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Curing behaviour of IPNs formed from model VERs and epoxy systems I amine cured epoxy

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Dedicated to Professor Karel Dusek in recognition of his contribution to the field of polymer networks

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Abstract

The curing behaviour for an Interpenetrating Polymer Network (IPN) formed from a model Vinyl ester resin (VER) and an amine cured epoxy resin has been studied by scanning DSC and isothermal mid-FTIR. The interactions between the VER initiating system (azobisisobutyronitrile or cumene hydroperoxide, benzoyl peroxide or methyl ethyl ketone peroxide/cobalt octoate) and the epoxy curative (aniline, diaminodiphenyl methane, butylamine or diamino-octane) have been examined. For most of the IPNs, there was evidence for a reduction in reaction rate due to the dilution of each reacting system by the other resin components. When cumene hydroperoxide, benzoyl peroxide or methyl ethyl ketone peroxide (with or without cobalt octoate) were used as the radical initiating systems, there was strong redox interaction between the peroxide and the amine, which caused acceleration of the peroxide decomposition in the early stages of reaction and also resulted in premature depletion of the initiator system. Evidence for a grafting reaction between the amines and the methacrylate groups by Michael addition was also found. In some systems cured isothermally at 70°C, the slow cure of the epoxy component allowed the unreacted DGEBA to plasticise the system and enhance the extent of cure of the VER components prior to vitrification of the IPN. As a consequence of the additional crosslinks introduced by the VER component, premature vitrification occurred during the slower cure of the DGEBA component, thus reducing the extent of cure of the epoxy groups in the IPN. Near full cure could be obtained for most of the IPN systems when post-cured at elevated temperature, indicating that the presence of each network imposed minimal topological restrictions on cure.

Keywords: IPN; Curing; DSC

1. Introduction

Thermosetting resins have a number of advantages over thermoplastics such as elevated heat distortion temperatures, good solvent resistance and high modulus, which results in their use in a wide range of commodity, engineering and specialty applications [1]. Most thermosetting resins are used with reinforcing fillers or fibres to produce a composite material for applications ranging from swimming pool liners and automotive components to corrosion resistant tanks and aircraft fuselages.

Optimisation of the properties of thermosetting polymers for a specific application has traditionally been achieved by modifying the structure of the monomer unit. For example, the addition of the bisphenol-A structure improves the rigidity of the polymer backbone and leads to improved mechanical properties [2,3]. Other property enhancement can be achieved by rubber or thermoplastic toughening or by reinforcement with inorganic fillers or fibres. Blending of thermosets to form "Interpenetrating Polymer Networks" (IPNs) is an entirely different route to extend the range of properties of these thermosets and hence increase the number of applications for the polymer product.

As first proposed by Sperling, [4] IPNs are ideally compositions 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). IPNs can be formed by one of two methods. A sequential IPN is one where the first network is formed and then swollen with a second crosslinking system, which is subsequently polymerised (see Fig. 2). Such systems have great potential for the

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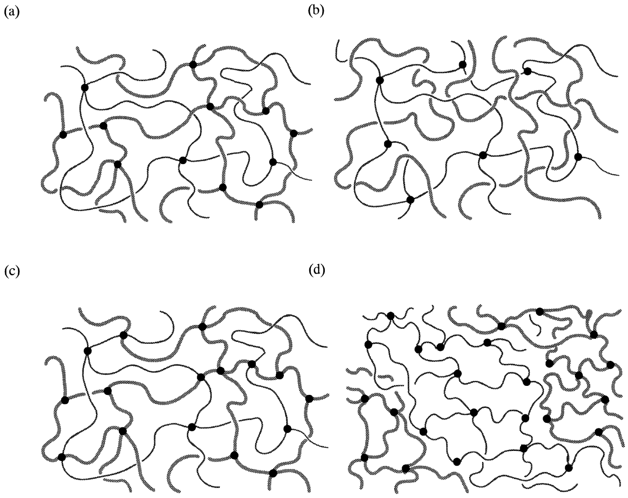


Fig. 1. (a) Idealised structure of an IPN; (b) semi-IPN; (c) grafted IPN; (d) phase separated IPN.

development of unusual gradient morphologies. The second type is the simultaneous IPN in which the two network components are polymerised together (see Fig. 3) and it is this type that is investigated in the present study.

There are a number of factors that could lead to complications in the curing of IPNs. First, interactions between the components of one network and the initiators of the other may accelerate or retard reaction. As an example, in a study of the cure of epoxy/polyester IPNs, Lin and Chang [6] observed an interaction between the cobalt salt catalyst of the polyester and the diamine curative for the epoxy. Second, the rate of reaction of one component might be expected to be reduced due to the dilutional effects by the other components [7]. In addition, it is known that during free radical polymerisation, the reaction may become diffusion controlled (such as with the termination process [8]) and so the change in viscosity of the IPN due to the reaction of one component may also affect the curing behaviour of the second component as suggested by Jin et al. [9]. If a thermosetting system is cured at a temperature below its maximally attainable T_g, vitrification occurs during cure, thus slowing the final stages of reaction and limiting the final degree of cure. But in an IPN, if the first component reacts more slowly than the second component, the former may act as a plasticizer to the cure of the latter, allowing faster reaction of the second component and full cure without vitrification. Evidence for this has been reported by Lin and Chang [6]. In contrast, a fast polymerisation of the second component may retard the reaction of the first component due to the presence of additional crosslinks in the system causing earlier vitrification and preventing further reaction of the first component. Also it is known that in some densely crosslinked polymers, the surrounding network architecture may trap reactive groups [10]. Hence it might be expected that in IPNs, the developing skeletal structure of one network might exert a topological restraint on the development of the other network, reducing the rate and final extent of reaction of the other component. Although the selection of different polymerisation modes of each of the crosslinking systems such as chain-growth and step growth mechanisms is intended to prevent copolymerisation, grafting reactions (depicted

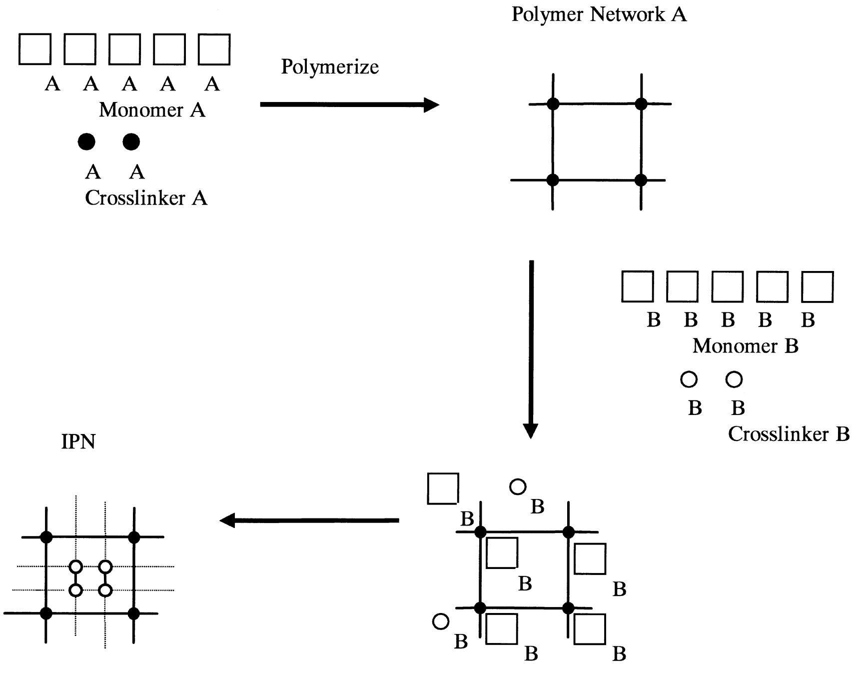


Fig. 2. Sequential IPN formation (adapted from Sperling et al.) [5].

