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Curing behaviour of IPNs formed from model VERs and epoxy systems
Part II. Imidazole-cured epoxy

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Dedicated to Prof. J.K. Gillham in recognition of his contribution to the understanding of vitrification in thermosetting systems.

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Abstract

The polymerisation kinetics for IPNs formed from a model vinyl ester resin (VER) and an imidazole-cured epoxy resin (DGEBA) has been studied by scanning DSC and isothermal FTIR. The chemical interactions between the VER initiating system (either cumene hydroperoxide, CHP; methyl ethyl ketone peroxide, MEKP; benzoyl peroxide, BPO; or azobisisobutyronitrile, AIBN) and the epoxy curative (1-methyl imidazole, 1-MeI) have been examined. IPNs containing AIBN showed minimal initiator interactions but a strong accelerating effect was observed by the imidazole curing agent on the peroxide initiator systems (at least in the early stages) due to enhanced radical production apparently via a redox reaction. For IPNs containing MEKP and BPO, the imidazole also appeared to cause a significant loss of initiator activity, perhaps by non-radical redox side reactions. During the isothermal cure of the IPN, the DGEBA monomer acted as a diluent on the polymerisation of the azo-initiated vinyl ester, resulting in a slower initial cure rate than in the neat VER. Due to the slower cure of the 1-MeI/DGEBA component, the DGEBA monomer acted as a plasticiser in the later stages of the isothermal VER cure, thus enabling higher final levels of vinyl cure prior to vitrification. As a consequence, the higher level of crosslinking of the VER component in the IPN reduced the maximum isothermal conversion of the epoxy component during its isothermal cure. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Vinyl ester resin; Epoxy resin; Thermosets

1. Introduction

In contrast to other methods of optimising the properties of thermosetting polymers (such as by modifying the structure of the monomer unit [1] or by the addition of particles [2,3]), the blending of thermosets to form 'Interpenetrating Polymer Networks' (IPNs) is an entirely different route of enhancing the properties of these thermosets and hence increasing the number of applications for the polymer product. As first proposed by Sperling [4], IPNs are ideally a composition of two (or more) chemically distinct polymer networks held together exclusively by their permanent mutual entanglements (Fig. 1a). This definition has been generalised to include semi-IPNs where only one of the components forms a network (Fig. 1b). Although the selection of different polymerisation modes of each of the crosslinking systems (such as polymerisation by a combination of chain-growth and step-growth mechanisms) is intended to prevent copolymerisation, grafting reactions (depicted in Fig. 1c) may occur between the two polymer networks [5,6] and this process has been observed by the present authors in IPNs formed from a vinyl ester resin (VER) and amine-cured epoxy resins. As discussed earlier [7] there are a number of additional factors, which could lead to complications in the curing of IPNs. For example, interactions between the components of one network and the initiators of the other may accelerate or retard the reaction — initiator interaction has been observed by the present authors [7] in IPNs employing amine and peroxide curatives. In addition, the rate of reaction of each component might be expected to be reduced due to the dilutional effects by the other components. Evidence for this has also been obtained for a VER and amine-cured epoxy resin system [7]. As suggested by Jin et al. [8], the change in viscosity of the IPN due to the reaction of one component may also influence the curing behaviour of the second component through an effect on the diffusion rate. Furthermore, the developing skeletal structure of one network might exert a topological restraint on the development of the other network reducing

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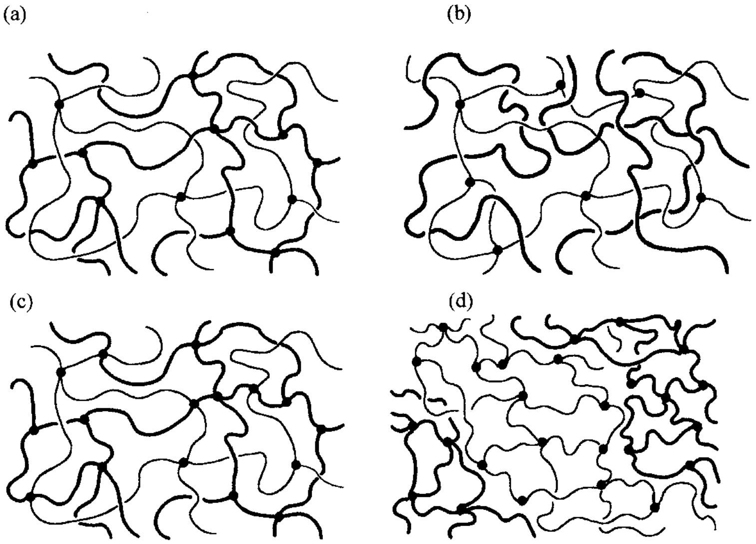
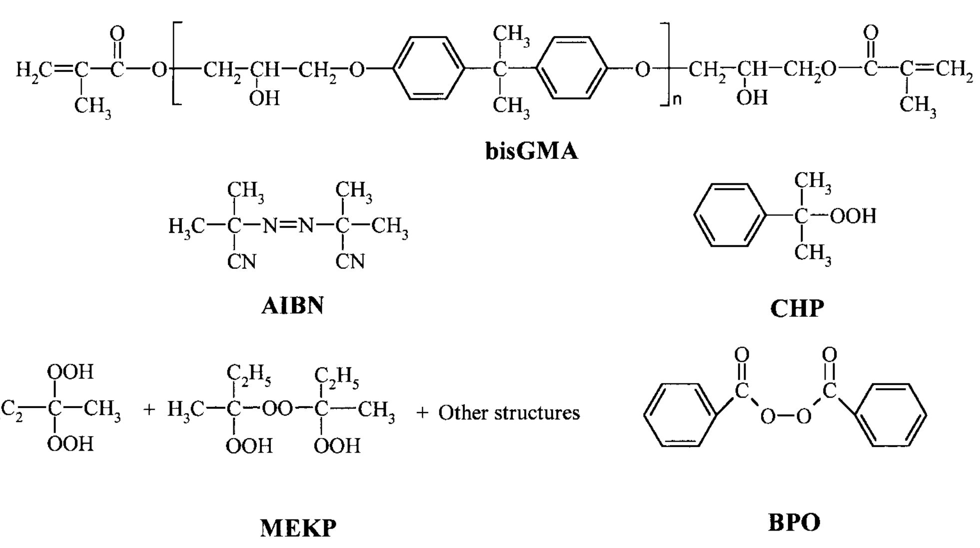


Fig. 1. (a) Idealised structure of an IPN; (b) semi-IPN; (c) grafted IPN; and (d) phase separated IPN.

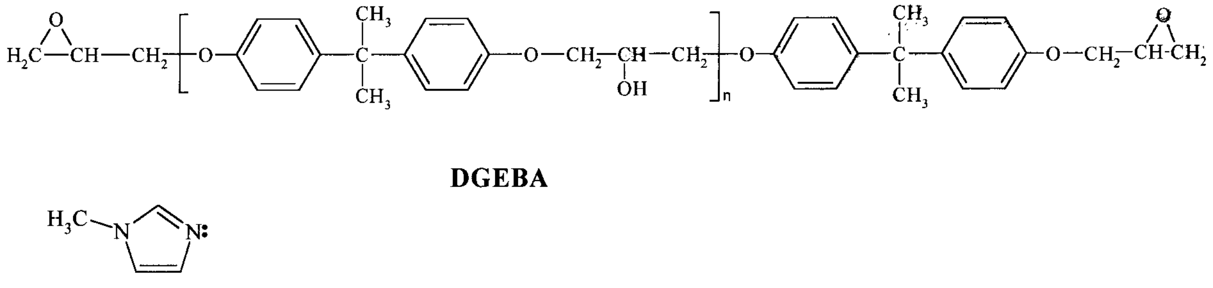
the rate and final extent of reaction of the other component. In addition, the vitrification of the system when crosslinking raises the T_g to the vicinity of the cure temperature [9] can play a complicating role. Thus, the presence of monomer from a more slowly reacting network may raise the extent of cure of the second network component by a plasticising effect which delays vitrification. However, as a result of the early development of one network component, the presence of these crosslinks in the IPN may restrict the degree of cure in the more slowly reacting component due to vitrification of the IPN when the overall crosslink density is sufficiently high. Both of these effects have been seen in VER and amine-cured epoxy resins [7]. Finally, although it is intended that the interlocking of the two networks prevent phase separation, demixing (see Fig. 1d) has been observed [10], and this process may be enhanced in semi-IPNs [11,12] where the absence of an interlocking structure can allow phase separation to occur.

