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Curing kinetics and morphology of IPNs from a flexible dimethacrylate and a rigid epoxy via sequential photo and thermal polymerization

Fei Chen, Wayne D. Cook *

Department of Materials Engineering, Rm 151/Building 19, Monash University, P.O. Box 69M, Victoria 3001, Australia

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ABSTRACT

The curing kinetics and morphology of Interpenetrating polymer networks (IPNs) formed from a rigid epoxy resin thermally cured by an anhydride, and a photocured flexible dimethacrylate resin, have been studied by temperature ramping differential scanning calorimetry (DSC), near-infrared (NIR), and dynamic mechanical thermal analyzer (DMTA). This combination of cross-linkable resins permits the partial or complete cure of each component independent of the other. Also, since the monomers are polar but chemically dissimilar thermosetting resins, their IPNs should offer considerable variation in properties. DSC studies showed that the possible interactions between each component in the IPN could be minimized, but that the curing rate and conversion of the second polymerizing component was affected by vitrification, network topology, or phase separation in the IPN. NIR was also used to confirm that virtually independent cure was achievable by the combination of the thermal and photochemical methods. Dynamical mechanical thermal analysis was used to investigate the effect of curing one or both components and of order of curing on the phase morphology of the IPN. The modulus in the rubbery region also provided information on loop formation and co-continuity of each network component through the polymer matrix. The modulus and tan δ curves showed large differences in the glass transition region of the IPNs with different curing schedules, however phase separation occurred in all fully cured IPNs. These observations conflict with a previously advanced hypothesis that rapid polymerization and gelation of the last-cured component interlocks the two networks into a single phase structure and leads to the inclusion of a caveat that the components require sufficient attraction for interlocking of the networks to occur.

1. Introduction

Interpenetrating polymer networks (IPNs) are blends of two or more crosslinking polymers [1], and appropriate blending should allow their properties to be tailored to the application [2]. Thermoplastic polymer blends have achieved widespread commercial use, however, IPNs have been slow to be commercialized because of difficulties in controlling their morphology during cure and the resulting structure that determines their properties.

The morphology and properties of IPNs are expected to be critically dependent not only on the miscibility of the components constituting the IPN but also on the polymerization kinetics of those components [3]. Thermodynamic miscibility of the two components within an IPN is governed by the Gibbs free energy of mixing. According to Flory–Huggins solution theory [4,5], the free energy of mixing (ΔG_M) is composed of entropy (ΔS_M) and enthalpy (ΔH_M) of mixing terms and can be expressed as

$$\begin{aligned}\Delta G_M &= \Delta H_M - T\Delta S_M \\ &= \phi_1\phi_2 V(\delta_1-\delta_2)^2 + RT\left(\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2\right)\end{aligned} \qquad (1)$$

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* Corresponding author. Tel.: +61 3 9905 4926; fax: +61 3 9905 4940.
E-mail address: wayne.cook@eng.monash.edu.au (W.D. Cook).

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where T is the temperature V is the total system volume and φ_i, V_i and δ_i are the volume fraction, molar volume and solubility parameter of component *i*. As the polymerization proceeds, the molecular weight of the two IPN components increases, which lowers the entropy of mixing and reduces the miscibility which may lead to phase separation. The morphology of the IPN is mainly controlled by the volume fractions of the components, the thermodynamics of mixing and the kinetics of network interpenetration. Thus the morphology is controlled by the specific order and rate of gelation of each components, and the rate of diffusion of the monomers and oligomers [6,7]. Originally IPNs were conceived by Sperling, Frisch, and others [1,3,8] as idealized structures where the polymerization of the individual components, and hence the interlocking of the two networks within the IPN, prevented phase separation. In reality, it is usually documented that entropically driven demixing and phase separation occur [9–12]. If phase separation precedes gelation of either component, then a rather coarse morphology may develop. If gelation precedes phase separation, the polymer which gels will tend to be more continuous. Thus, the degree of mixing is controlled by the balance between kinetics and thermodynamics of cure because large-scale macro-molecular diffusion and subsequent phase separation can not occur after crosslinking.

Yang et al. [13] investigated IPNs formed from photocured diacrylates and thermally cured urethanes and observed from the dynamic mechanical thermal analysis (DMTA) spectrum that if the acrylate was cured first, extensive phase separation occurred, however, reversal of the curing sequence gave a more homogeneous structure. Chou and Lee [10] studied the morphology and dynamic mechanical behavior of IPNs formed from a polyurethane and a photocured unsaturated polyester and found that the structure and properties were dependent on the cure order, however, no kinetic studies were undertaken. Nowers et al. [14] investigated structure–property relationships of IPNs formed from photocured diacrylates and thermally cured epoxy and revealed that the T_g was higher when the acrylate was cured first. It was also found from scanning electron microscopy that the morphology became less coarse (i.e. it was more homogeneous) with increasing acrylate component from 25% to 75% when the acrylate was cured first, but reversal of the curing sequence gave a more homogeneous structure for all of the IPNs. Recently, Fichet et al. [15] and Vidal et al. [16] studied the morphology and dynamic mechanical behavior of IPNs formed from polysiloxane and cellulose acetate butyrate and found that when the cure rates of the two components were similar, the networks were interpenetrated with no evidence of phase separation.

In our previous studies [7] we have shown that for IPNs prepared from an anhydride-cured epoxy and a photocured dimethacrylate, the phase structure can be controlled by the curing order of the components. When the dimethacrylate was photocured first and the epoxy was then cured thermally, the latter curing period was sufficiently long to allow phase separation of the networks before gelation of the epoxy component and so two glass transitions were observed. In contrast when the epoxy was thermally cured and the dimethacrylate subsequently photocured, the speed of gelation of the dimethacrylate interlocked the two networks before significant phase separation could occur and so a single T_g resulted. More recently, we investigated the effect of curing order in a dimethacrylate/epoxy IPN using two different activity peroxide [17] or azo initiators [18] for the dimethacrylate polymerization and confirmed [17] that the phase structure could be controlled by varying the curing procedure. However, in all of these works we used two structurally similar network components – the diglycidyl ether of bisphenol-A (DGEBA) and a dimethacrylate with the bisphenol-A backbone – so as to maximize the enthalpic interactions and thus the miscibility of the two networks, and so the mechanical properties were not very dependent on the level of phase separation. Therefore, it is of interest to extend these studies to new IPNs with structurally dissimilar network components.

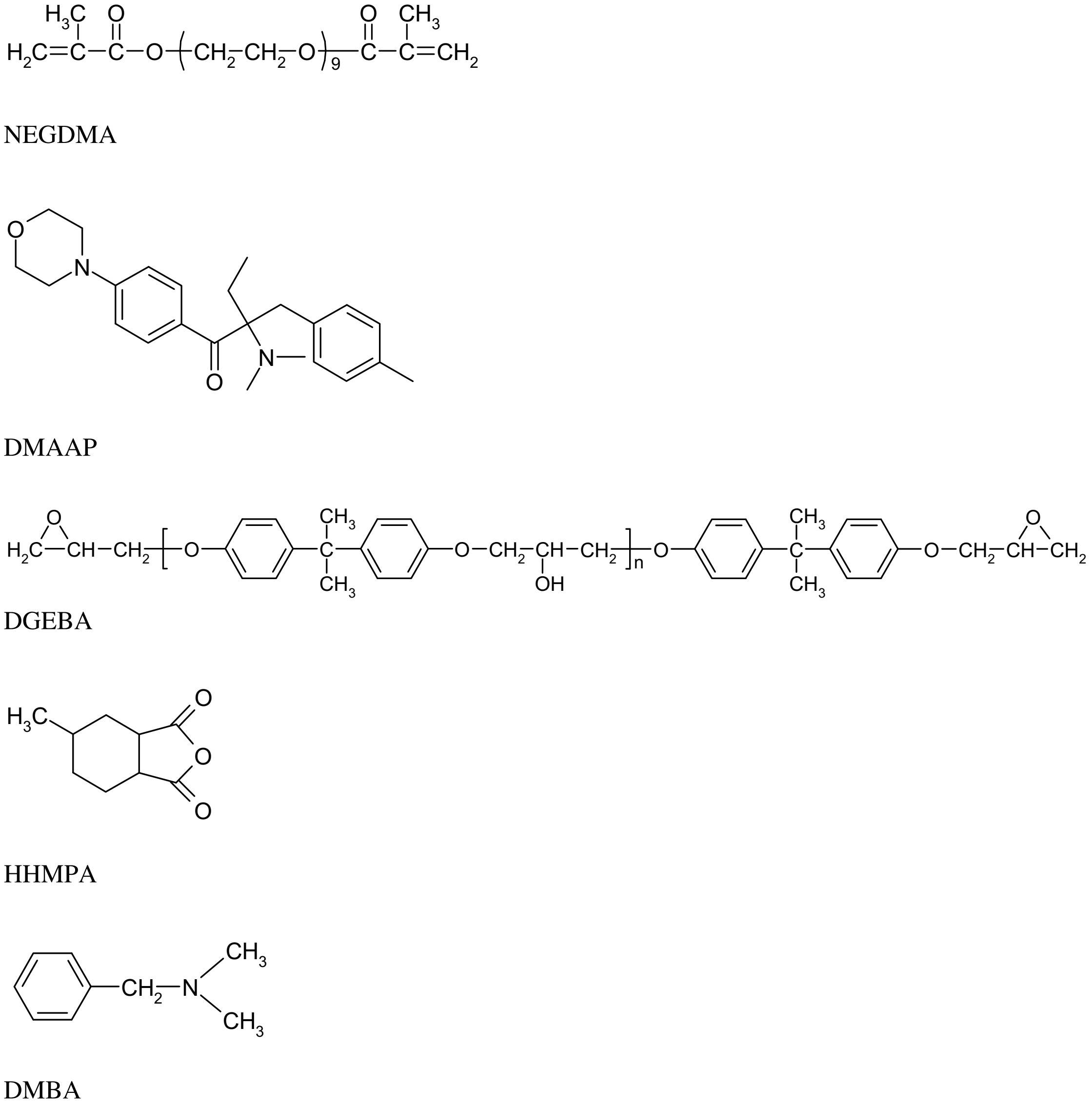
In the present study, we have prepared IPNs with a rigid anhydride-cured epoxy, and a flexible photocured dimethacrylate – these two chemically dissimilar thermosetting resins were chosen in order to increase properties such as toughness (with high levels of dimethacrylate in the IPN) or modulus (with high levels of epoxy in the IPN). The effect of changing the order of a dimethacrylate and epoxy system on the cure kinetics and phase structure in the IPN is investigated by using adaptable dual thermal/photochemical curing methods. This is achieved by either photocuring the dimethacrylate, followed by a thermal cure of the epoxy component, or by thermally curing the epoxy component, followed by the photocuring of the dimethacrylate. In addition, the effects of the curing sequence and composition on the miscibility during polymerization reaction and the reaction rate were studied and the different morphologies were examined by DMTA.

