

Studies on Interpenetrating Polymer Networks Based on Nitrile Rubber-Poly(vinyl chloride) Blends and Poly(alkyl methacrylates)

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SYNOPSIS

Several interpenetrating polymer networks (IPNs) based on nitrile rubber-poly(vinyl chloride) blends and various alkyl methacrylates have been synthesized. The rubber blends were swollen in methacrylate monomers containing required amounts of initiator and cross-linker for specific time periods and then polymerized at higher temperature. The composition of the IPNs could be varied by changing the swelling time. The IPNs were characterized for their glass-transition temperature, dynamic mechanical properties, and tensile properties. The effect of structure and composition on the vibration damping characteristics of these IPNs are discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs), because of their wide-range vibration damping characteristics,¹⁻⁸ have gained much importance in recent years. However, only a few references are available on IPNs based on rubbers.⁹⁻¹¹ Recently, the studies on IPNs based on nitrile rubber (NBR) and poly(vinyl acetate) were reported that were found to have a very broad glass transition.¹⁰ In order to obtain IPNs with improved mechanical properties NBR-poly(vinyl chloride) (PVC) blends have been selected. This blend is known to have good mechanical properties.^{12,13}

The present article deals with the synthesis and characterization of sequential IPNs based on NBR-PVC blends and poly(alkyl methacrylates). These IPNs are expected to have a broad glass transition around ambient temperature. Poly(alkyl methacrylates) were reported to have very high damping characteristics compared to many other polymer systems.⁷

Chang et al.^{7,14,15} have used the area under the E'' or $\tan \delta$ vs. temperature curves as measures of the

damping effectiveness of polymers and IPNs. Attempts have been made to correlate the structure and composition of the present IPNs on these two parameters as well.

EXPERIMENTAL

Materials

NBR-PVC blends of 70/30 (NVC 73) and 50/50 (NVC 55) compositions were obtained as raw stock (Rishiroop Polymers Limited, India). The NBR used for the above blends was of medium nitrile content (25%). Dicumyl peroxide (DCP) (Rubo Chem. Industries Ltd., India) a cross-linker for NBR was used without further purification. Butyl methacrylate (BMA), ethyl methacrylate (EMA), and methyl methacrylate (MMA) monomers (Fluka) were freed from inhibitor and distilled under reduced pressure before use. Tetraethylene glycol dimethacrylate (TEGDM) (Fluka) was used as received. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol before use.

Preparation of NBR-PVC Blend Sheet

NBR-PVC blends of both 70/30 and 50/50 composition were masticated and 3 phr of DCP was

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mixed in a roll mill. They were then cured into sheet form (1-mm thickness) at 150°C for 20 min under a pressure of 150 kgf/cm² using compression molding.

Synthesis of IPN

A preweighed sheet of cured NBR-PVC blend was swollen in alkyl MA monomer containing 0.2 wt % AIBN and 3 vol % TEGDM. A ratio of 1 : 10 (NVC: monomer) was maintained for all experiments. After swelling for a particular period (16 h), the NBR sheet was taken out, and adhering monomer on surface removed by wiping. It was then wrapped in aluminum foil and kept in between two stainless steel plates (to reduce the evaporation of monomer from the surface) in an oven at 80°C for polymerization for 1–2 h and then under reduced pressure at 80°C for 24 h to remove unreacted monomer. This ensured complete polymerization of MA monomer and no further weight loss. The composition was calculated from the total weight of IPN knowing the initial weight of the NBR-PVC blend. However, some monomers were lost during the polymerization and also during the vacuum treatment.

Swelling Characteristics

Preweighed NBR-PVC blends were swollen in various solvents such as *n*-hexane, cyclohexane, carbon tetrachloride, toluene, benzene, chloroform, dichloroethane, dioxane, acetonitrile, and methanol and the equilibrium swell ratio was determined. Blends

were also allowed to swell in various alkyl MA monomers for different time periods. The swell ratio of the blends in the various MA monomers were determined at an interval of 2–6 h and then after 16 h. The equilibrium swell ratio was also determined.

