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Near-Infrared and Rheological Investigations of Epoxy−Vinyl Ester Interpenetrating Polymer Networks

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ABSTRACT: Rheological and near-infrared (NIR) spectroscopic investigations have been undertaken for two different interpenetrating polymer networks (IPNs) based on a model vinyl ester (VER, composed of bisphenol A diglycidyl ether dimethacrylate, bisGMA, in 30 wt % styrene) cured with azobis(isobutyronitrile) (AIBN) and an epoxy monomer (diglycidyl ether of bisphenol A, DGEBA) cured either with 1-methylimidazole (1-MeI) or with a stoichiometric quantity of 4,4′-diaminodiphenylmethane (DDM). NIR studies showed that the vinyl ester resin component cured more quickly than the epoxy component. The rate of vinyl conversion within the 50:50 wt % VER/AIBN:DGEBA/DDM IPN system was slower than in the 50:50 wt % VER/AIBN:DGEBA/1-MeI IPN and was much slower than in the neat VER/AIBN system due to the dilution of the VER components by the epoxy system and retardation of the radical polymerization by the amines, as previously observed in DSC and mid-FTIR studies of similar systems. The rate of epoxy conversion in the 50:50 wt % VER/AIBN:DGEBA/1-MeI IPN was slower than in the neat 1-MeI cured epoxy, indicating that the presence of the vinyl ester component also had a dilutional effect within the IPN reducing the concentration of epoxy and imidazole species and hence slowing the reaction. In contrast, the rate of epoxy conversion in the 50:50 IPN of VER/AIBN:DGEBA/DDM was faster than in the neat DDM-cured epoxy, possibly due to the catalysis of the epoxy−amine reaction by the hydroxy groups in the bisGMA. The similarity between the rheology and gel times for the VER/AIBN system and the IPNs indicated that the gelation of the VER component determined the overall gel behavior of the IPN. The gel times correlated well with the vinyl NIR conversion data in that the gelation occurred first for the neat VER/AIBN resin and last for the VER/AIBN:DGEBA/DDM IPN. These observations are also consistent with the effects of dilution of the VER reactants by the epoxy component in the IPN and were confirmed by studies of VER/AIBN diluted with xylene. All systems appeared to vitrify after a period of time as the cure temperature was well below the maximally attainable glass transition temperature of all resins systems. The vinyl group conversion at the vitrification point was marginally higher in the IPNs than in the neat resin systems, but the epoxy conversions in the IPNs were significantly lower at vitrification. The neat resins approached vitrification faster than the IPNs which showed a much slower rise in modulus to the glassy plateau.

Introduction

Thermosetting polymers exhibit profound rheological changes during polymerization—in particular, the steady shear viscosity increases steadily and then diverges at the gel point, whereupon the equilibrium modulus becomes finite.[1,2] Scaling concepts developed by de Gennes[3] have recently been applied to the gelation singularity, and it has been found[4] that close to gelation a power-law expression relates the viscosity (η) and equilibrium modulus to the relative distance from the gel point. In addition, the viscoelastic properties exhibit power-law dependencies on time or frequency at the gel point, and in particular, the real (G') and the loss (G'') shear moduli scale with a power of the frequency:[5−10]

$$G' \propto \omega^n; \quad G'' \propto \omega^n \tag{1}$$

As a result, tan δ becomes frequency independent[6] at the gel point and is given by $\tan(n\pi/2)$.[10] After gelation, the polymer may vitrify if the glass transition temperature (T_g) approaches the curing temperature (T_{cure})[11]—if this occurs, then the real modulus (G') approaches the glassy state and the loss modulus is often seen to pass through a maximum[7,12] with cure time.

Interpenetrating polymer networks are ideally a composition of two (or more) chemically distinct polymer networks held together exclusively by their permanent mutual entanglements[13] (see Figure 1a). We have recently used mid-FTIR and DSC to study the cure of IPNs formed from a vinyl ester resin (VER) and amine-cured epoxy resins.[14,15] Although the selection of different polymerization modes of each of the cross-linking systems such as chain growth and step growth mechanisms is intended to prevent copolymerization, grafting reactions (depicted in Figure 1b) may occur between the two polymer networks[16,17] and has been observed in VER-epoxy IPNs by a competition of the amine−epoxy reaction with the Michael addition of the amine to the vinyl group.[14,15] A number of other interactions (including redox reactions between the amine and the peroxide initiators of the VER) have been observed by the present authors in some of these IPNs.[14] Also, although it is intended that the interlocking of the two networks prevents phase separation, demixing (see Figure 1c) has been observed in some IPN systems.[18,19]

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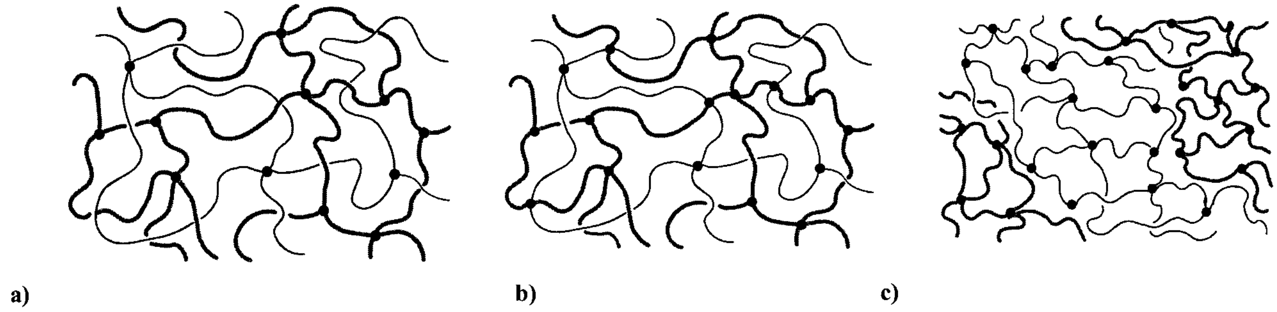

Figure 1. (a) Idealized structure of an IPN; (b) grafted IPN; (c) phase-separated IPN.