2. Experimental

2.1. Materials

The IPNs were prepared from a rigid epoxy resin and a flexible dimethacrylate resin. The epoxy resin was the diglycidyl ether of bisphenol-A (DGEBA, supplied by Ciba Geigy; see Fig. 1, where $n \approx 0.15$) with an average equivalent weight of 190 g/mol. The DGEBA was thermally cured by hexahydro-4-methylphthalic anhydride (HHMPA, supplied by Aldrich Chemicals, see Fig. 1) in stoichiometric ratio (1:1 anhydride to epoxy groups). The epoxy cure was accelerated with *N*,*N*-dimethylbenzylamine (DMBA, supplied by Aldrich Chemicals, see Fig. 1) which was used at a level of 2 wt % of the total epoxy/anhydride mixture.

The dimethacrylate resin was supplied by Aldrich Chemicals as polyethylene glycol dimethacrylate $M_n \sim 550$, and this molecular weight corresponds to nona-ethylene glycol dimethacrylate (NEGDMA see Fig. 1). It should be noted that although the average number of ethylene oxide units is nine, it is likely that the product contains a distribution of units as has been reported for a similar product [19]. The photo cure of the NEGDMA using UV radiation was initiated with 0.1 wt% of 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-



NEGDMA

DMAAP

DGEBA

HHMPA

DMBA

Fig. 1. Molecular structures of nona-ethylene glycol dimethacrylate (NEGDMA), 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (DMAAP), digylcidyl ether of bisphenol A (DGEBA, $n \approx 0.15$), hexahydro-4-methylphthalic anhydride (HHMPA), and *N*,*N*-dimethylbenzylamine (DMBA).

1-one (which is a dimethylamino acetophenone, abbreviated as DMAAP and supplied by Ciba Specialty Chemicals as Irgacure 379, see Fig. 1).

For IPN preparation, the dimethacrylate resin and the epoxy monomer were separately mixed with the respective radical initiator or curing agent before being combined in a 25:75, 50:50 or 75:25 weight ratio at ambient temperature to give a miscible blend. In some studies, certain components in these IPNs were omitted to determine if any interaction between initiator systems was occurring – the composition of these partially formulated systems was based on that employed in the fully formulated IPNs.

2.2. Differential scanning calorimetry

Photopolymerization studies were performed in a Perkin–Elmer DSC-7, operated in isothermal mode under a N_2 atmosphere at a flow rate of 20 mL min^{-1}. The instrument was modified to allow the irradiation of the sample as discussed by Cook [20]. The peak exotherm temperatures and the heats of polymerization of the samples (in J/g) were measured and the accuracy of these are estimated to be approximately ±1 °C and ±10 J/g, respectively. The calorimeter was calibrated for temperature and enthalpy using high purity zinc and indium standards.

For ultraviolet light photopolymerization during isothermal DSC experiments, the sample was initiated with a Spectroline S-100PC/FA ultraviolet lamp (Spectronics). A glass biconvex lens (Oriel, USA) was used to focus the UV radiation (predominantly 365 nm) on to the quartz fiber optic entrance. The unattenuated radiation intensity at the DSC sample pans, measured using an International Light IL 1700 radiometer fitted with a SED033/UVA/W detector, was 0.60 mW cm^{-2} at 365 nm. A shutter was used to allow an accurate control of the exposure time of the sample by the light source.

The kinetics of the thermal cure of the epoxy resin were measured with the DSC operated in temperature scanning mode (5 °C min^{-1}) under the same conditions as those for the isothermal mode and scanned from 50 to 200 °C. In cases where samples were temperature ramped after isothermal photocuring, the photocuring setup was dismantled and replaced with the standard DSC sample pan holder lid before the scanning temperature cure was undertaken. In the cases where the samples were partially temperature ramped before photocuring, the exotherm energy of the partial scan was calculated from a full temperature scan by integrating over the appropriate temperature limits. Subambient DSC scans of the neat NEGDMA/DMAAP and DGEBA/HHMPA/DMBA resins were used to determine the T_gs of the unreacted resins using the midpoint method. The DSC T_g is known to be approximately 10 °C lower than the T_g measured from the tan δ maximum [21], however as a first-order approximation we have ignored this difference.

2.3. Dynamic mechanical thermal analysis

A Rheometrics Mark IV dynamic mechanical thermal analyzer (DMTA) was employed to measure the viscoelastic properties of the partially cured and fully cured samples of DGEBA/HHMPA/DMBA, NEGDMA/DMAAP, and their blends as a function of temperature. The liquid resin was injected into a mould formed by a 3 mm thick silicone gasket which was sandwiched between two glass slides. For isothermal curing, the neat epoxy system, the sandwiched liquid sample was placed in an oven at 80 °C for 12 h. For UV light photopolymerization, the sandwiched liquid sample was placed in a thermostated cell and irradiated with 33 mW cm^{-2} radiation (in the range of 300–400 nm with 365 nm maximum) at the specimen plane using the DYMAX 2000-EC ultraviolet light source. The neat NEGDMA/DMAAP specimen was irradiated at 40 °C for 20 min on each side (40 min in total) to minimize radiation attenuation effects through the specimen. A number of different schedules were utilized for the IPN cure (see Table 1). The dynamic mechanical behavior of the partially cured and fully cured samples was measured on rectangular bars with dimensions 3 mm × 6 mm × 35 mm. The dual cantilever mode was used with a frequency of 1 Hz over the temperature range of −75 °C to 200 °C at a heating rate of 2 °C min^{-1}.

2.4. Near-infrared spectroscopy

The degree of cure of the 3 mm thick DMTA specimens was measured by near-infrared spectroscopy, using a Bruker Equinox 55 FT-IR fitted with MCT detector at a resolution of 4 cm^{-1}. The characteristic peaks in the infrared region for the epoxy group and methacrylate unsaturation occur at 6135 and 6166 cm^{-1}, respectively [22,23]. Since the peaks lie on a curved underlying spectrum, a fourth-order polynomial was fitted to the spectrum of the "fully cured" sample, and this approximation of the underlying spectral baseline was subtracted from the NIR spectra as suggested by Dell'Erba et al. [24]. The area under these peaks was used to calculate the conversion of the epoxy and methacrylate groups in the uncured, partially cured, and "fully cured" systems. Due to the greater baseline curvature underneath the epoxy peak in the NIR spectrum, it is estimated that the error in the conversion of the epoxy and methacrylate groups was approximately ±5% absolute.

3. Results and discussion

3.1. Interactions between the epoxy and dimethacrylate components of the IPNs

Fig. 2 shows the temperature ramping cure of DGEBA/HHMPA/DMBA which has an exotherm of 316 J/g. Assuming that this energy is primarily due to the ring opening of the epoxy group, the heat of reaction was 113 kJ/mol epoxy groups which is similar to that found for epoxy polymerization by primary or tertiary amines with the values in the range of 100–117 kJ/mol of epoxy groups [25], and for epoxy polymerization by anhydride with the values in the range of 110–113 kJ/mol of epoxy groups [26–28]. In order to confirm that the epoxy and dimethacrylate components could be thermally or photocured independently, the possible interactions between each component in the IPN were investigated by studies of the effects of components from each curing system on the curing behavior of the other. Fig. 2 exhibits the effects of the dimethacrylate components on the epoxy cure. Scanning DSC of the DGEBA/HHMPA/DMBA/DMAAP (see Fig. 2b) system revealed that the DSC peak shape and heat of polymerization were unaffected by the presence of 0.1 wt% of the tertiary amine, DMAAP, and in agreement with this, scanning DSC of DGEBA/DMAAP (not shown here) and DGEBA/HHMPA/DMAAP (see Fig. 2c) did not show any reaction between DGEBA and DMAAP (0.1 wt%) or between DGEBA/HHMPA and DMAAP (0.1 wt%) up to 200 °C, probably due to the low concentration of DMAAP amine. For the scanning DSC of NEGDMA:DGEBA/HHMPA/DMBA (see Fig. 2d), the DSC peak shifted from 124 °C to 136 °C, probably due to the dilution of the DGEBA/HHMPA/DMBA by the uncured dimethacrylate, which reduced the rate of epoxy cure, as observed in previous IPN studies [7,29,30]. The total heat of polymerization (163 J/g) of the NEGDMA:DGEBA/HHMPA/DMBA was approximately equal to that expected from the weight fractions of NEGDMA and DGEBA/HHMPA/DMBA.

The heat of photopolymerization of the NEGDMA/DMAAP (0.1%) system at 50 °C (which is above the T_g of the polymer, as measured below) was found to be 218 J/g or 60 kJ/mol of methacrylate groups. This compares reasonable well with previous studies of the thermal cure of NEGDMA [31] which gave 229 J/g or 63 kJ/mol and with the heat of polymerization of methacrylate groups 54.4 kJ/mol [32]. If NEGDMA/DMAAP was partially photocured for 24 s at 50 °C (giving a heat of polymerization of 61 J/g, equivalent to 30% conversion of methacrylate groups) and was then thermally scanned from 50 to 200 °C, no exotherm peak was detected (not shown here), suggesting there was no "dark reaction" in the system

Table 1

T_gs and conversions for the isothermally cured and photocured NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs and their parent resins using various cure schedules

