts. But the magnitude of the $\tan \delta$ peak decreases when there is an increase in the PH content or polyalkylmethacrylate content in the IPN. At a higher loading of PH, it is observed that

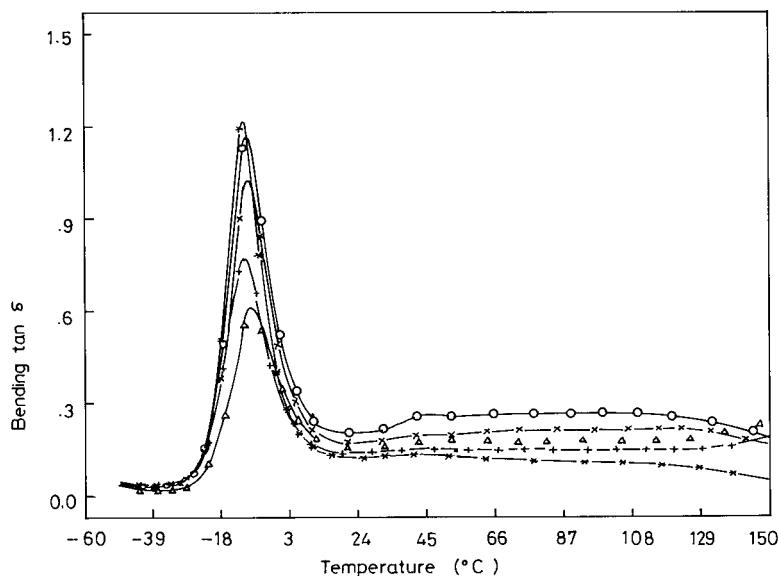


Figure 3 Plots of $\tan \delta$ versus temperature of NBR-PH blends at various PH loading: (*) 95 NBR/5 PH; (O) 90 NBR/10 PH; (x) 80 NBR/20 PH; (+) 70 NBR/30 PH; (Δ) 60 NBR/40 PH.

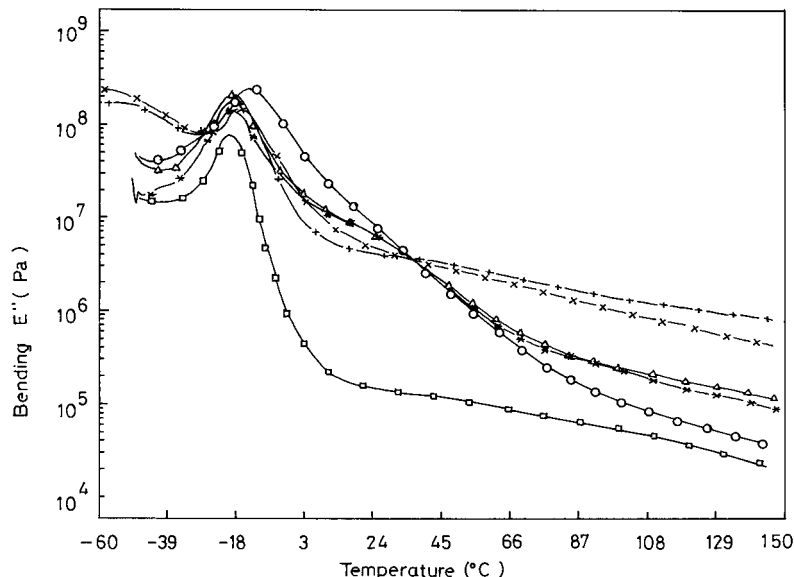


Figure 4 Plots of E'' versus temperature of NBR-PH blend and IPNs at various PH contents: (\square) 95 NBR/5 PH; (\circ) 54 NBR/3 PH/43 PBuMA; (\triangle) 59 NBR/6 PH/35 PBuMA; ($*$) 48 NBR/12 PH/40 PBuMA; (\times) 53 NBR/23 PH/24 PBuMA; ($+$) 47 NBR/31 PH/22 PBuMA.