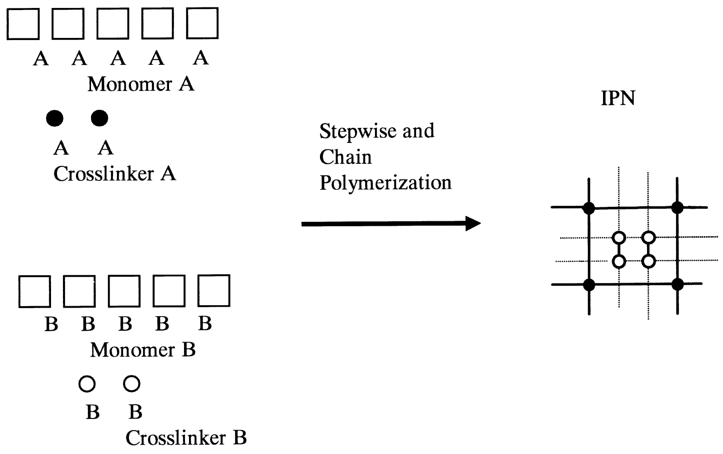


Fig. 3. Simultaneous IPN formation (adapted from Sperling et al.) [5].

in Fig. 1c), may occur between the two polymer networks [11,12]. Finally, although it is intended that the interlocking of the two networks prevents phase separation, demixing (see Fig. 1d) has been observed [13], and this process may be enhanced in semi-IPNs [14,15] where the absence of an interlocking structure can allow phase separation.

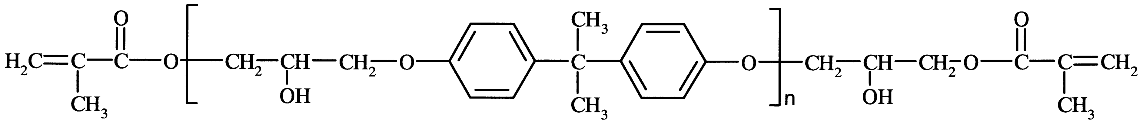
Recently, Lin and coworkers [16–18] have suggested an additional complication in which mutual entanglements formed during the polymerisation of IPNs lead to a process they termed “network interlock”, which provided a sterically hindered environment, reducing reactivity of the component systems. This process might be equivalent to topological restraint; however, Lin et al. [16–18] appear to suggest that the network interlock effect can occur quite early in the cure and is not restricted to the last stages of polymerisation as is found with the structurally-determined topological restraint. In their study of the cure of simultaneous IPNs formed from epoxy resin and unsaturated polyesters, Lin and Chang et al.[6] postulated that the interlock between the two polymer networks increased the activation energy for reaction and reduced the cure rates for both crosslinking systems. Further experimental results by Lin and Jeng et al.[17] on simultaneous IPNs based on poly(ethylene glycol) diacrylate and epoxy exhibited similar behaviour. Thus it would appear that their “network interlock effect” has a kinetic and not a thermodynamic basis.

In the present study, we investigate the curing kinetics of novel IPNs formed by an epoxy resin cured by condensation polymerisation and a model vinyl ester resin polymerised by several types of free radical initiators. Both the vinyl esters and epoxy resins used in this study contain the bisphenol-A diglycidyl structure and it is anticipated that this similarity will enhance miscibility in the IPN formed. Through these investigations we aim to form a more detailed understanding of the chemical interactions between initiating systems, the influence of each reactant on the development of the other network and the resultant morphologies of the IPNs.

2. Experimental

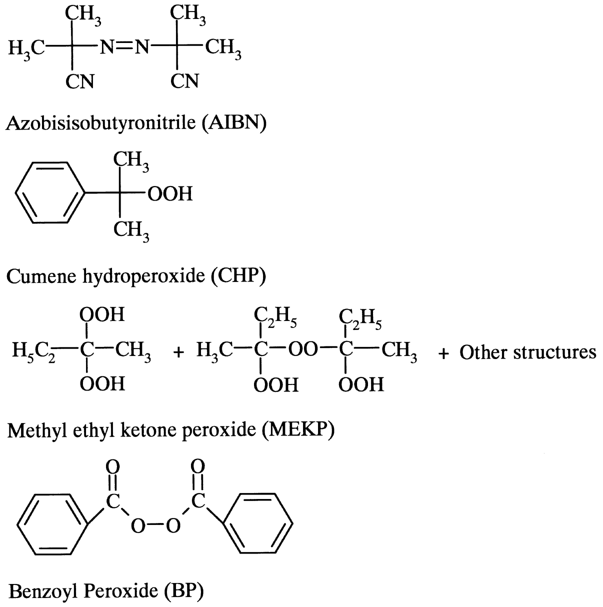
2.1. Materials

The model vinyl ester resin (VER) studied was prepared from a solution of bisphenol-A-diglycidyl-dimethacrylate (bisGMA ($n \sim 1$), Structure 1, supplied by Esschem Co., USA) in 30 wt% styrene monomer.



Structure 1

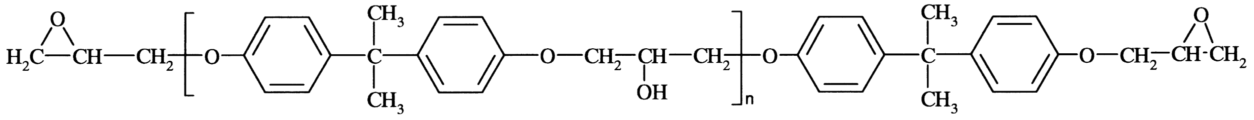
Four different types of radical initiators were used to cure this thermosetting component. Methyl ethyl ketone peroxide (MEKP, supplied by Laporte Pty Ltd as a 40 wt% solution in dimethyl phthalate), cumene hydroperoxide (CHP, supplied by Huntsman Chemical Company Australia Pty Limited as a 90 wt% solution 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 (Structure 2).



Structure 2

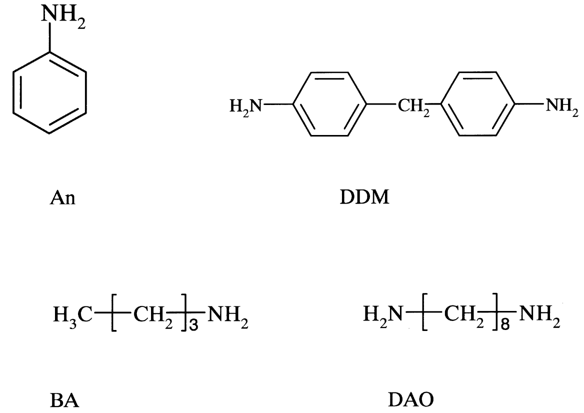
In some studies, cobalt octoate (Co, supplied by Thor Chemicals Australia as a 6 wt% solution in white oil) was used as an accelerator for MEKP at a level of 0.2 wt% based on the VER.

The epoxy oligomer was digylcidyl ether of bisphenol-A (DGEBA ($n = 0.15$), Structure 3, Araldite GY-9708-1 supplied by Ciba Geigy) and was reported to have an average equivalent weight of 190 g/mol.



Structure 3

The DGEBA was cured with a stoichiometric amount of the amine curing agents: butylamine (BA, supplied by Ajax Chemicals), 1,8-diamino-octane (DAO, supplied by Aldrich), aniline (An, supplied by Unilab) and 4,4-diamino-diphenyl methane (DDM, supplied by Aldrich). Butylamine and aniline are monomeric forms of the crosslinking diamines 1,8-diamino-octane and 4,4-diamino-diphenyl methane, respectively (Structure 4).



Structure 4

The glass transition temperatures of the fully cured model vinyl ester, the DGEBA/aniline polymer and DGEBA/butylamine polymer were 146, 85 and 32°C respectively, as determined by DSC.

The VER and DGEBA resins were mixed with their curatives (at slightly elevated temperature in the case of DGEBA cured by the crystalline DAO and DDM amines) and were studied neat or in a 50:50 (wt:wt) IPN mixture via scanning DSC or by isothermal FTIR. In some cases, studies were performed to investigate the effect of the omission of one of the reactive components (the amine or the radical initiator) in the IPN — in these studies the ratio of the individual components was maintained at the normal level as in the IPN.

2.2. Techniques

The kinetics of the cure and glass transition temperatures of the cured thermosets (T_g) were measured with a Perkin-Elmer DSC-7, operated in scanning mode (5°C/min). 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 sub-ambient runs from -10 to 300°C. After cure, the samples were re-run from 40 to 300°C to determine their T_gs, using the midpoint method. All exotherm energies are reported as Joules per gram of total resin (pure resin or IPN resin).

