

Studies on IPNs Based on Nitrile Rubber and Polyalkyl Methacrylates

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ABSTRACT: Sequential interpenetrating polymer networks (IPNs) based on nitrile rubber and various types of polyalkyl methacrylates such as poly(*n*-butyl methacrylate), poly(ethyl methacrylate), and poly(methyl methacrylate) were synthesized. The compositions of the IPNs could be varied by varying the reaction parameters such as swelling time and concentration of crosslinker. The tensile properties of the IPNs show that with increase in bulkiness of the ester group of the acrylates the tensile strength decreases, whereas elongation at break increases because of decreased stiffness of the acrylate phase. The dynamic modulus and loss tangent of the IPNs also show similar trend because of the above reason. All the IPNs were also tested for dynamic properties under multifrequency mode, and with the help of the WLF equation, the behavior of these IPNs in the frequency range of 1–10⁵ Hz were evaluated. The results showed reasonably high tan δ with good storage modulus in the entire frequency range for all the IPNs. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 549–554, 1997

INTRODUCTION

Polymeric materials are known for damping low-frequency vibration and sound waves appreciably in the sonic/ultrasonic range. The absorption of such waves in a polymer is a manifestation of mechanical relaxation of the segments of the long chains. The extent of absorption/damping is dependent on mechanical structure, thermodynamic state of the polymer, and the frequency of the wave. A polymer has a very well-defined temperature and frequency range where it shows pronounced absorption because it is related to its relaxation frequency. However, the range of temperature or frequency for high absorption is very narrow for common single polymers having well-defined glass transition temperatures. In order to broaden the range, the combination of polymers through formation of interpenetrating polymer networks has been reported by many researchers.^{1–7}

Interpenetrating polymer networks are a new

class of blends where two or more polymers are individually crosslinked in the immediate presence of another.¹ This results in tremendous improvement in the mechanical properties and also enhancement in the viscoelastic loss for a wider frequency and temperature range.^{1–7} Furthermore, due to the unique synthesis process, IPNs of fairly homogeneous phases can be made from completely immiscible polymers. The overall effectiveness of a vibration damper can be assessed by estimating the viscoelastic parameters such as dynamic moduli, loss moduli, and loss factors at frequencies of interest. The estimation of these properties at frequency ranges of 1–10⁵ Hz can be done through dynamic analysis with suitable time–temperature superposition principles.

The viscoelastic damping capability of a polymer is governed by the group-contribution as suggested by Sperling.² It is seen that acrylate, acrylonitrile, and acetate groups contribute more toward damping. The nitrile–vinyl acetate combination IPNs have been reported earlier.⁷ It has also been reported that polyalkyl methacrylates have high damping characteristics com-

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pared to many other polymers.⁸ In this paper, attempts are made to synthesize various IPNs with nitrile rubber–poly(*n*-alkyl methacrylate) combinations and characterization of these IPNs for tensile properties and viscoelastic properties at 1–10⁵ Hz.

EXPERIMENTAL

Materials

NBR (AN content 30%) was supplied by Rubo Chem (India) Ltd. Dicumyl peroxide (DCP) (Rubo Chem), a crosslinker for NBR, was used without further purification. Butyl methacrylate, ethyl methacrylate, and methyl methacrylate monomers (all from Fluka) were freed from inhibitor by standard methods. Benzoyl peroxide [(BPO)(BDH)] was recrystallized from methanol prior to use. Tetraethylene glycol dimethacrylate (TEGDM) (Fluka) was used as crosslinker for acrylates during IPN synthesis.

Preparation of NBR Sheets

NBR sheets were made using conventional methods. NBR was mixed with 5 parts of DCP 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 IPN

A preweighed sheet of cured NBR was swollen in acrylate monomer containing a 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 particular period, the NBR sheet was kept in an oven between two plates (to reduce the evaporation of monomer from the surface) at 60°C for polymerization. After polymerizing for the requisite time, the IPN samples were vacuum dried at 40°C to constant weight. Several IPNs were synthesized in this way by varying the reaction parameters such as swelling time and concentration of crosslinker.