Sample	Opaque	T_g/°C (from tan δ)	Conversion from NIR[a]/%	
			Methacrylate	Epoxy
Neat resins				
Neat NEGDMA/DMAAP (uncured)		−32 (by DSC)		
Neat DGEBA/HHMPA/DMBA (uncured)		−33 (by DSC)		
Neat NEGDMA/DMAAP (UV cure at 40 °C/ 40 min)	No	15	95	
Neat DGEBA/HHMPA/DMBA (isothermal cure at 80 °C/12 h, postcured at 150 °C/2 h)	No	158		92
25:75 IPN systems				
25:75 IPNs-partially cured				
25:75 IPN (UV cure at 40 °C/40 min)	No	4	96	7
25:75 IPN but without DMBA catalyst for epoxy (UV cure at 40 °C/40 min)	No	−13	96	0
25:75 IPN (isothermal cure at 80 °C/12 h)	No	ca. −25 and 85	0	95
25:75 IPNs-fully cured				
25:75 IPN (UV cure at 40 °C/40 min and then isothermal cure at 80 °C/12 h, postcured at 150 °C/2 h)	No	ca. 124 and 145	96	92
25:75 IPN (isothermal cure at 80 °C/12 h and then UV cure at 80 °C/40 min, postcured at 150 °C/2 h)	No	ca. 30 and 119	74	96
50:50 IPN systems				
50:50 IPNs-partially cured				
50:50 IPN (UV cure at 40 °C/40 min)	No	−3	96	12
50:50 IPN but without DMBA catalyst for epoxy (UV cure at 40 °C/40 min)	No	−11	96	0
50:50 IPN (isothermal cure at 80 °C/12 h)	No	−44 and 56	0	96
50:50 IPNs-fully cured				
50:50 IPN (UV cure at 40 °C/40 min and then isothermal cure at 80 °C/12 h, postcured at 150 °C/2 h)	No	Broad damping range from −5 to 150	96	95
50:50 IPN (isothermal cure at 80 °C/12 h and then UV cure at 80 °C/40 min, postcured at 150 °C/2 h)	No	ca. 20 and 123 with damping between	95	96
75:25 IPN systems				
75:25 IPNs-partially cured				
75:25 IPN (UV cure at 40 °C/40 min)	No	−1	93	18
75:25 IPN but without DMBA catalyst for epoxy (UV cure at 40 °C/40 min)	No	−5	93	0
75:25 IPN (isothermal cure at 80 °C/12 h)	Yes	−45 and −15	0	95
75:25 IPNs-Fully Cured				
75:25 IPN (UV cure at 40 °C/40 min and then isothermal cure at 80 °C/12 h, postcured at 150 °C/2 h)	No	Broad peak centred at 28	94	96
75:25 IPN (isothermal cure at 80 °C/12 h and then UV cure at 80 °C/40 min, postcured at 150 °C/2 h)	yes	19 and 94	98	96

[a] NIR samples were not postcured at 150 °C.

due to polymerization by residual trapped radicals in the matrix [7].

The effect of the IPN components on the dimethacrylate cure was also studied. Scanning DSC of the uninitiated NEGDMA (not shown here) and the initiated NEGDMA/0.1% DMAAP system (not shown here) revealed that there was no thermal cure of the dimethacrylate up to 200 °C. Temperature-ramping DSC of NEGDMA/HHMPA over the range 50–200 °C (Fig. 3a) showed an exotherm of 144 J/g and a peak at 150 °C. It appears that this exotherm is due to thermal polymerization of NEGDMA (with a polymerization heat of 40 kJ/mol) but it is unclear why the anhydride induces the reaction. In the case of the NEGDMA/HHMPA/DMBA system (Fig. 3b) when scanned from 50 to 200 °C, the exothermic peak shifted from 150 to 140 °C, but the heat of polymerization was unaffected. Temperature-ramping DSC of the NEGDMA/DMAAP/HHMPA system (see Fig. 3c) revealed that a reaction commenced at 118 °C and had a small exotherm peak at 128 °C (59 J/g, equivalent to 16 kJ/mol of methacrylate units), which may be due to thermal cure of the methacrylate groups, but the reason for this enhanced methacrylate reactivity is also unclear. When DMBA was added to this system (Fig. 3d), the exotherm peak shifted from 128 to 115 °C (and the onset of polymerization shifted to 102 °C), but the heat of reaction was unaffected. DSC scans of NEGDMA/DGEBA (Fig. 3e) showed an exotherm at high temperature 170 °C, possible due to the temperature thermal cure of NEGDMA.

From the above studies (Figs. 2 and 3) a number of interactions occur between the components in the IPN at elevated temperatures. However, if the isothermal curing is controlled below 100 °C, these interactions can be minimized. Therefore, the NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN is a suitable IPN system for sequential studies of cure, if an appropriate cure schedule is chosen.

3.2. Photochemical and thermal cure kinetics

Fig. 4 shows that the photopolymerization at 40 °C of the dimethacrylate component in the IPN (Fig. 4b and c) occurs reasonably quickly (<3 min) but that under the same conditions (Fig. 4a) no cure of the epoxy occurs. In fact, a reasonable rate of cure of the epoxy only occurs at

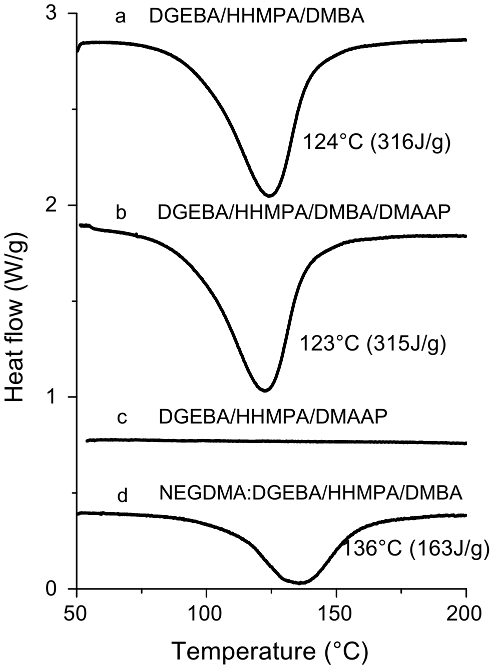


Fig. 2. Effect of initiator components on the cure of DGEBA: (a) temperature-ramping DSC of DGEBA/HHMPA/DMBA; (b) temperature-ramping DSC of DGEBA/HHMPA/DMBA/DMAAP; (c) temperature-ramping DSC of DGEBA/HHMPA/DMAAP; and (d) temperature-ramping DSC of NEGDMA:DGEBA/HHMPA/DMBA.

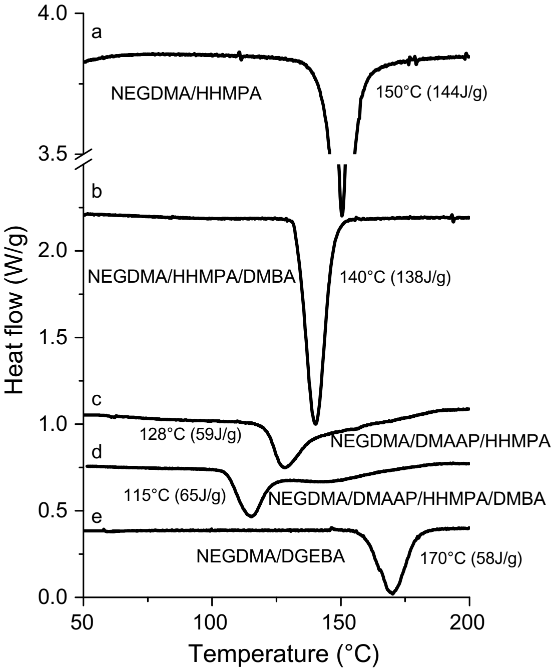


Fig. 3. Effect of interactions between the NEGDMA/DMAAP and DGEBA/HHMPA/DMBA and initiator components on the thermal cure of NEGDMA/DMAAP: (a) temperature-ramping DSC of NEGDMA/HHMPA; (b) temperature-ramping DSC of NEGDMA/HHMPA/DMBA; (c) temperature-ramping DSC of NEGDMA/DMAAP/HHMPA; (d) temperature-ramping DSC of NEGDMA/DMAAP/HHMPA/DMBA; and (e) temperature-ramping DSC of NEGDMA/DGEBA.

elevated temperatures (see Figs. 4 and 5). This shows that dimethacrylate photopolymerization occurs very fast in comparison to the slower cure of the epoxy component.

Fig. 4 also shows the effect of partial photocuring of the dimethacrylate component on the isothermal photocuring behavior of the epoxy component in the 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN system. When the IPN had not been photoirradiated (Fig. 4a), the DSC curing peak of the epoxy component has a shoulder at 128 °C which differs from that observed for the pure epoxy/anhydride system or the NEGDMA:DGEBA/HHMPA/DMBA semi-IPN (see Fig. 2), and this may suggest that an additional process is occurring, and presumably this is thermal cure of the dimethacrylate. The heat of polymerization of this system was 170 J/g which is slightly higher than the heat contributed from the cure of the epoxy in the NEGDMA:DGEBA/HHMPA/DMBA semi-IPN (163 kJ/mol, see Fig. 2d) or in the pure epoxy/anhydride system (158 J/g calculated from half of that observed for the pure DGEBA/HHMPA/DMBA system, 316 J/g, as seen in Fig 2a). When the dimethacrylate was partially photocured at 40 °C (Fig. 4b and c) prior to the temperature-ramping stage of the experiment, the peak became more symmetric and yielded a heat of polymerization that was close to that expected, suggesting that the exotherm was due primarily to epoxy cure. In addition, the peak temperature of the epoxy exotherm shifted from 138 °C for the IPN with no photoirradiation to 125 °C to for the photocured IPN which indicates that the epoxy cure is faster. One possible explanation for this observation is that phase separation of the epoxy components from the dimethacrylate network increases their local concentrations and thus increases the reaction rate.

Fig. 5 shows the effect of partial cure of the epoxy component on the isothermal photocuring behavior of the dimethacrylate component in the 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN system. As the maximum temperature attained in the temperature-ramping part of the experiment is raised, the amount of heat evolved rises because of an increase in the extent of epoxy cure, however this also results in a significant reduction in the exotherm (from 110 to 72 J/g) during the subsequent isothermal photopolymerization of the dimethacrylate components at 40 °C. This could be attributed to a reduction of segmental mobility as the IPN vitrifies (the “IPN vitrification effect” [6,7,17,18,29,30], where the mobility and hence reactivity of the methacrylate groups decreases as the epoxy conversion in the IPN and the T_g of the IPN network increases. It can be also noted from Fig. 5 that the maximum heat flow during dimethacrylate cure rises as the extent of prior cure of the epoxy component increases. In a similar manner to that discussed above, this could be interpreted as being a result of phase separation of the dimethacrylate components from the developing epoxy network, thus raising their concentration.

