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Photo-DSC cure kinetics of vinyl ester resins. I. Influence of temperature

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Abstract

Isothermal DSC was employed to monitor the photopolymerization kinetics of a commercial vinyl ester resin (VER) photoinitiated by the camphorquinone/amine photoinitiator system. The maximum rate of photopolymerization was found to increase tenfold as the isothermal cure temperature was varied from −30 to 90 °C due to faster propagation and greater initiator efficiency counterbalanced by a faster termination rate. After photopolymerization, the samples were temperature ramped in the DSC to monitor the dark polymerization reaction. The reduced polymerization rate increased with the scan temperature due to an increase in propagation rate. The summation of the isothermal and residual polymerization heats indicated that the final degree of cure after postcure was independent of the isothermal cure temperature. The onset temperatures for the recommencement of cure during the dark temperature scanning experiments were found to correspond closely with their respective isothermal cure temperatures as expected due to vitrification during the isothermal cure stage. © 2002 Published by Elsevier Science Ltd.

Keywords: Vinyl ester resin; Photopolymerization; Cure kinetics

1. Introduction

A vinyl ester resin (VER) typically consists of a bisphenol-A based dimethacrylate oligomer with styrene as a reactive diluent [1] and is commonly used as the matrix for large, high performance glass reinforced composites processed, for example, by the vacuum bag resin infusion technique. Conventionally, the resin is cured using thermal- or redox-activated peroxide initiators and so it is necessary to mix the initiator into the resin just before use to avoid premature cure. A more desirable curing process would utilize an adaptable 'cure-on-demand' system, where the resin is not initiated until it is required. Photopolymerization presents itself as one such curing system that allows a resin to be formulated with photoinitiator and yet remain stable as long as it is stored in the dark. Once the fibres are wetted by the formulated resin, the material can be irradiated when required thus decomposing the initiator to radicals and initiating the cure. A number of works [2–5] have discussed the potential of photocured VERs for composite applications, but as yet there has been no in-depth study into the kinetics of this process.

Photopolymerization can be an energy efficient process as the cure can proceed at room temperature. However, the temperature at which the cure occurs can have an impact on the kinetics of the cure and the final level of cure [6–8]. Additionally, heat is released during the exothermic polymerization process and so for thick mouldings the resin temperature may rise during cure. As a result, it is important to study the effect of temperature on the photopolymerization kinetics.

Photopolymerized dimethacrylate resins have been used in the coating and dental materials industries for many years and several studies [6–10] have examined the effect of temperature on the isothermal curing kinetics. At the start of irradiation of the resin, the rate of polymerization is typically low but it quickly rises to a maximum and then decreases. One of the present authors [6] found that for several isothermally photocured dimethacrylate resins, the conversion was reduced at low curing temperatures due to vitrification of the resin during cure. As the temperature was raised the conversion rose due to the enhanced molecular mobility which allowed the reaction to continue, however, a conversion maximum was exhibited at the highest temperatures, possibly due to depolymerization or decomposition of the polymer. Similar results were obtained by other workers [7].

Cook [6,9] and Young and Bowman [8] found that the maximum rate of cure for photopolymerized dimethacrylates also increased with raised temperature due to an

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increase in the propagation rate. Cook [6,9] found that the maximum rate of cure occurred at higher levels of conversion when the cure temperature was raised and modelling of the kinetics indicated that this was due to diffusion effects on the termination step [6] or due to the change in initiation efficiency as the network developed [9]. Young and Bowman [8] also found that the conversion at the maximum rate increased as the isothermal cure temperature was raised but explained this in terms of diffusion control of the propagation rate constant, arguing that the increased mobility of the system at higher temperatures delays the stage at which propagation becomes diffusion limited.

Less research has been undertaken in the more complicated area of polymerization of VERs, where the polymerization of two species (styrene monomer and methacrylate groups on either unattached or pendant oligomers) may add to the complexity of the kinetics. In particular, there do not appear to be any detailed examples in the literature of the effect of temperature, styrene concentration, radiation intensity or initiator on the photopolymerization kinetics of VER systems. In the present study, the effect of temperature on the kinetics of photopolymerization of VERs has been investigated using photocalorimetry—studies on the effects of monomer concentration, radiation intensity and initiator type and concentration will be reported in later papers.

