

# Preparation and Properties of a Poly(vinyl Isobutyl Ether)-Poly(ethyl Acrylate) Interpenetrating Polymer Network

## INTRODUCTION

Interpenetrating polymer networks (IPNs) constitute a group of composite materials in which two usually chemically distinct networks are intimately combined. They may be prepared in a number of ways.<sup>1-5</sup> In one procedure a three-dimensional network of the first component is formed in the monomer plus crosslinking agent of the second component which is subsequently polymerized to give the second three-dimensional network. Various aspects of IPNs have been reviewed recently.<sup>6-8</sup>

With the exception of Millar-type IPNs,<sup>9</sup> this class of polymeric composites usually shows two-phase morphology, with the size, shape, and extent of connectivity of the phases being considerably influenced by the mutual compatibility of the pair of networks,<sup>10</sup> the crosslink density, especially of the initially established network,<sup>11</sup> the method of synthesis,<sup>5,12</sup> and the composition.<sup>4,12</sup>

In this paper certain physical properties, including stress-strain and dynamic mechanical behavior, of an IPN formed from poly(vinyl isobutyl ether) and poly(ethyl acrylate) are reported. The IPN was synthesized by swelling cured poly(vinyl isobutyl ether) sheet in ethyl acrylate containing divinylbenzene and subsequently polymerizing these monomers to establish the second network.

## EXPERIMENTAL

The poly(vinyl isobutyl ether) (Lutonal ICK) used in this work was kindly donated by B.A.S.F., while the ethyl acrylate was supplied by B.D.H. Ltd. and the divinylbenzene, by Carabrian Chemicals. Table I shows some characterization data for the uncured poly(vinyl isobutyl ether). Cured sheets of poly(vinyl isobutyl ether) were prepared by milling the polymer on an unheated Farrell two-roll mill and then adding 2.5 g crosslinking agent, tertiary butyl peroxoate, per 100 g polymer. Following this addition the milling was continued for a further 10 min. Sheets were then cured for 30 min in a hot press at 120°C.

Pieces of this cured sheet were swollen in ethyl acrylate containing 30% by weight of divinylbenzene and 0.2% by weight of total monomer of initiator (AIBN) to give an overall composition of 60% by weight of crosslinked poly(vinyl isobutyl ether). The swollen gel was transferred carefully to a metal mold sealed with a Teflon-coated rubber gasket and the ethyl acrylate-divinylbenzene mixture was polymerized at 85°C for 8 hr. Prior to testing, the resulting sheets were placed in a vacuum oven at ambient temperature for about 10 days to ensure the complete removal of traces of unreacted ethyl acrylate and divinylbenzene. Cured poly(ethyl acrylate) sheet, also using 30% by weight divinylbenzene, was synthesized as in the second stage of the IPN preparation.

The stress-strain tests were conducted on standard dumbbell pieces using a Howden tensometer at a strain rate of 2.5 cm/min. A Rheovibron dynamic viscoelastomer (model DDV-II-B) was used at a frequency of 3.5 Hz to obtain the dynamic mechanical data. The rate of temperature change was 1-2°C/min. The longitudinal sonic velocity measurements<sup>13</sup> were made at 20°C with a Morgan pulse propagation meter (model PPM-5R) at a frequency of 15 kHz.

TABLE I  
Characterization Data for the Uncrosslinked Poly(vinyl Isobutyl Ether)

$\bar{M}_n \times 10^{-3}$	282 <sup>a</sup>
$\bar{M}_w/\bar{M}_n$	1.86 <sup>b</sup>

<sup>a</sup> Membrane osmometry. Toluene at 37°C.

<sup>b</sup> Gel permeation chromatography with chloroform as solvent.