The NIR spectra of the uncured 25:75 IPN mixture and of the 25:75 IPNs after various sequences of photochemical and thermal cure are illustrated in Fig. 6, and the conversion results for all IPNs are listed in Table 1. This data con-

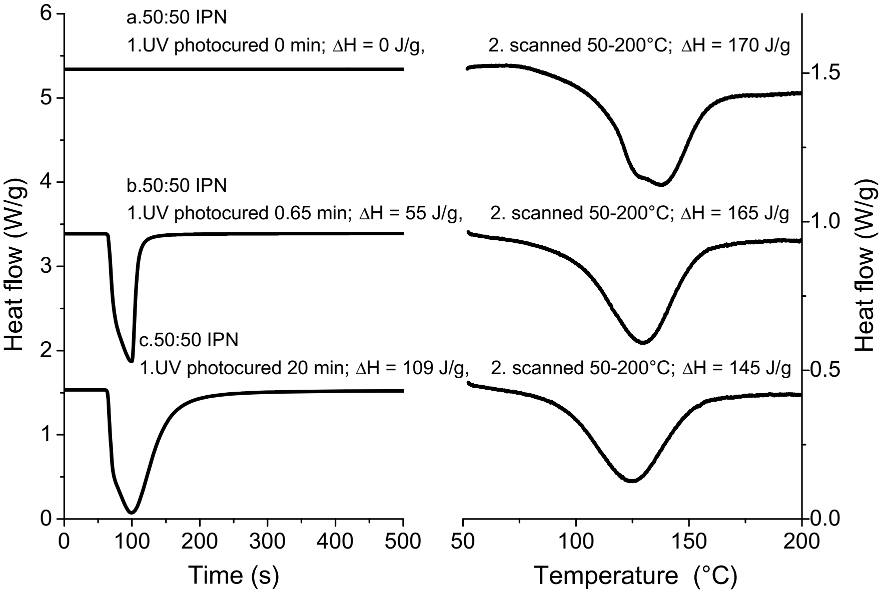


Fig. 4. Photocure behavior of 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs at 40 °C for varying times with UV light, followed by scanning DSC cure from 50 to 200 °C.

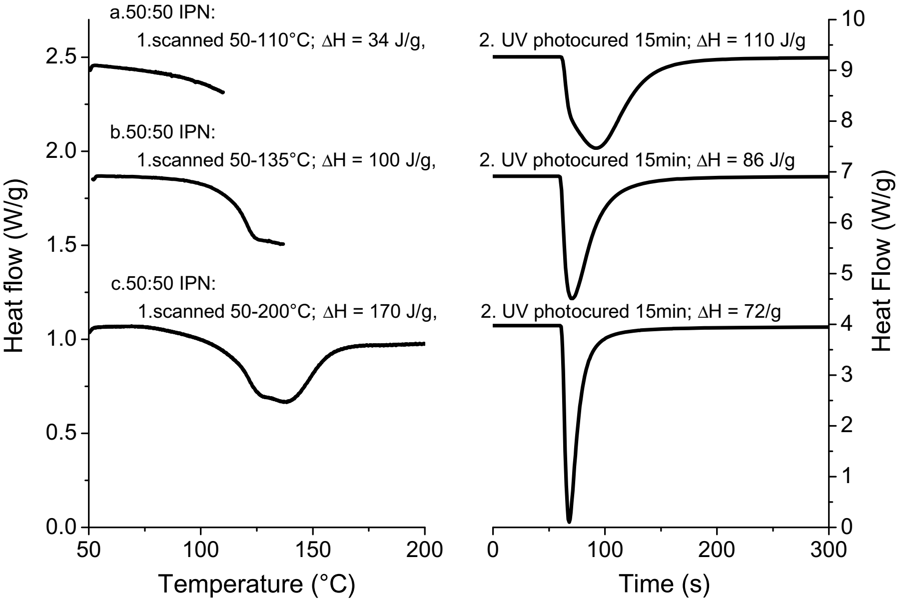


Fig. 5. Partial scan-cure of the epoxy component followed by photocuring of the dimethacrylate in 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs at 40 °C.

firms that in the absence of DMBA, UV irradiation of the IPN mixture at 40 °C for 40 min only causes methacrylate cure while the epoxy groups do not react. However, when DMBA was incorporated in the IPN systems and the dimethacrylate component was photocured at 40 °C, there was a small amount of thermal cure of the epoxy-anhydride system. The epoxy groups undergo significant polymerization only after thermal cure of the IPN at 80 °C for 12 h (see Table 1). This result is also consistent with the DMTA data which showed that the T_gs of the IPNs were slightly higher after photocuring when DMBA was included in the blend. In the case when the curing order was reversed, isothermal cure of the IPN at 80 °C for 12 h only resulted in the polymerization of the epoxy/anhydride network, and UV irradiation was required for methacrylate polymerization.

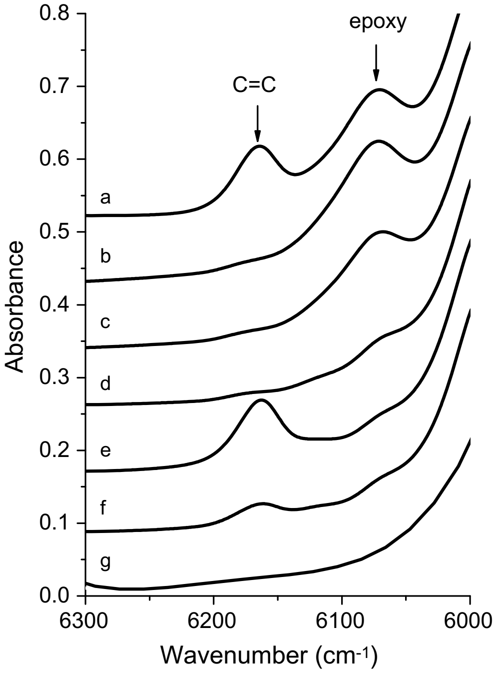


Fig. 6. NIR spectra of the IPN based on 25:75 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA components: (a) uncured IPN; (b) UV cure of IPN (without DMBA) at 40 °C for 40 min; (c) UV cure of IPN at 40 °C for 40 min; (d) UV cure of IPN at 40 °C/40 min and then isothermal cure at 80 °C/12 h; (e) isothermal cure of IPN at 80 °C/12 h; (f) isothermal cure of IPN at 80 °C/12 h and then UV cure at 80 °C/40 min; and (g) fourth-order polynomial fit to spectrum d to estimate the background spectra.

As discussed above, cross-reactions between the IPN components only became significant for cure temperatures over 100 °C. However the cure temperature in the first stage could not be too low because vitrification would occur, preventing full cure [33]. Assuming as a first approximation that the blends were miscible, measurements of the T_gs of the monomers and cured parent resins (discussed below and reported in Table 1) were used with the Fox equation[1] [34] to predict the T_gs of IPNs which had either or both components cured. Thus in the first curing stage of the IPN, for the dimethacrylate component of an IPN to be fully photocured, the curing temperature must exceed the final T_g of the blend – since this varies from –22 °C to 1 °C for blends ranging from 25 wt% to 75 wt% NEGDMA, a convenient photocuring temperature of 40 °C was employed. Conversely, a minimum required curing temperature of 80 °C in the first stage of curing was predicted for full cure of the epoxy component in blends varying from 25 wt% to 75 wt% epoxy component. In the cases where subsequent full cure of the second component was required, the curing temperature was 80 °C followed by post curing at 150 °C which is close to the maximum T_g of the components and so would allow full cure in the second curing stage.

3.3. Dynamical mechanical properties – effect of curing conditions

Dynamic mechanical thermal analysis is a common and useful technique to study the glass transition temperatures and thus phase-separation of IPNs [35,36], provided that the individual components of the IPN have clearly defined and well separated T_gs. Figs. 7–13 illustrate the tan δ and storage modulus traces for the 25:75, 50:50 and 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs prepared under different thermal/photo curing sequences, and for their parent resins. The corresponding T_gs of the networks are listed in Table 1. With the exception of some of the 75:25 IPNs (as discussed below), these materials were transparent. Although commonly used to study phase separation [37], the lack of turbidity (or the observation of transparency) in a blend does not necessarily mean that the system has a single phase, because blends with a small difference in the refractive indices of the components, domain sizes less than a micrometer or low volume fractions of one of the phases can also be transparent [37]. Thus the observation of turbidity in some of the 75:25 blends suggests that the transparency of the other IPNs either meant that they were essentially miscible or that the domain size (of the dispersed or co-continuous phase) was smaller than 1 μm, approximately.

The tan δ traces for the 25:75 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs and their parent network components are shown in Fig. 7. All of these blends were transparent, suggesting miscibility or small phase domains. The T_g values of the unreacted DGEBA/HHMPA/DMBA and NEGDMA/DMAAP rise from −33 °C and −32 °C, respectively (as measured by DSC) to 158 °C and 15 °C, respectively, after cure. In order to study the effect of curing only the dimethacrylate component on the DMTA behavior of the IPN, in one experiment DMBA was omitted from the 25:75 IPN components so that the thermal cure of the epoxy during the DMTA run was prevented by omission of the catalyst. Thus, after photocuring the 25:75 IPN at 40 °C, the T_g of the 25:75 IPN rises to −13 °C, which lies between the T_gs values of the uncured DGEBA/HHMPA/DMBA monomer (−33 °C by DSC) and the cured NEGDMA/DMAAP resin (15 °C by DMTA). For the completely formulated 25:75 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN, photocuring at 40 °C followed by isothermal curing at 80 °C for 12 h and at 150 °C for 2 h resulted in a peak at 145 °C but with a shoulder at 124 °C. Both of these T_g values are higher than the value of 110 °C predicted by the Fox equation [34]. It is not clear why the Fox prediction is not closer than observed since the conversions of both epoxy and methacrylate groups in this IPN are high and similar to that in the cured parent resins (see Table 1). Despite this, it appears that the two T_gs result from two epoxy-rich phases with small variations in their composition, suggesting a two-phase structure but with a narrow distribution of phase compositions.

In the opposite case where the epoxy component of the 25:75 IPN was thermally cured at 80 °C for 12 h without photoirradiation, the DMTA spectrum showed a small peak at –25 °C and a major peak at 85 °C. The former is presumably due to a minor NEGDMA monomer-rich phase since it

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[1] Note that this value is approximate because the T_gs of the monomers and polymers were measured using different methods.