Recently, Lin and co-workers [13,14] have suggested an additional complication to the cure behaviour of IPNs — they argue that mutual entanglements form during IPN polymerisation leading to a process they termed “network interlock” which reduces the reactivity of the component systems. It is not clear if this process is equivalent to topological constraint mentioned above.

In an earlier study, we reported on the curing behaviour of IPNs formed from a model VER and amine-cured epoxy resin [7]. These IPN systems showed complex cure behaviour, due in part to reactions of the primary amine curative for the epoxy with the vinyl unsaturation and with the radical initiators of the VER. The present study investigates the curing behaviour of novel IPNs formed from an epoxy resin



Scheme 1.



DGEBA

1-MeI

Scheme 2.

cured by anionic polymerisation and a VER polymerised by four types of free radical initiators.

2. Experimental

2.1. Materials

The model vinyl ester resin (VER) studied was prepared from a solution of bisphenol-A diglycidyl-methacrylate (bisGMA, see Structure 1, supplied by Esschem Co., USA) in 30 wt% styrene monomer (supplied by Huntsman-Chemical Company Australia Pty Limited). Four different types of radical initiators (see Scheme 1) were used to cure this thermosetting component. Methyl ethyl ketone peroxide (MEKP, supplied by Laporte Pty Ltd as a 40 wt% solution in dimethyl phthalate), cumene hydroperoxide (CHP, supplied by Huntsman Chemical Company Australia Pty Ltd as a 90 wt% solution in dimethylbenzyl alcohol), benzoyl peroxide (BPO, supplied by Aldrich Chemicals as a 70 wt% suspension in water) and azobisisobutyronitrile (AIBN, supplied by Aldrich Chemicals) were used separately as initiators at a concentration of 1 wt% of the VER component.

The epoxy oligomer was the diglycidyl ether of bisphenol A (DGEBA, see Structure 2 with $n \approx 0.15$, Araldite GY-9708-1 supplied by Ciba Geigy) and was reported to have an equivalent weight of 185–196 g/mol. The anionic initiator for the epoxy system was 1-methyl imidazole (1-MeI, supplied by Ciba Geigy), used at a level of 5 wt%.

The glass transition temperatures (T_gs) of the fully cured model vinyl ester and the DGEBA/1-MeI were 162 and 123°C, respectively, as measured from the tan δ maximum in the dynamic mechanical spectrum (at 1 Hz). Both the model vinyl ester and the epoxy resin were mixed with their respective initiators separately before being combined in a 50:50 (and in some cases in a 25:75 or 75:25) weight ratio at ambient temperature.

2.2. Techniques

The kinetics of the cure were measured with a Perkin–Elmer DSC-7, operated in scanning mode (5°C/min) under a N_2 atmosphere. The temperature and enthalpy were calibrated using high purity zinc and indium standards. Approximately 8–15 mg of the IPN resins were sealed in aluminium pans and scanned from 40 to 300°C. In a number of cases, the Perkin–Elmer Intracooler was also used for subambient runs from −10 to 300°C. All exotherm energies are reported as Joules per gram of total resin (pure resin or IPN resin). Table 1 lists the heats of polymerisation and the peak exotherm temperatures. In some cases, multiple peaks were recorded in the DSC scans and, where possible, the overlapping peaks were approximately resolved by dropping a vertical line from the heat flux curve to the baseline at the temperature corresponding to the lowest heat flux and integrating the underlying curve to obtain the individual heats of polymerisation.

Semi-quantitative isothermal cure information was obtained by infrared spectroscopy with a Perkin–Elmer FT1600 at a resolution of 4 cm^{-1}. Samples sandwiched between two KBr discs were placed in an oven (at 70°C or 110°C) for a timed period and then removed and scanned by FTIR before return to the oven. Final cure was attained by post-curing at 150°C for 3 h. Although this FTIR data is of comparative value, the cure time is not precise due to the delay in cooling and heating the sample. The epoxy absorption [15] at 915 cm^{-1}, the C=C resonance of styrene [16,17] at 778 cm^{-1} and 1630 cm^{-1} and the C=C methacrylate stretch [15] at 1645 cm^{-1} were used to calculate the conversion after allowance for overlapping peaks as discussed below. The vinyl group resonance of styrene at 778 cm^{-1} is a distinct and well resolved peak in the spectrum and so was used to monitor the styrene conversion, however the C=C peaks at 1630 and 1645 cm^{-1} overlap. Similarly the epoxy peak at 915 cm^{-1} overlaps with the resonance due to the styrene C=C bond at 910 cm^{-1}. Thus to monitor the methacrylate conversion, the contribution of the styrene component to the area of the C=C overlapping peaks near 1630–1645 cm^{-1} was subtracted by use of the ratio of the styrene peak areas at 778 and 1630 cm^{-1} in the spectra of pure styrene. Similarly to monitor the epoxy conversion, the contribution of the styrene component at 910 cm^{-1} was

Table 1
Summary of the DSC analysis of the VER cured with various radical initiators, DGEBA cured with 1-MeI and the IPNs formed from these resins

System	Heat of polymerisation (J/g)	Temperature of the peak exotherm
AIBN and 1-MeI initiators		
VER/1% AIBN	327	92°C
75:25 VER/1 wt% AIBN: DGEBA/5 wt% 1-MeI	Peak 1: 250	Peak 1: 85°C
	Peak 2: 114	Peak 2: 125°C
50:50 VER/1 wt% AIBN: DGEBA/5 wt% 1-MeI	Peak 1: 176	Peak 1: 101°C
	Peak 2: 239	Peak 2: 120°C
25:75 VER/1 wt% AIBN: DGEBA/5 wt% 1-MeI	444	Shoulder: 94°C
		Peak: 118°C
DGEBA/5 wt% 1-MeI	471	117°C
CHP and 1-MeI initiators		
VER/1 wt% CHP	318	125°C
75:25 VER/1 wt% CHP: DGEBA/5 wt% 1-MeI	Peak 1: 343	Peak 1: 104°C
	Peak 2: 102	Peak 2: 124°C
	Peak 3: 12	Peak 3: 242°C
50:50 VER/1 wt% CHP: DGEBA/5 wt% 1-MeI	Peak 1: 133	Peak 1: 95°C
	Peak 2: 254	Peak 2: 122°C
	Peak 3: 8	Peak 3: 244°C
25:75 VER/1 wt% CHP: DGEBA/5 wt% 1-MeI	Peak 1: 56	Peak 1: 83°C
	Peak 2: 375	Peak 2: 115°C
	Peak 3: 4	Peak 3: 245°C
DGEBA/5 wt% 1-MeI	471	117°C
1 wt% CHP:DGEBA/5 wt% MeI	468	114°C
VER/1 wt% CHP: 5 wt% 1-MeI	Peak 1: 308	Peak 1: 107°C
	Peak 2: 22	Peak 2: 191°C
MEKP and 1-MeI initiators		
VER/1 wt% MEKP	320	123°C
50:50 VER/1 wt% MEKP: DGEBA/5 wt% 1-MeI	Peak 1: 8	Peak 1: 87°C
	Peak 2: 232	Peak 2: 120°C
	Peak 3: 64	Peak 3: 225°C
DGEBA/5 wt% 1-MeI	471	117°C
MEKP:DGEBA/5 wt% MeI	470	114°C
VER/1 wt% MEKP:5 wt% 1-MeI	Peak 1: 302	Peak 1: 106°C
	Peak 2: 23	Peak 2: 233°C
BPO and 1-MeI initiators		
VER/1 wt% BPO	323	105°C
50:50 VER/1 wt% BPO: DGEBA/5 wt% 1-MeI	Peak 1: 34	Peak 1: 91°C
	Peak 2: 203	Peak 2: 121°C
	Peak 3: 34	Peak 3: 235°C
DGEBA/5 wt% 1-MeI	471	117°C
VER/1 wt% BPO:5 wt% MeI	Peak 1: 302	Peak 1: 93°C
	Peak 2: 19	Peak 2: 204°C
1 wt% BPO:DGEBA/5 wt% MeI	Peak 1: 472	116°C
Thermal cure		
VER	320	195°C