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 or 110°C) for a predetermined 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 quantitative due to the delay in heating-up the sample when it was returned to the oven. The epoxy absorption [19] at 915 cm^{-1}, the C=C resonances [20,21] of styrene at 778 and 1630 cm^{-1} and of the methacrylate stretch [21] at 1645 cm^{-1} were used to calculate the conversion after allowance for overlapping peaks. The C=C resonance of styrene at 778 cm^{-1} is a distinct and well resolved peak on the spectrum but the C=C peaks at 1630 and 1645 cm^{-1} overlap. Similarly the epoxy peak at 915 cm^{-1} and the resonance due to the styrene C=C bond at 910 cm^{-1} overlap. 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

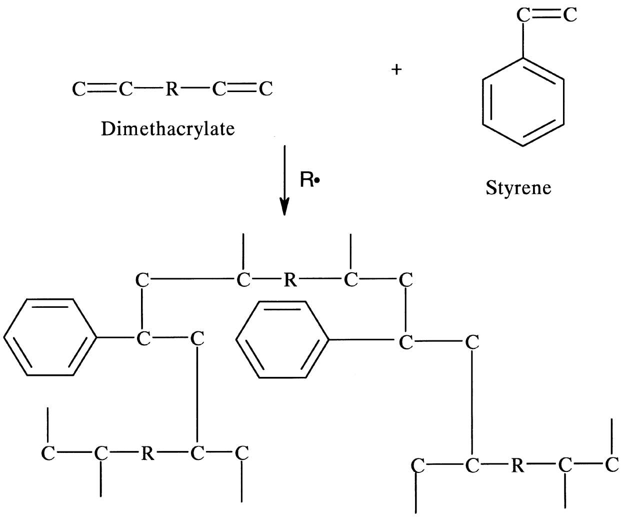


Fig. 4. Schematic of the cure of the model vinyl ester resin.

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 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. Thus the cure of the reactive groups in epoxy–vinyl ester IPNs was monitored via the decrease in intensity (area) of the above mentioned characteristic groups. The phenyl group of styrene exhibits a characteristic absorption at 700 cm^{-1}, which was used as an internal standard [22] to correct for small variations in specimen thickness during the early stages of cure.

3. Results and discussion

3.1. Reaction scheme

Vinyl ester networks are based on polyfunctional methacrylate monomers dissolved in styrene and are cured by free radical initiated polymerisation. Organic peroxides and aliphatic azo compounds are two of the more common families of free radical initiators used. A schematic of the general curing reaction of vinyl esters is illustrated in Fig. 4.

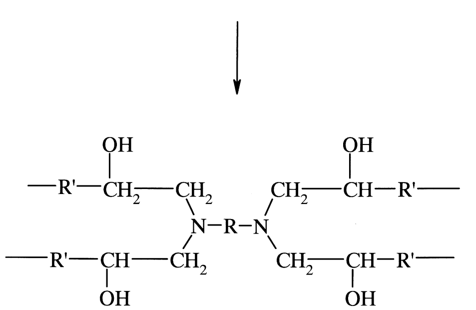


Fig. 5. Schematic of the cure of epoxy using an amine curing agent.

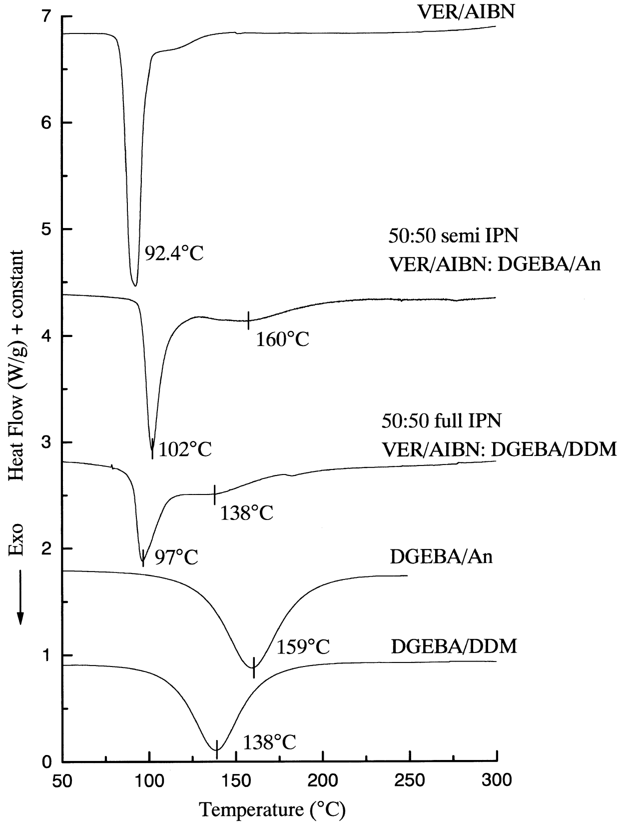


Fig. 6. DSC scans of the 50:50 VER/AIBN:DGEBA/An semi-IPN, the 50:50 VER/AIBN:DGEBA/DDM full-IPN and the parent resin systems.

In contrast, epoxy resins are commonly cured by step growth copolymerisation with aliphatic and aromatic amines [23]. The polymerisation sequence is illustrated in Fig. 5. The primary amine initially reacts with the epoxy group followed by the reaction of the secondary amine. A third possible reaction in the curing of the epoxy/amine system involves the reaction between the epoxy and hydroxyl groups.

3.2. Curing kinetics

3.2.1. AIBN initiated systems

The scanning DSC of the DDM- and An-cured DGEBA and the AIBN-initiated VER are shown in Fig. 6. The two epoxy systems show single exotherms at similar temperatures due to their chemical similarities [24]. The VER exhibits a sharp peak at 92°C with a small shoulder near 110°C — the cause for the shoulder is unclear but similar DSC traces have been observed previously for VER resins [25]. The scanning DSC curing traces of the semi-IPN of AIBN/VER:DGEBA:An and the full-IPN

Table 1
Heat of polymerisation and peak temperatures for individual peaks for IPNs involving aromatic amine cured epoxies

System	Curing peak (°C)	ΔH (J/g)
AIBN initiated systems		
VER/AIBN	92	327
50:50 VER/AIBN:DGEBA/An	Peak 1: 102 Peak 2: 159	373
50:50 VER/AIBN:DGEBA/DDM	Peak 1: 96 Peak 2: 133	400
DGEBA/An	159	421
DGEBA/DDM	138	373
CHP initiated systems		
VER/CHP	125	318
50:50 VER/CHP:DGEBA/An	Peak 1: 143 Peak 2: 161	378
50:50 VER/CHP:DGEBA/DDM	Peak 1: 140 Peak 2: 156	400
DGEBA/An	159	421
DGEBA/DDM	Peak 1: 138	373
BPO initiated systems		
VER/BPO	104	283
50:50 VER/BPO:DGEBA/An	Peak 1: 138 Peak 2: 213	260
DGEBA/An	Peak 1: 159	421
MEKP initiated systems		
VER/MEKP	123	320
VER/MEKP/Co	80	321
50:50 VER/MEKP:DGEBA/An	Peaks at: 93 150 209	380
50:50 VER/Co/MEKP:DGEBA/An	Peak 1: 75 Peak 2: 193	Peak 1: 21 Peak 2: 280
DGEBA/An	159	421
Other mixed systems		
VER/MEKP:An	Peak 1: 90 Peak 2: 220	Peak 1: 12 Peak 2: 94
VER/MEKP/Co:An	Peak 1: 84 Peak 2: 181	Peak 1: 84 Peak 2: 36
VER/Co:An	190 Decomposition of volatiles at 250–260°C	218
MEKP/Co:DGEBA/An	151	444
MEKP:DGEBA/An	149	449
VER:An	190	195

of AIBN/VER:DGEBA/DDM are also shown in Fig. 6. The DSC of the IPN system appears to shows two exothermic peaks: one narrow peak superimposed over a much broader peak, corresponding in part to the cure of the VER and of the epoxy–amine polymer, respectively. The VER peak in the IPN is shifted to higher temperatures than in the parent resin as a result of reduced reaction rates. This rate reduction is possibly due to dilution of the reactants by the other components. The epoxy peak occurs at similar temperatures in the parent resin and the IPN. This may be due to a combination of opposing factors — the effect of dilution would be to decrease the reaction rate; however, the presence of H-bonding OH groups on the bisGMA molecule could counter this effect as it is known [26,27] that the epoxy–amine reaction is catalysed by H-bonding groups. The overall heat of polymerisation associated with the peaks in the IPN corresponds closely to that expected of this blend (see Table 1). In addition, the similarity of cure behaviour of the VER and epoxy components in the IPN and in the neat resins suggests that the curing mechanism of each component is not greatly affected by the presence of the other, probably due to the lack of chemical interaction between the components of the parent systems, in particular between AIBN and the diamines. This is in accord with research showing that azo compounds are generally not susceptible to chemical induced decomposition, unlike that observed for peroxides [28]. Similar results were observed in the semi-IPN formed from AIBN-initiated VER and aniline cured DGEBA (see Table 1), which indicate that the curing behaviour of the IPN is not affected by the extent of network formation per se. As a result, the following studies of IPNs containing aromatic amine curatives were restricted to the monomeric amine species, aniline, because its liquid nature simplified the preparation of the IPN mixture.