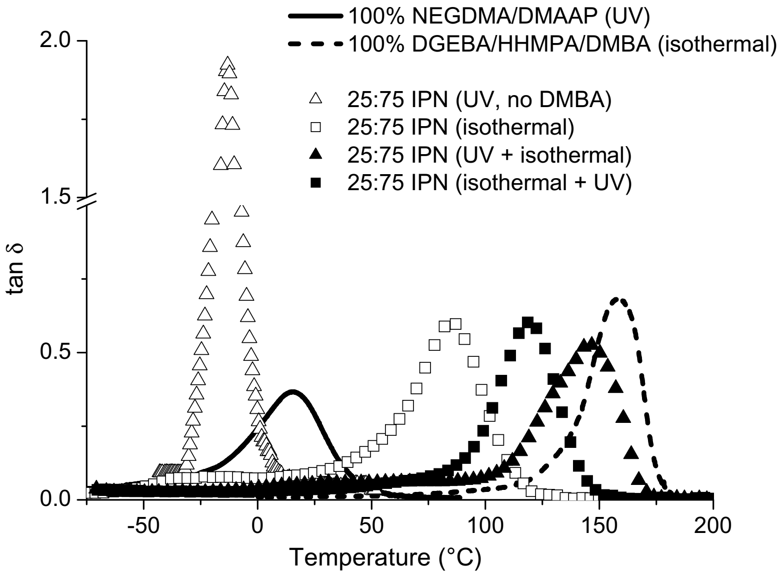

Fig. 7. Tan δ versus temperature for the photocured NEGDMA/DMAAP, thermally cured DGEBA/HHMPA/DMBA, and 25:75 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs using various cure schedules.

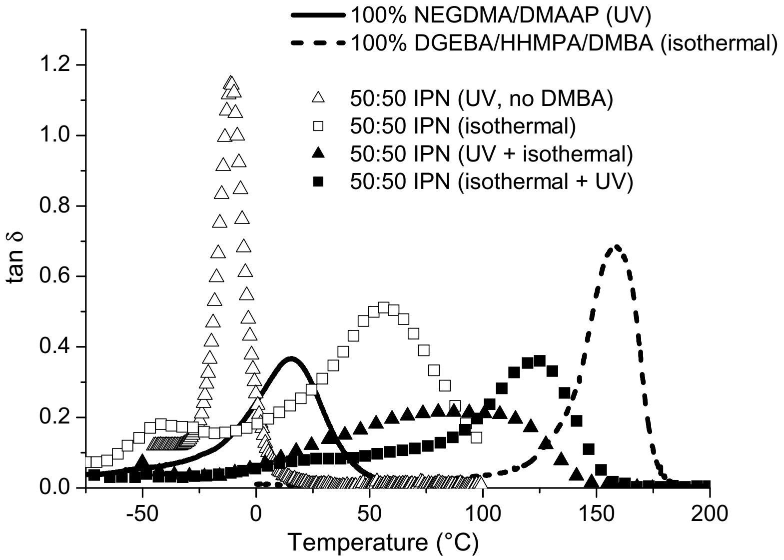

Fig. 8. Tan δ versus temperature for the photocured NEGDMA/DMAAP, thermally cured DGEBA/HHMPA/DMBA, and 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs using various cure schedules.

is close to the NEGDMA monomer T_g of −32 °C. The higher temperature peak at 85 °C, which lies between the T_g values of the NEGDMA monomer (−32 °C by DSC) and the cured epoxy resin (158 °C by DMTA), is due to the majority epoxy network component plasticized by NEGDMA. After subsequent photocure of the dimethacrylate component in this 25:75 IPN, a small tan δ shoulder occurred at ca. 30 °C and the major peak shifted to 119 °C. The lower temperature peak is probably due to a minor phase of crosslinked NEGDMA, possibly with a small amount of cured epoxy (the T_g of pure crosslinked NEGDMA is 15 °C). The major peak at 119 °C is probably due to the T_g of the cured epoxy-rich phase. However, estimation of its composition by the Fox equation [34] is complicated by the fact that the NEGDMA is not fully cured in this IPN (see Table 1) as discussed above, and so the uncured monomer could be distributed between either phase.

Table 1 shows that the conversion of both the epoxy and methacrylate groups was near to completion in the 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs after thermal and photochemical cure, irrespective of the cure order. All of these blends were transparent, suggesting

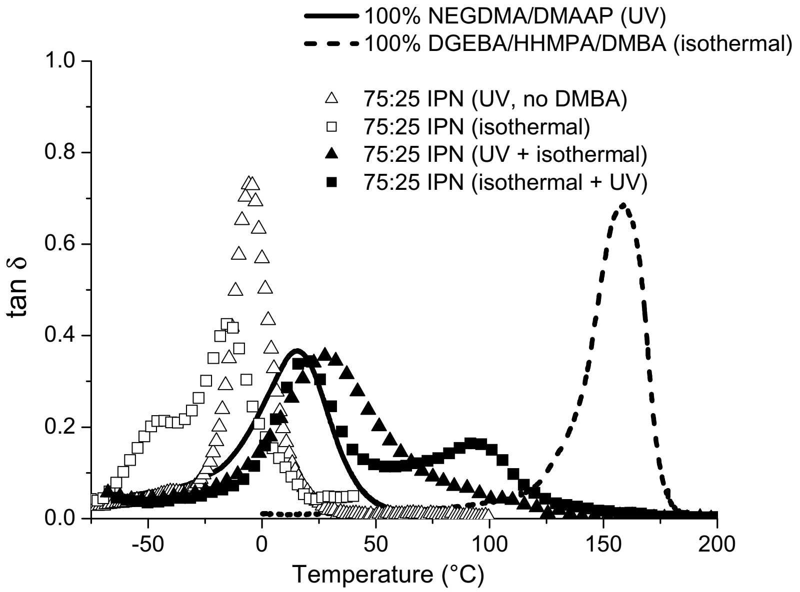

Fig. 9. Tan δ versus temperature for the photocured NEGDMA/DMAAP, thermally cured DGEBA/HHMPA/DMBA, and 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs using various cure schedules.

miscibility or small phase domains. Fig. 8 illustrates the tan δ traces for the 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs and their parent network components. The difference between the tan δ traces of the 50:50 IPN resins with different curing sequence is quite significant. As mentioned above, in order to study the effect of curing only the dimethacrylate component on the DMTA behavior of the IPN, DMBA was omitted from the 50:50 IPN components in one of the DMTA experiments so that the thermal cure of the epoxy during the DMTA run was prevented. Thus, after photocuring the 50:50 NEGDMA/DMAAP:DGEBA/HHMPA system at 40 °C, the T_g of the 50:50 IPN rises to −11 °C, which lies between the T_gs values of the uncured DGEBA/HHMPA/DMBA monomer (T_g is −33 °C by DSC) and the cured NEGDMA/DMAAP resin (15 °C by DMTA). For the completely formulated 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN, photocuring the dimethacrylate and then isothermal curing of the epoxy component resulted in an extremely broad damping range (from −5 °C to 150 °C) and ill-defined glass transition temperatures, suggesting a wide variation in phase intermixing.

In the case where the epoxy component in the 50:50 IPN was cured at 80 °C for 12 h, without photocuring, the IPN exhibited two T_gs at −44 °C and 56 °C. The lower T_g appears to be due to the uncured NEGDMA-rich region although it is unclear why the temperature is less than the T_g of −32 °C of the monomer. One possibility for this anomaly is that partitioning of some HHMPA from the epoxy-rich phase into the NEGDMA phase lowers its T_g as has been observed earlier for a related system [7]. However this would change the anhydride-epoxy stoichiometry resulting in undercure of the epoxy and this is not supported by the high conversion of epoxy groups in this IPN (see Table 1). The higher T_g in the 50:50 IPN is probably due to the epoxy-rich region. This temperature is much less than the cured DGEBA/HHMPA/DMBA network (T_g of 158 °C) and this difference may be due to plasticization by NEGDMA or due to incomplete cure due to the imbalance in anhydride-epoxy stoichiometry caused by phase partitioning as suggested above. Unfortunately this complexity makes it impossible to use the Fox equation [34] to predict the phase compositions. After subsequent photocuring of the dimethacrylate component in the thermally cured 50:50 IPN, both epoxy and methacrylate groups achieved high conversion and the material exhibited a quite broad damping range with a tan δ maximum at 123 °C and a smaller a shoulder observed at 20 °C. This broad damping range indicates that phase separation had also occurred in this IPN but that the variations in compositions of the various regions of the IPN was not as extensive as in the IPN formed by photopolymerization and then thermal cure. The tan δ shoulder at 20 °C in the thermally and then photocured 50:50 IPN system suggests a T_g due to a nearly pure NEGDMA phase (the neat NEGDMA/DMAAP T_g is 15 °C). The T_g due to the epoxy-rich phase at 123 °C is considerably less than that for the neat DGEBA/HHMPA/DMBA (T_g is 158 °C), suggesting partial mixing of epoxy and dimethacrylate networks. Use of the Fox equation [34] predicts that this phase is 80 wt% cured epoxy and 20 wt% cured NEGDMA. Between these two glass transition regions, the tan δ is relatively high suggesting that there also exist domains with other levels of intermixing.

The tan δ traces for the 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs and their parent network components are exhibited in Fig. 9. As mentioned above, in one experiment DMBA was omitted from the IPN components so that the thermal cure of the epoxy during the DMTA run was prevented. After photocuring the 75:25 IPN (with the omission of DMBA to prevent epoxy cure) at 40 °C, a transparent rubber was formed with a T_g of

