

Curing behaviour of fully and semi-interpenetrating polymer networks based on epoxy and acrylics

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Fully interpenetrating polymer networks (IPNs) based on diglycidyl ether of bisphenol A (DGEBA) and ethylene dimethacrylate (EDMA) were prepared by using isophoronediamine and benzoyl peroxide as curing agents. Semi-IPNs based on DGEBA and 2-hydroxyethyl methacrylate (HEMA) were also prepared using the same curing agents. Intermolecular interactions were investigated by Fourier transform infra-red spectroscopy. Curing behaviours were studied by dynamic differential scanning calorimetry (d.s.c.) and a Brookfield viscometer. Experimental results revealed that H-bonding in DGEBA/EDMA and DGEBA/HEMA occurred, in shifting of carbonyl and epoxide absorptions to lower wavenumber. Results also revealed that during curing reactions the dynamic d.s.c. thermograms for the fully IPNs showed a shift of the exothermic peaks to a higher and broader temperature range, while in HEMA/DGEBA semi-IPNs, the exothermic peaks shifted to a lower temperature range. On the other hand, a retarded viscosity increase was observed for fully IPNs, and an accelerated viscosity increase was found for semi-IPNs. An effect of network interlock was proposed to interpret this retarded curing behaviour of fully IPNs, while a catalytic effect of the OH group was found to explain the accelerated curing behaviour of semi-IPNs. These findings were reasonably consistent with the lower gel fractions and lower glass transitions found for fully IPNs. The calculated average molecular weight of chain length (M_c) between crosslinkages also conforms to the experimental results.

(Keywords: interpenetrating polymer networks; curing behaviour; intermolecular interactions)

INTRODUCTION

The effect of network interlock during interpenetrating polymer network (IPN) formation has been reported by our laboratory^{1,2}. This effect not only provides a sterically hindered environment for the curing reactions but also restrains the chain mobilities of the respective components, leading to lower rate constants and higher activation energies during IPN formation^{2,3}. Throughout this work, the epoxy is based on diglycidyl ether of bisphenol A, formed by a condensation reaction, and acrylics are based on ethylene dimethacrylate (for the fully IPNs) and 2-hydroxyethyl methacrylate (for the semi-IPNs), both formed by a free-radical reaction. The two networks formed simultaneously by independent and non-interfering reactions. Recently, we found that the network interlock had measurable influences on the curing behaviours and mechanical properties for both fully and semi-IPN materials. In this article we report the effect of network interlock on the curing behaviour of IPN formation. A paper dealing with the mechanical behaviour will be submitted separately.

EXPERIMENTAL

Fully IPNs based on diglycidyl ether of bisphenol A

(DGEBA) and ethylene dimethacrylate (EDMA), and semi-IPNs based on DGEBA and 2-hydroxyethyl methacrylate (HEMA) were prepared by using isophoronediamine (IPDA) and benzoyl peroxide (BPO) as crosslinkers. Thus, EDMA/DGEBA and HEMA/DGEBA were blended in various weight ratios: 0/100, 18/82, 25/75, 30/70, 37.5/62.5 and 50/50. BPO (0.5 phr on acrylics) and IPDA (on stoichiometric balance of DGEBA) were added. The mixtures, after being defoamed, were pre-cured at 45°C for 3 h, then cured at 70°C for 4 h and finally post-cured at 90°C for 2 h.

A Nicolet 520 FTIR with a resolution of 0.5 cm⁻¹ was employed to monitor the i.r. band shift. For curing dynamic differential scanning calorimetry (d.s.c.), liquid samples containing curing agents were sealed in the pressurized d.s.c. cells. All d.s.c. thermograms were obtained by running the samples in nitrogen atmosphere at a heating rate of 10°C min⁻¹. Gel fractions were measured with a Soxhlet extractor, after 48 h of continuous extraction by using acetone as solvent. Viscosity measurements were taken at 50°C with a Brookfield LVT viscometer.

RESULTS AND DISCUSSION

Molecular interactions

Molecular interactions in systems of EDMA/DGEBA and of HEMA/DGEBA were evidenced from the i.r.