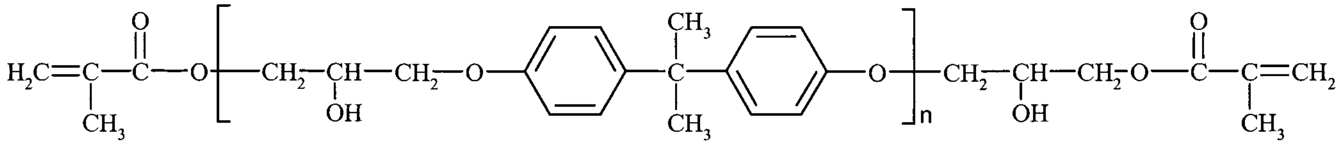

Figure 2. Structure of diglycidyl ether of bisphenol dimethacrylate (bisGMA)

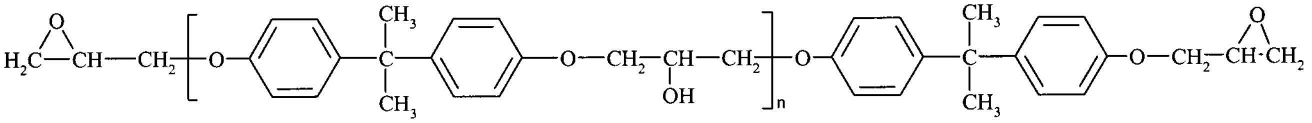

Figure 3. Structure of diglycidyl ether of bisphenol A (DGEBA)

Considerable research has been undertaken on the rheological behavior of single-component thermoset systems at the gel point and through the vitrification region;[5−9,11,12,20] however, rheological studies of IPNs are relatively scarce. Lin and Chang[21] have investigated the influence of H-bonding and cross-linking on the viscosity and gelation of epoxy−polyester IPNs and concluded that intermolecular hydrogen bonding prior to gelation increased the viscosity of these IPNs and extended the time for gelation. These workers[21] also suggested that the H-bonding also increased the compatibility of the components within the IPN, further enhancing IPN miscibility. Lin and Jeng[22] have also studied the effects of H-bonding and cross-linking on the viscosity of a diacrylate−epoxy IPN during cure and found similar behavior. Baidak et al.[19] investigated the gelation and phase separation in epoxy−acrylate IPNs, by measuring the time for the material to resist deformation or to become turbid, and proposed a metastable phase diagram which described gelation and phase separation. Chou and Lee[16] combined dynamic rheology with electron spin resonance to study the gelation behavior of a series of unsaturated polyester−polyurethane IPNs during isothermal cure. These workers[16] identified the polyurethane as the component causing the initial gelation of the IPN through rheological measurements, and they also determined the point where the polyester component formed a three-dimensional interlocking network by electron spin resonance. Chou and Lee[16] also found that in the IPN the polyurethane gelation was accelerated due to the presence of carboxyl groups terminating the unsaturated polyester molecules. Although the gelation of the polyester resin was found to be accelerated in the presence of isocyanate alone, in the complete IPN system the network formation of the unsaturated polyester component was retarded, and this was attributed[16] to a dilution effect and a strong "solidification effect" by the gelled polyurethane component.

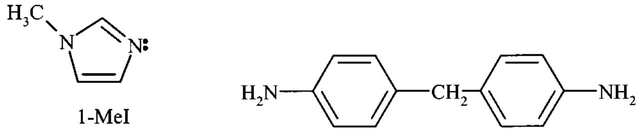

Figure 4. Structure of 1-methylimidazole and 4,4′-diaminodiphenylmethane

In the present study, we use near-infrared spectroscopy to investigate the curing kinetics of epoxy−vinyl ester resin IPNs based on the AIBN-initiated VER and either diamine-cured or imidazole-cured epoxy resin and correlate the curing behavior with the dynamic and steady shear rheology as the curing system passes through the gelation and vitrification stages.

Experimental Section

Materials. Vinyl ester networks[23] are generally based on polyfunctional methacrylate monomers dissolved in styrene and are cured by free-radical-initiated polymerization. In the present work a model vinyl ester resin (VER) studied was prepared from a solution of bisphenol A diglycidyl dimethacrylate (bisGMA, supplied by Esschem Co., see Figure 2) in 30 wt % styrene monomer (supplied by Huntsman Chemical Co. Australia Pty Limited). The equivalent weight of the bisGMA was determined to be 490 g/mol (by titration of the methacrylate groups using the morpholine method[24]) compared with the theoretical value (using $n = 1$ in Figure 2) of 514 g/mol. The radical initiator used with the VER component was azobis(isobutyronitrile) (AIBN, supplied by Aldrich Chemicals).

