

# Sequential Interpenetrating Polymer Network of Poly(ethyl methacrylate) and Carboxylated Nitrile Rubber: Dynamic Mechanical Analysis and Morphology

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**Abstract:** An interpenetrating polymer network (IPN) based on poly(ethyl methacrylate) (PEMA) and carboxylated nitrile rubber was synthesized. Peroxide crosslinked XNBR was swollen in ethyl methacrylate containing benzoyl peroxide as initiator and tetraethylene glycol dimethacrylate as crosslinking agent. A full and sequential IPN is formed by the two independently crosslinked phases of XNBR and PEMA. Dynamic mechanical analysis of the 50/50 XNBR/PEMA IPN shows a single, broad peak whereas a 50/50

blend shows two distinct peaks, indicating the pinning down of a microheterogeneous structure during the IPN formation rather than macrophase separation as in blends. SEM analysis confirms the development of a cocontinuous intimate structure of the IPN. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1487–1491, 2005

**Key words:** interpenetrating networks (IPN); phase separation; rubber; morphology

## INTRODUCTION

Interpenetrating polymer networks (IPNs) are special kinds of polymer blends that are defined as a mixture of two or more crosslinked polymer networks which have partial or total physical interlocking between them.<sup>1</sup> Consequently, there is a substantial improvement in the mechanical properties and an enhancement of the viscoelastic loss over a wider frequency and temperature range.<sup>1–5</sup> The use of IPNs in various fields is an area of potential development since it is easy to strike a balance between the dynamic and other properties such as strength, creep, and fatigue, by a judicious selection of polymer components.

Polymers have been widely used in many areas of technology for achieving acoustic and vibration isolation and damping due to a unique combination of low modulus and inherent damping.<sup>6,7</sup> The damping properties of a polymer are governed by its glass transition. When the chain segments in the polymer make deGennes reptation or Brownian motions, molecular vibrational energy is converted into heat energy and a loss peak appears in a temperature/frequency range. The extent of absorption or damping depends on the molecular structure, the thermodynamic state of the polymer, and the wave frequency.

However, for common polymers, the transition occurs at very high frequencies and within a narrow frequency/temperature range. As the acoustic spectrum covers frequencies in the range of 20 Hz to 20 kHz, it is practically not possible to design a damping material from a single polymer. One of the many ways to broaden the range and to lower the transition frequencies is the formation of an interpenetrating polymer network. This is because IPNs display a broad glass-to-rubber transition due to the microheterogeneities in the matrix and hence exhibit a broad range of temperatures and frequencies of damping.<sup>8,9</sup> This effect, hence, is especially useful for outdoor, machinery, and vehicular damping materials.

The viscoelastic damping capability of a polymer is governed by the inherent groups, as suggested by Sperling.<sup>8,9</sup> For example, acrylate, acrylonitrile, and acetate groups contribute more toward damping. IPNs based on nitrile rubber–poly(vinyl acetate),<sup>10</sup> nitrile rubber/phenolic blend–poly(alkyl methacrylate)s,<sup>11</sup> nitrile rubber–poly(alkyl methacrylate)s,<sup>12</sup> nitrile rubber/poly(vinyl chloride) blend–poly(alkyl methacrylate)s,<sup>13</sup> and poly(vinyl chloride-co-vinyl acetate)–poly(alkyl methacrylate)s<sup>14</sup> have been reported. These studies have shown the high damping characteristics of poly(alkyl methacrylate)s compared to many other polymers.

Carboxylated nitrile rubber (XNBR) is a high performance specialty rubber having pendent carboxyl groups at random along the chain. The introduction of carboxyl groups and the subsequent formation of ion-

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rich aggregates at these sites profoundly affect the vulcanizate properties and give high strength, excellent abrasion resistance, and improved adhesion to metal and other surfaces.<sup>15,16</sup> XNBR continues to find new applications under demanding conditions. Also, it has both acrylonitrile and acrylic acid groups that contribute to good damping. Hence, we have chosen XNBR as the matrix for our IPN.

We have earlier reported the sequential IPNs based on XNBR and PMMA.<sup>17</sup> This paper describes the study of an IPN of XNBR and poly(ethyl methacrylate) (PEMA) and the characterization of the microstructure by scanning electron microscopic and dynamic mechanical analysis.