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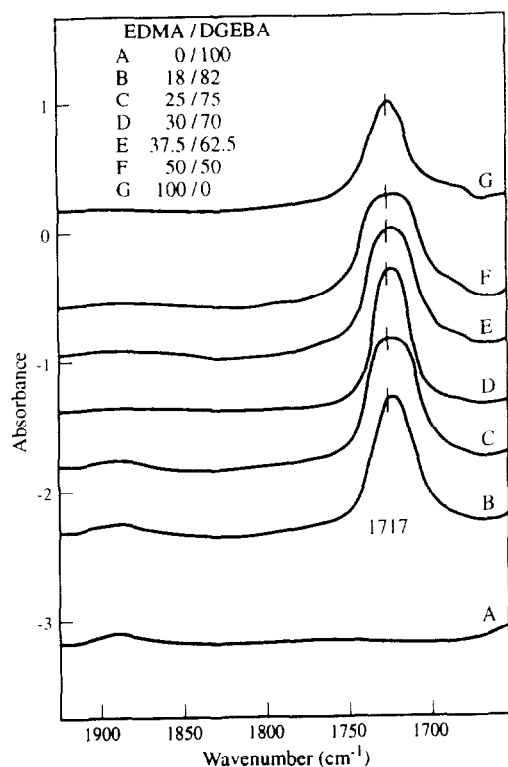


Figure 1 FT i.r. spectra of EDMA/DGEBA blends

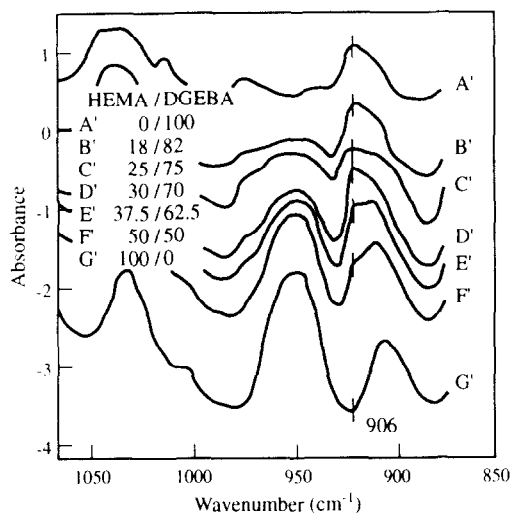


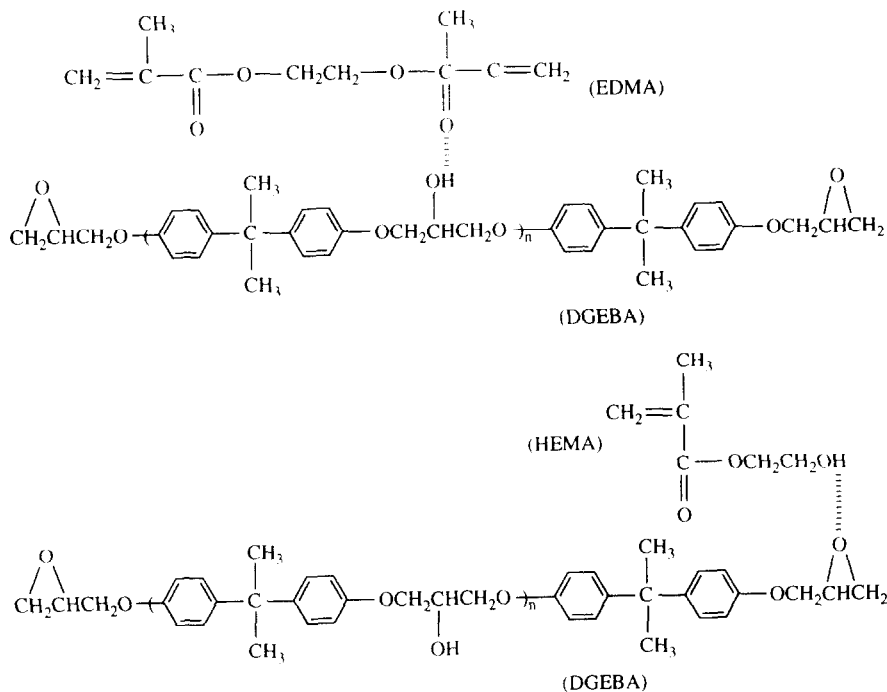
Figure 2 FT i.r. spectra of HEMA/DGEBA blends

