

Mechanical behaviours of fully and semi-interpenetrating polymer networks based on epoxy and acrylics

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Fully interpenetrating polymer networks (fully IPNs) based on diglycidyl ether of bisphenol A (DGEBA) and ethylene dimethacrylate (EDMA) were prepared using isophoronediamine and benzoyl peroxide as curing agents. Semi-interpenetrating polymer networks (semi-IPNs) based on DGEBA and 2-hydroxyethyl methacrylate (HEMA) were also prepared using the same curing agents. The average activation energies of transition for both these IPNs were calculated from rheometric dynamic spectroscopy (r.d.s.) data, which indicated higher values for the fully IPNs than the corresponding semi-IPNs. The more acrylic the interpenetrating polymer network (both fully and semi-IPNs) contained the lower the activation energy of transition. Broadened $\tan \delta$ peaks were observed for compatible materials, implying an enhanced cracking energy absorption. RDS data also revealed a maximum half-width of $\tan \delta$ at 30% of EDMA for the fully IPNs and at 25% of HEMA for the semi-IPNs. Beyond these compositions, decreased impact resistance and lower tensile modulus and elongation values were observed for these materials, presumably because of microphase-separation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: mechanical behaviours; fully IPN; semi-IPN; impact resistance)

INTRODUCTION

In our previous paper¹, we reported the curing behaviours of fully and semi-interpenetrating polymer networks (IPNs) based on the above epoxy and acrylic materials. These were partially compatible. As reported, the fully IPNs indicated a higher adjustable parameter, which is an indication of molecular interaction between components. Also the degree of network interlock between components had a measurable effect on the curing behaviour. Increased network interlock is expected to improve compatibility further, resulting in a broadening of the $\tan \delta$ peak. The overall area under the $\tan \delta$ curve increases, indicating an enhanced energy absorbing capability of both fully and semi-IPNs. The cracking energy was dissipated by the two compatible components, leading to improved impact resistance, Young's modulus and elongation.

EXPERIMENTAL

Materials

Fully IPNs of ethylene dimethacrylate/diglycidyl ether of bisphenol A (EDMA/DGEBA) ratios of 0/100, 18/82, 25/75, 30/70, 37.5/62.5 and 50/50 were blended. Iso-phoronediamine (IPDA, in a stoichiometric EEW of epoxy) and benzoyl peroxide (BPO, 0.5% on EDMA) were added as curing agents. The mixture was poured into Teflon moulds and was precured at 45°C for 3 h,

then cured at 70°C for 4 h, and finally postcured at 90°C for 2 h.

Semi-IPNs based on 2-hydroxymethyl methacrylate (HEMA)/DGEBA in exactly the same ratios were prepared with the same levels of IDPA and BPO, and by the same curing process.

Instruments

The dynamic mechanical behaviour was investigated with rheometric dynamic spectroscopy (r.d.s., Rheometric II) under a nitrogen atmosphere at a frequency of 1 Hz and a heating rate of 3°C min⁻¹, with 0.2% strain at 31.4 rads⁻¹. The temperature ranged from -100 to 200°C. The impact resistance was examined with a computer-added falling dart type impact tester, with a dart weight of 3.3 kg. The value of the dart weight times the height measures the impact energy, which was automatically recorded (as Newtons vs ms) during the cracking process. The area under this curve (Newtons vs ms) was integrated and taken as the cracking energy. An average of the test values of five specimens with 50 × 50 × 3 mm³ was reported for each composition. The tensile-elongation was measured according to an ASTM-D 638 type I dumb-bell specimen. The test speed was set at 5 mm min⁻¹.

RESULTS AND DISCUSSION

Generally, the maximum damping peak of a polymeric material is a function of composition^{2,3}. Figure 1 shows the maximum $\tan \delta$ peaks for various compositions of