2. Experimental

The photoinitiator, (±)-camphorquinone (CQ, Sigma Aldrich Pty Ltd), and photoreducer, *N*,*N*,3,5-tetramethyl aniline (TMA, Sigma Aldrich Pty Ltd) were used at a level of 0.25 and 0.30 wt%, respectively, as a visible photoinitiator system (Fig. 1). The commercial VER was Derakane 470-300 (Dow Chemical Ltd), a novolac epoxy based VER. This resin system has been characterized elsewhere [11].

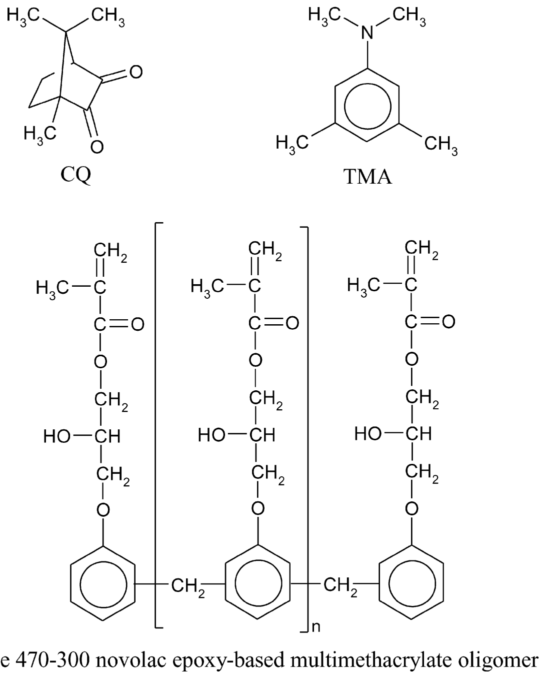

Fig. 1. Chemical structures of CQ, TMA and the constituent methacrylate oligomer of Derakane 470-300.

The isothermal photopolymerization (at temperatures ranging from −30 to 90 °C) and temperature-ramping cure of the resins was performed with a differential scanning calorimeter (Perkin Elmer DSC-7 and Intracooler). Indium and zinc standards were used to calibrate the temperature and enthalpy. The upper isothermal temperature limit of 90 °C was imposed by the excessive loss of styrene by evaporation at higher temperatures while the lower limit of −30 °C was dictated by the inability of the modified DSC to maintain control below this temperature during photopolymerization experiments. At −30 °C, there was no evidence of phase separation into styrene-rich and poor regions.

For isothermal photopolymerization studies, the DSC was modified [12] to allow uniform illumination of both the sample and reference pans. A PMMA block, with holes located directly above the DSC pan holders, was used in place of the standard DSC cover. Radiation from a Visilux-2 visible light curing unit (3 M), described elsewhere [12,13], was directed into a bifurcated glass fibre-optic light guide (7 mm diameter entry window, 5 mm diameter exit windows), the legs of which were fitted into the holes in the PMMA block. The irradiation time was controlled by a shutter between the curing unit and the light guide. Fine aluminium rings were placed on the ledge in each sample pan holder and 0.05 mm thick PET covers with two vent holes were allowed to rest on the rings to minimize thermal non-equilibrium and drafts which would normally cause thermal noise and an unstable baseline in the absence of the normal platinum covers. The relative radiation intensity was set at a nominal value of 1.0.

A typical DSC sample weight was 10 mg. PET coverslips (6 mm diameter) were placed over the DSC sample pans to minimize styrene loss due to evaporation during the experiment. After loading the sample in the DSC, N_2 (20 cm^3/min) was passed through the sample chamber for ~2 min to displace the air. No induction period due to O_2 inhibition was observed during photo-irradiation of the samples. The thermal imbalance in the DSC created by unequal absorption of the infrared component of the Visilux-2 light source by the sample and reference pans was corrected by repeating the illumination of the cured sample in a second isothermal DSC run and subtracting the data from the first run. Subsequent polymerization was not observed during the repeated illumination, confirming that the resins were fully vitrified at the isothermal cure temperature.