MEASUREMENT OF PHYSICAL PROPERTIES

Glass-Transition Temperature (T_g)

The T_g s of the IPNs was measured employing a DuPont 910 differential scanning calorimeter. The operating temperature was –80 to 100°C. A heating rate of 5°C/min was used and the sample weight was 5 mg.

Dynamic Mechanical Properties

The dynamic mechanical spectra were recorded using a dynamic mechanical analyzer (Dupont DMA model 983) at temperatures between –80 and 125°C. The measurements were carried out at a heating rate of 5°C/min and at the resonance mode.

Mechanical Properties

The tensile strength and elongation at break of the IPNs were measured by an Instron Testing Machine (Model 1123) using dumbbell-shaped specimens and cross-head speed of 20 mm/min, according to ASTM D638-85.

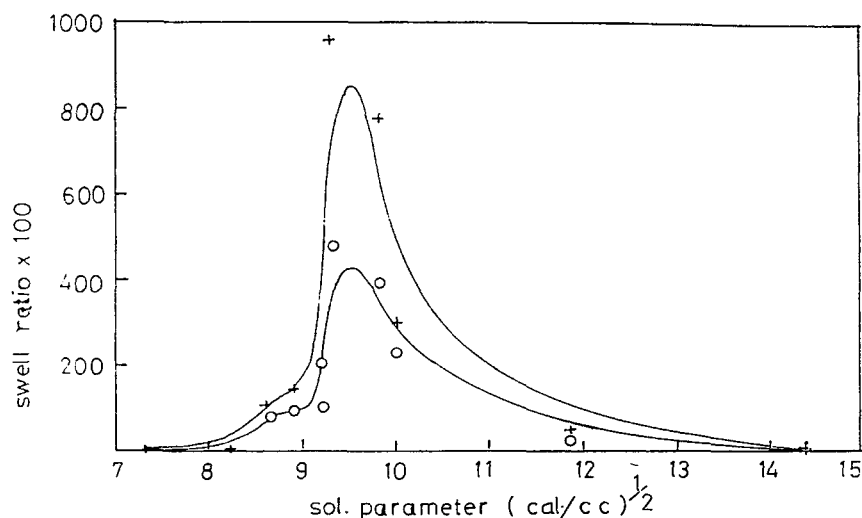


Figure 1 Equilibrium swell ratio $\times 100$ vs. solvent solubility parameter for (+-+-) NVC 73 and (-o-o-) NVC 55.

Table I Swelling of NVC Blends in Methacrylate Monomers

| Blend | Monomer | Swell Ratio $\times 100$ | | | | Equilibrium |
|--------|---------|--------------------------|-----|-----|------|-------------|
| | | 2 h | 4 h | 6 h | 16 h | |
| NVC 73 | MMA | 116 | 154 | 183 | 246 | 255 |
| | EMA | 96 | 135 | 176 | 226 | 230 |
| | BMA | 43 | 73 | 97 | 150 | 156 |
| NVC 55 | MMA | 82 | 106 | 120 | 130 | 140 |
| | EMA | 62 | 99 | 114 | 123 | 128 |
| | BMA | 37 | 61 | 80 | 101 | 102 |

RESULTS AND DISCUSSION

Swelling Behavior of NBR-PVC Blends

The swelling behavior of NBR/PVC blends were found to vary depending on the nature of the alkyl side group of the MA monomer. In order to understand the swelling characteristics of NRR-PVC blends, the solubility parameters were determined experimentally by the swelling method. Figure 1 shows the plot of equilibrium swell ratio vs. solvent solubility parameter. It can be seen that both compositions show a well-defined maxima at 9.5 (cal/cm³)^{0.5}.

Table I shows the swell ratio of the blends in different monomers. The uptake of MMA is the highest by both the blends and that of BMA is the

lowest. This could be attributed to the solubility parameter of the MMA (8.8), which is closer to that of NBR-PVC blends (9.5) whereas for EMA and BMA the values are 8.3 and 8.2, respectively.¹⁶ NVC 73 blends swell more in all monomers compared to NVC 55. The same observation was also made during the study of equilibrium solvent swell (Fig. 1).