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the EDMA/DGEBA fully IPNs. As more acrylic was incorporated in the IPN, the maximum $\tan \delta$ shifted to the lower temperature, because the acrylic component is a soft segment. A similar phenomenon was observed for the HEMA/DGEBA semi-IPNs (Figure 2). At the same time, the width of the $\tan \delta$ peaks changed significantly with composition. Some researchers have used the delta half temperature ($T_{1/2}$) as a measurement of compatibility for multicomponent polymer systems^{2,3}. The delta half temperature is the half width of the damping peak ($\tan \delta$). When two components are mixed in a compatible blend, chain mobilities are generally more restrained, making the α -transition more difficult, and

spanning a broader temperature range. Figure 3 shows the delta half temperature vs composition for both fully and semi-IPNs. Both curves are concave downwards. The maximum $\Delta T_{1/2}$ for the fully IPNs occurred at 30% of EDMA content, and 25% of HEMA content for the semi-IPNs. Beyond these compositions, presumably because microphase-separation occurred, and the chain mobilities were not so restrained, making the α -transition easier, in turn, reflected in a narrower transition peak. Unfortunately we do not have TEM micrographs to prove this morphology. However, Klemperer *et al.*⁴ in their study of energy-absorbing multicomponent interpenetrating polymer network elastomer and foams, reported a