subtracted from the total overlapping area near 910–915 cm^{-1} by knowledge of the ratio of the styrene peak at 778 and 910 cm^{-1} in the spectra of pure styrene. The phenyl group of styrene exhibits a characteristic absorption at 700 cm^{-1}, which was used as an internal standard [18] to correct for small variations ($<5\%$) in specimen thickness during the early stages of cure. Thus the cure of the reactive groups in the epoxy–vinyl ester IPNs were monitored via the decrease in area of the above mentioned characteristic peaks.

3. Results and discussion

3.1. Curing mechanism

VER networks are based on polyfunctional methacrylate monomers copolymerised with styrene. A schematic of the general curing reaction of vinyl esters is illustrated in Fig. 2. For the anionic polymerisation of epoxide groups with 1-substituted imidazoles, such as 1-methylimidazole (1-MeI), Dearlove [19] has proposed a mechanism in which the

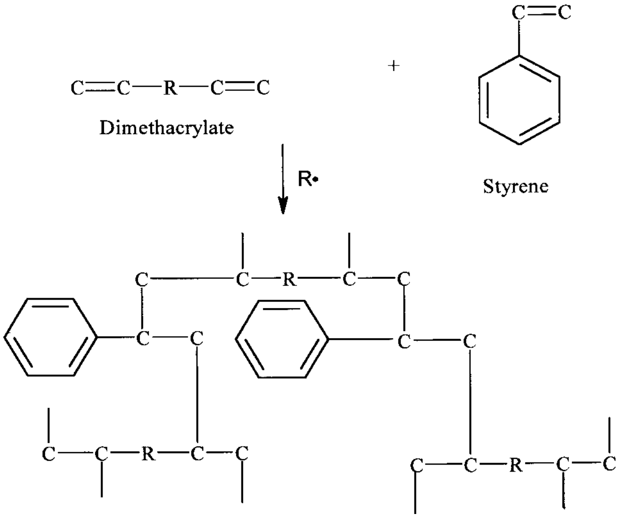


Fig. 2. Schematic of the cure of the model vinyl ester resin.

initiating species was the 1:1 adduct (produced via the attack of the pyridine-type nitrogen) as illustrated in Fig. 3.

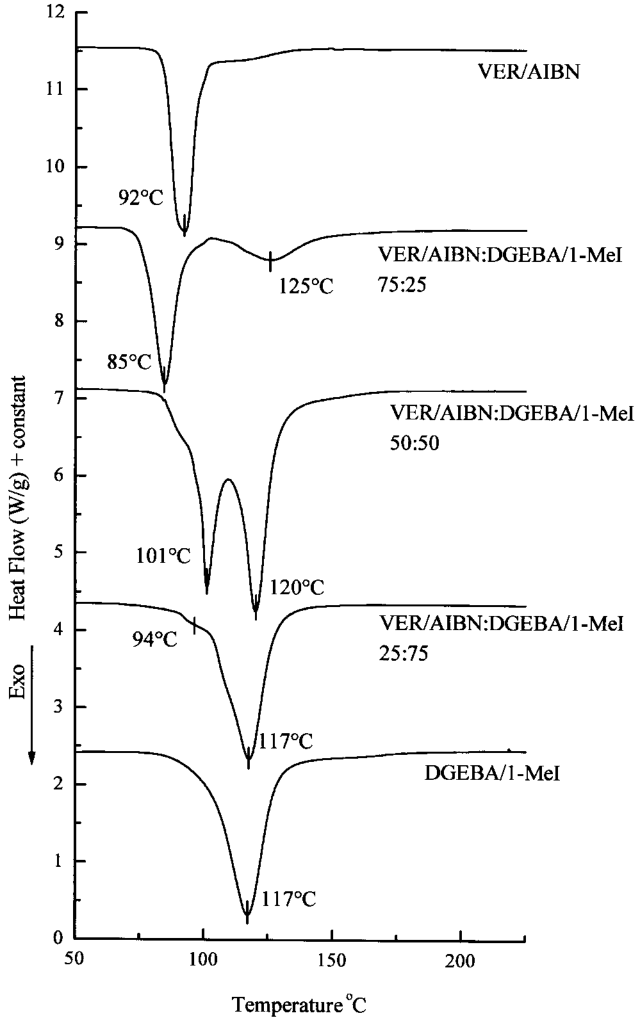


Fig. 4. DSC scans of VER/AIBN, DGEBA/1-MeI and their IPNs.

3.2. VER/AIBN blended with DGEBA/1-MeI

The cure behaviours of the AIBN-initiated VER, the 1-MeI initiated DGEBA and their IPNs are shown in Fig. 4. The DSC thermograms of the neat VER and the DGEBA epoxy exhibit single peaks with slight shoulders at the higher temperature side of the exotherms whereas the IPNs of the VER and DGEBA epoxy (Fig. 4) shows two distinct exotherms. Based on the close correspondence of peak temperatures in the neat and blended systems, the lower and upper exotherms in the DSC trace of the 50:50 IPN can be attributed to the vinyl ester and DGEBA cure, respectively. The designation of the lower and upper exotherms to the cure of vinyl ester and epoxy, respectively, is confirmed by the analysis of both the 75:25 and 25:75 blends of this system. The resolved contributions to the DSC exotherm show that the areas of the lower and upper peaks are approximately proportional to the weight fractions of VER and epoxy components in the IPN, respectively. As shown in Table 1, the total polymerisation enthalpies for the 75:25, 50:50 and 25:75 blends of VER/AIBN:DGEBA/1-MeI are 364, 415 and 444 J/g, which are comparable with the weighted averages of the enthalpies for the individual components of 362, 399 and 435 J/g, respectively, suggesting that 'full' cure was achieved at moderate temperatures