After each isothermal cure was complete, the temperature of the DSC cell was maintained while the PET covers,

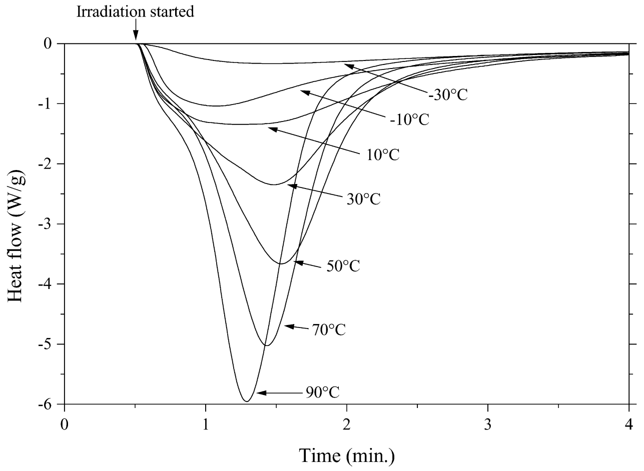

Fig. 2. Isothermal DSC traces of Derakane 470-300 cured at various temperatures (as shown) and a relative intensity of 1.0.

Table 1
Summary of results from isothermal photo-DSC and subsequent temperature scanning DSC of Derakane 470-300 resins cured at various temperatures

Temperature (°C)	Isothermal ΔH_p (J/g)	Isothermal conversion (%)	Residual ΔH_p (J/g)	Total conversion (%)
90	290	89	15	93
80	282	86	21	93
70	284	87	28	95
60	273	83	33	93
50	269	82	40	94
40	266	81	53	97
30	236	72	60	90
20	196	60	61	79
10	181	55	86	82
0	151	46	133	88
− 10	135	41	166	92
− 20	98	30	196	90
− 30	71	22	–	–

aluminium rings and PET coverslips were quickly removed and replaced with the normal vented platinum sample holder covers. The sample was then scanned from a minimum of 5 °C below the isothermal curing temperature up to 220 °C, at a rate of 5 °C/min, to determine the residual heat of polymerization due to dark polymerization.

The theoretical heat of polymerization (ΔH_p) of the Derakane 470-300 was calculated by addition of the fractional amounts of heat evolved by each component, using a ΔH_p for styrene [14] of 67.4 kJ/mol and a ΔH_p for a methacrylate of 54.4 kJ/mol (based on the ΔH_p for methyl methacrylate [15] since methacrylates generally have similar ΔH_p values [16]). The fractional conversion of monomer to polymer was estimated by dividing the measured heat evolved by the theoretical heat of polymerization (ΔH_p) of the Derakane 470-300.

3. Results and discussion

3.1. *Effect of photopolymerization temperature*

Isothermal photopolymerization experiments were performed with Derakane 470-300 at different temperatures ranging from −30 to 90 °C (Fig. 2; Table 1). Fig. 2 shows that the time taken to reach the exotherm peak is essentially independent of the isothermal curing temperature and that the maximum rate of cure only increases tenfold even though the cure temperature is raised by more than 100 °C. For a peroxide initiated polymerization, the polymerization rate would be expected to change more markedly with variations in temperature due to its effect on the rate of decomposition of the initiator. The rate of decomposition of a photoinitiator, however, is not dependent on the temperature. The rate of photopolymerization can be expressed by the equation [17]

$$-\frac{d[M]}{dt} = k_p[M][R\cdot] = \left(\frac{fk_p^2}{k_t}\right)^{1/2}(\Phi I_{abs})^{1/2}[M] \qquad (1)$$