band shifts, which are given in Figures 1 and 2. In Figure 1, the carbonyl absorption of pure EDMA (spectrum G) occurs originally at 1726 cm^{-1} . When mixed with DGEBA the carbonyl absorption shifts to lower wavenumber. This i.r. band shift can be reasonably interpreted by the formation of H-bonding between EDMA and DGEBA, as shown in Scheme 1. Similarly, in the HEMA/DGEBA mixture (Figure 2) the original

epoxide absorption occurs at 926 cm^{-1} (curve A'), and shifts to lower wavenumber when mixed with HEMA, resulting from H-bonding between HEMA and DGEBA, as shown in Scheme 1. Both H-bonding interactions between components result in the promotion of compatibility for both fully and semi-IPNs. The compatibility is supported by a single glass transition temperature (Figures 8 and 9) and a single damping peak of rheometric dynamic spectroscopy (RDS) curve⁴.

Dynamic curing d.s.c.

Figure 3 shows the curing dynamic d.s.c. thermograms for the fully IPN cure behaviour. Curve A is the exothermic peak for the pure epoxy cured by IPDA. Curve G is the exothermic peak for the pure EDMA cured by BPO. Compared with curve A, when more EDMA was added to the epoxy, the exothermic peaks



Scheme 1

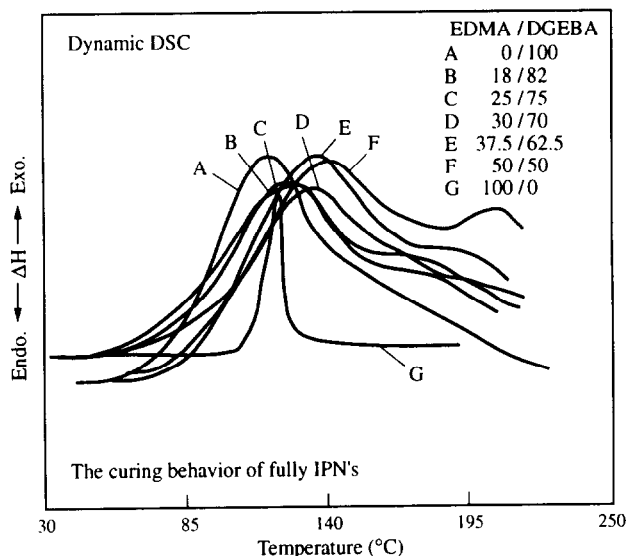


Figure 3 Curing dynamic d.s.c. for EDMA/DGEBA fully IPNs

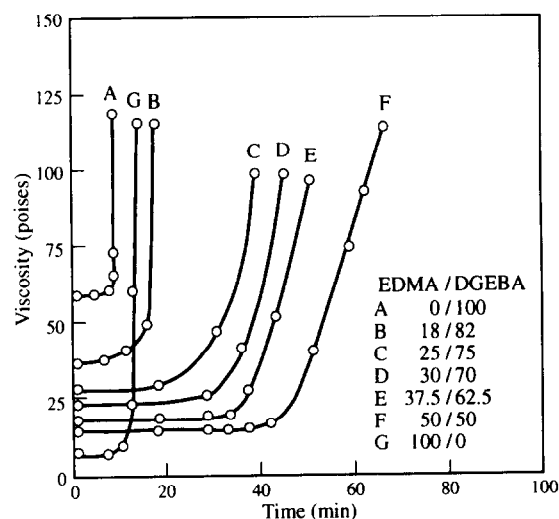


Figure 5 Viscosity increases of EDMA/DGEBA fully IPNs

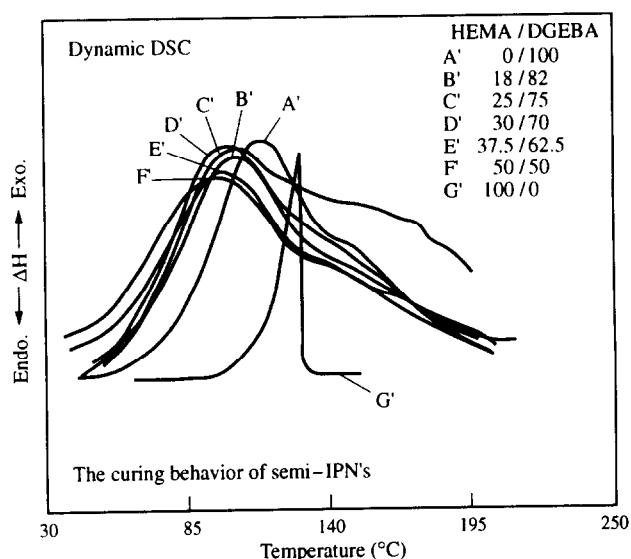


Figure 4 Curing dynamic d.s.c. for HEMA/DGEBA semi-IPNs

shifted to a higher and broader temperature range. A possible interpretation of this phenomenon could be the effect of network interlock. When two networks grow simultaneously, the cure rate of one network is retarded in the presence of the other network, because first, the crosslinking reaction occurs in a hindered environment, and second, the chain mobilities of both components are restrained. An increase of temperature would compensate these two factors. As seen from *Figure 3*, especially curve F for a 50/50 blend of EDMA/DGEBA, the exothermic peak reached a higher and extremely broad temperature range, so presumably this composition possesses a large amount of network interlock.