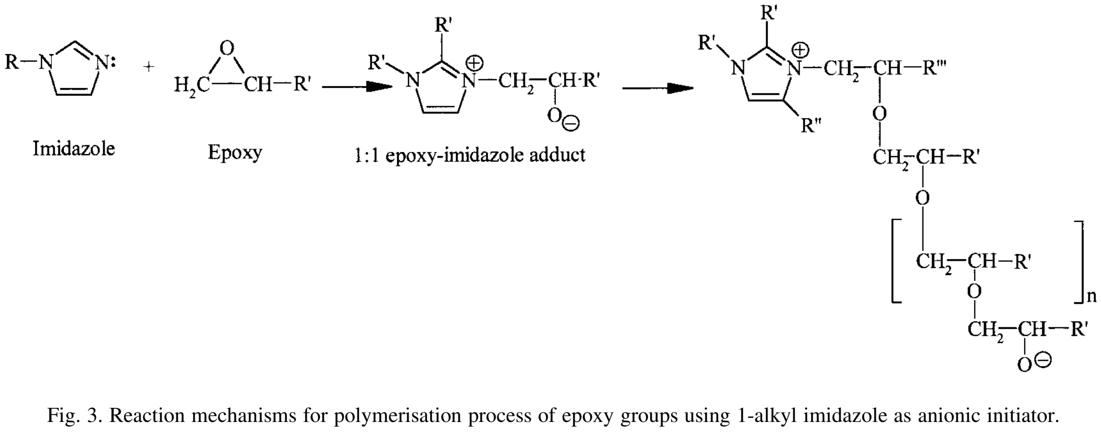


Fig. 3. Reaction mechanisms for polymerisation process of epoxy groups using 1-alkyl imidazole as anionic initiator.

and that blending had not impaired the curing ability of each resin.

The curing exotherm peak of the vinyl ester component shifted from 92 to 101°C in the 50:50 VER/AIBN:DGEBA/1-MeI IPN and the epoxy exotherm shifted from 117 to 120°C in the 50:50 IPN (Fig. 4). This behaviour was also observed for IPNs prepared from diamine-cured DGEBA and VER [7] and may be due to dilution of the reactants, which therefore reduces the rates of cure and raises the peak temperature. However the 75:25 VER/AIBN:DGEBA/1-MeI IPN exhibits an acceleration of the cure of the VER — the reason for this observation is unclear. In a similar study of the cure of an IPN formed from diamine-cured DGEBA and a radically cured diacrylate resin, Lin and Chang [13] proposed a "network interlock effect" in which mutual entanglements between the two polymer networks produced a sterically hindered environment resulting in the reduction in the rate constant of the diacrylate resin. However this argument does not seem to be applicable to the data shown in Fig. 4 because the epoxy network does not start to develop until the cure of the VER is nearly complete.

Fig. 5 illustrates the variation in the FTIR spectrum during the cure of the VER/AIBN:DGEBA/1-MeI IPN — the main changes appear to be the reduction of the magnitude of the absorption peaks associated with the methacrylate (1645 cm^{-1}), styrene (778, 910 and 1630 cm^{-1}) and epoxy (915 cm^{-1}) groups.

Typical conversion-time data for the reaction of the vinyl groups in the neat VER are shown in Fig. 6. As predicted from the similar reactivity ratios of the methacrylate groups of dimethacrylate, and styrene [16], both groups copolymerise at similar rates. The VER shows incomplete cure at 70°C but nearly full cure was observed (but not shown) during isothermal cure at 110°C. This difference can be attributed to the effect of vitrification during cure, which occurs when crosslinking raises the glass transition temperature to the curing temperature [9]. Thus, when the polymerisation was conducted at an isothermal cure temperature that was significantly below the T_g of the fully cured VER (123°C), incomplete cure resulted. However, regardless of the initial isothermal cure temperature, nearly complete cure occurred upon postcure of the resin at 150°C.

During the isothermal cure of both the vinyl ester system and the 50:50 IPN, the styrene and methacrylate conversion data exhibit brief induction periods (see Fig. 6), presumably due to the presence of free radical inhibitors in the resins. Isothermal infrared spectroscopy undertaken at 110°C (not shown) showed shorter induction periods as would be expected for a rate acceleration. At each given temperature, the methacrylate groups within the IPN initially polymerise more slowly compared with the pure resin. This decrease in reaction rate can be attributed to the dilution of the reactants by the DGEBA resin, in agreement with the DSC results for this IPN. Previous FTIR investigations [7] of semi-IPNs formed from a VER and DGEBA cured by a stoichiometric amount of primary amine (either aniline or butylamine) also showed similar reduced polymerisation rates for styrene and methacrylate, suggesting that a dilutional effect was operative. However, when this earlier IPN data is compared (see Fig. 6) with that for the present IPNs containing imidazole, it is apparent that the IPN containing a primary amine reacts more slowly. This difference in cure rates may be attributed to the retardation of the vinyl ester polymerisation by the large quantities of aniline or butylamine that are present in a much higher concentration than the imidazole curing agent.

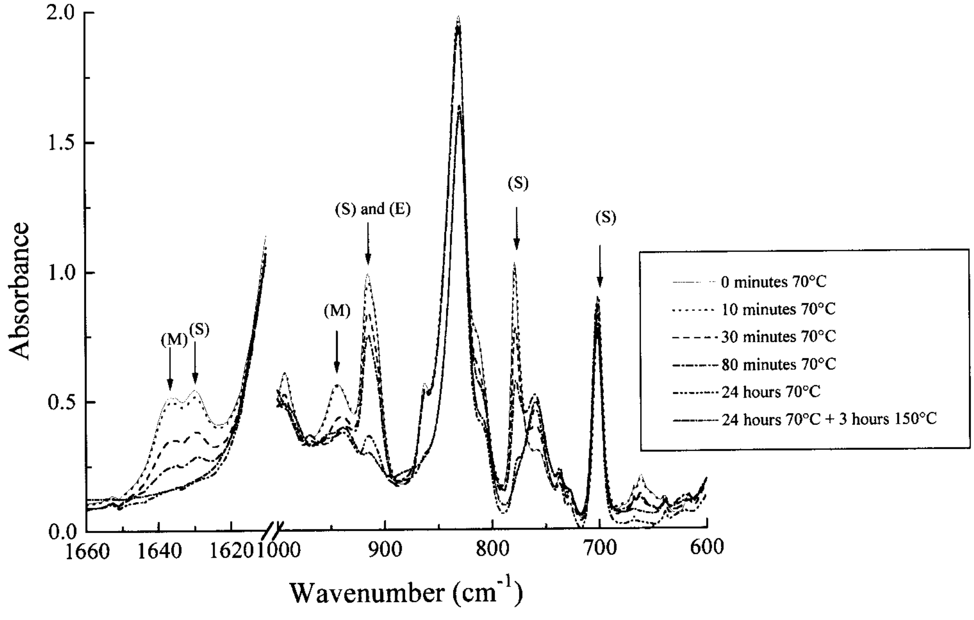


Fig. 5. FTIR spectra in the region from 1660 to 1600 cm^{-1} and from 1000 to 600 cm^{-1} of the 50:50 VER/AIBN:DGEBA/1-MeI IPN cured at 70°C for varying times and after post-cure at 150°C for 3 h, showing the methacrylate (M), styrene (S) and epoxy (E) peaks.