The epoxy monomer was the digylcidyl ether of bisphenol A (DGEBA, supplied by Ciba Geigy; see Figure 3) and was claimed to have an average equivalent weight of 190 g/mol. The DGEBA was cured via anionic chain growth polymerization[25] with 2 wt % 1-methylimidazole (1-MeI, supplied by Ciba Geigy; see Figure 4) or was condensed with a stoichiometric (equimolar amino hydrogens and epoxy groups) amount of the aromatic amine, 4,4′-diaminodiphenylmethane (DDM, supplied by Aldrich Chemicals; see Figure 4).

For IPN preparation, the model vinyl ester and the epoxy monomer were separately mixed with the respective radical initiator and curing agents before being combined in equal parts by weight (50:50) at ambient temperature to give a miscible blend.

Techniques. The cure kinetics were monitored by Fourier transform near-IR spectroscopy via a Nicolet 550 FTIR using a resolution of 4 cm^{-1}. Approximately 10 g of each liquid sample was contained by a silicone gasket which was sandwiched between two glass plates coated with conductive indium–tin oxide and having a path length of 1 mm. A voltage was applied across the glass plates which heated the sample in the assembly as described by Rey et al.[26] The reaction temperature was maintained at 70 °C as measured with a thermocouple, which was inserted into the liquid. The characteristic peaks in the near-IR region for the epoxy group, styrene unsaturation, and methacrylate unsaturation are 6073, 6135, and 6166 cm^{-1}, respectively.[26,27] The area under the epoxy absorption peak at 6073 cm^{-1} was used directly to calculate the conversion of the epoxy groups. Unfortunately, the vinyl resonances of the styrene (6135 cm^{-1}) and methacrylate (6166 cm^{-1}) groups overlap. Since previous mid-FTIR investigations[14,15] have indicated that the rate of cure of styrene and methacrylate vinyl groups are very similar, the NIR vinyl resonances were not separated in the present study, but their total area was measured to give the total vinyl group conversion. An estimate of the vitrification time was taken as the time when the conversion of reactive group (or least reactive group in the case of the IPNs) approached a plateau value. After isothermal cure at 70 °C for 450 min the samples were postcured at 160 °C for 2 h. Since the spectra obtained from these postcured samples indicated that essentially full cure of epoxy and vinyl groups was achieved, these spectra were used as the baseline for the calculation of conversion vs cure time.

The changes in the steady shear viscosity during cure of the neat resins and their IPNs were followed via a Contraves Rheomat 115 type viscometer at 70 °C using a cup and bob arrangement (1 mm gap) at a shear rate of 10 s^{-1}. Gelation is commonly determined as the stage when the steady shear viscosity diverges to infinity,[1,2] and so the gel times were obtained by extrapolating the reciprocal of the viscosity to zero.

Dynamic rheology of the systems was investigated at 70 °C with angular frequencies varying from 1 to 100 rad/s via a Rheometrics dynamic analyzer (RDAII) using 40 mm diameter parallel plates, ca. 0.5 mm gap, and an average shear strain of 40% which enhanced the sensitivity of the instrument to the gelation phenomena. Gelation was determined by two criteria from this dynamic rheology data. The time at which the real (G') and the loss (G'') shear moduli showed similar power law behavior and at which tan δ became frequency-independent was one definition.[6] In addition, since gelation is accompanied by the formation of an elastic network, the time at which G' attained a value of 1 Pa, was also used as an operational definition.

Dynamic rheology which accentuated the vitrification phenomena of the systems was also performed at 70 °C as above but using the Rheometrics RDAII and the Bohlin CS-50 with ca. 10 mm diameter parallel plates and average shear strains varying from 40% (when liquid) to 0.016% (when solid). The onset of the glass transition temperature is often defined[28] as occurring where the real shear modulus attains a value in the region of 10^7–10^8 Pa. Since the rheometers become insensitive for stiff materials, the vitrification time was operationally defined when $G' = 10^7$ Pa.

The glass transition temperatures (T_g's) of the fully cured VER/AIBN, DGEBA/DDM, and DGEBA/1-MeI were measured to be 123, 158, and 163 °C, respectively, with a Rheometrics RDAII (rectangular specimens in torsion) at the maximum in tan δ at 1 Hz. Bar samples for this experiment were cured at 70 °C for 24 h and then postcured at 180 °C for 2 h (except for the neat VER/AIBN system which was postcured up to 150 °C). The glass transition temperatures of all samples were also measured via scanning DSC at 40 °C/min (to emphasize the heat capacity step at T_g)—a subsequent rescan confirmed that the samples were fully cured using the above-mentioned curing schedule.