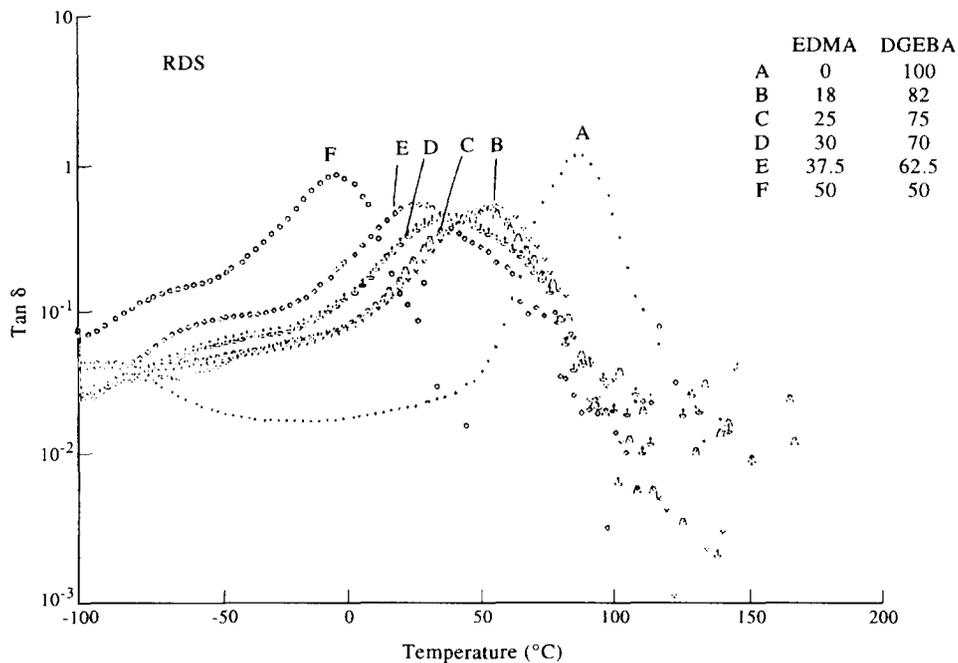


Figure 1 Plots of $\tan \delta$ vs composition for EDMA/DGEBA fully IPNs

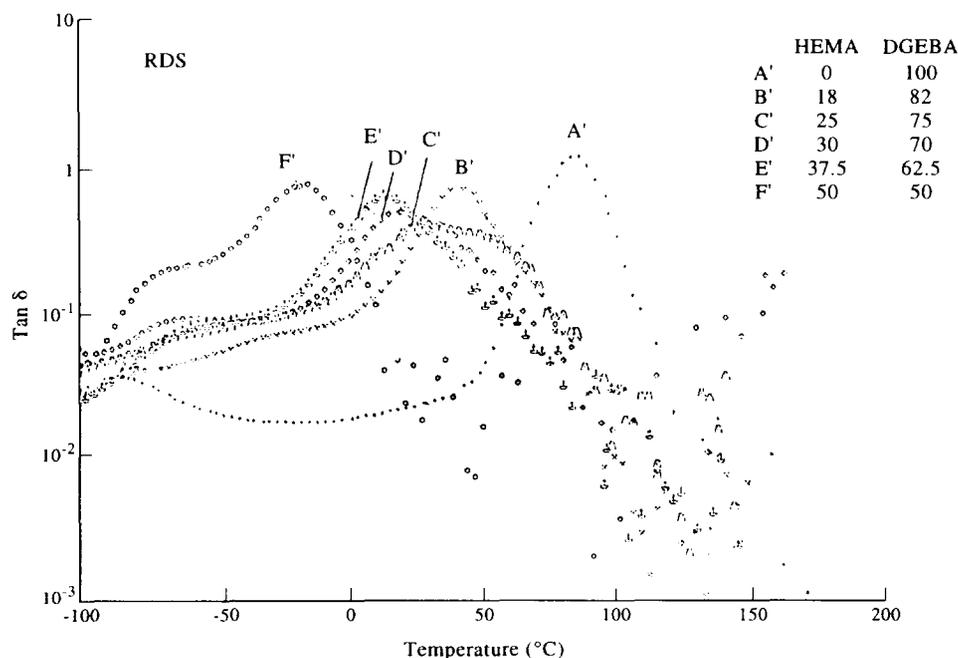


Figure 2 Plots of $\tan \delta$ vs composition for HEMA/DGEBA semi-IPNs

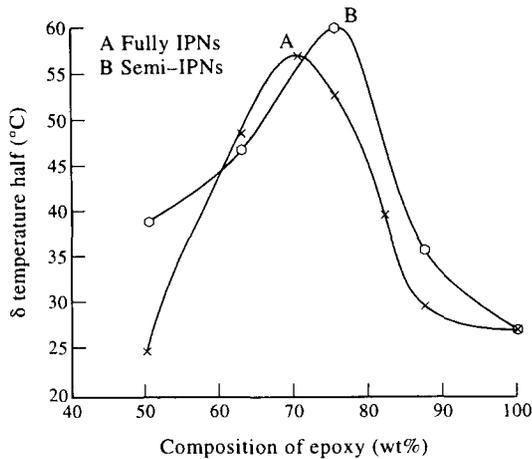


Figure 3 Plots of $\Delta T_{1/2}$ vs composition for (A) fully IPNs, and (B) semi-IPNs

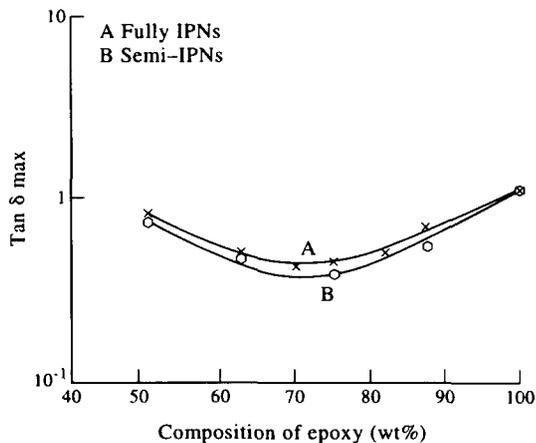


Figure 4 Plots of $\tan \delta_{\max}$ vs composition for (A) fully IPNs, and (B) semi-IPNs

broadening of the $\tan \delta$ peak and shifting it to around room temperature, resulting in enhancement of miscibility.

As the $\tan \delta_{\max}$ peaks broaden, the overall area under the $\tan \delta$ curve increases, indicating the enhancement in energy absorbing capability of both the fully and semi-IPNs. Since increasing the overall area under the $\tan \delta$ peak means a network interlock effect, polymer chains are more entangled and more restrained, making transition more difficult, thus the transition spanned a wider temperature range. In the meantime, the broadening of the damping peak also means a relative increase of storage modulus and a relative decrease of loss modulus. The applied energy was expected to be dissipated by the compatibly entangled polymer chains, leading to improved impact resistance of these materials, as was the case in our study.

Figure 4 compares the $\tan \delta_{\max}$ values for both fully and semi-IPNs. Both are concave upward curves. The minimum value for the fully IPNs occurs at 30% EDMA, and that for the semi-IPNs occurs at 25% HEMA. To the right side of the minimum point, both fully and semi-IPN materials are transparent. Only one damping peak was observed, indicating good compatibility. As the ratio of EDMA/DGEBA increases and approaches 30/70 of EDMA/DGEBA, the storage shear modulus G' increases relatively (*Figures 5 and 6*), and the loss shear modulus G'' decreases relatively (*Figures 7 and 8*), and the ratio of G''/G' (i.e. $\tan \delta$) goes down to a minimum point. On the contrary, to the left side of the minimum in *Figure 4*, the samples are somewhat opaque, which might indicate more or less incompatibility. As the ratio of EDMA/DGEBA is higher than 30/70, the loss shear modulus G'' is increasing relatively, the storage shear modulus G' is decreasing relatively, and the ratio of G''/G' increases again. Possible microphase-separation may probably occur at the minimum point where the ratio of EDMA/DGEBA is 30/70, as mentioned previously. Klemperer *et al.*⁴ reported a similar broadening of $\tan \delta$, which is related to the miscibility of