Fig. 7 shows the variation in the FTIR spectrum during the cure of the VER/AIBN: DGEBA/An semi-IPN. The main change appears to be the reduction in magnitude of the methacrylate (1645 cm^{-1}), styrene (778, 910 and 1630 cm^{-1}) and epoxy (915 cm^{-1}) peaks as cure proceeds. The conversion with time of styrene, methacrylate and epoxy groups is shown in Fig. 8. The conversions of styrene and methacrylate groups are significantly delayed in the VER/AIBN:DGEBA/An system compared with the neat VER/AIBN system, as suggested by the DSC studies. The decrease in the rate of C=C conversion in the semi-IPN may be partly attributable to the dilution of the reactants by the DGEBA resin. However after 300 min cure at 70°C, the IPN system exhibits a higher level of conversion of both styrene and methacrylate groups, compared with the neat VER. Since the reaction of DGEBA is very slow in the IPN, the increased conversion of vinyl groups in the IPN may be due to the presence of unreacted DGEBA in the IPN, which acts as a plasticizer by enhancing mobility within the system and hence enabling a higher degree of reaction before vitrification occurs. This behaviour is similar to that observed by Jin et al. [9] for polyurethane–monomethacrylate/trimethacrylate IPNs. However, post-curing of the VER and of the IPN at 150°C caused almost complete vinyl conversion in both networks.

As shown in Fig. 8, the rate of epoxy conversion in the VER/AIBN:DGEBA/An semi-IPN is very similar to that in the neat DGEBA/An system up to 100 min. The apparent similarity of epoxy cure rate up to 100 min may be the

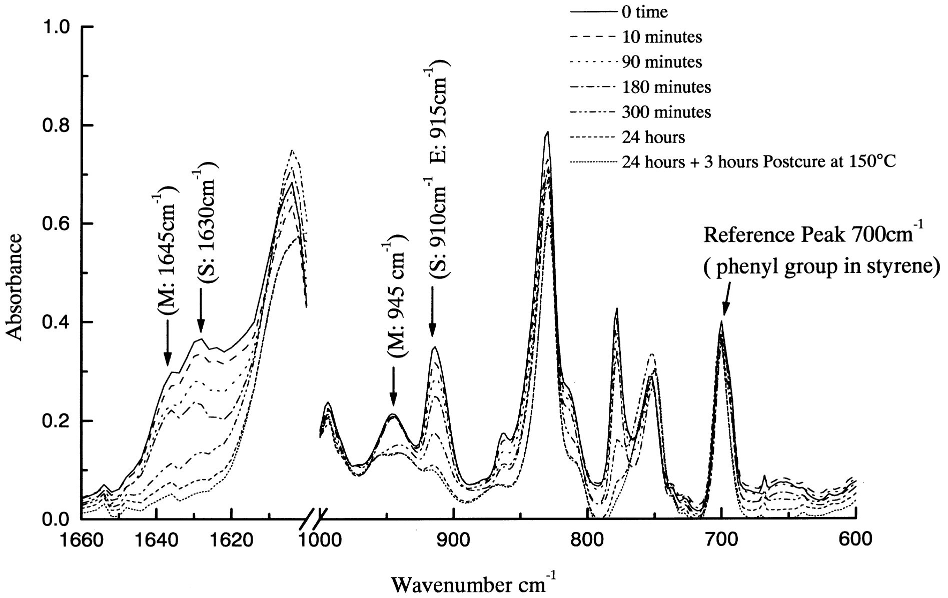


Fig. 7. FTIR spectra for the cure of 50:50 VER/AIBN:DGEBA/An at 70°C illustrating the epoxy (E), methacrylate (M) and styrene (S) characteristic peaks.

combined result of a dilutional effect and a rate accelerating effect in the IPN, discussed above. However after 100 min, the epoxy conversion in the IPN is retarded in comparison with the neat resin, which may be due to the dominance of the dilutional effect. The final extent of cure of the epoxy component of the resin appears to be less than 100%. Assuming the IPN to be 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 occurs. Despite this, nearly full conversion of the epoxy was observed after post-cure at 150°C, which is above the T_g of the two components' T_gs, indicating that the presence of the VER network does not produce a significant topological restraint on the cure of the epoxy.

Analogously to the investigations of the IPNs involving

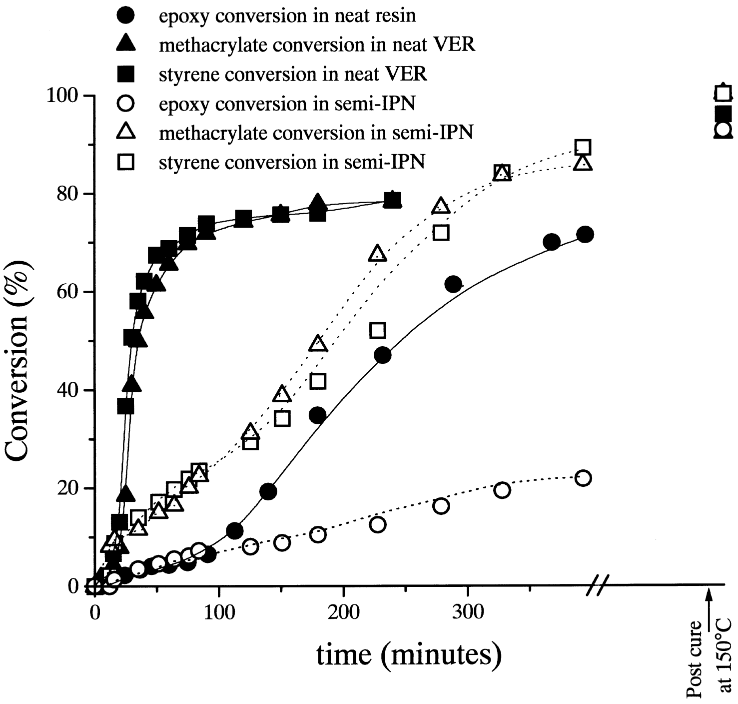


Fig. 8. Conversion versus time for the epoxy, methacrylate and styrene in the 50:50 VER/AIBN:DGEBA/An and the parent resins at a cure temperature of 70°C.

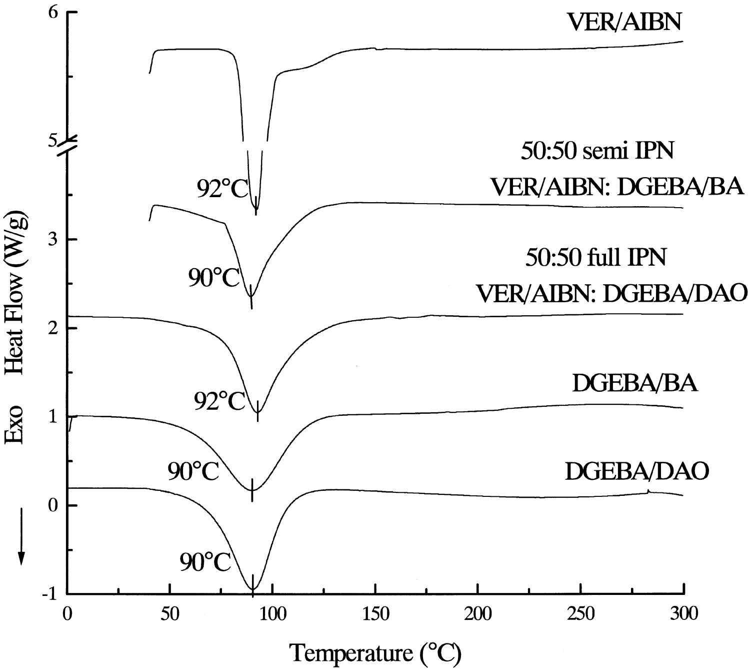


Fig. 9. DSC scans of 50:50 VER/AIBN:DGEBA/BA, semi-IPN, 50:50 VER/AIBN:DGEBA/DAO, full-IPN, and the parent resin systems.

aromatic amine cured DGEBA systems, the IPNs involving aliphatic amines of butylamine and crosslinking diaminooctane have also been studied. The DSC curves of the neat VER/AIBN and DGEBA/DAO (or DGEBA/BA) resins exhibit narrow and broad exothermic peaks, respectively during cure (Fig. 9). Due to the proximity of the exotherm curves for the parent resins, it is not possible to comment on dilutional or catalytic effects of each component on the other. The DSC traces of the 50:50 semi-IPN and 50:50 full-IPN are similar to those obtained from the sum of the neat resin components, with the total heat of polymerisation for the semi-IPN and full-IPN being close to that predicted from the average of the cure of the component resin systems (see Table 2). As a result of the similarity between the curing behaviour of the semi-IPN and full-IPN, further studies of IPNs containing aliphatic amine curatives were restricted to the monomeric amine species, butylamine, because its liquid nature simplified the preparation of the IPN mixture.