the swelling in the monomer during IPN preparation is less. As a result, the content of the third phase, that is, the polyalkylmethacrylate phase, is less. Hence, the $\tan \delta$ peak in the case of IPN containing a higher amount of PH is predominantly due to the NBR phase. But in the case of systems containing a lesser amount of PH, the

NBR content is higher. During IPN formation, the swelling due to the monomer is high and, hence, the percentage of the third phase (polyalkylmethacrylate) is also high. The lower magnitude of $\tan \delta$ in these systems can be explained on the basis of a group contribution toward damping.¹ It was reported that the contributions of methacrylate,

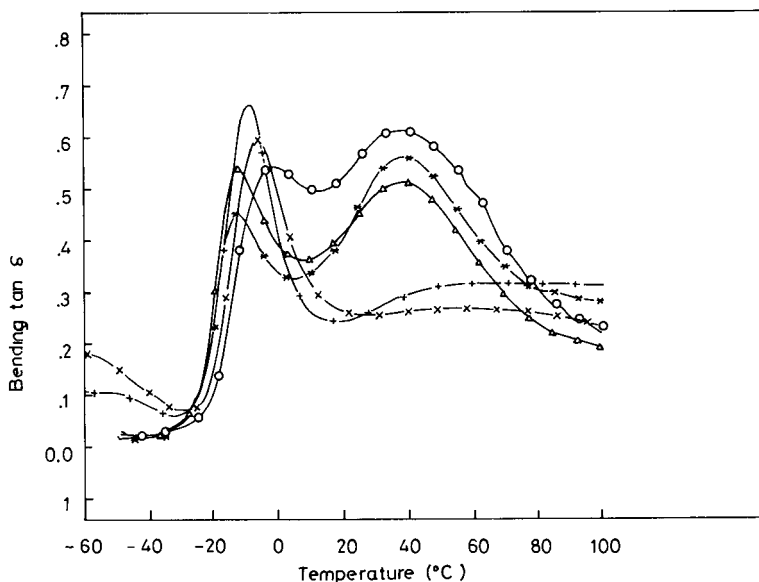


Figure 5 Plots of $\tan \delta$ versus temperature of NBR-PH/PBuMA IPNs at various PH contents: (\circ) 54 NBR/3 PH/43 PBuMA; (\triangle) 59 NBR/6 PH/35 PBuMA; ($*$) 48 NBR/12 PH/40 PBuMA; (\times) 53 NBR/23 PH/24 PBuMA; ($+$) 47 NBR/31 PH/22 PBuMA.

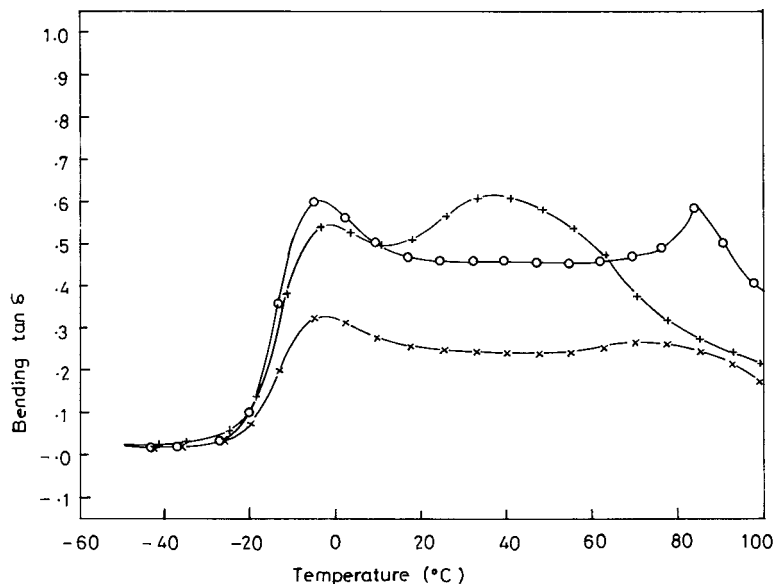


Figure 6 Plots of $\tan \delta$ versus temperature of IPNs with various methacrylates: (+) 54 NBR/3 PH/43 PBUmA; (O) 65 NBR/4 PH/31 PEMA; (X) 55 NBR/3 PH/42 PMMA.