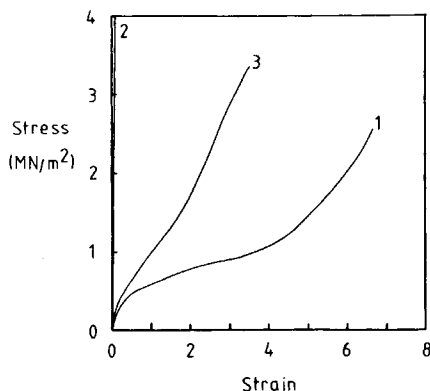


Fig. 1. Stress-strain curves for crosslinked poly(vinyl isobutyl ether) (1), crosslinked poly(ethyl acrylate) (2), and the IPN (3) at 20°C.

### RESULTS AND DISCUSSION

The stress-strain properties of the IPN and of the two networks alone are shown in Figure 1. It is clear that the moduli and stress and elongation at break of the IPN, which contains 60% of crosslinked poly(vinyl isobutyl ether), are intermediate between those of the poly(ethyl acrylate) and poly(vinyl isobutyl ether) networks but are closer in magnitude to the poly(vinyl isobutyl ether) network values. As the poly(vinyl isobutyl ether) constitutes the first formed network and consequently is a continuous phase at this composition, it is not surprising that the IPN stress-strain behavior should be more similar to that of the cured poly(vinyl isobutyl ether). The stress-strain curve for the poly(ethyl acrylate) network indicates the expected very high level of crosslinking leading to a stress at break of 6.8 MN/m<sup>2</sup> and an elongation at break of 15%. The toughness of the IPN is approximately 80% of that of the poly(vinyl isobutyl ether) network.

The longitudinal sonic velocities ( $V_L$ ) of the cured poly(vinyl isobutyl ether), the IPN, and the poly(ethyl acrylate) network are 0.5, 0.68, and 1.24 km/sec, respectively. The experimental error for these  $V_L$  measurements is  $\pm 8\%$ . In other semi- and fully interpenetrating networks it has been found<sup>14</sup> in plots of  $V_L$  versus composition that  $V_L$  varies linearly with composition up to quite high levels of the second formed network, but beyond some critical composition the slope of the  $V_L$ -composition plot changes substantially. This has been taken to indicate that the first formed network constitutes the continuous phase up to this critical composition. If the very limited data for this system are plotted against composition, it appears to fit the above situation, indicating that the IPN is a two-phase material with the poly(vinyl isobutyl ether) network as the continuous phase.

Tan  $\delta$ -versus-temperature plots (3.5 Hz) are shown in Figure 2 for the poly(vinyl isobutyl ether)

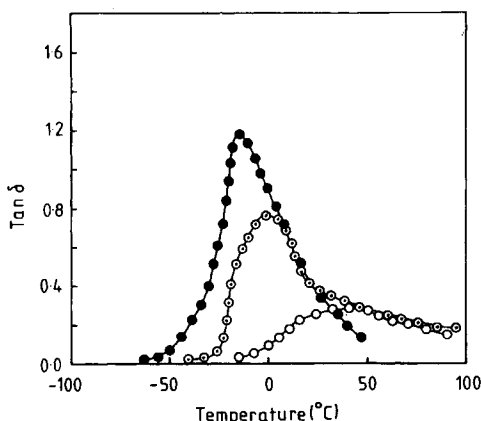


Fig. 2. Tan  $\delta$  vs. temperature of crosslinked poly(vinyl isobutyl ether) (●), crosslinked poly(ethyl acrylate) (○), and the IPN (⊙). Frequency, 3.5 Hz.

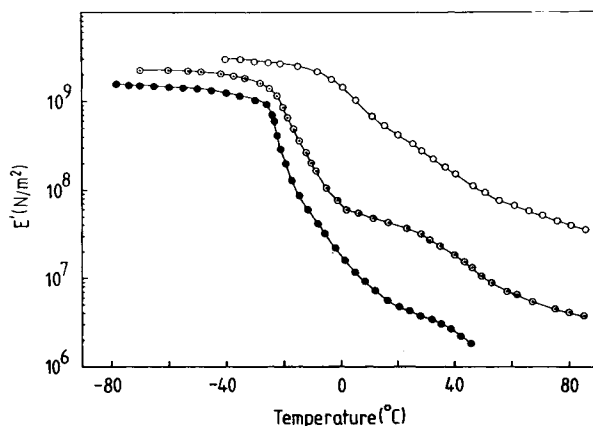


Fig. 3. Dynamic storage modulus ( $E'$ ) vs. temperature of crosslinked poly(vinyl isobutyl ether) (●), crosslinked poly(ethyl acrylate) (○), and the IPN (⊙). Frequency, 3.5 Hz.

and poly(ethyl acrylate) networks and for the IPN, while the dynamic storage modulus ( $E'$ )- and the dynamic loss modulus ( $E''$ )-versus-temperature plots of these materials are presented in Figures 3 and 4, respectively.