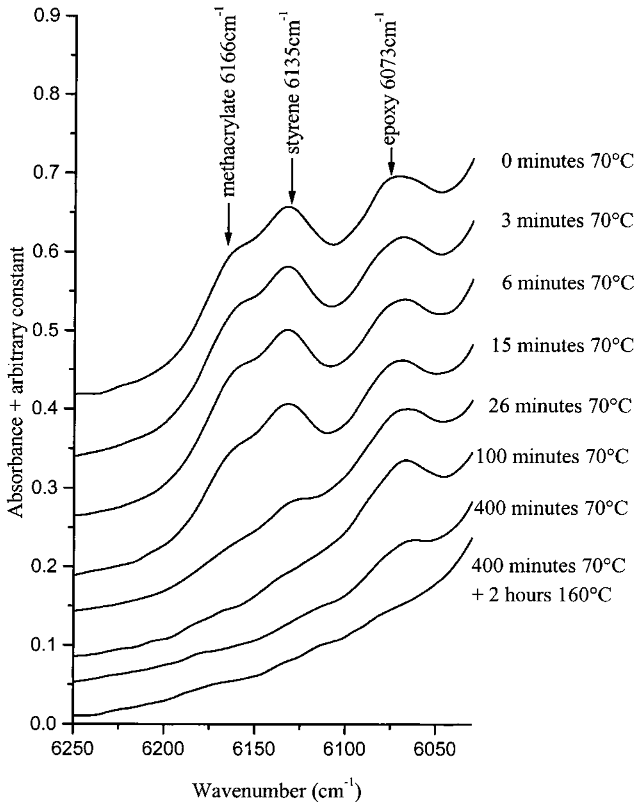

Figure 5. Near-infrared spectra during cure of the 50:50 wt %VER/AIBN:DGEBA/1-MeI IPN at 70 °C.

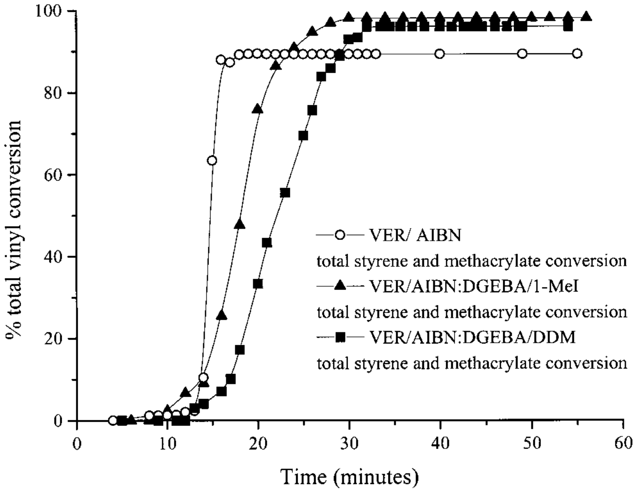

Figure 6. Comparison of the total vinyl conversion in the neat VER/AIBN system and the 50:50 wt % VER/AIBN:DGEBA/1-MeI and VER/AIBN:DGEBA/DDM IPNs at 70 °C.

Results and Discussion

Curing Kinetics. Typical NIR spectra of VER/AIBN:DGEBA/1-MeI are shown in Figure 5 obtained during isothermal cure at 70 °C. The absorptions due to the styrene (6135 cm^{-1}) and methacrylate (6166 cm^{-1}) species rapidly decrease in the initial 25 min of isothermal cure at 70 °C while the epoxy group absorption (6073 cm^{-1}) decreases less rapidly due to its lower polymerization rate. After postcure at 160 °C, however, the epoxy reaction appeared to be essentially complete. Figure 6 shows that the rate of conversion of styrene and methacrylate species in the neat VER/AIBN is faster than in the 50:50 IPN of DGEBA/1-MeI:VER/AIBN and more significantly faster than in the 50:50

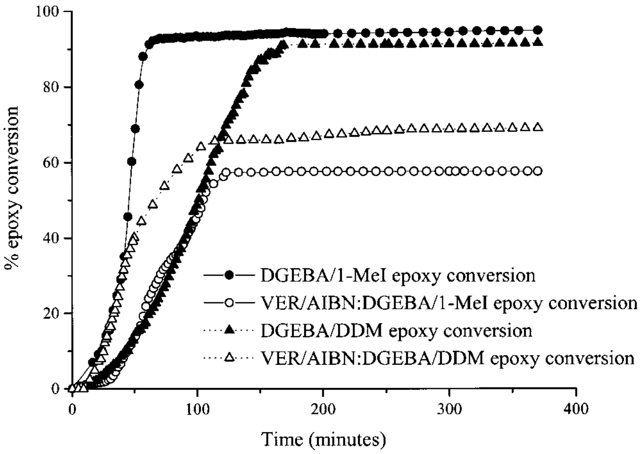

Figure 7. Comparison of epoxy conversion in the neat DGEBA systems and the 50:50 wt % VER/AIBN:DGEBA/1-MeI and VER/AIBN:DGEBA/DDM IPNs at 70 °C.

IPN of DGEBA/DDM:VER/AIBN. If the effect of dilution of the VER component by the epoxy component on the rate constant is ignored, then one would expect the VER to polymerize more slowly in the IPN than in the neat resin system due to the reduction in reactant components. Thus, the lower rate of vinyl group conversion in the IPNs may be due (in part) to the dilution of the VER reactants, as we have observed elsewhere.[14,15] A similar conclusion has been made by Chou and Lee[16] for polyester−polyurethane IPNs. Figure 6 also shows that the vinyl groups in the VER/AIBN:DGEBA/DDM IPN cure more slowly than in the VER/AIBN:DGEBA/1-MeI IPN. This may result from the reaction of the isobutyronitrile radicals or the polymer chain radicals with the DDM amino groups forming less reactive amine radicals. This explanation is consistent with similar observations that the polymerization of methyl methacrylate can be inhibited by aromatic primary amines.[29] This is also supported by Imoto's[30] study of AIBN-initiated methyl methacrylate in the presence of dimethylaniline where it was found that the formation of less reactive amine radicals reduced the rate of polymerization of the methacrylate. In the VER/AIBN:DGEBA/DDM system, the DDM concentration is much higher than the 1-MeI concentration in the VER/AIBN:DGEBA/1-MeI system, and so the DDM radical reaction would be more likely and may explain its slower cure.