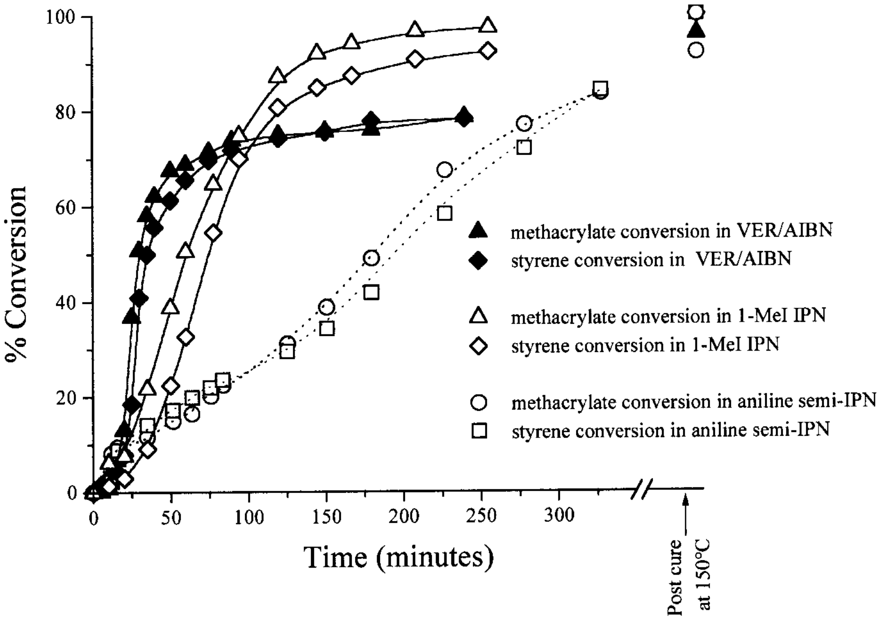


Fig. 6. Dimethacrylate and styrene conversion versus time in the pure VER/AIBN system and in the 50:50 blend of VER/AIBN:DGEBA/1-MeI at 70°C. The dashed lines show the cure behaviour, previously reported, of the IPN formed with VER/AIBN:DGEBA/aniline.

This hypothesis is supported by the work of Imoto et al. [20] who showed that dimethyl aniline reduced the polymerisation rate in the AIBN-initiated methylmethacrylate and suggested that this effect was due to radical transfer to the amine, which was incapable of re-initiating the polymerisation.

Similar to that found previously [7] for IPNs formed by VER and diamine-cured DGEBA, the present IPN system exhibits a higher level of conversion of both styrene and methacrylate units compared with the neat resins (see Fig. 6). This increase in final conversion of styrene and methacrylate groups may be attributed to the presence of the unreacted DGEBA in the system since the cure of the epoxy resin is much slower than that of the VER (compare Figs. 6 and 7). Thus, if the IPN is considered to be miscible (or partly miscible), the unreacted DGEBA can act as a plasticiser during the cure of the VER components, enabling greater mobility within the system and hence a greater degree of conversion for the styrene and methacrylate units prior to vitrification of the resin.

The isothermal conversion-time plots for the epoxy groups in neat DGEBA as measured by FTIR at 70 and 110°C are illustrated in Fig. 7. Although the FTIR conversion-time data was only semi-quantitative (see Section 2), the epoxy conversion curve at 70°C suggests a two stage cure process. This process has been previously observed

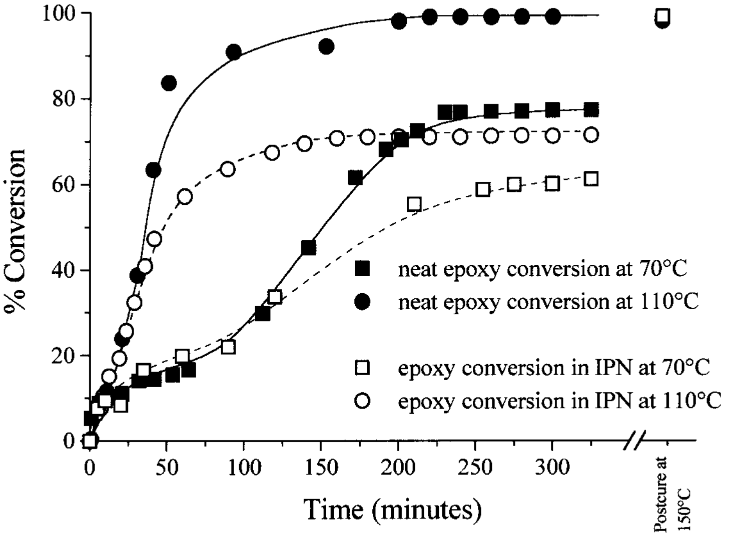


Fig. 7. Epoxy conversion versus time for the neat DGEBA/1-MeI resin and in the 50:50 blend of the VER/AIBN: DGEBA/1-MeI IPN.

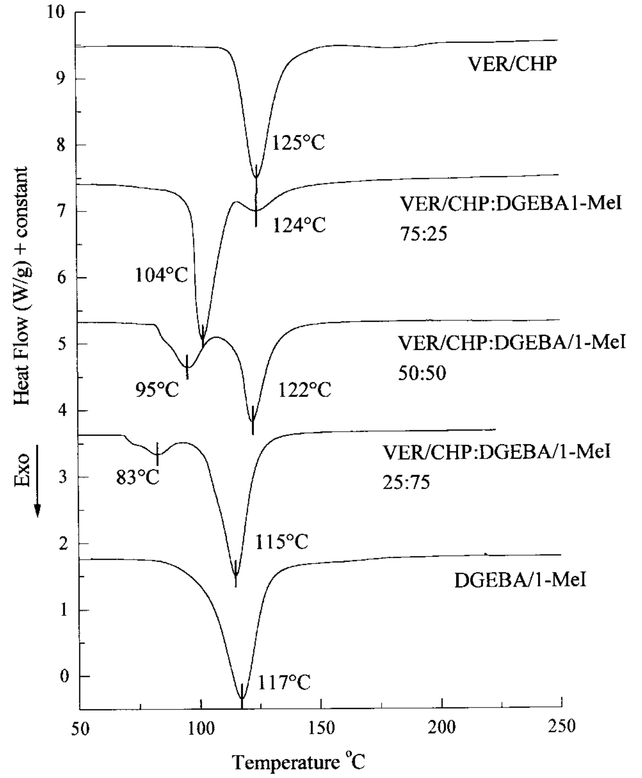


Fig. 8. DSC scans of VER/CHP, DGEBA/1-MeI and their IPNs.

[21] during isothermal (but not scanning) DSC cure studies and is believed to be associated with the distinct stages of formation of the 1:1 adduct and of polymerisation (see Fig. 3). As discussed above for the VER system, the epoxy groups are not fully reacted (80% conversion) after 24 h at 70°C because this temperature is well below the T_g of the fully cured epoxy resin (162°C by DMTA) and so vitrification occurs during cure [9].

In the early stages of cure, the conversion of the epoxy groups in the neat epoxy system and the IPN appear similar — the data is not sufficiently accurate to distinguish between them. However, as the reaction proceeds, the cure rate in the IPN is slower than in the neat system, possibly due to a dilutional effect. It is interesting to note that the plateau conversions of the epoxy groups in the IPN cured at 70 and 110°C were significantly lower than in the neat resin at these temperatures. This may be explained in terms of the vitrification of the IPN during cure [9], as suggested elsewhere [7] for a related IPN. A comparison of Fig. 6 with Fig. 7 indicates that the VER components polymerise at a much faster rate than does the epoxy component. Thus if the IPN is considered as a single-phase material, an increase in its crosslink density by the curing of the VER component may raise the T_g of the IPN so much that the material vitrifies before complete reaction of the DGEBA. In partial support of this explanation, Fig. 7 shows that nearly full conversion of the epoxy groups can be attained when the IPN is postcured at 150°C. Alternatively, the “network interlock” effect [13,14] may retard the cure of the epoxy in the presence of the already formed VER network, due to steric hindrance and restricted chain mobility. However, the network interlock mechanism does not explain why postcuring at 150°C produces near complete epoxy cure in the IPN.