where [M] and [R·] are the monomer and active radical concentrations, k_p and k_t are the propagation and termination rate constants, f is the initiation efficiency, Φ is the quantum yield and I_{abs} is the absorbed radiation intensity. It is generally accepted that f, k_p and k_t vary with molecular mobility and so are dependent on temperature and, in particular, on conversion [9,18–25]. The initiator efficiency is constant at low conversions, but decreases when the segmental mobility of the medium decreases, because this prevents the initiator radicals from escaping the surrounding solvent cage [9,22–24]. The termination constant varies throughout the entire reaction conversion [9,18–21,25] due to changes in the dominant diffusion mechanism—at low conversions k_t is controlled by segmental and translational diffusion and so decreases rapidly with conversion. Segmental diffusion involves the motion of only a segment of a polymer chain whereas translational chain diffusion involves the movement of the entire polymer chain. At higher conversions the diffusion of radicals occurs by the successive addition of monomer units (reaction diffusion) and so k_t becomes proportional to the rate of propagation and so is relatively constant [9,18–21,25]. The propagation rate rises with increased temperature but is independent of conversion unless the material starts to vitrify as the cure proceeds [25,26]. Since Φ and I_{abs} in Eq. (1) are constant, the variation of the polymerization rate with temperature is only dependent on the ratio $(fk_p^2/k_t)^{1/2}$. If, for the moment, one puts aside any temperature dependence of the initiator efficiency (f) and accepts that at low conversions the activation energy for termination is nearly zero [17], the overall activation energy should be close to that for

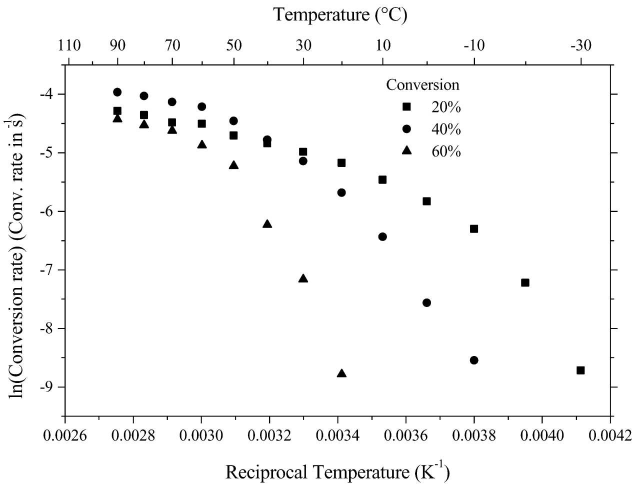

Fig. 3. Natural logarithm of the conversion rate (in s^{-1}) versus reciprocal temperature for photocured Derakane 470-300 at various conversions.

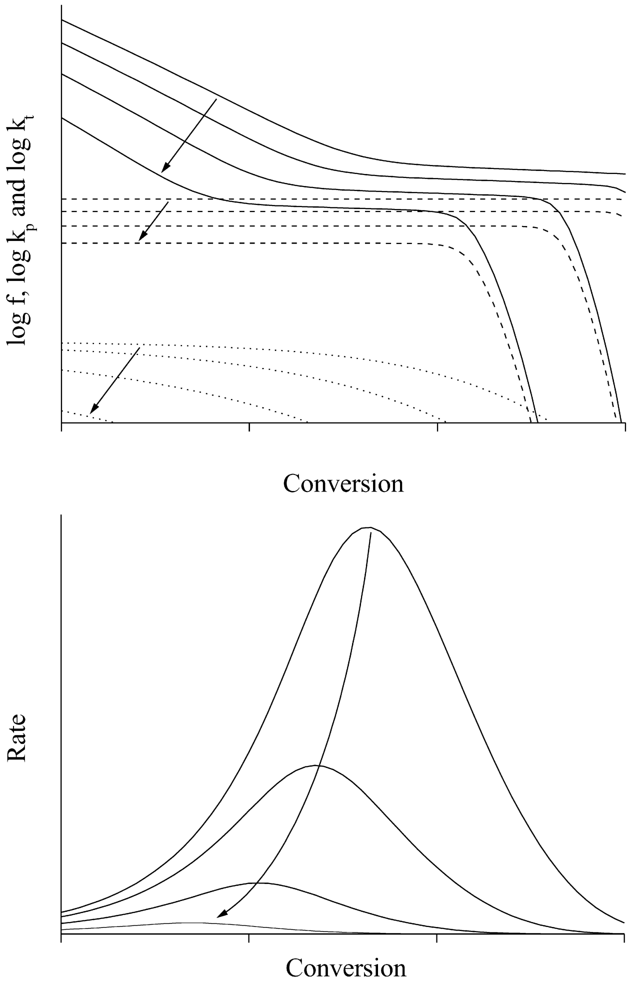

Fig. 4. Schematic diagrams of the initiator efficiency (f) (dotted line), the propagation rate constant (k_p) (dashed line), the termination rate constant (k_t) (solid line) and the reaction rate as a function of conversion at four equidistant temperatures, based on the model presented by Cook [9]. Decreased temperature is as indicated by the arrows.