To provide further information of the curing behaviour in the IPNs, studies were made of IPN systems containing only some of the components. For example, a DSC scan of the VER/AIBN:BA combination (where the weight ratio of components is as in the IPN except that it contains no DGEBA — this corresponds approximately to an equimolar ratio of NH and methacrylate groups), indicated a large exotherm attributable to the VER exhibiting a total heat of polymerisation (309 J/g, allowing for the dilution of the resin by BA), which is close to that expected for full polymerisation of the neat VER/AIBN system (327 J/g). However, some evidence of grafting reactions between the IPN components can be observed. For example, the systems bisGMA:An and bisGMA:BA (which are analogs to VER/AIBN:DGEBA/An and VER/AIBN:DGEBA/BA) should not show significant reaction of the methacrylate groups due to the absence of AIBN — thermal cure of VER in the absence of radical initiator was found to require temperatures above 200°C. However mid-FTIR spectroscopy indicated that a reaction occurred at 70°C, leading to a consumption of methacrylate groups, as shown in Fig. 10. This reaction is presumably the Michael addition [29], in which a nucleophile (the amine) attacks the electron deficient double bond (the methacrylate group) followed by the transfer of a proton. The Michael reaction between secondary amino hydrogen and the fumarate double bond in unsaturated polyester resins is well documented [29–31]. The extent of methacrylate reaction in the bisGMA:BA system is higher than for bisGMA:An — this is what would be expected for Michael addition because the aliphatic amine is a stronger base [32]. A comparison of the curing kinetics of the VER component in the IPN with the bisGMA/amine reaction suggests that although the consumption of methacrylate double bond due to the Michael reaction is less than that due to free radical polymerisation by AIBN, it is still significant. It is interesting to note that cure at 70°C for 24 h did not produce complete reaction of the methacrylate groups in the bisGMA/amine systems and that post-cure at 150°C for 3 h only resulted in approximately 20% conversion.

3.2.2. CHP initiated systems

The VER/CHP:DGEBA/An system shows two DSC

Table 2
Heat of polymerisation and peak temperatures for individual peaks for IPNs involving aliphatic amine cured epoxies

System	Curing peak (°C)	Δ*H* (J/g)
AIBN initated systems		
VER/AIBN	92	327
50:50 VER/AIBN:DGEBA/BA	90	379
50:50 VER/AIBN:DGEBA/DAO	92	395
DGEBA/BA	90	398
DGEBA/DAO	90	424
CHP initiated systems		
VER/CHP	125	318
50:50 VER/CHP:DGEBA/ BA	Peak 1: 86	259
	Peak 2: 136	
	Peak 3: 205	
50:50 VER/CHP:DGEBA/DAO	Peak 1: 88	Peak1: 158
	Peak 2: 113	Peak2: 165
	Peak 3: 229	Peak3. 113
DGEBA/BA	90	398
DGEBA/DAO	90	424
BPO initiated systems		
VER/BPO	105	283
50:50 VER/BPO:DGEBA/BA	Peak 1: 86	Peak 1: 101
	Peak 2: 229	Peak 2: 148
DGEBA/BA	90	398
MEKP initiated systems		
VER/MEKP	123	320
VER/MEKP/Co	80	321
50:50 VER/MEKP:DGEBA/BA	Peak 1: 89	Peak 1: 245
	Peak 2: 218	Peak 2: 72
50:50 VER/MEKP/Co:DGEBA/BA	Peak 1: 91	Peak 1: 162
	Peak 2: 204	Peak 2: 78
DGEBA/BA	90	398
Other mixed systems		
MEKP:DGEBA/BA	89	390
Co/MEKP:DGEBA/BA	89	341
VER/MEKP/Co:DGEBA	Peak 1: 85	Peak 1: 134
	Peak 2: 193	Peak 2: 19
VER/MEKP/Co:BA	Peak 1:118	Peak 1: 16
	Peak 2: 197	Peak 2: 42
VER/Co:DGEBA/BA	Peak 1: 91	Peak 1: 142
	Peak 2: 203	Peak 2: 82
VER/MEKP:BA	Peak 1: 89	Peak 1: 19
	Peak 2: 190	Peak 2: 40
VER/BA	Peak 1: 125	Peak 1: 20
	Peak 2: 195	Peak 2: 40
VER (thermal cure)	195	320
VER/MEKP:DGEBA	131	161
VER:DGEBA/BA	Peak 1: 89	Peak 1: 202
	Peak 2. 220	Peak 2: 108

exothermic curing peaks (Fig. 11) that are similar to the DSC peaks found for the VER/AIBN:DGEBA/An system (Fig. 6), with the exception that the lower peak in the VER/CHP:DGEBA/AN semi-IPN is smaller and appears to be broader. The dominant curing exotherm at 161°C in the IPN corresponds to that of the DGEBA/An component, which exhibits a peak at 159°C in the parent resin. As discussed above, the invariance of the epoxy peak temperature in the IPN and the neat resin, which indicates a constant epoxy cure rate, may be due to the combination of a rate reduction due to dilution in the IPN and the rate acceleration due to the catalytic effect of H-bonding of the epoxy–amine transition state [27,28] with the bisGMA hydroxy groups. The smaller peak observed at 143°C in the IPN DSC trace occurs at a significantly higher temperature than that in the neat VER/CHP resin (125°C), indicating a reduction in the VER cure rate. This may be due to a dilutional effect from the DGEBA or due to a reduction of the activity of the CHP. The latter may be caused by redox interations between the peroxide and the amine — it is known that in some cases amines can catalyse the decomposition of peroxides [33] to radicals but perhaps in the present case, the redox reaction may result in non-radical products, which causes a reduction in radical formation. The total heat of polymerisation for the IPN (378 J/g) is very close to the average of the individual components (370 J/g), suggesting that full cure can be obtained for this system under reasonable curing conditions.

The conversion of the reactive groups at 70°C in the neat resins and the 50:50 VER/CHP:DGEBA/An semi-IPN is shown in Fig. 12. The cure of styrene and the methacrylate groups is significantly slower in the IPN than in the VER resin, in agreement with the DSC results. The IPN and the neat VER both show full conversion of the styrene and methacrylate groups when post-cured at 150°C (above the maximum T_g of the parent resins). While it was found in the VER/AIBN:DGEBA/An system that the epoxy component enhanced the VER cure through a plasticising mechanism, in the VER/CHP:DGEBA/An system, the epoxy reacts at a similar rate to the VER components and so there are fewer small molecules able to act as plasticizers of the VER component. This may account for the lower level of cure of the VER components when cured at 70°C due to vitrification of the IPN.

The epoxy conversion is initially faster in the VER/CHP:DGEBA/An semi-IPN (Fig. 12) than in the neat resin. As mentioned earlier, this may be a catalytic effect of the hydroxy groups in the bisGMA molecule on the diamine/epoxy reaction [27]; however, it is not clear why the initial epoxy cure rate is faster in the CHP-initiated IPN (Fig. 12) than in the AIBN-initiated IPN (Fig. 8). After approximately 250 min, the cure rate of the neat epoxy exceeds that of the epoxy in the IPN. This may be partly due to a dilution effect. In addition, this may also be partly due to vitrification of the IPN. Similar to that observed with the VER/AIBN:DGEBA/An semi-IPN (Fig. 8), in the VER/CHP:DGEBA/An semi-IPN (Fig. 12) the epoxy groups did not completely react. As discussed above, if the IPN is assumed to be 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.