3.3. VER/CHP blended with DGEBA/1-MeI

The DSC thermograms of the VER/CHP resin and the DGEBA/1-MeI resins each exhibit a single major peak while the 50:50 IPN exhibits two well resolved exotherms (Fig. 8). Based on the size of the peaks for the three IPN blends (75:25, 50:50 and 25:75), the lower and higher temperature exotherms observed in the IPNs may be attributed to the cure of vinyl ester and epoxy components, respectively. The polymerisation enthalpy and temperature and the peak for each system are listed in Table 1. The total heat of polymerisation (from 50 to 180°C) for the 50:50 blend is 387 J/g which is only slightly less than the average of the enthalpies for the individual exotherms (395 J/g), suggesting that nearly full cure can be obtained with the IPN at moderate temperatures. However, the enthalpy associated with the first peak (133 J/g) is less than that expected for complete polymerisation of the VER (159 J/g) — the remainder of this enthalpy may be included in the epoxy cure exotherm at 122°C and in the broad exotherm (8 J/g) at temperatures above 200°C, which has previously been attributed to thermal cure of the VER component [7].

The small shift of the temperature of the epoxy exotherm peak from 117 to 122°C in Fig. 8 can be attributed to dilution effects within the 50:50 blend as found above with the AIBN-cured IPN. In contrast, dilution effects cannot account for the downward shift of the VER exotherm peak from 125 to 95°C (in the 50:50 blend) for the vinyl ester cured with CHP. This unusual behaviour may be attributed to a redox reaction between the CHP and 1-MeI — similar redox reactions between aromatic amines and peroxides have been observed by Walling and Indicator [22] and Brinkman et al. [23]. These redox reactions may cause premature decomposition of the peroxide and enhance radical production, resulting in the observed acceleration of the cure of the vinyl ester component. To confirm the acceleration of the cure of the VER by the imidazole in the 50:50 blend, a separate sample of the VER/CHP systems was blended with 5% 1-MeI and studied by scanning DSC (see Table 1). Close to full cure of the VER was observed, with a small amount of thermal cure (20 J/g) occurring at 191°C. The temperature of the main exotherm peak for the VER/CHP:1-MeI shifted to 107°C compared with 125°C for the VER initiated with CHP alone, confirming that the imidazole accelerates the rate of radical production and hence rate of cure. Surprisingly this peak occurs at a lower temperature (95°C) in the IPN than in the VER/CHP:1-MeI system — the reason for this is unclear.

Fig. 9 illustrates the conversion of styrene and methacrylate species obtained by FTIR at 70°C in the neat and IPN

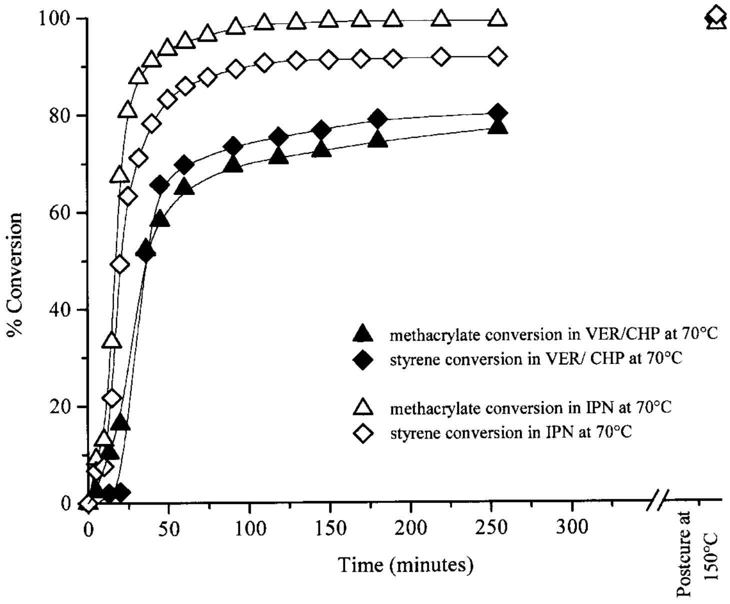


Fig. 9. Dimethacrylate and styrene conversion versus time in the VER/CHP system and in the 50:50 blend of VER/CHP:DGEBA/1-MeI at 70°C.

systems. The reaction of the methacrylate and styrene groups in the neat VER exhibited a short induction period, probably due to radical inhibition, however this induction period is significantly reduced for the IPN systems. In contrast to the AIBN initiated VER systems, the conversion of both styrene and methacrylate is faster in the IPN which agrees with the DSC data and confirms that the imidazole does act as a promoter causing enhanced radical production from the CHP. As observed in the IPN systems initiated with AIBN, the final isothermal conversion of both styrene and methacrylate groups is higher in the IPN than in the neat system due to the plasticisation of the developing VER network by the unreacted DGEBA, thus delaying vitrification in this time regime. Accelerated cure behaviour was also observed in FTIR studies of the IPN at 110°C but here full cure was observed during the isothermal phase.

The conversion of the epoxy groups in the neat 1-MeI/DGEBA resin and the VER/CHP:DGEBA/1-MeI IPN, obtained from isothermal FTIR at both 70 and 110°C, is illustrated in Fig. 10. As expected, the rate of polymerisation is faster at the elevated isothermal temperature of 110°C compared with 70°C. The initial rate of conversion of epoxy groups in the IPN is slower than in the neat epoxy system, perhaps due to dilution by the surrounding VER, as suggested for the VER/AIBN:DGEBA/1-MeI IPNs. Also in agreement with the previously presented data, the final

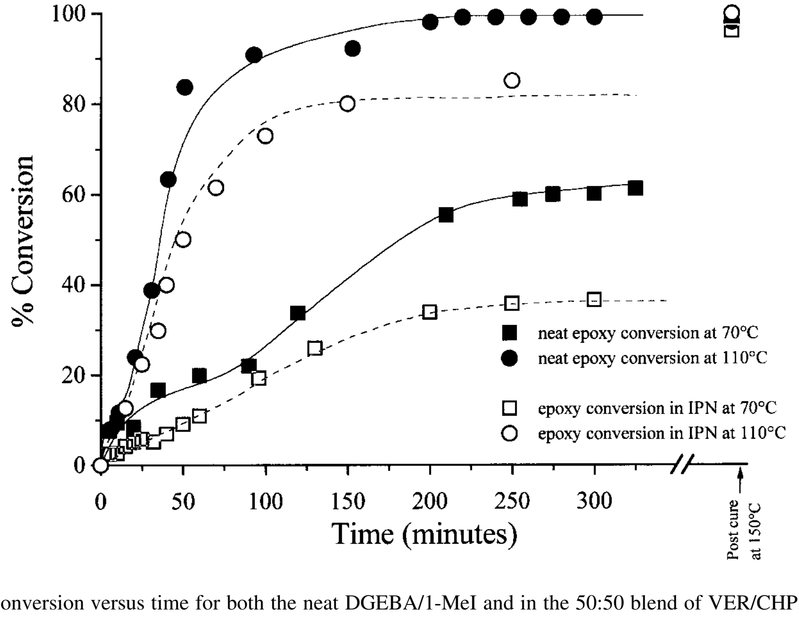


Fig. 10. Epoxy conversion versus time for both the neat DGEBA/1-MeI and in the 50:50 blend of VER/CHP:DGEBA/1-MeI.