Differential Scanning Calorimetric (DSC) Studies

The T_g s of the NBR-PVC blends and the IPNs were measured using DSC. A few representative spectra are shown in Figure 2. The NVC 73 shows a T_g at -25°C and NVC 55 at -22°C . It may be noted that pure NBR shows a T_g around -32°C .¹⁰ Thus the presence of the PVC phase raised the T_g of the nitrile phase owing to the partial miscibility of the two components.¹³ The acrylonitrile content of the NBR used was 25% and this is not completely compatible with PVC.¹⁷

The DSC thermograms of the IPNs (Fig. 2) showed the onset of T_g at the same temperature as that of the starting blends. The IPNs are having a very broad glass transition ranging between the two starting polymers. In the present system, only the onset of T_g could be clearly obtained. However, there was no separate T_g present for the MA system, confirming the formation of IPN. Dynamic mechanical analysis was more helpful in understanding the phase transition clearly.

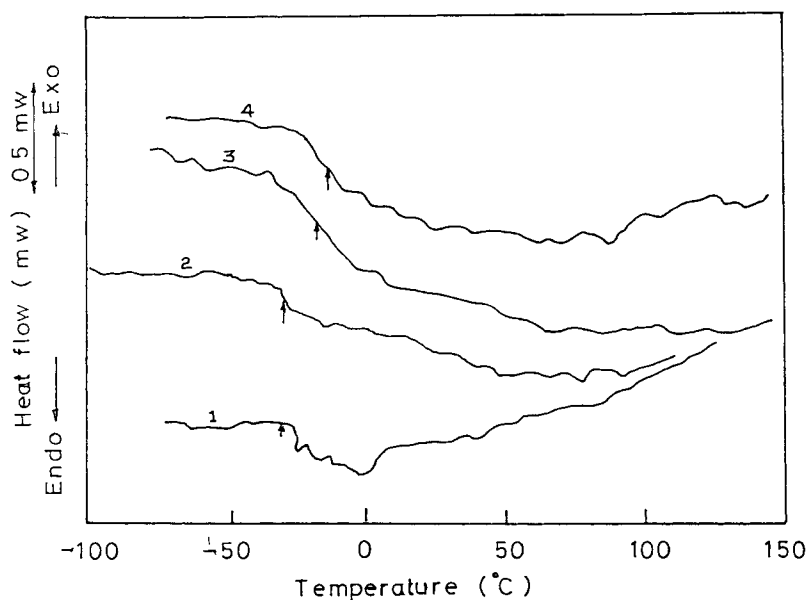


Figure 2 DSC thermograms of NVC blends and IPNs: (1) NVC 73; (2) 58 BMA/42 NVC 73; (3) NVC 55; (4) 40 BMA/60 NVC 55.

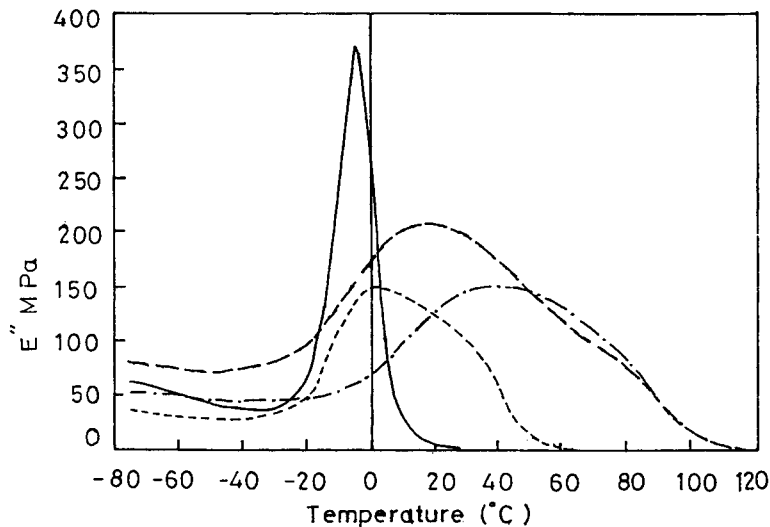


Figure 3 E'' vs. temperature plots for NVC 73 and IPNs: (—) NVC 73; (---) 58 BMA/42 NVC 73; (----) 63 EMA/37 NVC 73; (-·-·-) 68 MMA/32 NVC 73.