Figure 4 shows the curing dynamic d.s.c. for HEMA/DGEBA semi-IPNs. Curve A' shows the exothermic peak of pure DGEBA, and curve G' is that of pure HEMA. When HEMA was added to epoxy, the exothermic peak did not shift to higher temperature as the fully IPNs did. Rather, they shifted to a lower temperature range. This is probably due to the fact that

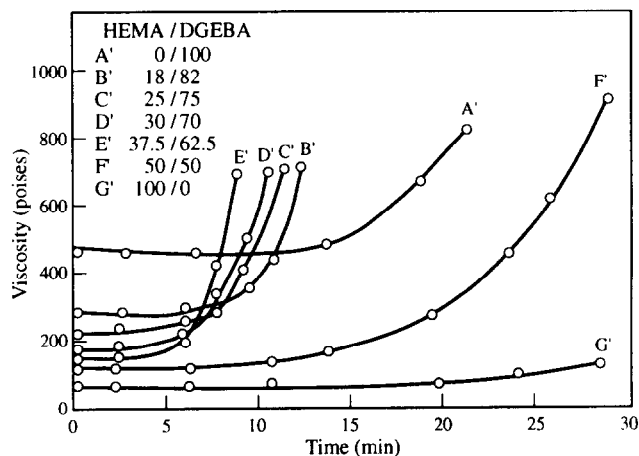


Figure 6 Viscosity increases of HEMA/DGEBA semi-IPNs

there is only one network growing, there is no network interlock between the two components, and the cure rate of the components was not retarded. Moreover, the OH group in HEMA played a catalytic role in the epoxy cure, thus shifting the exothermic peak to a lower temperature range. The catalytic effect of OH on epoxy cure is well known from the literature^{5,6}. Ohashi and co-workers recently reported a catalytic effect by curing epoxy resin having a hydroxymethyl group⁶.

Viscosity increase

The effect of network interlock was reflected in the slow viscosity increase during the curing reaction. *Figure 5* shows the viscosity increase for various fully IPNs cured at 50°C. Curve A is the viscosity increase of pure DGEBA cured by IPDA, and curve G is that of pure EDMA cured with BPO. Both DGEBA and EDMA alone cured rapidly. When 18% of EDMA was blended with DGEBA, with an equivalent amount of IPDA (based on the epoxy equivalent weight of DGEBA) and 0.5% BPO (based on EDMA), and cured at 50°C, a retarded cure rate was observed, which is reflected in a slow viscosity increase. When more EDMA was added to DGEBA (curves C, D, E and F), the retarded cure rate was more pronounced, especially composition F, a 50/50