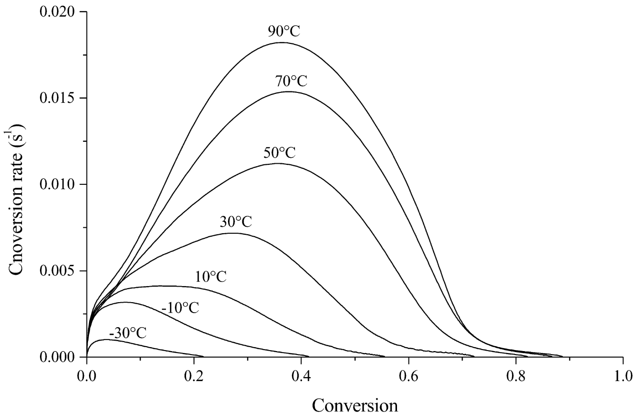

Fig. 5. Rate versus conversion for Derakane 470-300 photocured at various temperatures (as shown) and a relative intensity of 1.0.

propagation (between 22 kJ/mol for MMA [27] and 33 kJ/mol for styrene [27]). At higher conversions, where termination is controlled by reaction diffusion, k_t is proportional to k_p[M] [19,28] and so the overall rate is proportional to $k_p^{1/2}$ which would predict an activation energy between 11 kJ/mol for MMA [27] and 16.5 kJ/mol for styrene [27]. Arrhenius plots of the rate data are shown in Fig. 3 for Derakane 470-300 and are not in full agreement with these predictions. Although the activation energy at high temperatures is of the order of 12 kJ/mol, which is close to these simple predictions, the Arrhenius plot is curved, especially at low temperatures. This may be due to a non-chemical dependency of the rate constants such as would be found if the propagation or termination steps were diffusion controlled [6,9]. Alternatively this may result from the non-Arrhenius temperature dependence of the initiation efficiency associated with the rate of diffusion of the radicals from the solvent cage [9,22–24]. In both of these cases, as the temperature and molecular mobility drops, the rate of reaction becomes markedly slower than that predicted by the Arrhenius equation. These effects have been modelled by Cook [9] and are shown schematically in Fig. 4.

Fig. 5 shows that the maximum cure rate of the VER occurs at lower conversion as isothermal cure temperature decreases and similar behaviour has been observed in the photocuring of neat dimethacrylates [6,8,9]. Chemico-diffusion modelling of the polymerization kinetics [6,9], schematically illustrated in Fig. 4, has also predicted this behaviour. The shift in the conversion at the maximum rate appears to occur partly because the change in dominant termination mechanism (from segmental/translational chain diffusion to reaction diffusion) occurs at lower conversions when the temperature is reduced [6,9] and partly because the initiation efficiency drops rapidly as the temperature is lowered [9] as noted above.

Figs. 5 and 6 show that raising the isothermal cure temperature also results in increased heat evolution, as has been found in other thermosetting systems [6,9,29–32]. In the early stages of isothermal cure, the molecules increase in size, branch, crosslink and then form a gel, reducing the

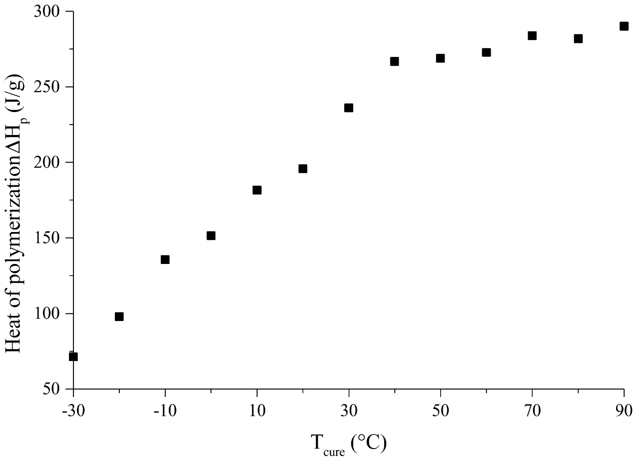

Fig. 6. Heat of polymerization versus isothermal photocure temperature for Derakane 470-300.