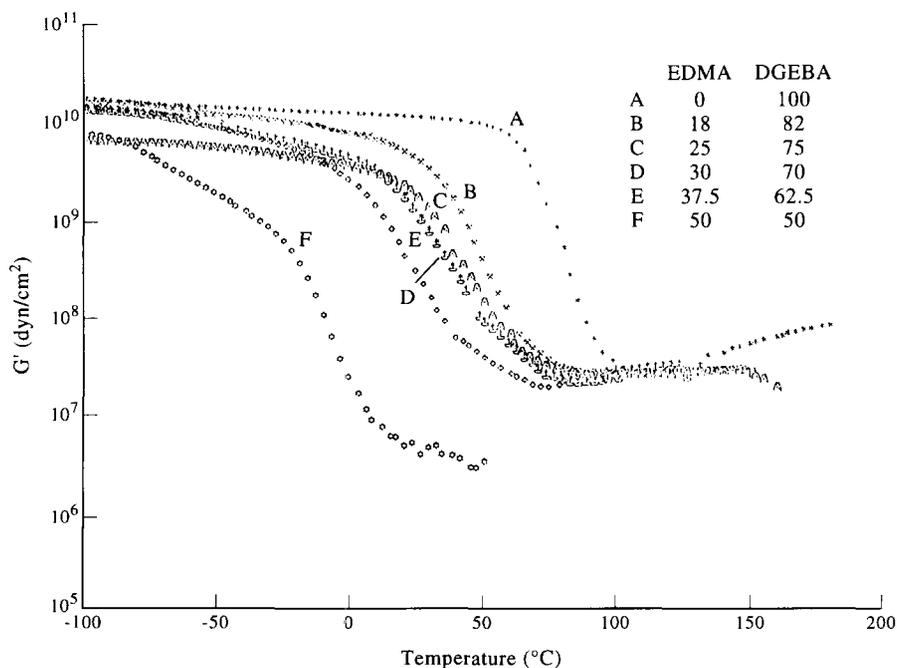


Figure 5 Storage shear modulus vs temperature for EDMA/DGEBA fully IPNs

multiphase polymer. A similar phenomenon occurs for the semi-IPNs, at a different minimum point where HEMA/DGEMA is 25/75.

The average activation energy of transition for IPN material can be calculated from the dynamic mechanical data, which was reported in the literature⁶⁻⁸. We have extended the proposed equation to calculate the average activation energy of transition for both fully and semi-IPNs:

$$tA = (\ln G'_g - \ln G'_r) \times R(E_a)_{\text{avg}} \times P_i/2 \times T_g^2$$

where tA is the area under the $\tan \delta$ peak. G'_g and G'_r are

the shear moduli of the glassy and rubbery states, respectively. $(E_a)_{\text{avg}}$ is the average activation energy of transition to be calculated. Figures 5 and 6 give the G' values for the fully and semi-IPNs of corresponding compositions. The G'_g values were taken from the data before the α -transition (the storage modulus at -100°C in Figures 5 and 6) while the G'_r values were taken from the data after the α -transition (the storage modulus at 120°C , except sample F at 50°C , in Figures 5 and 6). Tables 1 and 2 list the tA , G'_g , G'_r and the calculated $(E_a)_{\text{avg}}$ for the fully and the semi-IPNs. It was found that the fully IPNs had higher $(E_a)_{\text{avg}}$ values because they