nitrile, and acetate groups are very high, nitrile contributing the highest. Hence, the effectivity of the nitrile group decreases due to the presence of less contributing methacrylate groups. The $\tan \delta$ peak due to PBUmA is not well separated from the NBR peak. Instead, the $\tan \delta$ humps appear as a broad peak with reasonable splitting. Interestingly, the IPNs have $\tan \delta$ (0.4–0.6) in the temperature range of 25–50°C. This indicates that these IPNs can be used as a low-frequency vibration damper.

Figure 6 shows the $\tan \delta$ versus temperature peak of IPNs made from a blend containing the least PH (5 phr). It can be seen that the $\tan \delta_{\max}$ increases as the monomer is varied from methyl methacrylate to butyl methacrylate. This may be attributed to the variation of the bulkiness of the ester group. The segments of PMMA are stiff due to less bulkiness, whereas those of PBUmA are flexible due to increased bulkiness. Hence, IPNs from PBUmA and NBR/PH have a high damping factor.

Solvent Resistance

The solvent-resistance behavior of NBR–PH and the corresponding IPNs were studied in a range of solvents. The swelling data of few representative blends and the IPNs are incorporated in Table III. It can be seen that the swelling values of the NBR–PH blend decrease on IPN formation. A

large decrease was observed for PMMA, whereas the decrease due to PEMA and PBUmA is low. This may be attributed to the smaller size of the pendant alkyl group compared to other two methacrylates, which, in turn, causes a maximum compactness in the resulting IPN. Moreover, the smaller size of the pendant alkyl group in PMMA can lead to a higher T_g , resulting in greater polarity. Hence, IPNs with the PMMA phase swells to a maximum in polar solvents (Table III).

CONCLUSION

The IPNs were synthesized from several NBR–PH blends using polymethacrylates as the third component. The IPNs were formed between the NBR phase and poly(alkyl methacrylate)s. The presence of a hard PH segment increases the strength of IPNs while maintaining high damping characteristics. It is observed that the IPNs made are of higher strength compared to the corresponding NBR–PH blends. The strength of the PMMA-based IPN was found to be maximum. The $\tan \delta$ peaks of the IPNs are broad and have a split, showing a semicompatible nature. At a lower PH content, a broad $\tan \delta$ peak with distinct splitting was observed. However, at higher PH loading (>30 parts), the $\tan \delta$ value for polymethacrylate decreases drastically. The damping factor ($\tan \delta_{\max}$) for polymethacrylate reaches a maximum

Table III Swelling Behavior of NBR/PH Blends and IPNs in Various Media (%)

Composition	CCl ₄	MIBK	Xylene	Engine Oil C104	C ₂ H ₄ Cl ₂	NaCl Saturated Solution
95 NBR/5 PH	166	155	164	0	810	0
51 NBR/3 PH/46 PMMA	101	6	7	0	518	0
90 NBR/10 PH	160	134	97	0	538	0
53 NBR/6 PH/41 PMMA	110	64	41	0	342	0
80 NBR/20 PH	137	157	130	0	393	0
45 NBR/11 PH/44 PBuMA	120	140	115	0	236	0
70 NBR/30 PH	133	100	79	0	501	0
50 NBR/22 PH/28 PEMA	110	85	68	0	401	0

value of 0.6. The IPNs thus synthesized may find application as a vibration damper over a temperature range of -10 to 60°C .

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