## EXPERIMENTAL

### Materials

Carboxylated nitrile rubber (Krynac X7.4, carboxyl content 6.9%, ML (1+4)<sub>100°C</sub>: 39) was obtained from Polysar, USA. Dicumyl peroxide obtained from S.D. Fine Chemicals, India was used as received. EMA monomer (from Fluka, Switzerland) was used as received. Tetraethylene glycol dimethacrylate (TEGDM) (Fluka, Switzerland) was the crosslinker for methacrylates. Benzoyl peroxide (BPO) (BDH Chemicals, India) was recrystallized from methanol prior to use. Poly(ethyl methacrylate) (molecular weight  $\bar{M}_n = 65,000$  g/mol) was synthesized by free radical polymerization using azobisisobutyronitrile (AIBN) as initiator.

### Preparation of XNBR sheet

XNBR was compounded on a two-roll mill with 2 phr of DCP. The compound was compression molded at 150°C for 20 min in an electrically heated press at 150 kg/cm<sup>2</sup>. Prior to use, the rubber sheets were washed with water and dried in a vacuum oven at 80°C.

### Preparation of blend

The blend of XNBR and PEMA was prepared in a Brabender Plasticorder (model LABSTATION) mixing station. PEMA was softened for 2 min at 150°C and 100 rpm. XNBR, masticated and cut into small pieces, was then added and mixing continued for 5 min. The blend was taken out immediately and sheeted in a two-roll mill. Molding was done at 150°C for 3 min in a compression molding press at 150 kg/cm<sup>2</sup> pressure.

### Synthesis of IPN

XNBR sheets were weighed and swollen in an excess amount of ethyl methacrylate containing 0.5% BPO (initiator for EMA polymerization) and 4% TEGDM

(crosslinker for EMA) for a particular time. The swollen sheets were kept at 60°C for polymerization. After polymerizing for the required time, the IPN samples were vacuum dried to constant weight at 80°C. The percent increases in weight of XNBR sheets, when swollen for 1 h in TEGDM and EMA were 26 and 129%, respectively, which shows that the components actually swell and penetrate the rubber prior to the IPN formation.

### Dynamic mechanical analysis

The dynamic mechanical analysis of the samples was carried out on a Rheometric Scientific Dynamic Mechanical Thermal Analyzer model PL Mk III. The samples were scanned from -75 to +125°C at a heating rate of 3°C/min. The dynamic stress applied on the sample was such as to produce a dynamic (oscillatory) strain amplitude of 32  $\mu\text{m}$ , at a fixed frequency of 1 Hz.

### Scanning electron microscopy

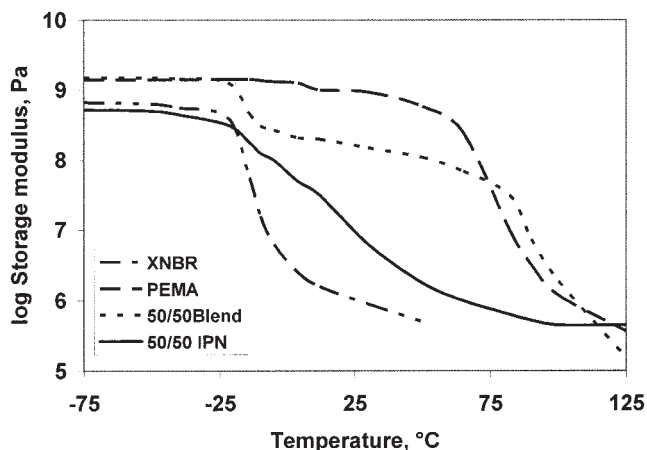
The morphological studies were carried out using a Leo 1477 (UK) scanning electron microscope. Low-temperature fractured samples were either etched with solvent or used as such and coated with gold for the study.

## RESULTS AND DISCUSSION

A full IPN is a system in which both the polymer components are crosslinked, each through a different curing mechanism. This produces either a simultaneous (if both networks are cured simultaneously) or sequential (if one component is polymerized followed by swelling with the second monomer which is then reacted) IPN.<sup>1</sup> Hence, the present system can be termed as a full and sequential IPN considering that both the components are crosslinked through different curing mechanisms and that the formation of IPN has taken place in a sequential mode.

### Dynamic mechanical analysis

Dynamic mechanical testing is a versatile and sensitive tool enabling a complete exploration of relaxational mechanisms in viscoelastic materials. The most common use of DMA is the determination of the glass transition temperature ( $T_g$ ), where the molecular chains of a polymer obtain sufficient energy, usually from thermal sources, to overcome the energy barriers for segmental motion. This is also the region where there is maximum loss of applied energy is observed, usually as a peak in the traces of  $\tan \delta$  or loss factor versus frequency or temperature.



**Figure 1** Dynamic storage modulus versus temperature of single polymers, 50/50 XNBR/PEMA blend, and 50/50 XNBR/PEMA IPN.