Measurements of Physical Properties

Tensile Measurement

The tensile strength and elongation at break of IPNs were measured by an INSTRON (1123) at room temperature at a cross-head speed of 20 mm/

min using dumbbell-shaped specimens according to ASTM D638.

Elastic Moduli and Loss Tangent

The dynamic mechanical spectra of the IPNs were obtained by using a PL MK III Dynamic Mechanical Thermal Analyzer (DMTA). The samples were heated from –60°C to 110°C at a heating rate of 3°C/min. The samples were tested in the fixed frequency (1 Hz) mode. From the spectra, storage modulus (E') and loss tangent ($\tan \delta$) were obtained. Tests were also carried out at frequencies 0.3, 1, 3, 10, and 30 Hz in step-iso mode with a 5°C step in the temperature range of –55°C to 110°C. The isotherms obtained from this experiment were shifted around a reference temperature of 25°C with the help of time–temperature superposition software. Finally, the shifted isotherms produced master curves for E' and $\tan \delta$ in the frequency scale of 1–10⁵ Hz.

RESULTS AND DISCUSSION

Tensile Properties

The tensile properties of nitrile rubber and IPNs were studied and results are presented in Table I. From the results it can be seen that NBR shows very low tensile strength. It is quite obvious because of the fact that NBR is a random copolymer having no regular structure. However, on IPN formation the strength increases due to intimate mixing of the second crosslinked phase.⁹ Moreover, as concentration of the crosslinker increases, the strength further augments for all the IPNs. This is possibly due to reduced domain size³ and increased crosslink density.⁴ The value of elongation at break for IPNs has reduced considerably as compared to NBR. This is attributed to the presence of hard polymethacrylate segments in the NBR matrix. Furthermore, the decrease is more significant in case of NBR/PMMA IPNs. Similar trends have been observed for other systems.¹⁰ The stiffness of the segments is inversely related to the bulkiness of the ester group. The bulkiness of ester group in case of PMMA being lowest, the NBR/PMMA IPNs are stiffest in the present series. Hence NBR/PMMA IPNs show lower elongation at break.

Dynamic Mechanical Properties

The dynamic mechanical properties of NBR as well as IPNs are evaluated by DMTA and few of

Table I Mechanical Properties of IPNs

Composition	% TEGDM	Tensile Strength (MPa)	% Elongation at Break
NBR	—	1.2	176
NBR/PBuMA			
75/25	2	3.9	79
80/20	4	3.4	88
80/20	6	5.5	85
65/35	8	6.5	104
NBR/PEMA			
50/50	2	3.1	76
50/50	4	3.9	70
NBR/PMMA			
85/15	2	2.3	56
70/30	4	3.2	65
70/30	6	4.1	65
70/30	8	5.8	65

the representative spectra of dynamic modulus (E') and loss factor ($\tan \delta$) are given in Figures 1 and 2, respectively. From the figures, temperatures of E''_{\max} and $\tan \delta_{\max}$, value of $\tan \delta_{\max}$, half peak ($\tan \delta$) width, and area under the $\tan \delta$ temperature curve (t_a) are calculated and depicted in Tables II and III.

The storage modulus plot shows that NBR has a low dynamic modulus temperature plateau com-

pared to the IPNs. NBR, being a random copolymer of butadiene, and acrylonitrile will have a low modulus. Introduction of hard acrylate segments through IPN formation can result in high modulus material. In the case of IPNs, as the bulkiness of the ester group in poly(alkyl methacrylates) decreases, the modulus as well as temperature range increases. This is again due to increased stiffness of the chains or decreased bulkiness of the acrylate group.