Fig. 13 shows the DSC curing exotherms for the 50:50 VER/CHP:DGEBA/BA system. In this particular semi-IPN,

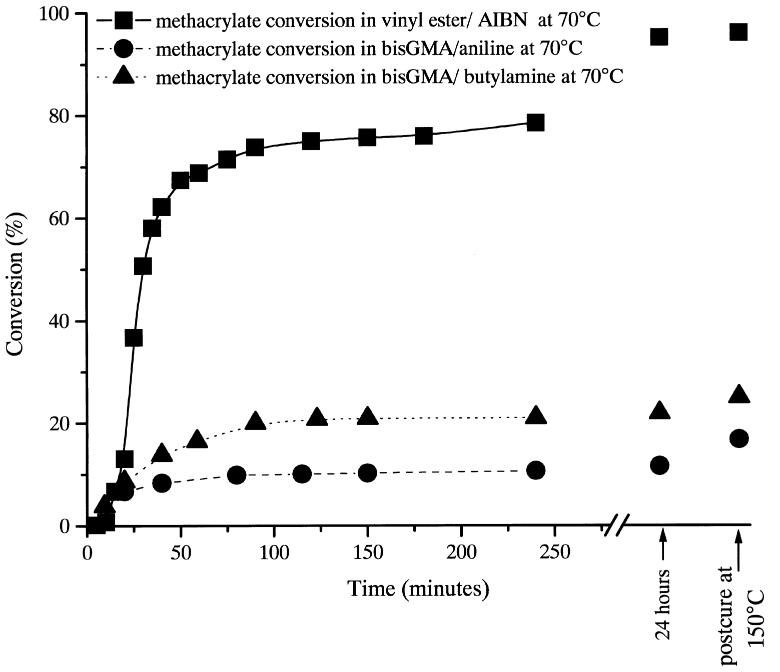


Fig. 10. Mid-FTIR methacrylate conversion versus time for the VER/AIBN, bisGMA/BA and bisGMA/An at 70°C.

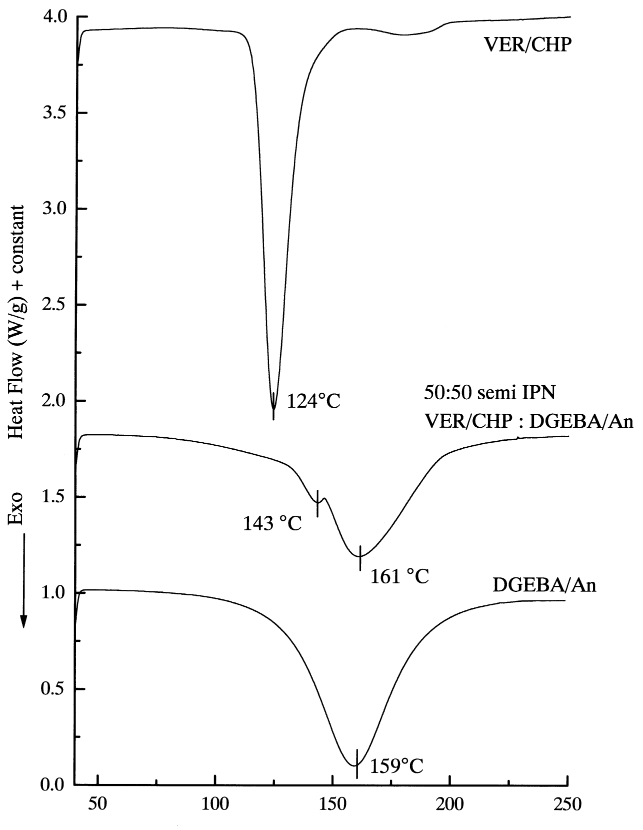


Fig. 11. DSC scans of the CHP-initiated VER, the An-cured DGEBA and the 50:50 VER/CHP:DGEBA/An semi-IPN.

the DGEBA/BA cures faster than the VER/CHP and so the first exotherm peak of the 50:50 IPN represents the cure of the epoxy component. The second DSC peak at 136°C presumably represents the partial cure of the VER network by CHP-derived radicals. However, this system appears to have significant inter-component interaction. A broad exothermic peak is observed in the IPN at 220°C, which may be attributed to thermal cure of the VER resin. This assignment is confirmed by the DSC scan of VER:DGEBA/BA (omitting the peroxide), which shows the peak cure of the epoxy at 89°C and a broad exotherm at 220°C, which is close to the exotherm found during non-catalysed thermal cure of VER (see Fig. 13 and Table 2). This thermal cure of residual vinyl groups in the IPN indicates that the CHP has been unable to fully cure the VER component, perhaps due to catalytic decomposition of CHP by butylamine, causing a significant loss of radicals. It is interesting to note that even after scanning up to 300°C, the IPN is not fully cured as shown by the small heat of polymerisation (259 J/g, Table 2) compared with the expected average value of the parent resins (358 J/g). This is in contrast to the VER/AIBN: DGEBA/BA system, which showed full cure (Fig. 9 and Table 2).

3.2.3. *BPO initiated systems*

The IPN systems containing the BPO initiated VER resin are analysed in Fig. 14. The 50:50 VER/BPO:DGEBA/BA semi-IPN exhibited two DSC peaks the lower temperature exotherm at 86°C corresponds very closely to the curing exotherm in the neat DGEBA/BA system (90°C) and the second peak at approximately 229°C corresponds closely to that of the VER thermal curing

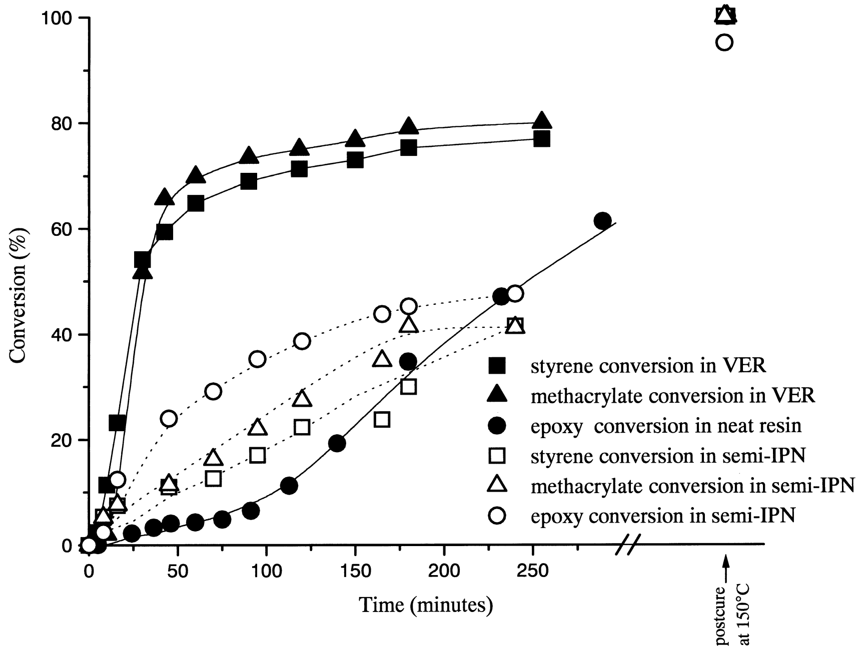


Fig. 12. FTIR conversion versus time for VER/CHP:DGEBA/An and the parent resins at 70°C.

temperature (195°C). The total heat of polymerisation was measured to be approximately 249 J/g which is lower than that expected and may result from interactions between the amine and peroxide as discussed above. The DSC traces in the semi-IPN also exhibited considerable noise above 250°C, possibly due to volatilization from unreacted species within the system.