The dynamic mechanical properties—storage modulus ( $E'$ ) and loss factor ( $\tan \delta$ )—of all the samples are illustrated in Figures 1 and 2. The magnitude and nature of the change in the dynamic modulus of elasticity are determined both by the intermolecular and intramolecular interactions, the latter having greater influence in the different physical states of the polymer.<sup>18</sup> In the glassy state, when the intermolecular interactions are sufficiently great, the dynamic modulus is in the range of  $10^9$  Pa. But in the rubbery state, when the energy of intermolecular interactions is appreciably lower, the dynamic modulus of the same polymer is in the range of  $10^6$  Pa. Any change in the energy of intermolecular interactions, which will affect molecular motion in polymers, also has an appreciable influence on the magnitude and nature of the mechanical loss.

XNBR, being a random copolymer of butadiene, acrylonitrile, and acid monomer, will have a low modulus. Figure 1 shows that XNBR has a sharp glass-to-rubber transition and a low dynamic modulus-temperature plateau compared to the IPN or the blend. PEMA, being a plastic, shows the highest modulus and a sharp transition. The 50/50 XNBR/PEMA blend shows two distinct transitions representing the individual polymers XNBR and PEMA, clearly indicating the immiscibility of the components. The IPN shows a broad transition, typical of the interpenetrating network formation.<sup>1,5</sup>

The loss tangents versus temperature plots are shown in Figure 2. As the temperature is increased, the damping goes through a maximum in the transition region and then decreases in the rubbery region. The damping is low below  $T_g$  since the chain segments are frozen in that region. Below  $T_g$ , the deformations are primarily elastic and the molecular motions resulting in viscous flow are less. Above  $T_g$ , the damping is

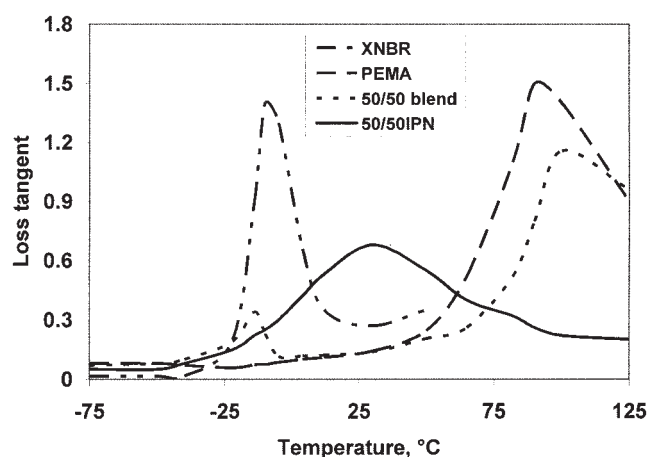
low because the molecular segments are free to move and there is no resistance to flow. The damping is high in the transition region because of the initiation of micro-Brownian motion of the macromolecules and their stress relaxation, although not all the segments will be able to take part in such relaxation together. The micro-Brownian movement is concerned with the cooperative diffusional motion of the main chain segments. The maximum damping occurs in a region where most of the chain segments take part in this cooperative motion under harmonic stress.

It is seen that both XNBR and PEMA have sharp loss tangent peaks at  $-5$  and  $90^\circ\text{C}$ , respectively. The immiscibility of the 50/50 blend is clearly evident from two distinct transitions at  $-14$  and  $100^\circ\text{C}$  corresponding to the individual polymers. The slight shifting of  $T_g$ s in blends from individual  $T_g$ s of components has been attributed to the apparent immiscibility of the components.<sup>19</sup> The IPN, on the other hand, shows a broad loss tangent peak that is shifted to a temperature between the  $T_g$ s of XNBR and PEMA. The broad, but single peak of the IPN indicates that there is no macrophase separation between the two crosslinked phases.