mixture of components, which shows a much slower viscosity increase. This composition is expected to have much network interlock. Comparing *Figures 3 and 5*, both dynamic d.s.c. and viscosity increase are very consistent. *Figure 6* gives the viscosity increase of semi-IPNs. The catalytic effect of the OH group on epoxy cure is reflected in a fast viscosity increase. Curve A' is the viscosity increase of pure epoxy at 50°C, while curve G' is that of pure HEMA at the same temperature. The more HEMA was added to DGEBA, as in curves B', C', D' and E', the faster was the viscosity increase. An exception is curve F', a 50/50 blend of HEMA/DGEBA: its rate of viscosity increase lies between those of pure DGEBA and pure HEMA, but is slower than compositions B', C', D' and E', probably because excess HEMA may act as solvent for epoxy, and the low DGEBA concentration exhibits a lower cure rate and a slower viscosity increase.

Gel fractions

Figure 7 shows the plots of gel fraction versus DGEBA content for both fully and semi-IPNs. The fully IPNs (curve A) give higher gel fractions than the semi-IPNs (curve B), because in fully IPNs, both components form networks and are expected to have higher crosslinking density than the semi-IPNs which contain only one DGEBA network. Furthermore, the semi-IPNs show a linear relationship with composition, while all the fully IPNs show decreased gel fractions, compared with the two respective components, DGEBA and EDMA. This decreased gel fraction in fully IPNs probably resulted from the retarded cure behaviour which, in turn, leads to difficult and incomplete cure.

Glass transition temperature (T_g)

Figure 8 shows the d.s.c. thermograms of semi-IPNs. As more HEMA is incorporated, the T_g goes down, and the sharp single transitions are very clear. The glass transitions for fully IPNs are given in *Figure 9*. When more acrylic polymer, EDMA, is incorporated, the T_g goes down like the semi-IPNs, but the glass transitions span a broader temperature, probably because the network interlock restrains the chain mobilities of fully IPNs at the glass transition temperature. These single T_gs support the conclusions concerning the compatibility of

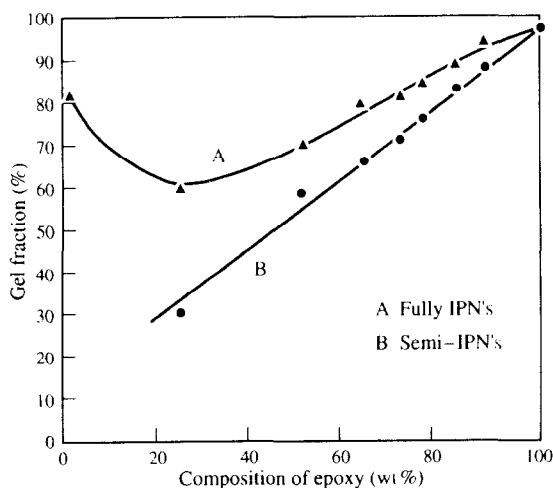


Figure 7 Plots of gel fractions versus epoxy content for (A) fully IPNs, and (B) semi-IPNs