The conversion of the vinyl groups in the neat VER reaches a plateau value of ca. 90% at 70 °C (see Figure 6). This premature cessation of the reaction is presumably due to vitrification of the matrix[11,12] which reduces the molecular mobility and hence reactivity, because the T_g of the postcured VER (123 °C) is much greater than the isothermal cure temperature employed (70 °C). Both IPN systems exhibit a higher final conversion of styrene and methacrylate groups compared with the neat VER/AIBN system. As suggested earlier,[14,15] this increase in conversion may be due to the presence of the unreacted DGEBA from the more slowly reacting epoxy component of the IPN which acts as a plasticizer providing greater mobility within the system and hence allowing a higher degree of vinyl conversion before vitrification occurs.

The dependence of epoxy group conversion on cure time is illustrated in Figure 7. For both IPNs and their parent resins, the rate of consumption of epoxy groups is not as rapid as observed for the styrene and methacrylate groups as noted above. For the imidazole-cured system, the rate of epoxy conversion in the IPN is lower than in the neat resin. This observation is consistent with previously reported scanning DSC and isothermal mid-FTIR studies[15] and can be explained in terms of a dilution effect such that the presence of the vinyl ester component within the IPN reduces the concentration of 1-MeI and epoxy species and thus slows the rate of the polymerization reaction. In contrast, Figure 7 shows an enhanced rate of epoxy conversion in the VER/AIBN:DGEBA/DDM IPN system compared with the epoxy conversion in the neat system. Similar findings have been reported by the present authors[14] in DSC and mid-FTIR cure studies of the IPNs. It is well-known that the amine/epoxy reaction is catalyzed by H-donors,[31,32] and it is possible that the presence of the hydroxy groups in the bisGMA molecule act as a catalyst of the epoxy−amine reaction which offsets any dilutional effect, with the result that the rate of epoxy conversion within the VER/AIBN:DGEBA/DDM IPN is actually enhanced.

The epoxy conversion approaches a plateau of approximately 90−95% (after 450 min at 70 °C) in the neat DGEBA/1-MeI and DGEBA/DDM systems (see Figure 7). This conversion limit may be caused by vitrification of the network during cure at 70 °C because the fully cured resins have T_g's of 162 °C (DGEBA/1-MeI) and 157 °C (DGEBA/DDM), which are greater than the curing temperature. More significantly, the conversion of the epoxy group approaches a plateau of approximately 60% and 70% (after 450 min at 70 °C) in the VER/AIBN:DGEBA/1-MeI and VER/AIBN:DGEBA/DDM IPNs, respectively, which is significantly lower than in the neat systems. Similar finding have been reported from previous mid-FTIR studies.[14,15] If it is assumed that the IPN is one phase (or if a certain level of miscibility exists), then the difference between the plateau conversions of the neat epoxy resin and in the IPN can be interpreted in terms of the degree of cross-linking in the VER component as suggested previously.[14,15] After curing at 70 °C for only 30 min, the VER component in the IPN is nearly fully cured (see Figure 6), and so its contribution to the cross-link density of the IPN would be high. Therefore, the T_g of the IPN (or the epoxy-rich phase if partially phase separated) would have been raised by the prior cross-linking of the VER component so that during cure at 70 °C, the epoxy component may only polymerize partially before the IPN vitrifies. In fact, full conversion of the epoxy component in the IPNs is not observed until after postcuring above the T_g of both pure components, indicating that vitrification was responsible for incomplete epoxy cure. The observation that the epoxy component in the IPN can be fully cured shows that the presence of the VER network does not exert a significant topological restraint on the capability of the epoxy to cure.

Gelation. The changes in the steady shear viscosity during cure of the thermoset blends and their respective pure components at 70 °C are shown in Figure 8. Using the gel point criteria of viscosity divergence, the neat VER/AIBN system gelled at 8 min. The two neat epoxy systems, DGEBA/1-MeI and DGEBA/DDM, gelled at 57 and 115 min, respectively. It would appear that the neat VER/AIBN system gels earlier than the epoxy resin (see Figures 6 and 7) because the VER/AIBN system polymerizes faster and because gelation of divinyl systems occurs at low conversions[33]—in fact, a comparison of the NIR and rheology data for the VER/AIBN system

Table 1. Summary of Rheology and Kinetics at the Gel Point at 70 °C

system	VER/AIBN	DGEBA/1-MeI	DGEBA/DDM	VER/AIBN: DGEBA/1-MeI	VER/AIBN: DGEBA/DDM
gel time from steady shear viscosity	8 min	57 min	115 min	12 min	21 min
gel time determined from the time when $G' = 1$ Pa	5 min	46 min	98 min	9 min	11 min
gel time from tan δ crossover	not clearly obsd	52 min	112 min	11 min	13 min
tan δ at gelation and power-law exponent (in parentheses)	not clearly obsd	5.5 (0.88)	43.2 (0.98)	1.25 (0.57)	0.94 (0.48)
NIR conversion of total C=C groups at gelation (tan δ crossover)	<ca. 2%			<ca. 2%	<ca. 2%
NIR conversion of epoxy groups at gelation (tan δ crossover)		70%	60%	<ca. 1%	<ca. 1%