For the cured poly(vinyl isobutyl ether) Figure 2 shows that the glass transition occurs at  $-15^{\circ}\text{C}$  and the maximum value of  $\tan \delta$  ( $\tan \delta_{\text{max}}$ ) is 1.2. In an earlier publication<sup>15</sup> the apparent activation energy for this transition was calculated to be around 87 kJ/mole. Schmieder and Wolf<sup>16</sup> and Thurn and Wolf<sup>17</sup> have reported a number of minor transitions for various poly(vinyl ethers). For the poly(vinyl isobutyl ether) network used in this study there was an indication of such a secondary transition<sup>15</sup> at about  $-45^{\circ}\text{C}$  in both the  $E'$ - and  $E''$ -versus-temperature plots. Above the glass transition temperature the poly(vinyl isobutyl ether) softens at about  $35^{\circ}\text{C}$ , which agrees with earlier work.<sup>16</sup>

The dynamic mechanical behavior of poly(ethyl acrylate) has been investigated<sup>17-19</sup> by several groups, and the findings have been reviewed by McCrum, Read, and Williams.<sup>20</sup> The network used in these studies is very extensively crosslinked, as is shown by the low value of  $\tan \delta_{\text{max}}$ , by the increase in the glass transition temperature which is reported<sup>20</sup> to be  $-24^{\circ}\text{C}$  for the linear polymer, and by the breadth of the transition region.

From Figures 2, 3, and 4 it is clear that the IPN is a two-phase material. The  $\tan \delta$ -temperature dispersion shows a maximum at  $-1^{\circ}\text{C}$ , which is about  $14^{\circ}\text{C}$  higher than the maximum for the pure poly(vinyl ether). This shift, which is also seen in the  $E'$  and  $E''$  plots, could be explained on the grounds that there is some mixing of the two networks causing constraints to be placed on poly(vinyl isobutyl ether) segmental motion by the densely crosslinked poly(ethyl acrylate). The dynamic

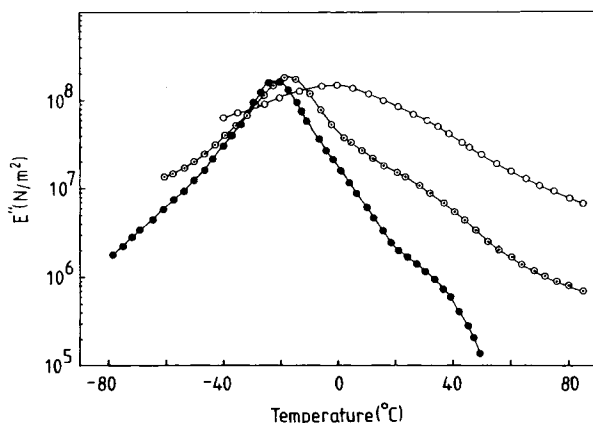


Fig. 4. Dynamic loss modulus ( $E''$ ) vs. temperature of crosslinked poly(vinyl isobutyl ether) (●), crosslinked poly(ethyl acrylate) (○), and the IPN (⊙). Frequency, 3.5 Hz.

storage and loss moduli of the IPN show a transition at about 35°C, which is ascribed to the glass transition of the poly(ethyl acrylate) phase. This transition is occurring at a significantly higher temperature than for the poly(ethyl acrylate) network alone. This again may result from restrictions on the movement of segments in the IPN. If this is so, then some significant degree of entanglement of the two networks must exist.

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