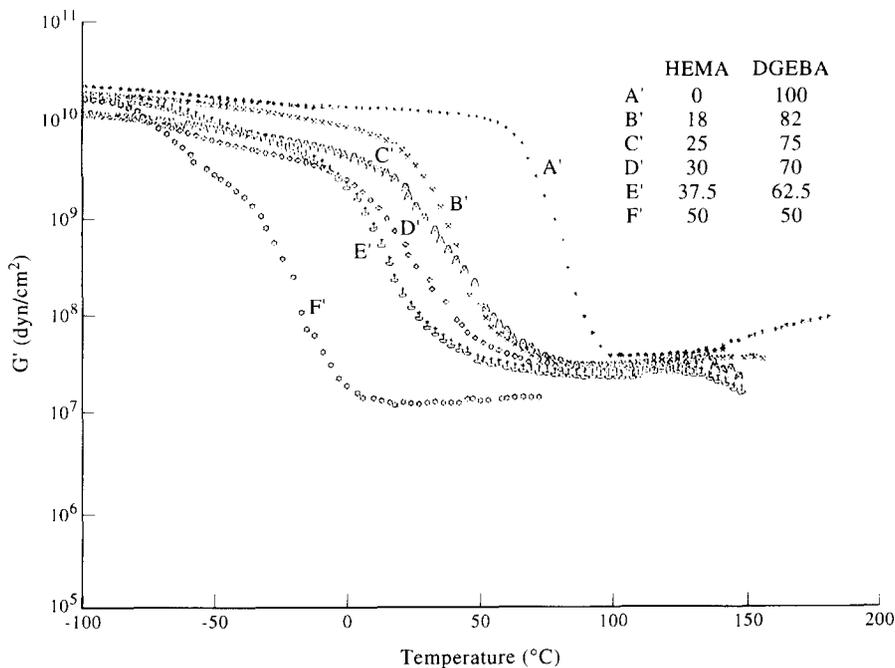


Figure 6 Storage shear modulus vs temperature for HEMA/DGEBA semi-IPNs

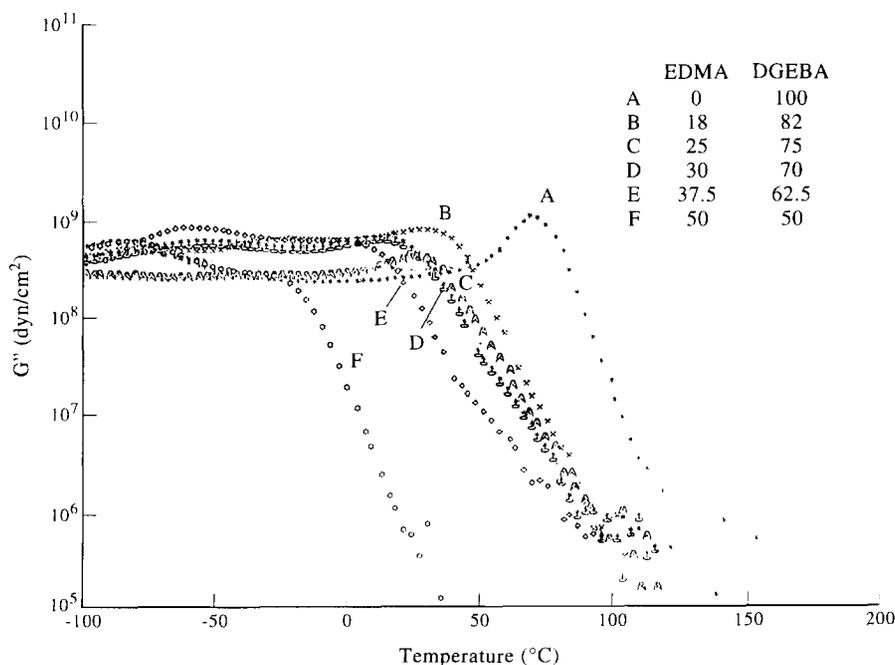


Figure 7 Loss shear modulus vs temperature for EDMA/DGEBA fully IPNs

have more network interlock which results in less chain mobility. The greater the acrylic content of an IPN (both fully and semi-IPNs), the lower the $(E_a)_{\text{avg}}$ is found, because the acrylic moiety is a soft segment. Furthermore, as found in our previous study¹, the uncured portion of the fully IPN material may act as a plasticizer which may increase the chain mobility. As mentioned before, when the $\tan \delta_{\text{max}}$ peaks broaden, the overall area under the peak increases, indicating an enhancement of energy absorbing potential for both fully and semi-IPN material. Figure 9 shows the cracking energy dissipated vs epoxy composition for both fully (curve A) and semi-IPNs (curve B). Again the maximum cracking energy occurs at 30% EDMA for the fully IPNs, and 25% HEMA for the semi-IPNs. Both results are in good agreement with the $\Delta T_{1/2}$ data (Figure 3). To the

right-hand-side of the maximum in both curves in Figure 9, because both IPNs are compatible, the cracking energy was dissipated by the two compatibly entangled polymer chains, the enhancement in energy absorbing is expected, as mentioned before. The more the second component is incorporated, the larger the extent of chain entanglement is expected, and an improved impact resistance was found. On the contrary, to the left-hand-side of the maximum for both fully and semi-IPNs in Figure 9, decreased impact resistance was found, presumably because of decreased compatibility. Fox *et al.*⁵ have discussed the relation of a broadening dampening peak in close relation with phase-separation.