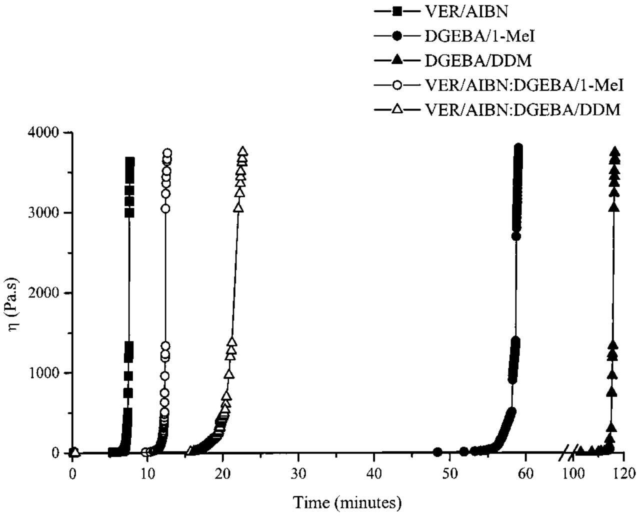

Figure 8. Steady shear viscosity vs time for the pure components and respective blends at 70 °C.

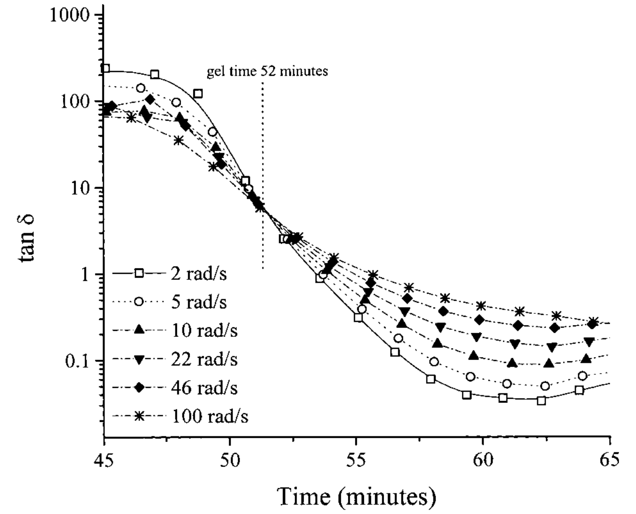

Figure 9. Frequency dependence of tan δ as a function of reaction time for neat DGEBA/1-MeI at 70 °C.

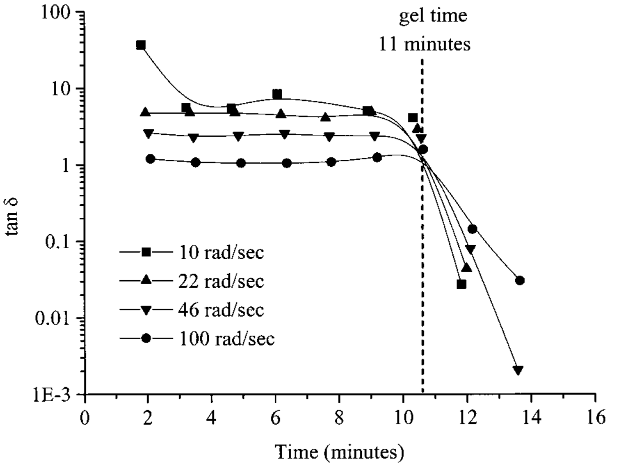

Figure 10. Frequency dependence of tan δ as a function of reaction time for the 50:50 wt % VER/AIBN:DGEBA/1-MeI IPN at 70 °C.

suggests the gel point is less than 2% (Table 1). In contrast, the epoxy systems polymerize more slowly, and the conversions at the gel points are expected to be higher. For DGEBA/DDM, the high gel point (measured to be 60%, as listed in Table 1, compared to the theoretical value[1,34] of 57%) is a result of the step growth nature of the reaction. The DGEBA/1-MeI system should gel at a relatively high conversion for a chain growth polymerization because the kinetic chain length of the anionic chain growth polymerization of epoxy groups is relatively low;[35] however, the measured value (70%; see Table 1) is higher than expected. The VER/AIBN:DGEBA/1-MeI IPN and the VER/AIBN:DGEBA/DDM IPN gelled (as determined by steady shear rheometry) at 12 and 21 min, respectively. The proximity of the gel times for the VER/AIBN:DGEBA/1-MeI and VER/AIBN:DGEBA/DDM IPNs to that of the neat VER system is close, and the resemblance of their viscosity indicates that gelation in the IPNs is determined by gelation of the VER component. The gelation times of VER/AIBN, VER/AIBN:DGEBA/1-MeI, and VER/AIBN:DGEBA/DDM also correlates well with the near-FTIR data, which shows that the rate of vinyl conversion in the VER/AIBN resin is fastest, the rate in the VER/AIBN:DGEBA/1-MeI IPN is intermediate, and that for the VER/AIBN:DGEBA/DDM IPN the vinyl cure is slowest.