Dynamic Mechanical Analysis

Results of dynamic mechanical analysis of the blends and the IPNs are summarized in Table III. Plots of E'' , $\tan \delta$, and E' vs. temperature for all IPNs are given in Figures 3–8. Both NVC 73 and NVC 55 blends show a narrow E'' or $\tan \delta$ peaks (Figs. 3–8). Temperature corresponding to E''_{\max} was found to be -4°C for NVC 73 and $+5^{\circ}\text{C}$ for NVC 55 whereas for pure NBR it was around -10°C .¹⁰ This again confirms the fact that the presence of PVC increased the T_g of the NBR phase and was in conformity with the DSC results.

The DMA studies show that E'' and $\tan \delta$ vs. temperature curves of the various IPNs are very broad compared to the starting NVC blends. For example, the E'' vs. temperature ranges from -20 to $+5^{\circ}\text{C}$ for NVC 73, whereas for the IPN based on NVC 73 PBMA it begins at -20°C and ends at $+60^{\circ}\text{C}$. NVC 55/PMMA showed the maximum broadness for E'' -temperature curve, that is, from -20 to $+100^{\circ}\text{C}$. The damping characteristics of the IPNs should not be judged in terms of half peak width because the areas under the curves differ mainly due to the broadness at the low E'' or $\tan \delta$. Sperling et al.^{11,14,15} quantified the chemical group contribution toward damping

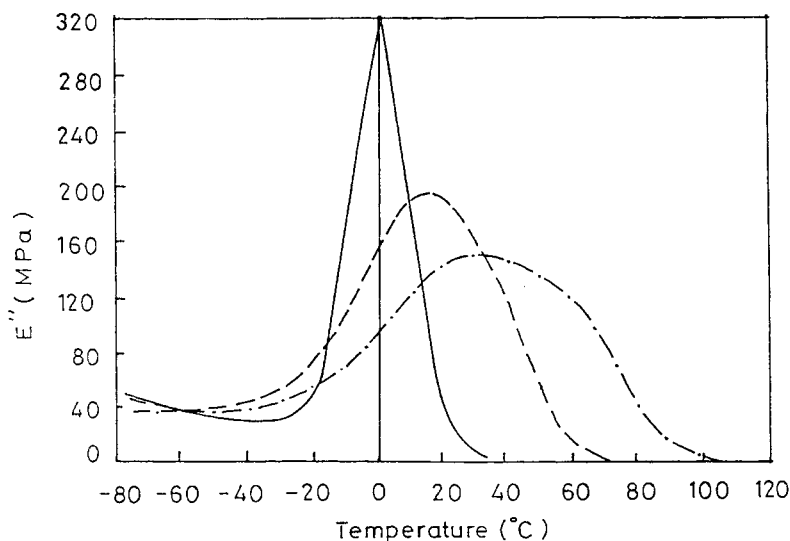


Figure 4 E'' vs. temperature plots for NVC 55 and IPNs: (—) NVC 55; (---) 55 EMA/45 NVC 55; (-·-·-) 58 MMA/42 NVC 55.