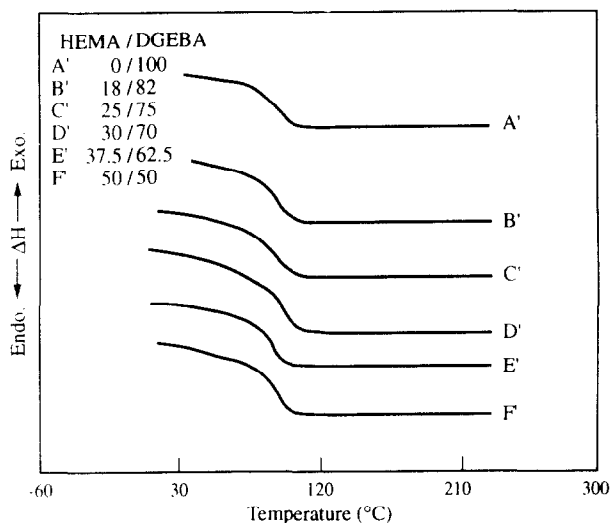


Figure 8 D.s.c. thermograms for HEMA/DGEBA semi-IPNs

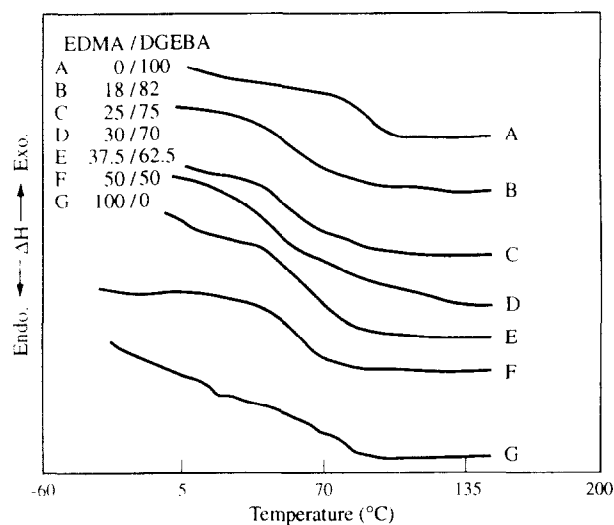


Figure 9 D.s.c. thermograms for EDMA/DGEBA fully IPNs

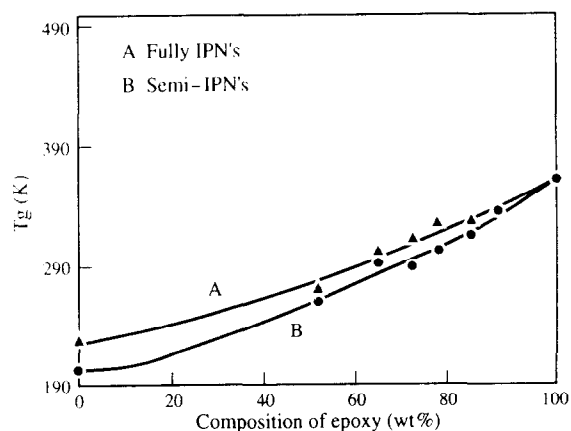


Figure 10 Plots of glass transition temperatures versus epoxy content for (A) fully IPNs, and (B) semi-IPNs

blends. The H-bonding, mentioned previously, must play an important role in promoting this compatibility⁷. *Figure 10* compares the T_g values for fully and semi-IPNs. Obviously, fully IPNs have higher T_gs because the

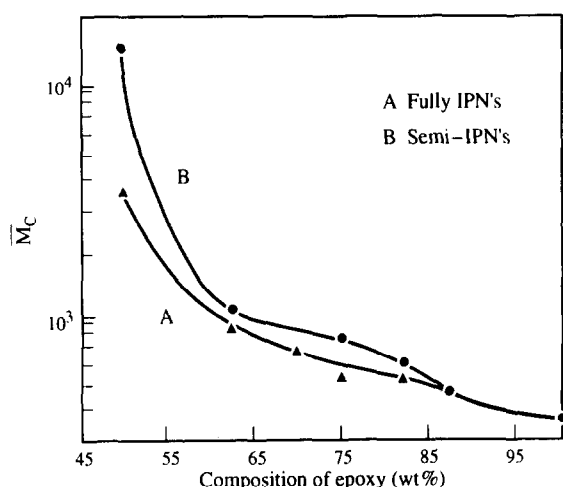


Figure 11 Comparison of the average molecular weight between two crosslinkages (\bar{M}_c) for (A) fully IPNs, and (B) semi-IPNs

Table 1 Characterizations of fully IPNs

Sample	EDMA/DGEBA	T_g (°C)	Gel content	
			(%)	$\bar{M}_c \times 10^2$
A	0/100	90.0	99.8	3.66
B	18/82	66.0	96.3	4.72
C	25/75	54.0	91.1	5.52
D	30/70	37.0	85.6	5.68
E	37.5/62.5	26.0	81.0	9.15
F	50/50	-5.0	71.1	33.5
G	100/0	-	81.8	-