The frequency independence of tan δ at the gel point is commonly observed[5,8,9]as a “frequency crossover point”—below the gel point, the tan δ decreases with increasing frequency whereas the reverse is observed above the gel point. A frequency crossover in tan δ for the pure DGEBA/1-MeI system is illustrated in Figure 9, indicating the gel point at 52 min. This value agrees quite well with the steady shear viscosity experiments, which indicated a gel point at 57 min (Table 1). The corresponding dynamic rheometry behavior for the VER/AIBN:DGEBA/1-MeI IPN is illustrated in Figure 10 and shows a frequency crossover for the IPN at 11 min, in good agreement with the 12 min gel time determined by steady shear rheometry (see Table 1). Table 1 shows that the value of the power-law exponent n (see eq 1), calculated from tan δ, varies from 0.48 to 0.98, which lies within the range 0.33−1.0 predicted from various gelation theories.[10]

Figure 11 illustrates the dependence of real modulus (G') on cure time for the pure components and their respective blends. In each system, there is a time regime

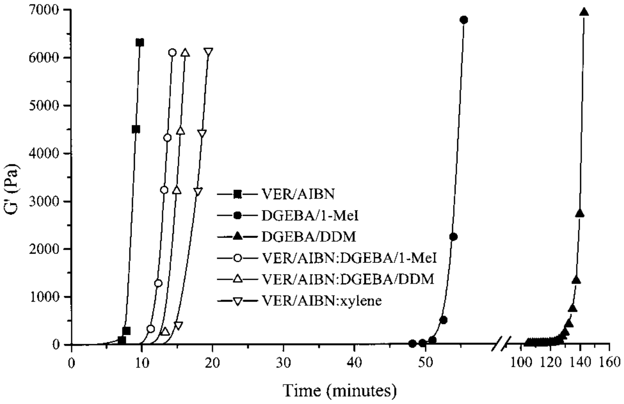

Figure 11. Real modulus (G') at 22 rad/s as a function of reaction time for the neat resins and the 50:50 wt % IPNs and for a 50:50 wt % mixture of VER and xylene at 70 °C near the gelation point.

in which the modulus starts rapidly rising because of the increasing number of cross-links being added to the hyperbranching structure as it develops into a three-dimensional gel. As revealed in Table 1, the operational definition of gelation as the stage where G' equals 1 Pa gives an approximation to the gel time which agrees reasonably well with the more rigorous methods.

The gel times of the network-forming systems and the corresponding conversions of the reactive functional groups (obtained by NIR) are listed in Table 1. For the free radical polymerized VER/AIBN system, gelation occurs at such low conversions that the crossover of tan δ could not be observed; hence, the times when G' equals 1 Pa and when the steady shear viscosity diverged to infinity were used to determine the gel point. The gel points of the IPNs are close to that of the VER/AIBN system and occur at low conversions of the vinyl groups, showing that the gelation of the IPN is very much dependent on the gelation of the VER/AIBN component of the IPN. Table 1 reveals that the gel times of the IPNs are longer than for the neat VER, and this is consistent with the effect of dilution on the reaction rate (for VER/AIBN:DGEBA/DDM and VER/AIBN:DGEBA/1-MeI) and cure retardation by amine–radical interactions (for VER/AIBN:DGEBA/DDM) as suggested earlier. The effect of dilution on the polymerization rate of the IPN components is further supported by dilution studies of the VER with xylene; Figure 11 shows that the gelation of the resin was delayed when it was diluted by 50 wt % xylene.

Vitrification. Figures 12 and 13 show the development of the real modulus with time, highlighting the rheological changes occurring in the final stages of cure. The vitrification times (taken to be the time when G' equals 10^7 Pa) and the corresponding vinyl and epoxy conversions at the onset of vitrification for the neat resins and IPNs are listed in Table 2. All neat resin systems vitrified at high conversions when cured at 70 °C. The VER/AIBN system was the first to approach the vitrification region, with the real modulus attaining a value of 10^7 Pa after curing at 70 °C for approximately 30 min. The neat epoxy resins reached the vitrification region well after this time; vitrification occurs at 145 min for DGEBA/1-MeI and at 180 min for the DGEBA/DDM system. In contrast, the IPNs vitrify at much later times of 260 min for the VER/AIBN:DGEBA/1-MeI IPN and 435 min for the VER/AIBN:DGEBA/DDM IPN.

For the parent resins, there is a correlation between the rheological vitrification time and that measured from the NIR conversion data (see Table 2), although the latter values are generally significantly smaller than the former. Similarly, for the IPNs, the vitrification times determined by NIR are smaller than the rheological values; however, there is no correlation between the two. This lack of agreement may be a reflection of the fact that small changes in reaction can have dramatic effects on the modulus in the transition region and that this is further complicated in an IPN because there are two reaction processes building up the structure.

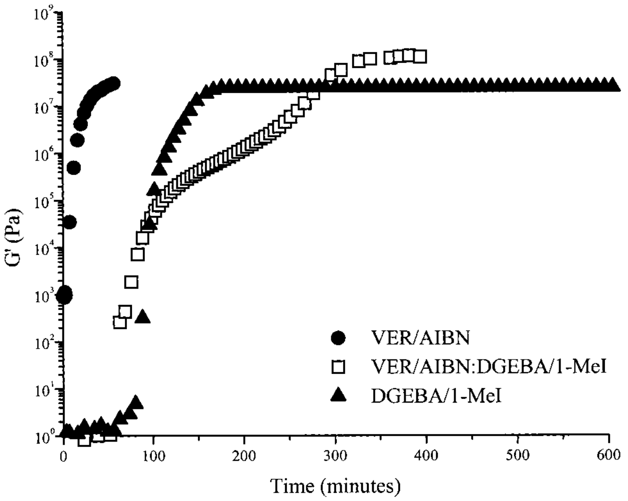

Figure 12. Real modulus (G') at 22 rad/s as a function of time for the VER/AIBN:DGEBA/1-MeI IPN and the parent resins in the vitrification region at 70 °C.