Figure 10 shows plots of Young's modulus vs composition. Generally the fully IPNs have higher

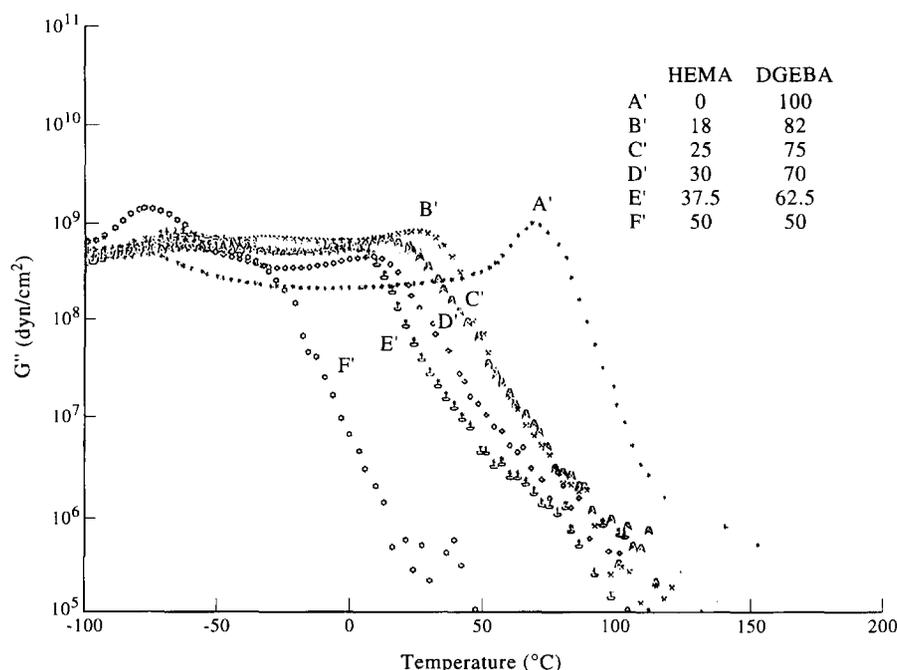


Figure 8 Loss shear modulus vs temperature for HEMA/DGEBA semi-IPNs

Table 1 The average activation energy of transition for fully IPNs

EDMA/DGEBA	G'_g ($\text{Nm}^{-2} \times 10^8$)	G'_r ($\text{Nm}^{-2} \times 10^5$)	tA	$(E_a)_{\text{avg}}$ (kcal mol^{-1})
0/100	13.80	26.78	27.49	92.07
18/82	15.00	27.14	21.51	98.15
25/75	5.87	25.10	19.99	90.13
30/70	11.34	22.49	21.77	85.91
37.5/62.5	12.97	20.45	31.53	57.26
50/50	7.56	5.23	36.51	44.74

Table 2 The average activation energy of transition for the semi-IPNs

EDMA/DGEBA	G'_g ($\text{Nm}^{-2} \times 10^8$)	G'_r ($\text{Nm}^{-2} \times 10^5$)	tA	$(E_a)_{\text{avg}}$ (kcal mol^{-1})
0/100	13.80	26.78	27.49	92.07
18/82	15.78	29.66	22.65	71.81
25/75	9.73	27.75	23.58	64.92
30/70	13.40	24.39	25.38	51.47
37.5/62.5	7.85	28.25	29.35	57.26
50/50	11.77	40.34	26.69	44.63

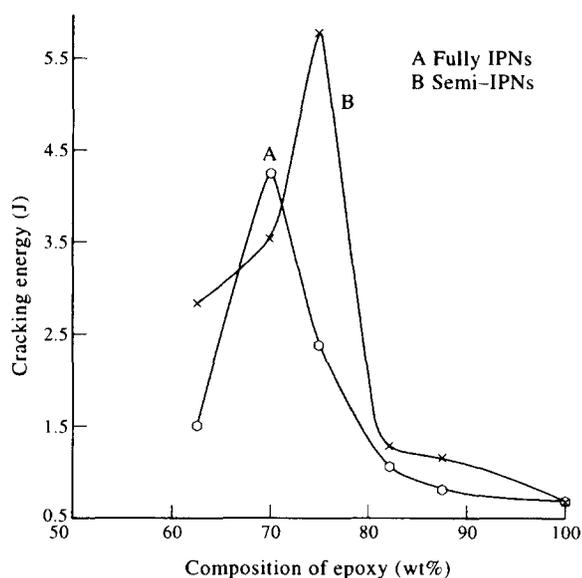


Figure 9 Plots of cracking energy vs composition for (A) fully IPNs, and (B) semi-IPNs