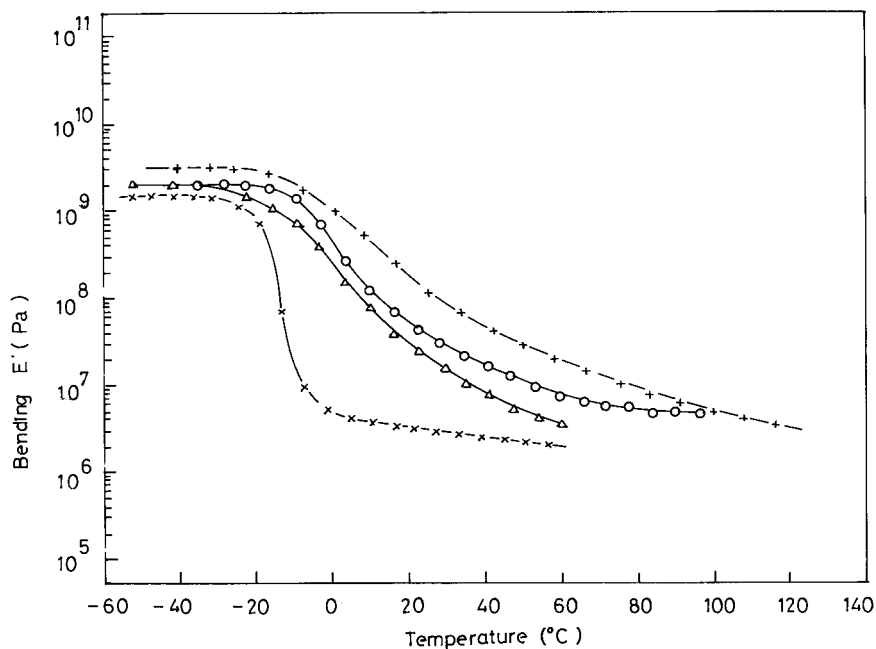


Figure 1 Dynamic modulus versus temperature for NBR and IPNs: (x) NBR; (Δ) 85/15 NBR/PBuMA (2% TEGDM); (O) 50/50 NBR/PEMA (2% TEGDM); (+) 70/30 NBR/PMMA (4% TEGDM).

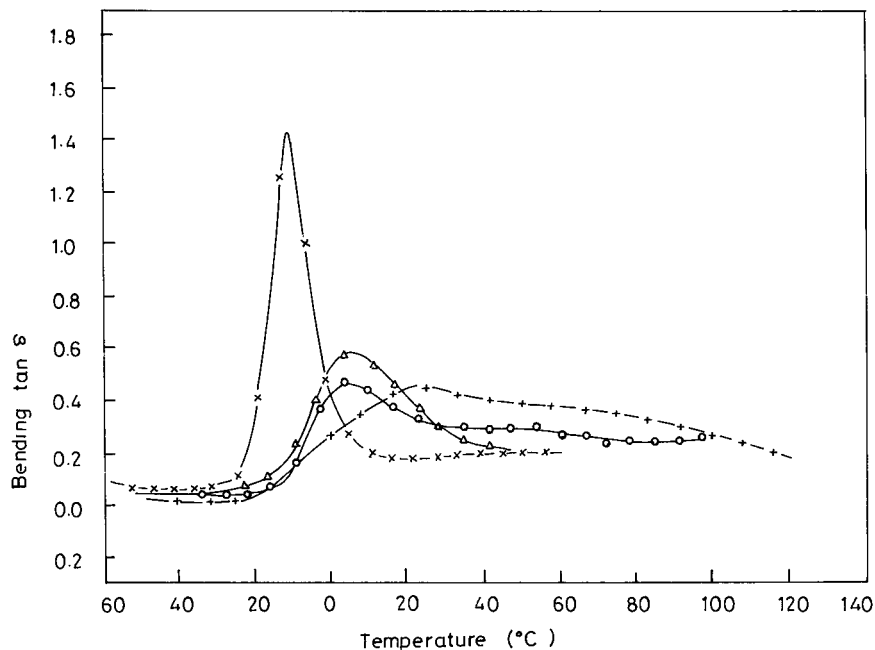


Figure 2 $\tan \delta$ versus temperature for NBR and IPNs: (x) NBR; (Δ) 85/15 NBR/PBuMA (2% TEGDM); (\circ) 50/50 NBR/PEMA (2% TEGDM); (+) 70/30 NBR/PMMA (4% TEGDM).