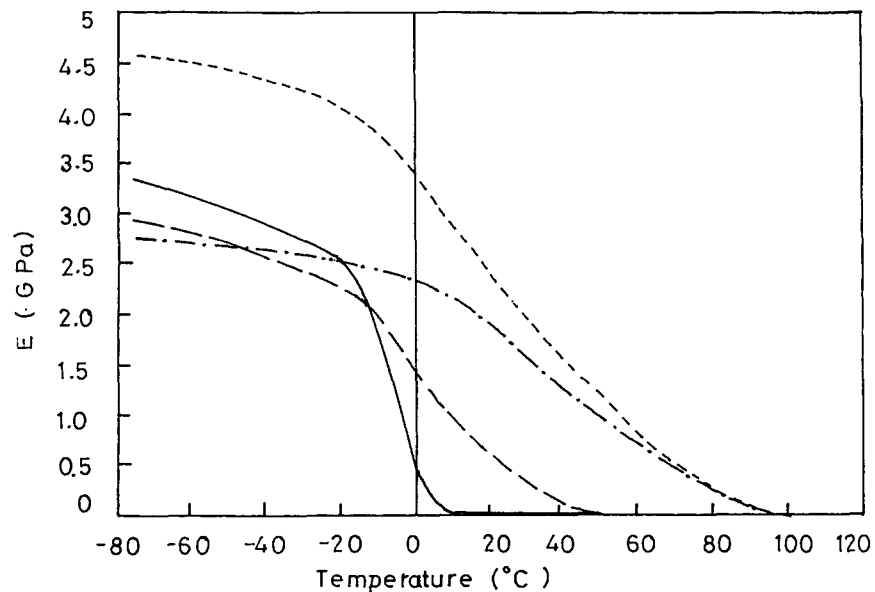


Figure 5 E' vs. temperature plots for NVC 73 and IPNs: (—) NVC 73; (---) 58 BMA/42 NVC 73; (- · - · -) 63 EMA/37 NVC 73; (····) 68 MMA/32 NVC 73.

and found that the loss area (LA) is a valuable tool in designing polymeric damping materials based upon chemical composition. On the other hand, the area under the $\tan \delta$ -temperature curve, tA , was not found to obey a group contribution analysis. This may be attributed to the fundamental difference between the loss modulus and $\tan \delta$. Whereas, E'' is a measure of the amount of mechanical energy converted to heat during the DMA experiment and dependent upon chemical structure, $\tan \delta$ is equal to

the ratio E''/E' . The decrease in E' in the glass-transition region has no quantitative theory as yet in relation to chemical structure of the material. However, tA is considered because it has relevance to designing constrained layer vibration dampers.

The LA and the $\tan \delta$ area was calculated for the NVC blends and the IPNs. The values are summarized in Table II. Both LA and tA increased substantially for the IPNs compared to the starting NBR/PVC blends. The MA structure was found to

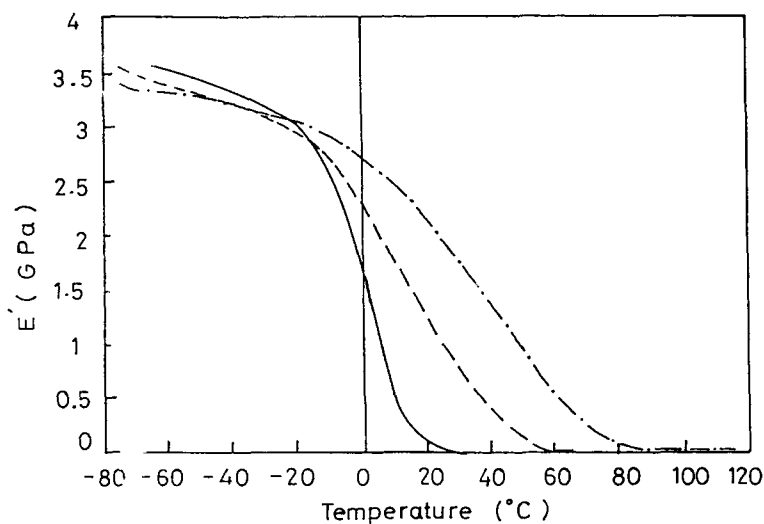


Figure 6 E' vs. temperature plots for NVC 55 and IPNs: (—) NVC 55; (---) 55 EMA/45 NVC 55; (- · - · -) 58 MMA/42 NVC 55.