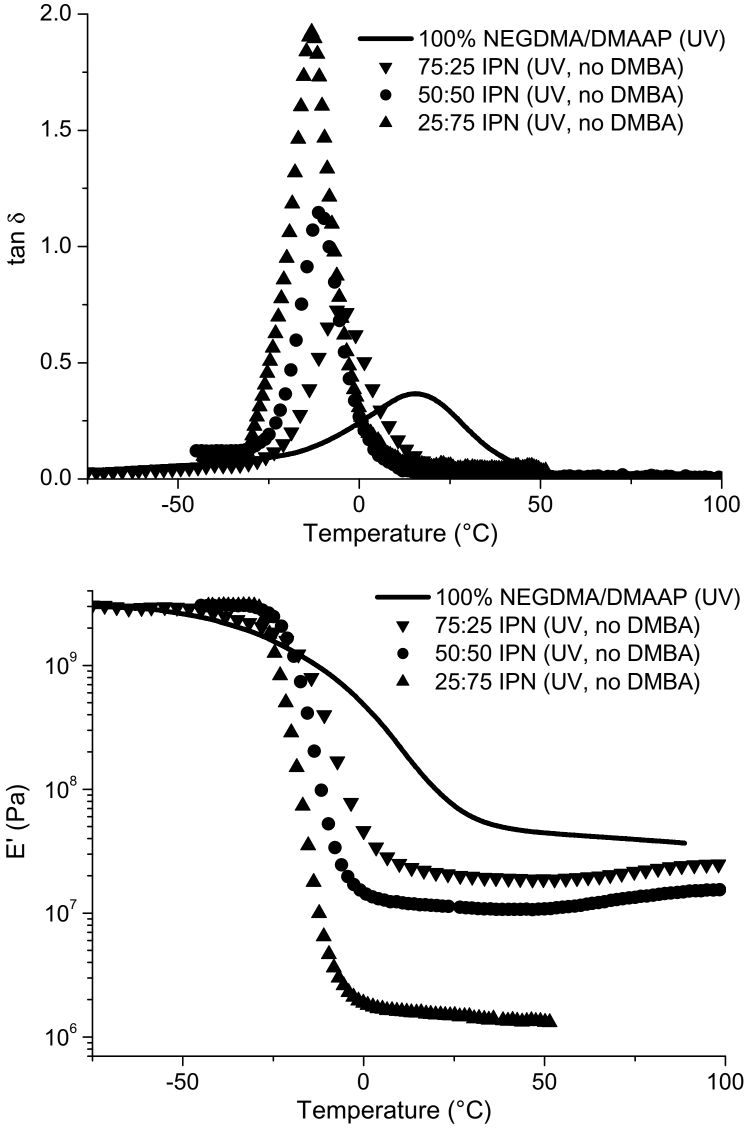

Fig. 10. Tan δ and storage modulus (E') versus temperature for the 25:75, 50:50, 75:25 NEGDMA/DMAAP:DGEBA/HHMPA IPNs and the neat NEGDMA/DMAAP resin after photocuring.

−5 °C which lies between the fully cured NEGDMA (15 °C by DMTA) and the uncured DGEBA/HHMPA/DMBA monomer mixture (−33 °C by DSC). This suggests a single phase structure. Photocuring followed by thermal cure of the fully formulated 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN at 80 °C for 12 h and 150 °C for 2 h resulted in a well cured IPN (see Table 1) which was transparent and had a single, broad tan δ peak at 28 °C. This T_g is a little lower than the value of 41 °C predicted by the Fox equation [34]. Although the single transition might suggest that the blend was miscible, the breadth of the transition implies that there are small domains with a narrow distribution of phase compositions. As discussed later, scanning electron microscopy (SEM) studies (these will be reported in a later paper) of freeze fractured samples show that this system has phase separation with domains of <200 nm.

In the case when the minority epoxy component in the 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN was thermally cured at 80 °C for 12 h (but not photocured), the material was a very soft and opaque rubber, indicating a two-phase structure with micrometer-sized domains in which the epoxy network was co-continuous throughout the structure (hence providing a rubbery modulus as discussed below). The IPN exhibited two T_gs at −45 and −15 °C (see Fig 9). The lower and more prominent peak is similar to the T_g of −44 °C found for the 50:50 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN prepared under the same curing conditions, and appears to be due to the uncured NEGDMA-rich region. In the analogous 50:50 IPN, it was suggested above that unreacted HHMPA plasticized the unreacted NEGDMA, however once again, this is not supported by the high conversion of epoxy groups in this

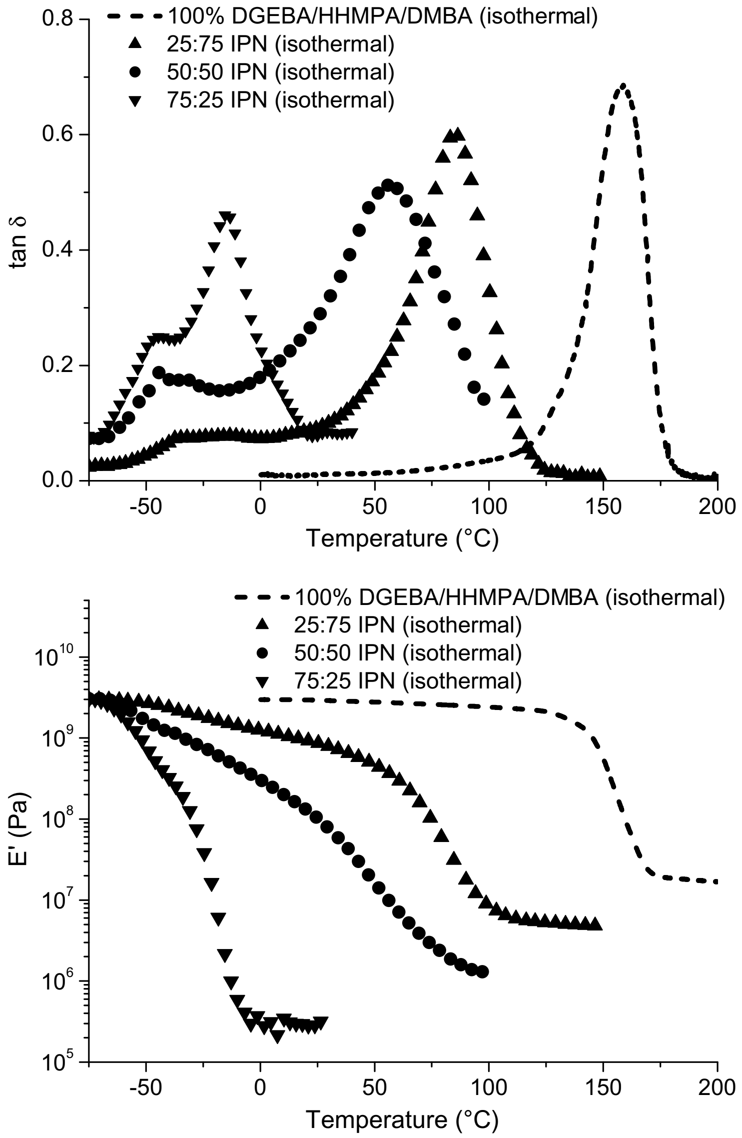

Fig. 11. Tan δ and storage modulus (E') versus temperature for the 25:75, 50:50, 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs after thermal cure of the epoxy component and the neat DGEBA/HHMPA/DMBA resin.

IPN (see Table 1). The higher T_g of −15 °C in the thermally cured 75:25 IPN is probably due to the epoxy-rich region – the T_g is much less than the cured DGEBA/HHMPA/DMBA network (T_g of 158 °C) because the uncured NEGDMA (T_g of −32 °C by DSC) plasticizes the IPN. After subsequent photocure of the dimethacrylate component in the 75:25 IPN, the resulting 75:25 IPN remained opaque and exhibited two distinct relaxations at 19 °C and 94 °C. The lower temperature relaxation corresponds to the relaxation of a NEGDMA-rich phase which is relatively pure (the neat NEGDMA/DMAAP T_g is 15 °C). The high temperature peak at 94 °C corresponds to the relaxation of the epoxy-rich phase but the significant reduction in the T_gs from the parent value (the neat DGEBA/HHMPA/DMBA T_g is 158 °C) and the fact that the conversion of both methacrylate and epoxy groups were high (see Table 1) suggests that this phase is a blend with some of the low T_g NEGDMA component – use of the Fox equation [34] predicts that 35 wt% of this phase is cured NEGDMA. For simplicity, if it is assumed that the lower temperature is pure polymerized NEGDMA and the upper peak is a 35:65 blend of cured NEGDMA and epoxy/anhydride, then from a mass balance, the fractions of the two phases are 61.5 wt% NEGDMA and 38.5 wt% NEGDMA/epoxy-anhydride. This estimated ratio of phases is consistent with the observation that the larger DMTA transition is observed for the NEGDMA phase in Fig. 9.

3.4. Dynamical mechanical properties – effect of IPN composition

In order to compare the thermomechanical properties of the IPNs with different compositions but under the same

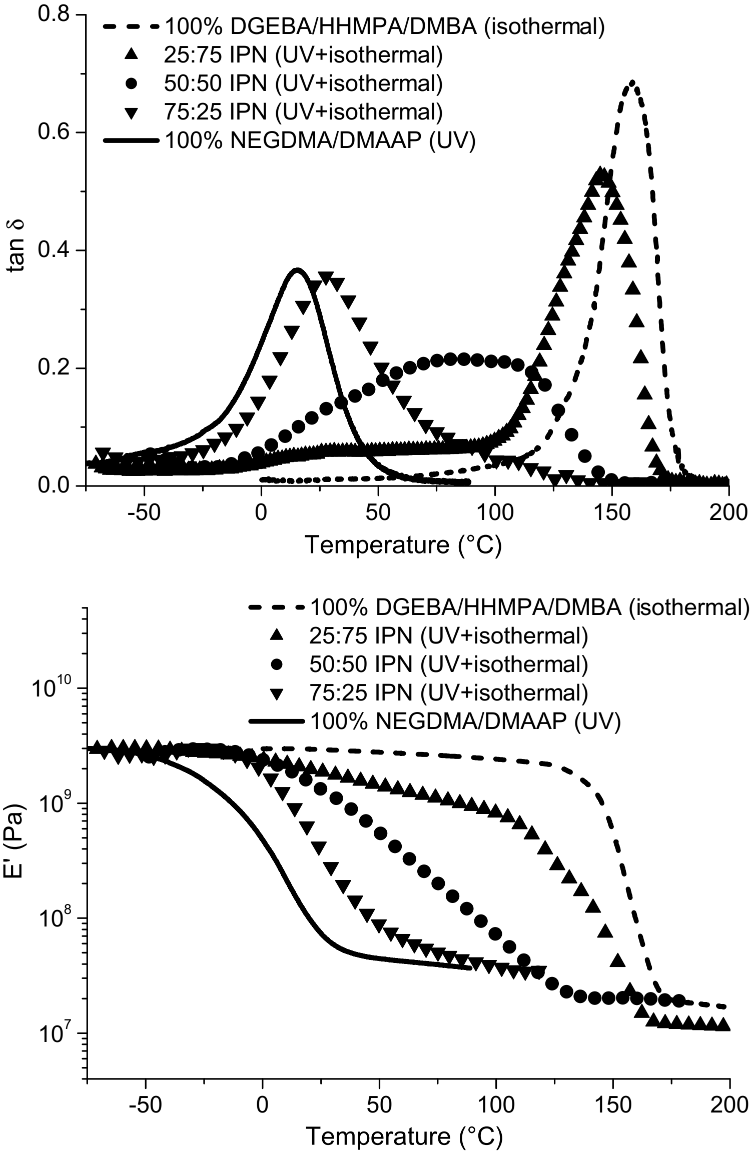

Fig. 12. Tan δ and storage modulus (*E*') versus temperature for the photocured and thermally cured 25:75, 50:50, 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs after photocuring first then thermally curing and for the cured parent resins.

curing condition, the DMTA spectra for the 25:75, 50:50 and 75:25 NEGDMA/DMAAP:DGEBA/HHMPA IPNs and the neat NEGDMA/DMAAP resin after photocuring at 40 °C for 40 min are shown in Fig. 10. The 100:0, 75:25, 50:50 and 25:7 systems exhibited a single tan δ peak at 15 °C, −5 °C, −11 °C and −13 °C, respectively, which decreased as the epoxy fraction was raised, due to plasticization by the DGEBA and HHMPA monomers. The modulus curves in Fig. 10 support these conclusions, showing only one step in the transition.