Table 2 Characterizations of semi-IPNs

Sample	HEMA/DGEBA	T_g (°C)	Gel content	
			(%)	$\bar{M}_c \times 10^2$
A'	0/100	90.0	99.8	3.66
B'	18/82	44.0	85.1	6.43
C'	25/75	31.0	77.7	8.19
D'	30/70	20.0	72.8	10.65
E'	37.5/62.5	16.0	67.6	11.95
F'	50/50	-14.0	59.9	148.3
G'	100/0	-	-	-

fully IPNs are expected to have higher crosslinking density and thus higher gel fractions than the corresponding semi-IPNs. It is also noted that the semi-IPNs show a relatively linear relationship, while the fully IPNs show a concave-upward curve (lower T_g s than their respective components) because of incomplete cure. The T_g data are in good agreement with those of the gel fractions.

The average molecular weight between crosslinkages

Hourston⁸ proposed a method to calculate the average molecular weight (\bar{M}_c) between two linkages for a crosslinked polymer:

$$T_g - T_{g,0} = 3.9 \times 10^4 / \bar{M}_c$$

where T_g is the glass transition temperature of a specific IPN material, and $T_{g,0}$ is the glass transition of the uncured epoxy resin (-16.6°C). The calculated \bar{M}_c values are plotted in *Figure 11* and are listed in *Tables*

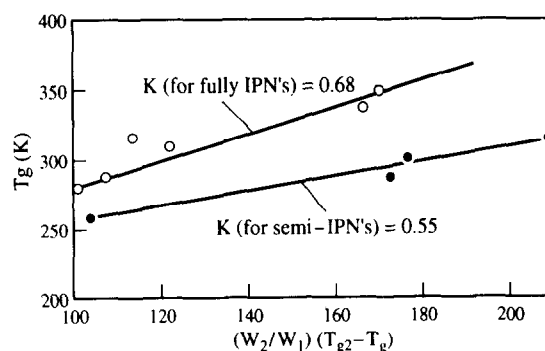


Figure 12 Plots of Gordon-Taylor equation for fully IPNs (upper), and semi-IPNs (lower)

1 and 2. It is found that the \bar{M}_c value of a specific IPN increases with decreasing epoxy content and that the fully IPN, reflected in a higher gel fraction, has lower \bar{M}_c value than the corresponding semi-IPN.

Fox and co-workers⁹ applied the Gordon-Taylor equation¹⁰ to estimate the intermolecular interaction in polymer blends:

$$T_g = T_{g1} + K(W_2/W_1)(T_{g2} - T_{g1})$$

where W_1 and W_2 are the weight fractions of acrylate and epoxy in the IPN compositions, T_{g1} and T_{g2} are the glass transitions for acrylate and epoxy network, and K is the adjustable parameter, which increases with the extent of interaction between components. A plot of the Gordon-Taylor equation is given in *Figure 12*. The measured K values (0.68 for the fully IPNs and 0.55 for the semi-IPNs) might suggest that the fully IPNs have stronger molecular interaction than the semi-IPNs. Although both fully and semi-IPNs originally have strong H-bondings between components, as mentioned before, the network interlock in the fully IPNs obviously plays a predominant role in governing the molecular interaction.

CONCLUSIONS

H-bonding between components improved the compatibility of both fully and semi-IPN systems. During the EDMA/DGEBA cure and fully IPN formation, the network interlock not only provides a sterically hindered environment to the curing reactions, but also restrains the chain mobilities of the respective components, thus leading to a difficult and incomplete cure for fully IPN materials. This network interlock was overcome by increasing the cure temperature, as reflected in a shift of the exothermic peak to higher and broader temperature range in dynamic d.s.c. thermograms. In contrast, during the HEMA/DGEBA semi-IPN formation, the OH group in HEMA showed a catalytic effect which, in turn, lowered the curing temperature, as was evidenced from the shift of exothermic peak to a lower and broader temperature range. This curing behaviour was confirmed by the viscosity increase during IPN formation. Furthermore, the more network interlock an IPN material contained, the higher the gel fraction, the higher the T_g , the lower the \bar{M}_c , and the higher the value of the adjustable parameter K were found to be for the IPN materials.

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