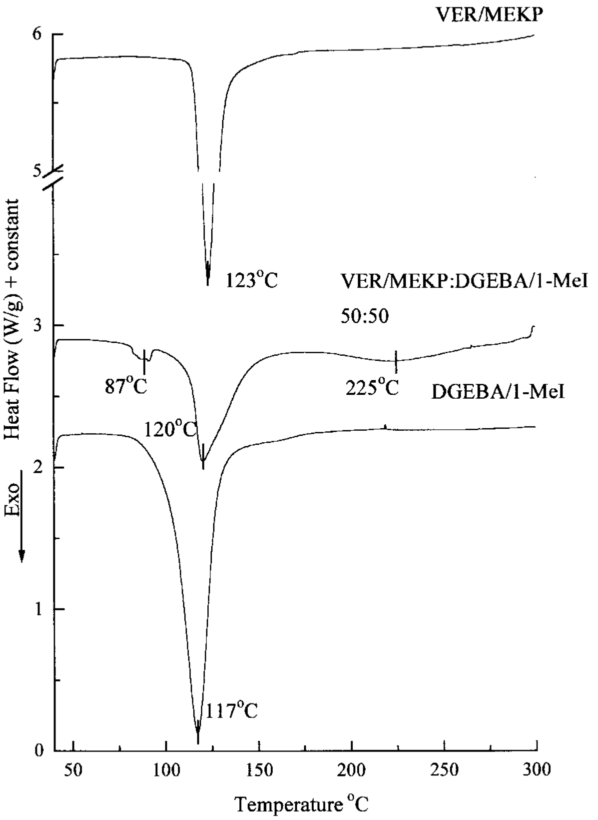


Fig. 11. DSC scans of VER/MEKP, DGEBA/1-MeI and their 50:50 IPN.

epoxy conversion at 70°C is higher for the neat DGEBA resin than for the IPN, possibly due to vitrification caused by the high level of crosslinking of the VER component in the IPN. However, post-curing at 150°C (which is higher than the T_gs of the component resins) leads to an epoxy conversion of greater than 95% in the IPN.

3.4. VER/MEKP blended with DGEBA/1-MeI

The DSC thermograms of the VER/MEKP and the DGEBA/1-MeI resins exhibit single exothermic peaks, respectively, however the DSC thermogram of the 50:50 IPN of epoxy and vinyl ester exhibits three significant exothermic peaks (Fig. 11), indicating that much more complex interactions are occurring between the components in the IPNs. The total polymerisation enthalpy and the temperature at each exotherm peak are listed in Table 1 for each system. The total heat of polymerisation for the 50:50 blend (304 J/g) is substantially less than that predicted from the average of the enthalpy for the individual component exotherms (average of the VER/MEKP and DGEBA/1-MeI, i.e. 396 J/g). One possible explanation for the reduction in heat of polymerisation is that the MEKP concentration is rapidly consumed by redox reactions with the imidazole, causing premature peroxide decomposition and subsequent depletion of radicals similar to the effect of dead-end radical polymerisation [24]. Alternatively, the 1-MeI may also reduce the MEKP by a side reaction, which does not produce radical species, thus also causing premature depletion of the peroxide. These processes would be observed as a decrease in the heat of polymerisation and a lower peak exotherm temperature for the VER component. On this basis, the small peak at 87°C could be due to the accelerated but incomplete polymerisation of the VER. This assignment is consistent with the accelerated VER cure when 5 wt% 1-MeI was added to the VER/MEKP system (see Table 1) resulting in a large peak at

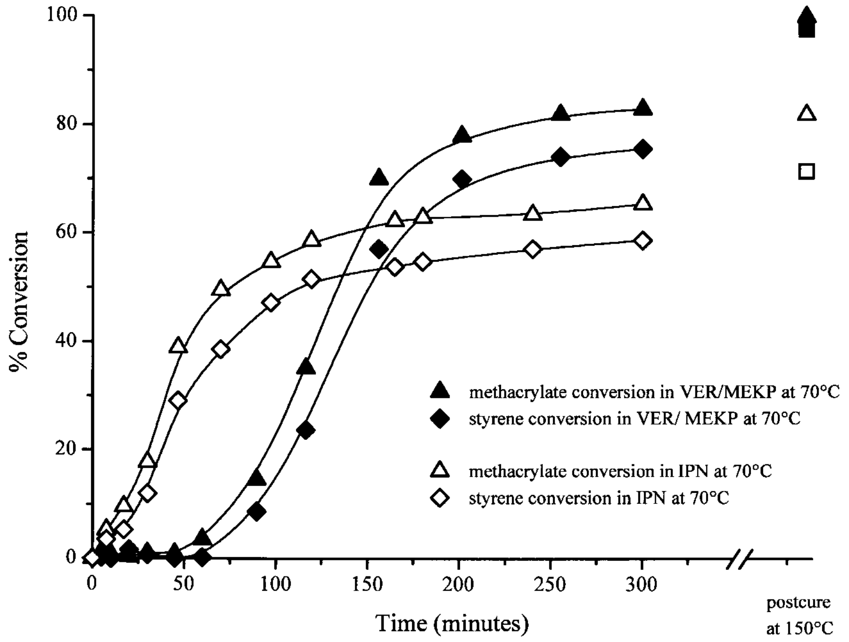


Fig. 12. Dimethacrylate and styrene conversion versus time in the pure system of VER/MEKP and in the 50:50 blend of VER/MEKP:DGEBA/1-MeI at 70°C.

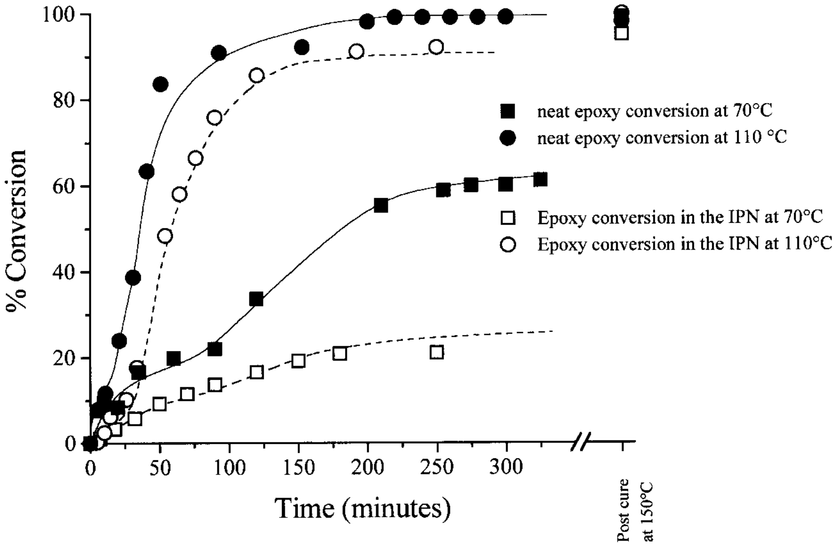


Fig. 13. Epoxy conversion versus time for both the neat system of DGEBA/1-MeI and in the 50:50 blend of VER/MEKP:DGEBA/1-MeI at 70 and 110°C.

106°C due to accelerated VER cure. Surprisingly, this peak occurs at a higher temperature and develops a greater exotherm than in the IPN — the reason for this is unclear. The VER/MEKP:1-MeI system also shows a small, broad peak at 233°C. This peak occurs close to the peak around 225°C in the IPN and is similar to the broad exotherm at 195°C observed for the VER when thermally cured without added initiator. In contrast, the DSC cure of the MEKP:DGEBA/1-MeI blend (containing no VER) shows no significant decrease in polymerisation enthalpy of the epoxy groups compared with the pure system (see Table 1). On this basis, the middle peak at 120°C in the IPN may be identified with cure of the epoxy component — the enthalpy of this peak (232 J/g) is similar to the contribution expected from the pure epoxy system (236 J/g) suggesting that the epoxy achieves close to full cure. The shift of the peak exotherm of the epoxy from 117°C in the neat resin to 120°C in the IPN may be attributed to dilution effects within the blend as found with the AIBN- and CHP-containing IPN systems.