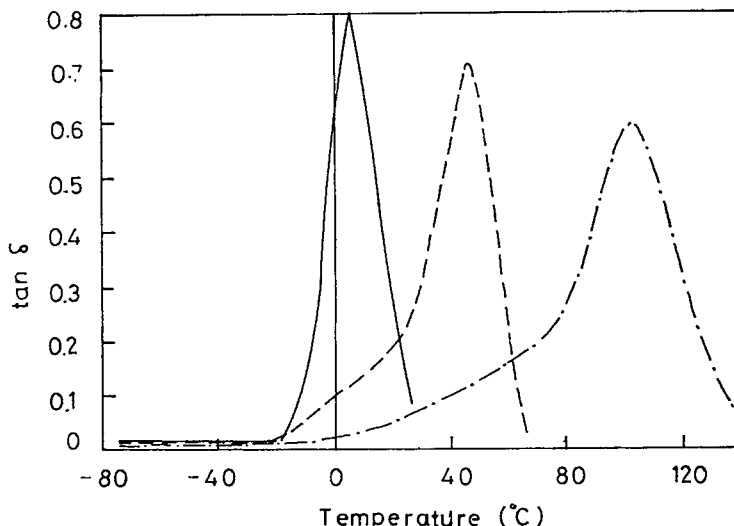


Figure 7 Tan δ vs. temperature plots for NVC 73 and IPNs: (—) NVC 73; (---) 58 BMA/42 NVC 73; (-·-·-) 63 EMA/37 NVC 73.

affect the damping effectiveness of the IPN. PMMA-based IPNs showed the maximum loss area and PBMA-based IPNs had the lowest LA among the IPNs. The highest value of PMMA was primarily attributed to the strong secondary transitions occurring in this temperature region; secondary transitions for PBMA occur at much lower temperatures.

NBR/PVC 50/50 blend shows a higher loss area compared to 70/30 blend (Table II) but the tan δ areas show an opposite trend. This might be due to the high E' value of the NVC55 blend and because tan δ is inversely related to E' , its value is smaller.

It may also be noted that the tan δ_{max} values (Table III) do not show any direct relation with the LA and tA values. This is because in IPNs, although the maximum value is slightly lower, the curves broadened resulting in an increase in the area or damping.

From Figures 5 and 6 it can be seen that the IPNs have a high modulus-temperature plateau compared to NVC blends and this plateau increases continuously when the MA structure was changed from butyl to methyl. The E' values at room temperature given in Table III also show the same trend.

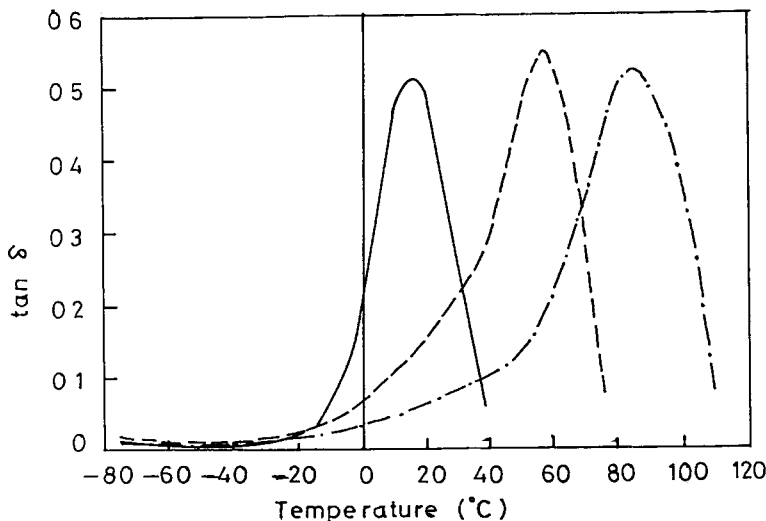


Figure 8 Tan δ vs. temperature plots for NVC 55 and IPNs: (—) NVC 55; (---) 55 EMA/45 NVC 55; (-·-·-) 58 MMA/42 NVC 55.