The DMTA spectra for the 25:75, 50:50, 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs after thermal cure of the epoxy component and the DGEBA/HHMPA/DMBA network are shown in Fig. 11. These IPNs exhibited two T_gs with a minor peak at ca −40 °C and the main tan δ peak at 85 °C, 56 °C and −15 °C. This decrease in the T_g of the IPNs major peak with increasing NEGDMA content is due to plasticization by uncured NEGDMA. The minor tan δ peak appears to be associated with the uncured dimethacrylate phase increased with increasing NEGDMA composition but only shifting marginally to lower temperature. The modulus curves in Fig. 11 support these conclusions, showing two steps in the transition regions of the IPNs. In addition, the rubbery modulus of IPNs increases with higher epoxy concentration, because the epoxy-anhydride network provides the network strands in these thermally cured IPNs.

Fig. 12 illustrates the DMTA spectra for the 25:75, 50:50, 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs after photocuring the dimethacrylate component first

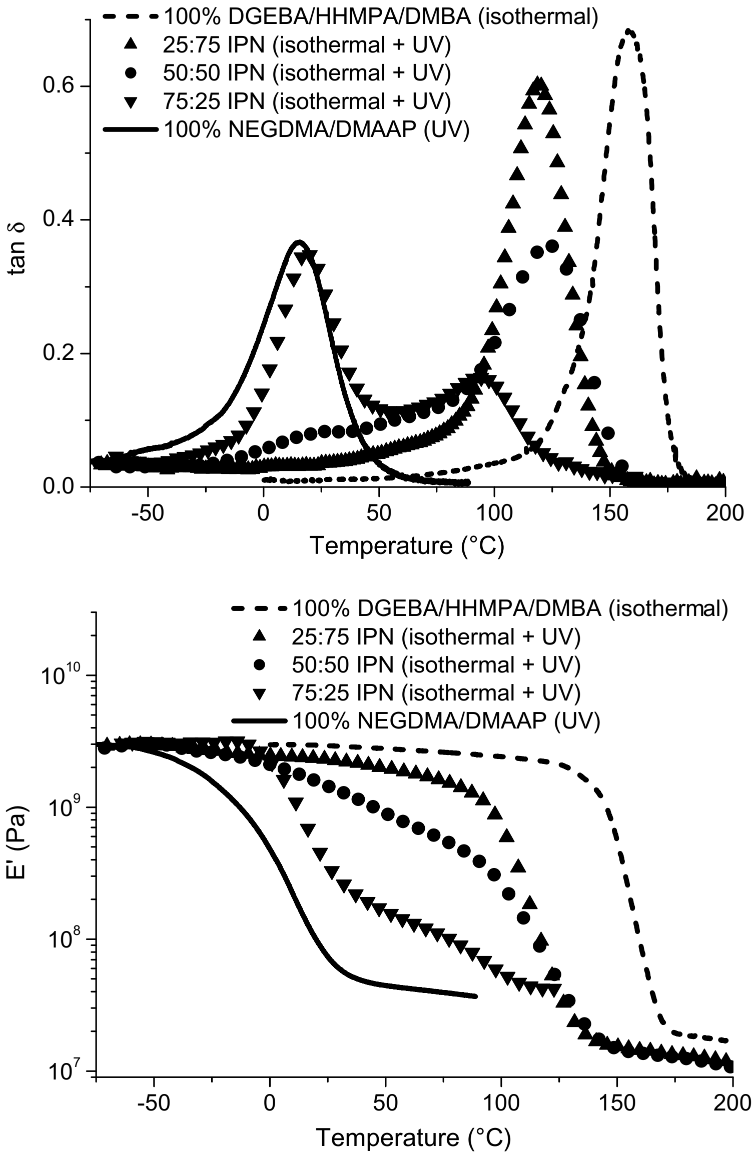

Fig. 13. Tan δ and storage modulus (E') versus temperature for the photocured and thermally cured 25:75, 50:50, 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs after isothermally curing first then photocuring and for the cured parent resins.

and then isothermally curing the epoxy, and compares them with the photocured NEDGMA/DMAAP resin, and thermally cured DGEBA/HHMPA/DMBA resin. As expected from the rigidity of the bisphenol-A backbone segments, the main T_g of the IPNs rose with increasing DGEBA content, but the extent of phase separation was at a maximum for the 50:50 IPN. The 25:75 IPN exhibited a tan δ curve with a peak at 145 °C and a slight shoulder at 124 °C, suggesting a relatively narrow distribution of phases, whereas the glass transition of the 50:50 IPN shifted to lower temperature and became significantly broader over a wide damping range which suggests a wide variety of phase separation, while the T_g of the 75:25 IPN was lowest and the transition was relatively narrow, suggesting that the material is close to a single phase structure. Thus it appears that the heterogeneity passes through a maximum with increasing NEGDMA content [38]. The modulus curves in Fig. 12 support these conclusions, showing a double step for the 25:75 IPN, an extremely broad multiple steps transition for the 50:50 IPN and a single step in the 75:25 IPN. Allowing for the experimental error in the DMTA flexural modulus, the rubbery modulus passes through a minimum and appears to be associated with loop formation of the 50:50 and 25:75 IPNs as is discussed below.

The DMTA spectra for the 25:75, 50:50, 75:25 NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs, after isothermal curing first and then photocuring are exhibited in Fig. 13 and compared with the photocured NEDGMA/DMAAP and thermally cured DGEBA/HHMPA/DMBA. The dominant T_g of the IPNs decreased with increasing NEGDMA content due to

Table 2
Calculated (Eq. (2)) and theoretical strand density for the photocured and isothermally cured NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPNs and their parent resins using various cure schedules

Samples	Curing process	Phase morphology	Calculated strand density (mol/g)	Weighted strand density (mol/g)
NEGDMA		1 phase	0.00563	0.00563
DGEBA/HHMPA		1 phase	0.00163	0.00163
25:75 IPN	UV	1 phase	0.00022	0.00141
25:75 IPN	Iso	1 major and 1 minor phase	0.00057	0.00122
25:75 IPN	UV + iso	Partially phase separated	0.00109	0.00263
25:75 IPN	Iso + UV	1 major and 1 minor phase	0.00141	0.00263
50:50 IPN	UV	1 phase	0.00165	0.00282
50:50 IPN	Iso	2 phase	0.00015	0.00082
50:50 IPN	UV + iso	Multiphase	0.00202	0.00363
50:50 IPN	Iso + UV	2 phase	0.00135	0.00363
75:25 IPN	UV	1 phase	0.00307	0.00422
75:25 IPN	Iso	2 phase	0.00004	0.00041
75:25 IPN	UV + iso	Mainly 1 phase	0.00552	0.00463
75:25 IPN	Iso + UV	2 phase	0.00455	0.00463

the chain flexibility of the ethylene oxide segments. It appears that for the 25:75 IPN (rich in epoxy), the blend is almost homogeneous and the NEGDMA component acts as a plasticizer, whereas the 50:50 IPN exhibits a two-phase structure with a peak at 123 °C and a shoulder at 20 °C. In NEGDMA-rich 75:25 IPN system, two glass transitions, corresponding to NEGDMA-rich phase and the epoxy-rich phase, are clearly observed in the tan δ trace as peaks could be detected at 19 °C and 94 °C, as discussed earlier. The modulus curves in Fig. 13 support these conclusions obtained from the tan δ traces, showing two steps in the transition regions of the 75:25 and 50:50 IPNs and a single transition in the 25:75 IPN. As observed for the photocured and then thermally cured IPNs, discussed above, the rubbery modulus passes through a minimum with composition which appears to be associated with loop formation as is discussed below.

3.5. Rubber elasticity

According to the theory of affine rubber elasticity [39], the rubbery modulus (E) is dependent on the concentration of elastically active network strands:

$$E = 3\nu dRT \tag{2}$$

where ν is the concentration on active network strands (moles/kg), d is the mass density (assumed here to be 1000 kg/m^3), R is the gas constant and T is the absolute temperature in the region when E attained a plateau. This theory assumes that the strands obey a Gaussian distribution for the end-to-end distances, whereas some of the strands emanating from the trifunctional junction points of the methacrylate and epoxy unit are very short. Despite this, the theory of rubber elasticity (Eq. (2)) has been found to be very useful for estimating the strand [40] and therefore crosslink densities. Figs. 10 and 11 show the effect of IPN composition on the DMTA behavior where the systems were either photocured or thermally cured only. As expected, the rubbery modulii of the IPNs were reduced with decreasing concentration of the cured NEGDMA or DGEBA/HHMPA component, respectively, because in these IPNs, the network strands are provided by those molecules.

The strand densities for the pure networks were calculated from the rubbery modulus values (see Table 2) – for simplicity it was assumed that full cure of the epoxy/anhydride and methacrylate groups occurred. Surprisingly for photocured NEGDMA, the theoretical (0.0055 mol/g) and calculated (0.0056 mol/g) strand densities agree well. However, given the non-idealities of the present systems and the recognition that the moduli measured by DMTA in flexure are not highly accurate (due to the non-uniform stresses around the DMTA specimen grips), this high level of agreement is fortuitous. As listed in Table 2, the experimentally determined strand density (0.0016 mol/g) of DGEBA/HHMPA/DMBA system was significantly lower than that predicted (0.0042 mol/g) and this may be due to loop formation [41] between one epoxy functionality and an anhydride (to form a cycle with two ester groups) which reduces the concentration of active strands. As a result, the agreement between the calculated and theoretical values strand densities in IPNs containing a cured epoxy component were also poor, except for systems with high levels of cured NEGDMA. To allow for this effect, a theoretical concentration of strands in the IPNs was calculated from the experimental values of the parent resins and the weight fraction of each cured component and this is also given in Table 2. The agreement between this theoretical strand density and the value calculated from the modulus of the IPN was reasonable for the fully cured IPNs and some of the partly cured IPNs. However, large differences of fivefold or more between the experimentally calculated strand densities and the predicted values were observed in two groups. The first group of IPNs with low strand densities was those where only the minor component (with a concentration of 25 wt%) had been cured. It is well known [41] that networks formed in a solvent have a high fraction of loop structures which are not active network strands and so it would be expected that for these IPN systems dimethacrylate or epoxy-anhydride loop formation would be extensive, thus causing the disagreement in the strand densities. In addition, for the 75:25 NEGDMA/epoxy system in which only the epoxy component had been cured, phase separation of the minor epoxy network phase is likely to form a dispersed phase which contributes little to the modulus and this additional effect may be the cause of the 10-fold difference between predicted and measured strand densities. The other group which showed significant (>5-fold) differences was for the 50/50 IPN where only the epoxy component was cured and this IPN underwent extensive phase separation, thus lowering the effective strand density.