From Figure 2 it is observed that NBR has a sharp $\tan \delta$ peak at a relatively lower temperature (-11.4°C) indicating its suitability as a high-frequency narrow band damper. On the other hand, the $\tan \delta$ peaks for all the IPNs are broad and have inwardly shifted to a temperature between the transition peaks of NBR and corresponding polyalkyl methacrylates. All IPNs showed a broad $\tan \delta$ peak, indicating that there was no macro phase separation between two crosslinked matri-

ces. The magnitude of $\tan \delta$ peak for NBR is maximum (1.4) but on IPN formation the value of $\tan \delta_{\max}$ decreases.⁷

It can be explained, based on the observation by Sperling,² that the nitrile group contributes the maximum toward damping. Hence, in IPN the effectivity of $-\text{CN}$ group is reduced because of the presence of lesser contributing acrylate groups. Even in case of acrylates the extent of damping is dependent on the bulkiness of ester

Table II Dynamic Mechanical Properties of IPNs

Composition	% TEGDM	Temperature ($^\circ\text{C}$) for E''_{\max}	Temperature ($^\circ\text{C}$) for $\tan \delta_{\max}$
NBR	—	-15.5	-11.4
NBR/PBuMA			
85/15	2	-5.0	5.0
80/20	4	-10.0	0.0
80/20	6	0.0	10.0
65/35	8	-3.0	13.0
NBR/PEMA			
50/50	2	-5.5	4.6
50/50	4	-3.5	10.1
NBR/PMMA			
70/30	4	-15.0	-10.0
65/35	6	-6.0	10.0
65/35	8	0.0	25.3

Table III Damping Characteristics of IPNs

Composition	% TEGDM	$\tan \delta_{\max}$	t_a (°C)	1/2 Peak Width of $\tan \delta$ curve (°C)
NBR	—	1.4	24.5	15.0
NBR/PBuMA				
85/15	2	0.61	19.5	26.5
80/20	4	0.63	16.7	30.0
80/20	6	0.45	16.8	30.0
65/35	8	0.43	17.9	43.0
NBR/PEMA				
50/50	2	0.46	16.5	58.0
50/50	4	0.38	21.2	76.0
NBR/PMMA				
70/30	4	0.45	15.5	32.0
65/35	6	0.36	16.2	57.0
65/35	8	0.34	23.3	75.0

groups. Thus, IPNs based on NBR/PBuMA show the highest $\tan \delta$ peak and the lowest in case of NBR/PMMA. This is due to the increased stiffness of the PMMA segment. The extent of mechanical damping is measured from broadness as well as the area under the $\tan \delta$ -temperature curve.¹¹ Table III shows that area under $\tan \delta$ -temperature (t_a) curve for NBR and IPNs does not vary appreciably. But the temperature range of damping, as measured in terms of $\frac{1}{2}$ peak width of the $\tan \delta$ curve, is higher for all the IPNs compared to NBR. The broadness is maximum for NBR/PMMA IPNs because of the wider separation of their corresponding relaxation temperatures. The viscoelastic properties in temperature scale is logarithmically related to those in frequency scale as per the phenomenological relaxation theory.¹² Hence, these IPNs having broad bands in temperature scale are expected to damp vibrations over a wide range of frequency.