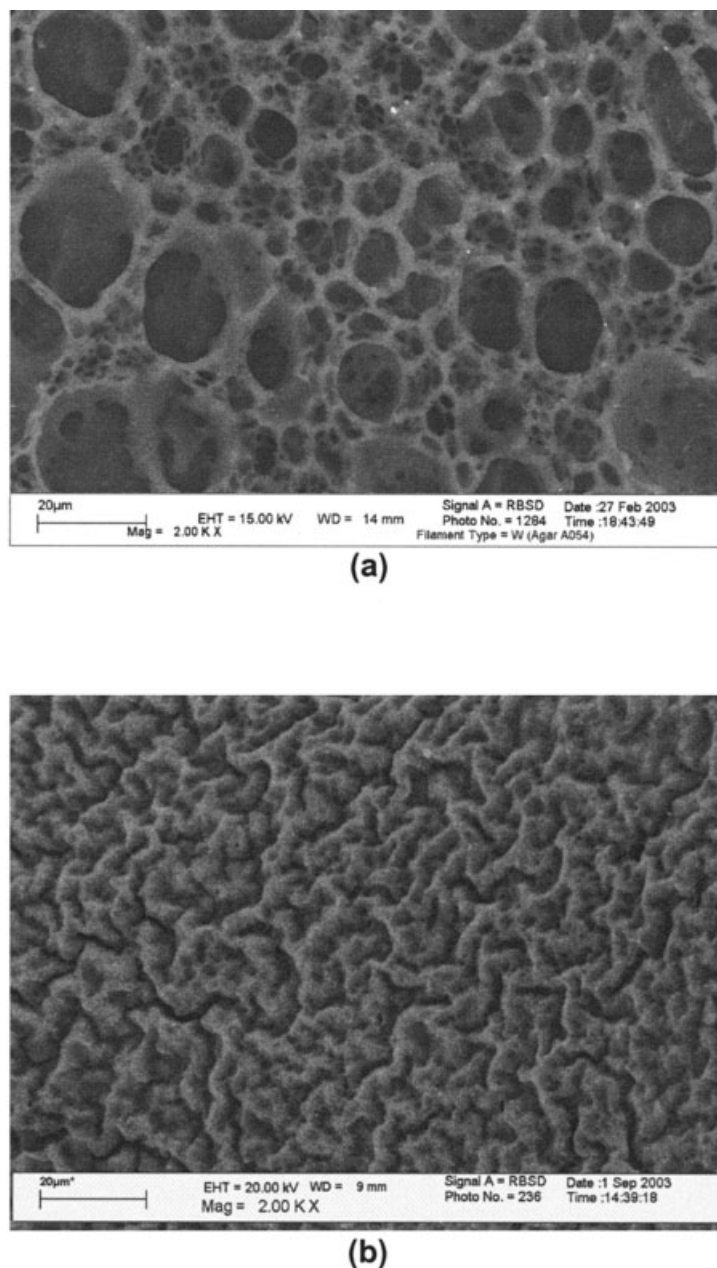
The magnitude of  $\tan \delta$  peak for XNBR is the maximum (1.4), but the value decreases to 0.68 on IPN formation. Based on the observation by Sperling, it can be explained that the nitrile group contributes the maximum toward damping.<sup>8,9</sup> Hence, the effectiveness of the nitrile group is reduced in the IPNs because of the presence of lesser contributing ethacrylate groups.

### SEM Analysis

To get an insight into the microstructure of the IPN, the IPN and the blend were analyzed by SEM. The



**Figure 2** Loss tangent versus temperature of single polymers, 50/50 XNBR/PEMA blend, and 50/50 XNBR/PEMA IPN.



**Figure 3** SEM microphotographs of (a) 50/50 XNBR/PEMA blend and (b) 50/50 XNBR/PEMA IPN.

microphotographs clearly illustrate the difference in the formation of phases in the blends and the IPN, as shown in Figure 3. The blend shows spherical holes of size 20–40 μm due to the etched out PEMA phase, which indicate a two-phase globular morphology. On the other hand, in the case of the IPN, the two phases are not clearly distinguishable in the entire region and there is considerable phase-mixing at the microlevel. It appears that the structure is pinned down by the interpenetrating network thus preventing macrophase separation.

Thermodynamically, when the free energy of mixing is near zero, there exist two possibilities for the

phase formation. First, the glass transitions may be shifted toward each other, reflecting the presence of polymer 2 in the polymer 1- rich phase and vice versa. In the second case, a microheterogeneous phase composition occurs where the phases are very small. The composition within these phases varies greatly from one microlocation to other, but overall it produces a single, broad  $T_g$ .<sup>19,20</sup> This is exemplified in the present case. The interpenetrating nature of the network produces microheterogeneous phases rather than macroheterogeneous phases, thus leading to distinct SEM features and dynamic mechanical properties.



## CONCLUSION

Sequential interpenetrating polymer network (IPN) based on poly(ethyl methacrylate) and carboxylated nitrile rubber was synthesized and the microstructure characterized by dynamic mechanical analysis and SEM. DMA of the 50/50 XNBR/PEMA blend shows two distinct peaks indicating immiscibility. The 50/50 XNBR/PEMA IPN shows a single, broad peak, indicating the change in the microstructure from macrophases in blend to microheterogeneous phases during the IPN formation. The difference in the phase formation and structure is further confirmed by SEM analysis.

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