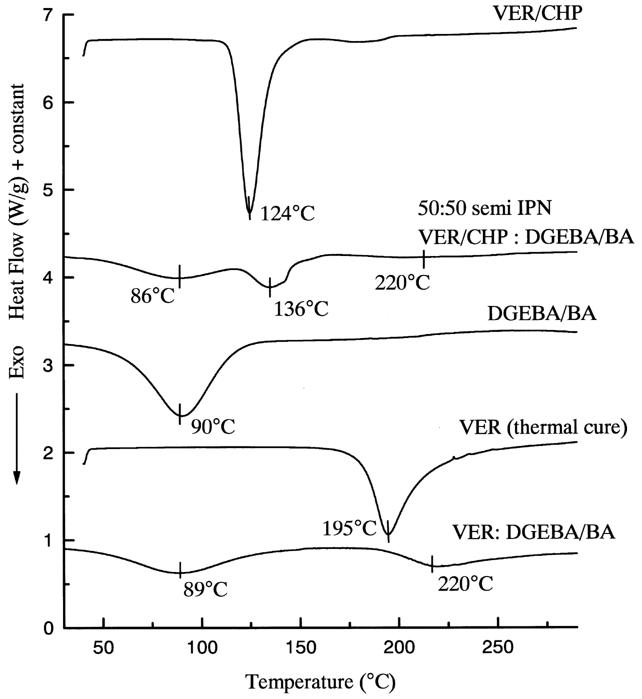


Fig. 13. DSC scans of the VER/CHP:DGEBA/BA semi-IPN, the parent resins, the thermal cure of VER and the system VER:DGEBA/BA (without radical initiator).

The 50:50 VER/BPO:DGEBA/An system (Fig. 14) also exhibits two exothermic peaks, at approximately 140 and at 213°C. The peak at 138°C, which would be expected to be due to epoxy cure, occurs at a lower temperature than the epoxy cure peak in the neat DGEBA/An (150°C), possibly due to acceleration of the DGEBA/An reaction by the bisGMA hydroxyl groups. Alternatively it may an artifical result caused by an overlap of the epoxy peak with a lower temperature peak due to partial cure of the VER. The higher temperature curing exotherm in the IPN corresponds closely to the thermal VER cure (see Table 2) — the total heat of polymerization (378 J/g–Table 1) suggests that full cure can be attained for this IPN.

3.2.4. MEKP initiated systems

The DSC scan of the VER/MEKP system (Fig. 15) shows a sharp exotherm at 123°C while DGEBA cured with aniline exhibits a broad exotherm at 159°C. The 50:50 blend of the two systems has a very broad exotherm region with overlapping peaks at 93, 150 and 209°C, suggesting that complex interactions have occurred between the components. The first peak may be due to the cure of VER by the accelerated decomposition of MEKP by aniline — Walling et al.[33] have reported that aromatic amines can undergo a redox reaction with peroxides, resulting in enhanced radical production. The second peak at 150°C may be associated with the DGEBA/An cure, perhaps accelerated by the bisGMA hydroxyl groups, as discussed above. The final peak at 209°C

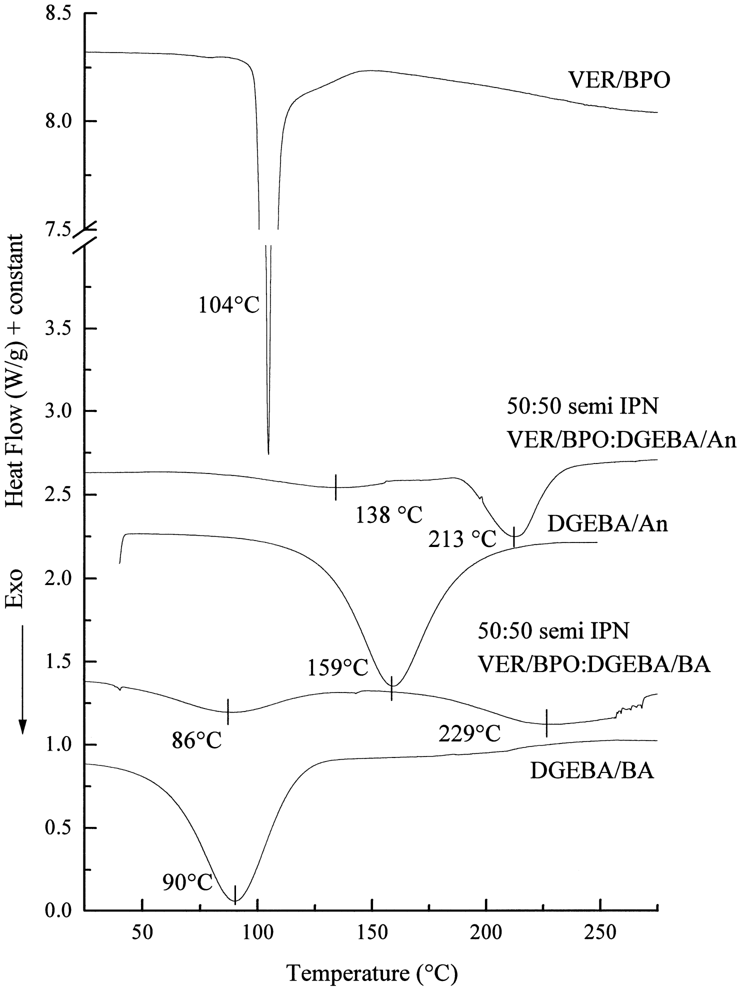


Fig. 14. DSC scans of the 50:50 VER/BPO:DGEBA/An and VER/BPO:DGEBA/BA semi-IPNs and the parent resins.

may be due to thermal cure of the VER components due to premature loss of radical initiator in the early stages of the VER cure. The total heat of polymerisation of the IPN is 380 J/g, which is similar to the average of the enthalpies of the pure systems (370 J/g), suggesting that full cure has been attained.

The scanning DSC of DGEBA cured with butylamine (Fig. 16) exhibits a broad low temperature DSC peak (90°C) compared with the higher temperature and narrower peak at 124°C, due to VER/MEKP cure. However the blend of the two systems produces two quite broad peaks at 89 and 218°C. The heat of polymerisation for the lower temperature peak of the IPN (approximately 245 J/g) is greater than 50% (199 J/g) of the heat of polymerisation of the DGEBA/BA system, suggesting that partial cure of the VER component is also occurring within this lower temperature peak at a temperature much less than for neat resin. Such behaviour has been suggested above for the VER/MEKP:DGEBA/An system. One possible explanation of the apparent absence of a separate peak due to MEKP cure of the VER may be the amine-accelerated peroxide decomposition [33], as discussed previously. However the presence of a residual exotherm peak at 218°C, which is close to the peak at 195°C found in the thermal cure of VER without initiator (Table 2), suggests that the redox reaction between the MEKP and BA also causes premature depletion of the peroxide before full VER cure is attained. The total heat of polymerisation for the two exothermic peaks of the 50:50 semi IPN of VER/MEKP:DGEBA/BA is 317 J/g, which is less than the weighted average of the VER/MEKP cure and the DGEBA/BA (359 J/g), suggesting a significant degree of undercuring for this particular system.

Variations of the VER/MEKP:DGEBA/BA system were studied to provide more complete explanations for the unusual cure behaviour in this series of IPNs. The top DSC curve in Fig. 17 shows the interfering effects of BA on the VER/MEKP cure — the first curing exotherm peak at 89°C has a heat of polymerisation of only 19 J/g in comparison with the parent resin of VER/MEKP, which exhibits an exotherm peak at 123°C and a heat of polymerisation of 320 J/g (see Table 2). The second peak near 190°C in the VER/MEKP:BA system is consistent with thermal cure of the VER

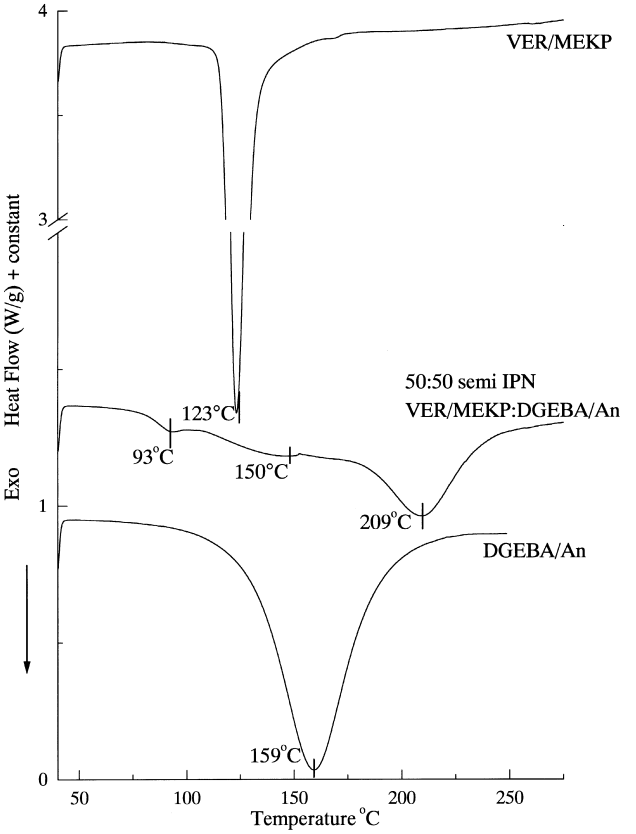


Fig. 15. DSC scans of the 50:50 VER/MEKP:DGEBA/An semi-IPN and the parent resins.