For vibration damping, the material should have higher loss properties and appreciable dynamic modulus at low frequencies typically 0–10³ Hz. In order to evaluate the properties (E' and $\tan \delta$) in frequency scale, a time-temperature superposition principle based on the WLF equation¹³ was applied to two representative IPNs, NBR/PBuMA and NBR/PMMA. The samples were subjected to dynamic analysis in the multi-frequency mode from 0.3 to 30 Hz within a temperature range of –55°C to 110°C. The resulting curves were shifted with respect to a reference temperature of 25°C to obtain master curves of E' and $\tan \delta$ in the frequency scale with the help of

time-temperature superposition principle software of the PL-DMTA instrument. Figure 3 shows the dynamic modulus of NBR/PBuMA and NBR/PMMA in the frequency range of 1–10⁵ Hz and Figure 4 shows the $\tan \delta$ of these IPNs in the same frequency range. From these results it is clear that both the IPNs have reasonable storage modulus and $\tan \delta$ over the entire frequency range. It can also be seen that dynamic modulus of NBR/PMMA is marginally higher than that of NBR/PBuMA, but the $\tan \delta$ value of NBR/PBuMA is higher than that of NBR/PMMA in the entire range of frequency. Moreover, the differ-

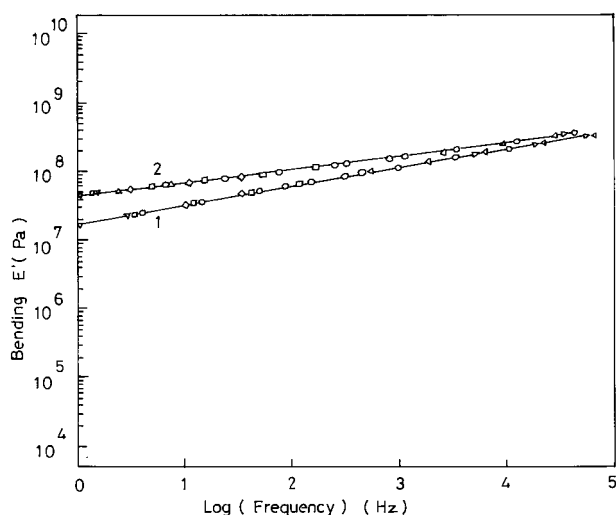


Figure 3 Master curve for dynamic modulus versus frequency for IPNs: (1) 50/50 NBR/PBuMA (2% TEGDM); (2) 50/50 NBR/PMMA (2% TEGDM).

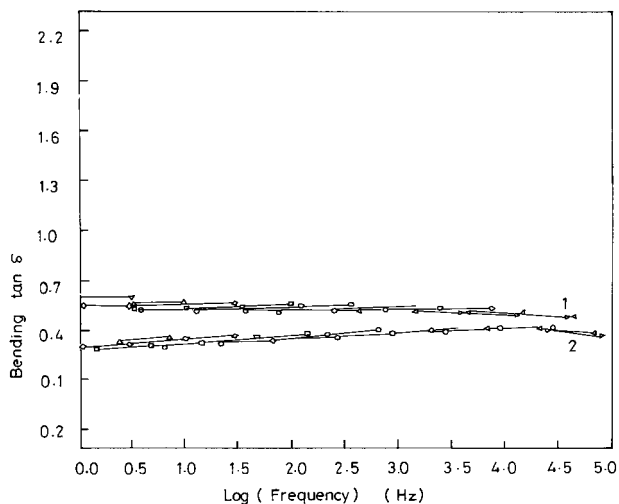


Figure 4 Master curve for $\tan \delta$ versus frequency for IPNs: (1) 50/50 NBR/PBuMA (2% TEGDM); (2) 50/50 NBR/PMMA (2% TEGDM).

ence in the lower frequency range (0–100 Hz) is significant for NBR/PBuMA (0.52–0.56) compared to NBR/PMMA (0.32–0.36). It can also be seen that the $\tan \delta$ values at higher frequency (10^2 – 10^5 Hz) for both the IPNs are appreciable. Therefore, it can be concluded that these materials find applications both as vibration damper as well as acoustic absorber.

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