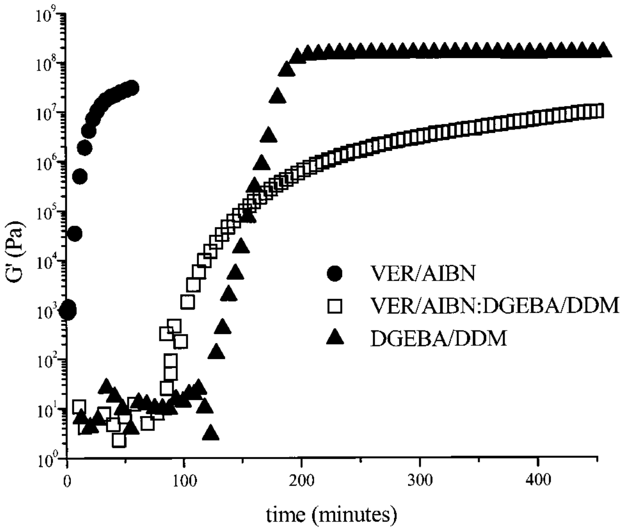

Figure 13. Real modulus (G') at 22 rad/s as a function of time for the VER/AIBN:DGEBA/DDM IPN and the parent resins in the vitrification region at 70 °C.

It is interesting to note that for the IPNs the modulus slowly rises to the plateau over a long period of time compared to the parent resins. For VER/AIBN:DGEBA/1-MeI, there appears to be two steps in the development of the modulus. These observations are qualitatively consistent with the conversion data because the modulus of the VER/AIBN:DGEBA/1-MeI IPN develops from the point where the first component (the VER) gels through to the stage where the more slowly reacting component (the epoxy resin) finally vitrifies. In contrast, a two-stage development of the real shear modulus is not evident for the VER/AIBN:DGEBA/DDM IPN, pos-

Table 2. Summary of Rheology and Kinetics at the Onset of Vitrification (at $G' = 10^7$ Pa) at 70 °C

system	VER/AIBN	DGEBA/1-MeI	DGEBA/DDM	VER/AIBN: DGEBA/1-MeI	VER/AIBN: DGEBA/DDM
vitrification time at $G' = 10^7$ Pa	30 min	145 min	180 min	260 min	435 min
vitrification time (plateau in conversion)	15 min	60 min	170 min	140 min	90 min
NIR conversion of total C=C groups at vitrification	90%			98%	96%
NIR conversion of epoxy groups at vitrification		93%	90%	57%	68%

sibly due to the greater overlap of the time regimes where the VER and the DGEBA/DDM components are curing (see Figures 6 and 7).

Table 2 shows that the conversion of vinyl and epoxy groups at the vitrification point was incomplete in the neat parent resins because the curing temperature (70 °C) was less than the maximally attainable T_g. However, the vinyl group conversion was marginally higher in the IPNs than in the neat resin system while the epoxy conversions in the IPNs were significantly lower at vitrification. This is consistent with the observations that the VER is the faster polymerizing component, and its reaction is aided by the plasticizing effect of the more slowly reacting DGEBA component—in contrast, the cure of the DGEBA is prematurely interrupted by vitrification as a result of the high level of cross-linking in the VER component.

Conclusion

IPNs were prepared from a model vinyl ester resin and two epoxy resin systems, and the cure kinetics were monitored via NIR and rheometry at 70 °C. For all systems, the rate of consumption of epoxy groups was slower than that found for the vinyl groups. The rate of vinyl (styrene and methacrylate) conversion in the 50:50 VER/AIBN:DGEBA/DDM was found to be slower than in the 50:50 VER/AIBN:DGEBA/1-MeI, and the rates of vinyl conversion in both IPNs were slower than in the neat VER/AIBN resin. This decrease in rate in the IPNs is partly due to the dilution of the VER reactants by the other components as previously observed by DSC and mid-FTIR studies of similar systems.[14,15] In addition, for the VER/AIBN:DGEBA/DDM IPN, the DDM amino groups interacted with the radicals and retarded the cure rate. The rate of epoxy conversion in VER/AIBN:DGEBA/1-MeI was slower than in the neat DGEBA/1-MeI, which is also consistent with dilutional effects. In contrast, for the 50:50 VER/AIBN:DGEBA/DDM IPN, the epoxy group reaction was faster compared with the epoxy conversion in the neat system, due to the presence of the hydroxy groups in the bisGMA molecule acting as a catalyst of the epoxy—amine reaction, which offset any dilutional effect by the VER components.

The similarity between the gel point for the VER/AIBN system and the IPNs indicated it was the gelation of the VER component rather than the gelation of the epoxy component that had the dominant effect on the overall gel point of the IPN. The gelation was fastest in the neat VER/AIBN system and was slowest in the VER/AIBN:DGEBA/DDM IPN which correlated well with the NIR vinyl conversion data for VER/AIBN, VER/AIBN:DGEBA/1-MeI, and VER/AIBN:DGEBA/DDM systems. The delayed gelation of the IPNs was due, in part, to a dilutional effect (confirmed by the study of a xylene diluted VER/AIBN resin) and in part due to amine—radical interactions.

All systems vitrified in the latter stages of the reaction because the isothermal cure temperature was well below the glass transition temperature of the resin components. Compared with the parent resins, the real modulus for both IPNs rose more slowly to the glassy region and was consistent with the NIR results. The degree of conversion of the vinyl and epoxy groups when the parent resins and their IPNs vitrified was interpreted in terms of the plasticization of the VER component by DGEBA and the vitrification of the IPN prior to full cure of the epoxy component caused by the high level of cross-linking contributed by the VER component.

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