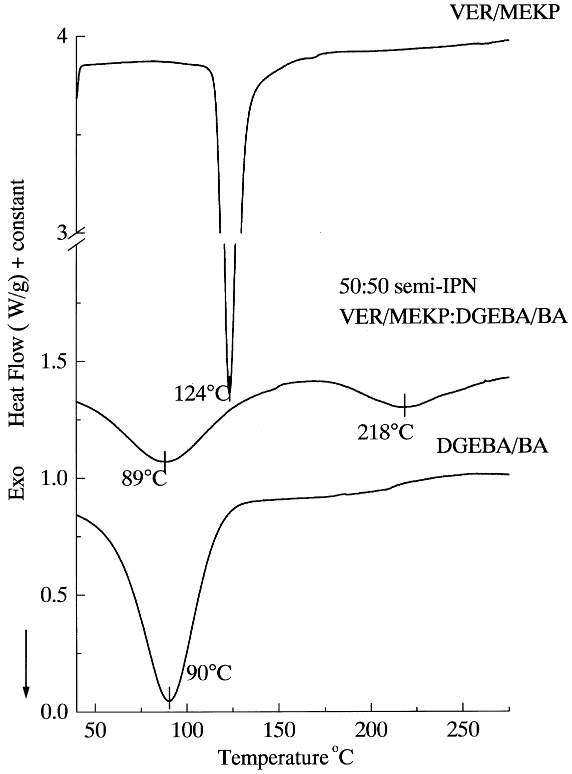


Fig. 16. DSC scans of VER/MEKP:DGEBA/BA and the parent resins.

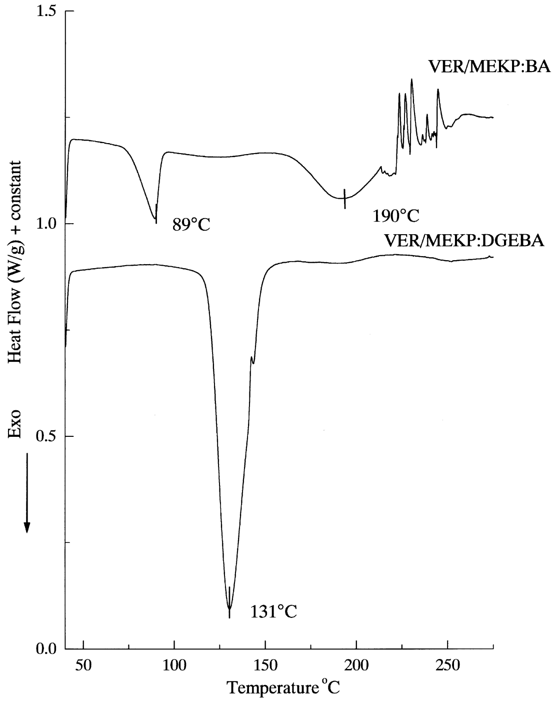


Fig. 17. Variations of the VER/MEKP:DGEBA/BA semi-IPN system — DSC thermograms of VER/MEKP:BA and VER/MEKP:DGEBA.

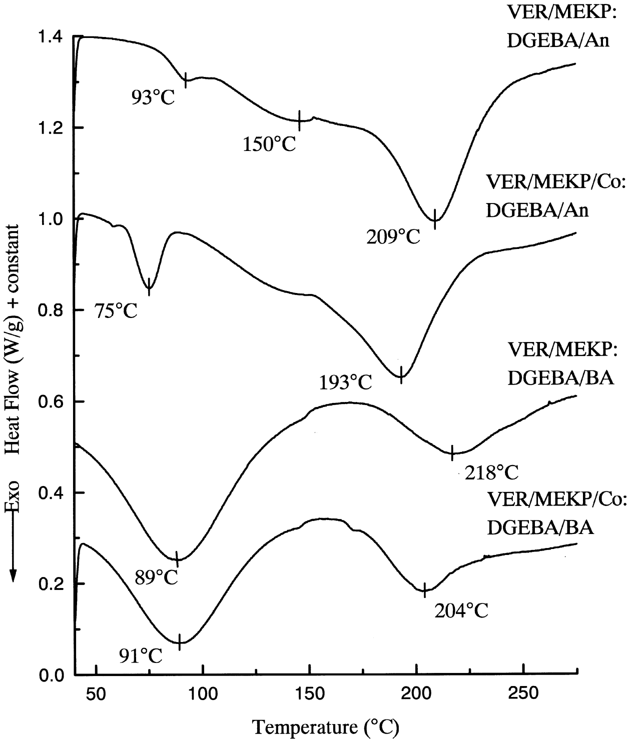


Fig. 18. The effects of cobalt octoate accelerator on the scanning DSC cure of VER/MEKP/Co:DGEBA/An and VER/MEKP/Co:DGEBA/BA.

(cf. Fig. 13). The DSC trace shows considerable noise above 210°C and this may be due to loss of the volatile amine by evaporation. A comparison of Figs. 16 and 17 also reveals the dilutional effect of uncured DGEBA resin on the cure of the VER/MEKP resin — the VER curing peak is shifted from 124°C in the neat resin to 131°C in the DGEBA-diluted resin.

Fig. 18 illustrates the differences between two semi-IPNs cured with and without the presence of the accelerator cobalt octoate. As discussed above and shown in Fig. 15, the VER/MEKP:DGEBA/An semi-IPN exhibits a complicated DSC curve with peaks at 93, 150 and 209°C — when cobalt octoate is included in the system, the small peak at 93°C is magnified and shifted to a lower temperature (75°C), confirming that the production of radicals from MEKP has been enhanced by the redox reaction of cobalt and MEKP. However this peak at 75°C in the VER/MEKP/Co:DGEBA/An system is much smaller (approximately 21 J/g) than is observed for VER/MEKP/Co cure (321 J/g with a peak at 80°C — see Table 2) so that some of the activity of the MEKP must have been lost by interactions with aniline. However the VER/MEKP:DGEBA/BA system showed similar DSC curves with and without Co indicating that much of the MEKP activity was destroyed by side reactions with the amine.

4. Conclusions

The polymerisation behaviour of IPNs formed from radically-initiated vinyl ester resin and amine-cured epoxy has been investigated by temperature-ramping DSC from 30 to 300°C and by isothermal mid-FTIR at a curing temperature of 70°C. Apart from a dilutional (solvent) effect by the other components on the VER cure, the DSC studies showed that IPNs formed with AIBN-initiated VER exhibited the most independent cure behaviour. In contrast, initiation of the VER component by BPO, CHP and MEKP all showed strong interactions between the peroxide and the amine, particularly for aliphatic amine curatives. The cure of the DGEBA resin was less affected by the radical initiator; however, there is evidence that the hydroxy groups of bisGMA may cause acceleration of the epoxy cure by H-bonding catalysis.

More detailed studies of the IPN cure by FTIR showed that the cure rate of one of the components affected the level of cure of the second component. Thus the presence of unreacted components (such as DEGBA or amines) of the epoxy system could plasticise the IPN and enable a higher level of reaction in the VER before vitrification occurred. In addition, if one of the components (such as the VER component) attained a high level of cure early in the formation of the IPN, the high level of crosslinking contributed to premature vitrification, which limited the extent of cure of the other component. None of the curing behaviour could be attributed to the “network interlock” process suggested by Lin and co-workers.[17–19] In most cases, near-complete cure of the IPN components could be attained by post-curing above the T_g of the component networks. No evidence was found for a topological constraint by one network on the full cure of the other component.

Evidence for grafting reactions (presumably by Michael addition) between the amine groups of the epoxy-amine system and the methacrylate groups of the VER was demonstrated by FTIR.

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