3.6. Heterogeneity in the IPNs

It is clear from the above results that significant differences in the glass transition temperature region are observed for the IPNs with the same compositions but different reaction sequences, and also for the IPNs with the same reaction sequences but different compositions. In the case where the dimethacrylate component in the 50:50 IPN is photocured first, the system appears to remain miscible (see Figs. 8 and 10). Possibly this occurs because this reaction transforms only one molecule (NEGDMA) into a network, so that the change in the entropy from a mixture of three monomers to a mixture of the DGEBA and HHMPA monomers with the dimethacrylate network is not sufficient to cause significant change in free energy (see Eq. (1)) and thus phase separation. When the epoxy component is subsequently polymerized (see Figs. 8 and 12), the entropy of mixing further decreases and the free energy of mixing is raised and this makes the IPN less miscible. Since the epoxy cures slowly and does not gel until high conversion (between 30% and 50% for DGEBA/HHMPA/DMBA [42,43], this allows diffusion of the growing epoxy/anhydride out of the flexible dimethacrylate gel and results in a high degrees of phase separation with a range of different phase compositions as evidenced by the extremely broad damping curve (see Figs. 8 and 12).

When the order of curing is reversed in the 50:50 IPN and the epoxy component is cured first, the situation is different (see Figs. 8 and 11) because both DGEBA and HHMPA react together to form the epoxy network and so there is a large change in the entropy from a mixture of the three monomers to a mixture of NEGDMA monomer and epoxy network. This reduction in the entropy of mixing increases the free energy of mixing (see Eq. (1)) and causes the partially cured IPN to separate into two phases primarily consisting of unreacted dimethacrylate and of epoxy network. When the dimethacrylate is subsequently photopolymerized into a network, the entropy of mixing is reduced further and hence results in further phase separation. In previous work on epoxy/dimethacrylate IPNs [17,36], it was argued that after epoxy cure, fast photopolymerization and early gelation of the dimethacrylate resin tended to interlock the two networks thus reducing phase separation. Similarly in the present case, the extent of further phase separation in this 50:50 IPN during photocure of the dimethacrylate component is reduced because the dimethacrylate locks the IPN into its pre-existing phase structure. As a result the DMTA (see Figs. 8 and 13) shows a broad low temperature peak with a peak near 20 °C due primarily to the cured NEGDMA and a high temperature peak at 123 °C due primarily to the epoxy network.

In the case of the 25:75 NEGDMA:DGEBA/HHMPA IPNs, when the dimethacrylate component (comprising 25 wt% of the blend) is photocured first, the system remains miscible (see Figs. 7 and 10) because the change in the entropy of mixing is small as a result of the majority of the molecules (DGEBA and HHMPA) remaining unconnected to the network. When the remaining epoxy component (75 wt% of the IPN) begins to polymerize (see Figs. 7 and 12), this slow epoxy cure and relatively high gel point conversion [42,43] allows some diffusion of the growing epoxy/anhydride out of the flexible dimethacrylate gel and results in phase separation but the extent of this is limited because the majority component is the epoxy network. The situation is different when the order of curing is reversed and the majority epoxy component in the 25:75 IPN is cured first (see Figs. 7 and 11) – here the large change in entropy due to the loss of DGEBA and HHMPA molecules results in phase separation as revealed by a glass transitions peak of the epoxy-rich network at 85 °C with a significant low temperature peak near –25 °C due to the uncured NEGDMA. When the subsequent 25% dimethacrylate is rapidly photopolymerized, the pre-existing phase structure is substantially retained and both glass transitions shift to higher temperatures (see Figs. 7 and 13) as the NEGDMA is cured.

In the case where the majority dimethacrylate component of the 75:25 IPN is photocured first (see Figs. 9 and 10), the system remains miscible, apparently because the decrease in the entropy of mixing as a result of the polymerization of one species is not sufficiently large. When the remaining DGEBA/HHMPA (25 wt% of the total) slowly polymerizes (see Figs. 9 and 12), the transition broadens, suggesting a range of phase mixing. When the order of curing is reversed, the situation is different. In this case, when the minority epoxy component of the 75:25 NEGDMA:DGEBA/HHMPA IPN is thermally cured, the reduction in the entropy of mixing due to loss of the anhydride and epoxy molecules causes phase separation (see Figs. 9 and 11). When the remaining dimethacrylate monomer (75 wt% of the blend) is rapidly photocured, the pre-exisiting phase structure is retained and two separate phases with two well-defined glass transitions result (see Figs. 9 and 13).

In summary, the data presented above shows that, with the exception of IPN mixtures that were only photocured, most of the IPNs were immiscible (see Table 2). This has been confirmed by SEM of freeze fractured samples - for brevity this will be reported elsewhere. The photocured-only IPNs showed completely featureless surfaces down to less than 50 nm. The SEM images of the other IPNs showed phase separation but with domain sizes of less than 500 nm except for the course structure (domains of greater than 2 μm) found for the 75:25 IPN which had been thermally cured and then photocured.

The phase separation observed appear to contradict the hypothesis previously advanced [7,17] that dimethacrylate free radical polymerization in the second cure stage locked the IPN into a single phase before large-scale diffusion and phase separation could occur. As discussed above, this discrepancy is probably related to the differences in enthalpy of mixing of the systems. To estimate these differences, the solubility parameters (see Eq. (1)) were calculated using Fedor's method [44] for the cured epoxy component and the unreacted dimethacrylate. In the present system, the solubility parameters were 23.0 and 19.5 $\text{MPa}^{0.5}$ for cured DGEBA/HHMPA and uncured NEGDMA, i.e. a difference of 3.5 $\text{MPa}^{0.5}$. This compares with the differences in solubility parameters of 2.0 [17] and 0.8 [7] for the corresponding epoxy-methacrylate components of the single phase IPNs studied previously. Therefore it appears that the difference in miscibility of the present IPN systems and those studied previously [7,17] is due to the inferior enthalpy of mixing. Thus the previous advanced hypothesis [7,17] appears to require a revision to state that rapid curing and gelation of the second component of the IPN can cause interlocking of the networks only if the enthalpy of mixing is sufficiently attractive.

4. Conclusions

Interpenetrating polymer networks have been formed from a thermally cured, rigid epoxy/anhydride resin (DGEBA/HHMPA), and a photocured, flexible dimethacrylate resin (NEGDMA). These two chemically and structurally dissimilar thermosetting resins were chosen in order to vary the range of properties of their IPNs. The curing kinetics and morphology of the IPNs have been studied by temperature ramping DSC, isothermal near-infrared (NIR), and DMTA. This combination of thermal and photochemical initiation has facilitated studies of the effect of curing order, i.e. either photocuring the dimethacrylate followed by thermal cure of the epoxy or thermally curing the epoxy first followed by photocuring of the dimethacrylate.

DSC studies showed that by appropriate choice of curing temperatures, the possible chemical interactions between each component in the IPN could be minimized, and therefore the NEGDMA/DMAAP:DGEBA/HHMPA/DMBA IPN was found to be a model system for studying the effect of curing sequence on the phase morphology. The polymerization kinetics of the 50:50 epoxy/methacrylate IPNs was investigated by combinations of isothermal and temperature-ramping DSC. When the dimethacrylate component was photocured at 40 °C before the epoxy cure, the rate of photopolymerization was reduced compared with neat resin due to a dilution effect, but almost complete conversion could be attained. Similarly, the subsequent thermal cure of the epoxy component was almost complete, however the dilution effect on its kinetics depended on the level of photocure and thus phase separation of the dimethacrylate component. When the order of cure was reversed, the thermal epoxy cure in the blend was retarded with respect to neat epoxy cure due to a dilution effect, however complete cure could be attained. In contrast, the subsequent photopolymerization of the dimethacrylate photocured at 40 °C was limited by vitrification and/or topological restraint of the IPN, and the dimethacrylate photocure rate was dependent on the extent of pre-cure of the epoxy due to phase separation, however postcuring also resulted in near-complete conversion of the dimethacrylate. Thus the curing rate of the first component to be polymerized is effected by dilution by the second component while the curing rate and conversion of the second polymerizing component is affected by phase separation, vitrification and network topology of the first-formed network in the IPN, as has been found previously [7,36]. NIR was also used to confirm that virtually independent cure was achievable by the combination of the thermal and photochemical methods.

Dynamical mechanical thermal analysis was used to investigate the effect of curing sequence and composition on the phase morphology of the IPNs. The 25:75 IPNs showed a narrow distribution of phase compositions no matter which component was cured first. The 50:50 IPNs showed a various degrees of phase separation – a broad damping range when the dimethacrylate was photocured before the cure of the epoxy component, but when the epoxy was cured first the IPN showed a narrower range of damping. The 75:25 IPNs showed a narrow distribution of phases when the dimethacrylate was photocured first, but revealed two distinct phases when the epoxy was cured first. SEM studies (not shown here) confirmed that IPNs that had been photocured only were miscible blends. However, fully cured IPNs were phase separated and had domain sizes of less than 500 nm, except for the thermally and then photochemically cured 75:25 blend which had micron-sized domains.

The modulii in the rubbery region of the IPNs were not simply defined by an additivity relationship of the modulus contributions of the components, but were interpreted in terms of loop formation due to dilution effects and the effect of phase separation on the continuity of each phase through the polymer matrix.

The previously advanced hypothesis [7,17] relating to rapid polymerization and gelation of the second curing component was found to require a revision which acknowledged the need for sufficient attraction between the components to offset the loss in the entropy of mixing during IPN formation.

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