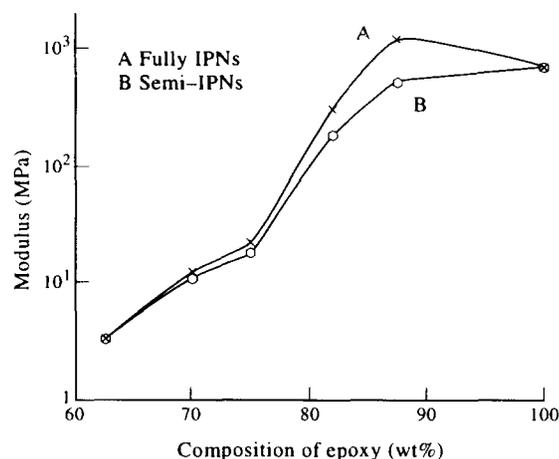


Figure 10 Plots of Young's modulus vs composition for (A) fully IPNs, and (B) semi-IPNs

moduli than the semi-IPNs of corresponding compositions. Young⁹, in their study of the structure/property relationship in highly crosslinked polyurethanes, reported an enhancement of Young's modulus for a material with a broadened damping peak. We found similar results for both IPN systems. Figures 11a and b show the elongation vs composition for both IPN systems. The maximum elongation for the fully IPNs occurs at 30% EDMA content, and that of semi-IPNs occurs at 25% of HEMA. This finding is consistent with the $\Delta T_{1/2}$ data in Figure 3. Recently, we found similar mechanical behaviours for fully and semi-IPNs based on epoxy and other unsaturated polyesters¹⁰.

CONCLUSIONS

Compatible IPN materials (both fully and semi-IPNs) indicated broadened damping peaks which was reflected in an enhancement of cracking energy absorbing capability by the entangled networks. The greater the extent of the compatibly entangled network, the better the energy absorbing of the IPN materials. Improved

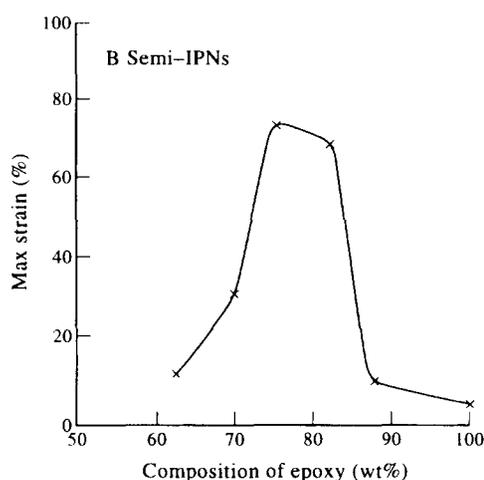
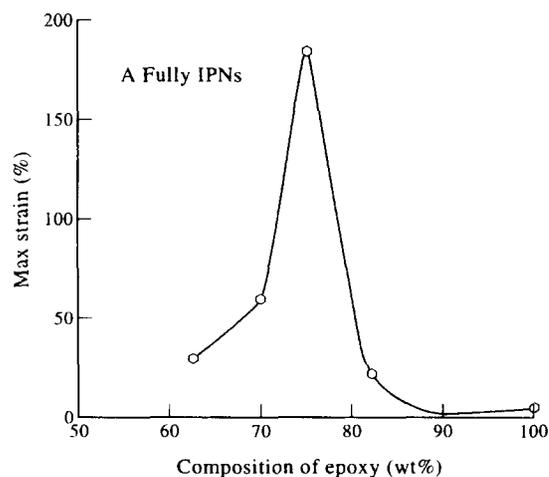


Figure 11 Plots of maximum strain vs composition for (A) fully IPNs, and (B) semi-IPNs

impact resistance, Young's moduli and elongation were observed. A possible microphase-separation was presumed at 30% EDMA content for the EDMA/DGEBA fully IPNs, and at 25% HEMA content for the HEMA/DGEBA semi-IPNs.

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