The FTIR conversions of styrene and methacrylate units in both the pure VER/MEKP resin and the IPN at 70°C are shown in Fig. 12. In contrast to the extensive induction period found for the conversion of vinyl ester components in the neat resin, a minimal induction period is observed for both the styrene and methacrylate groups within the IPN at 70°C (see Fig. 12) and the initial polymerisation rate is higher in the IPN. These results support the DSC data (Fig. 11) suggesting accelerated decomposition of the MEKP initiator by the 1-MeI. For the neat resin, the conversion of styrene and methacrylate groups at 70°C attains a plateau conversion at approximately 70 and 80%, respectively, and both groups reach close to full cure after post-curing at 150°C. In contrast, the IPN conversion of the styrene and methacrylate groups level out at approximately 50 and 60%, respectively, and even after the postcure at 150°C, the styrene and methacrylate units within the IPN only reach 70 and 80% conversion, respectively. This is consistent with the DSC studies of this system (Table 1) and further confirms the degradation of the MEKP by the imidazole causing either a dead-end effect [24] or depletion of radicals by a non-radical-producing side reaction.

Fig. 13 compares the epoxy conversion in the neat DGEBA/1-MeI and the MEKP-initiated IPN. As found for the IPN systems radically initiated by CHP and AIBN, the epoxy conversion within the IPN is significantly retarded in comparison with the neat system, due to a dilution effect and perhaps due to the crosslinking of the VER component prior to significant epoxy cure, as discussed earlier. Full cure of the epoxy groups in the IPN was attained on postcure at 150°C.

3.5. VER/BPO blended with DGEBA/1-MeI

The DSC thermograms (see Fig. 14) of the BPO-initiated VER and the 1-MeI initiated epoxy resin both exhibit single primary peaks whereas the 50:50 IPN of the epoxy and VERs exhibits three exotherms — an exotherm at 91°C, a larger peak at 121°C and a broad exotherm around 235°C. On the basis of their proximity to the parent resins, the lower and intermediate temperature exotherms observed in the 50:50 blend may represent the (partial) cure of vinyl ester and epoxy, respectively, whereas the broad peak at high temperatures can be assigned to thermal cure of the remaining VER components, as discussed earlier. The exothermic VER curing peak at 91°C is significantly lower than in the neat VER system (104°C) and can be attributed to the reduction of the BPO by the 1-MeI causing accelerated radical production similar to that observed in both the CHP and MEKP cured IPNs. This is confirmed by the shift of the curing peak of VER/BPO from 104 to 93°C when 5 wt% of 1-MeI is added (see Table 1) and is similar to that found

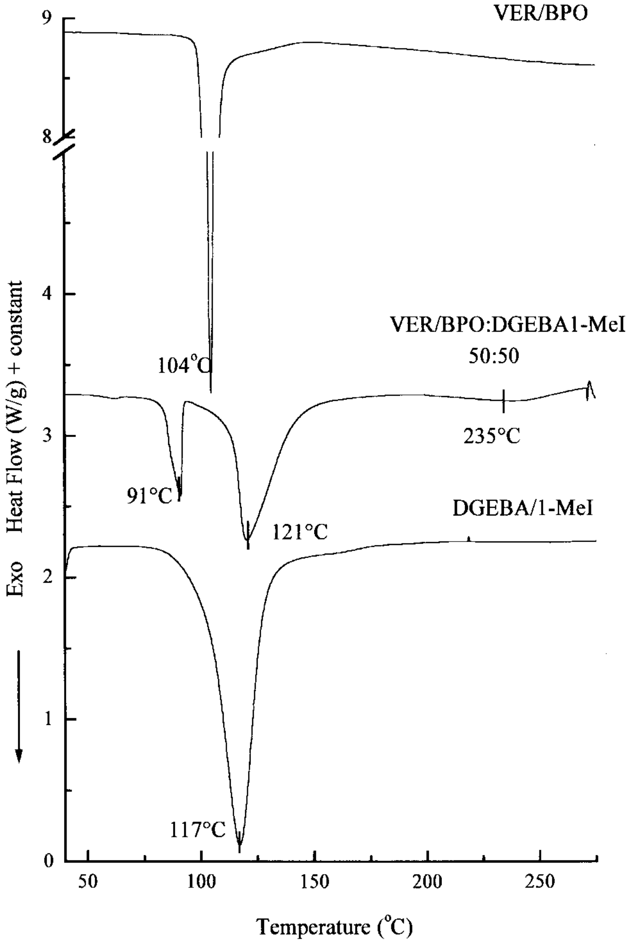


Fig. 14. DSC scans of the VER/BPO and DGEBA/1-MeI resins and their 50:50 IPN.

for MEKP-cured systems. The broad peak around 235°C in the IPN is close to the broad, high temperature exotherm at 203°C in the VER/MEKP:1-MeI system and corresponds with the exotherm at 195°C observed for the VER when thermally cured without added initiator. The total heat of polymerisation for the 50:50 blend (237 J/g not including the thermal component of the VER cure of 34 J/g at 235°C) is substantially reduced from the average of the enthalpies for the individual exotherms of VER/BPO and DGEBA/1-MeI (i.e. 397 J/g) suggesting that the VER component does not fully cure at normal curing temperatures. This decrease in size of the VER component exotherm in the IPN can be explained by the premature decomposition of the BPO by the 1-MeI, as discussed above, which causes dead-end radical polymerisation [24]. Alternatively BPO may be depleted by a side reaction, which does not produce radical species, thus decreasing the heat of polymerisation.

The upwards shift of the peak temperature of the epoxy component exotherm in the VER/BPO:DGEBA/1-MeI IPN, from 117° to 121°C, can be attributed to dilution effects within the 50:50 blend as found in the AIBN, CHP and MEKP cured IPNs. The exotherm enthalpy of the epoxy peak in the IPN (203 J/g) is less than that expected for full cure (236 J/g); however, this may be within the experimental error associated with the separation of overlapping peaks.

4. Conclusions

IPNs were prepared from imidazole-cured DGEBA and radical-cured VER. The AIBN-containing IPNs did not show significant interaction effects between the VER and epoxy components, and for the AIBN- or CHP- initiated systems, full cure of the VER was achieved at moderate temperatures as indicated by the scanning DSC heat of polymerisation and from the isothermal FTIR conversion-time data. However, all of the peroxide-initiated IPN systems exhibited an apparent redox reaction between the 1-MeI amine and the peroxide, causing accelerated decomposition of the peroxides to radicals, and hence this accelerated the rate of cure of the vinyl ester component. In the case of MEKP and BPO, the cure of the vinyl species was incomplete due to loss of initiator activity, perhaps by non-radical redox reactions — full cure was not achieved even at high temperatures for these two IPNs.

The extent of epoxy cure was nearly complete at moderate temperatures for all IPN systems. This suggests that even if interactions occurred between the initiator systems, there was sufficient residual imidazole to allow full cure.

In general, dilution effects of the reacting DGEBA system by the VER components were observed for the IPNs in the early stages of the cure. In addition, during isothermal cure at 70°C, unreacted DGEBA monomer plasticised the IPN allowing a higher plateau conversion of the vinyl groups in the IPN, provided there were no strong interactions between the 1-MeI and the radical initiators. In contrast, when the conversion of the VER component was near complete, the subsequent reaction of the epoxy was limited by vitrification of the IPN associated with the high level of crosslinking in the VER component.

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