Table II Damping Characteristics of NVC Blends and IPNs

| Composition | LA (GPa K) | tA (K) |
|------------------|---------------|-----------|
| NVC 73 | 4.14 | 16.23 |
| 58 BMA/42 NVC 73 | 6.14 | 21.68 |
| 63 EMA/37 NVC 73 | 8.53 | 28.21 |
| 68 MMA/32 NVC 73 | 11.05 | — |
| NVC 55 | 6.56 | 14.64 |
| 55 EMA/45 NVC 55 | 9.27 | 21.14 |
| 58 MMA/42 NVC 55 | 10.03 | 22.91 |

(—) Sample failed at the $\tan \delta$ peak maxima. LA, loss area; tA, area under $\tan \delta$ -temperature curve.

Tensile Properties

The NBR-PVC blends have high tensile strength and elongation compared to pure NBR (Table IV). The IPNs based on the nitrile blends and MAs were also found to have good mechanical properties. The tensile strength increases from PBMA-based IPNs to PMMA-based IPNs. The elongation at break of the IPNs, however, decreases from PBMA IPNs to PMMA IPNs. This is evident because the elastic modulus of MA polymers decreases as the bulkiness of the pendent alkyl group increases. Therefore PMMA will have the highest mechanical strength out of these three MA polymers.

CONCLUSION

A number of IPNs based on nitrile-PVC blends and various alkyl MAs were synthesized. The composi-

Table IV Tensile Properties of IPNs

| Composition | Tensile Strength (MPa) | Elongation (%) |
|----------------------|------------------------------|-------------------|
| NBR | 1.18 | 176 |
| NVC 73 | 5.20 | 370 |
| 58% BMA + 42% NVC 73 | 4.12 | 206 |
| 63% EMA + 37% NVC 73 | 6.27 | 146 |
| 68% MMA + 32% NVC 73 | 17.64 | 40 |
| NVC 55 | 15.29 | 300 |
| 40% BMA + 60% NVC 55 | 11.07 | 210 |
| 55% EMA + 45% NVC 55 | 14.41 | 110 |
| 58% MMA + 42% NVC 55 | 29.11 | 50 |

tion of the IPN can be varied by changing the swelling time of the rubber blend in the MA monomer. The swelling behavior of the rubber blend also depends on the MA structure. The IPNs were characterized for their T_g , dynamic mechanical properties, and tensile properties.

The glass transition was broadened as obtained from the DSC and DMA studies. DMA studies also show that both the loss area and the area under the $\tan \delta$ curve, which refers to the magnitude of the damping factor, increases substantially in the IPNs. Thus this study shows that these IPNs will find application as broad range vibration dampers that can damp sound and vibration over a wide range of temperatures. The tensile studies show that the IPNs have good mechanical properties. By changing the MA structure and the composition, IPNs of desirable strength and damping can be obtained.

Table III Dynamic Mechanical Properties of NVC Blends and IPNs

| Composition | E' at RT (GPa) | E'' Peak Temp. (°C) | Tan δ_{\max} Value | Temp. for Tan δ_{\max} |
|------------------|---------------------|--------------------------|------------------------------|----------------------------------|
| NVC 73 | 0.008 | -4 | 0.80 | 5 |
| 58 BMA/42 NVC 73 | 0.485 | 2 | 0.71 | 35 |
| 63 EMA/37 NVC 73 | 1.75 | 38 | 0.60 | 90 |
| 68 MMA/32 NVC 73 | 2.2 | 20 | 0.52 | 98 |
| NVC 55 | 0.044 | 5 | 0.52 | 15 |
| 55 EMA/45 NVC 55 | 0.998 | 18 | 0.54 | 55 |
| 58 MMA/42 NVC 55 | 1.97 | 30 | 0.53 | 85 |

RT, room temperature.

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