mobility of the molecular segments and raising the glass transition temperature (T_g). Once the T_g of the material exceeds the isothermal curing temperature, the material vitrifies, freezing in the mobility of the reactive vinyl groups and radicals and preventing further reaction [6,29]. When the material is isothermally cured at a low temperature, the material will vitrify at an early stage in the reaction, releasing a small amount of heat. As the isothermal cure temperature is raised, the reaction is able to proceed further before vitrification occurs, thereby producing a greater heat of polymerization as observed in Fig. 6.

Fig. 7 shows the DSC ramps after isothermal cure (Fig. 6). When the sample is cooled to a low temperature after the isothermal photopolymerization and then temperature ramped in the dark in a temperature-scanning DSC experiment, the material will initially be in the glassy state and therefore not capable of reacting until the scanning temperature is in the vicinity of the glass transition temperature of the partially cured resin [29,30,32,33]. As the temperature is increased further, the molecular segments will become more mobile, allowing the chain radicals to reinitiate polymerization.[1] As a result, the rate of polymerization rises and an exothermic peak is shown in the DSC due to the dark polymerization (Fig. 7). Thus, the heat of polymerization during the temperature ramp should increase for samples that were isothermally cured at a lower temperature because these samples had been previously cured to a lower extent and this is shown in Fig. 7 and Table 1.

Fig. 7 also shows that the maximum rate of polymerization decreases when the prior isothermal cure temperature is higher. This appears to be a consequence of the lower concentration of monomer remaining in the sample after isothermal cure at the higher temperature. As is observed in Fig. 7, the shapes of the temperature-ramped DSC curves for

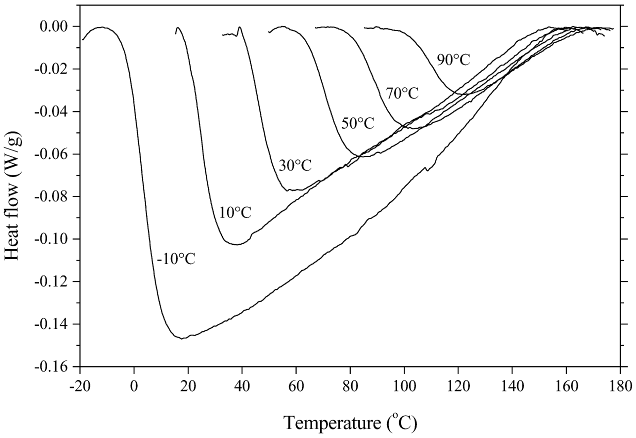

Fig. 7. Postcure scanning DSC traces of Derakane 470-300 which had been previously photocured isothermally at the temperatures indicated.

each isothermal curing temperature are similar. Since the heat flow is proportional to the reaction rate and the residual heat is proportional to the monomer concentration, the DSC trace is a measure of the polymerization rate $k_p[M][R\cdot]$ (Eq. (1)). Thus the similarity of the DSC traces in the temperature ramped (dark reaction) stage is expected because at each temperature (after the re-initiation of the reaction) both the residual monomer concentration and the rate constant are independent of the original photocuring temperature and the radical concentration should vary with ramping temperature in a similar manner. The quotient of the heat flow and the residual heat is equal to the reduced rate $k_p[R\cdot]$ (Eq. (1)). In each case, the reduced rate rises abruptly from zero as the scanning temperature is raised above the isothermal cure temperature (see Fig. 8) and then slowly rises with temperature, presumably due to the increase in k_p with temperature. Note that no new radicals are being formed by decomposition of initiator during the temperature ramp because no thermally sensitive initiator is present. It is interesting to note that after the initial rise, the reduced rate curves overlap with one another, indicating that $k_p[R\cdot]$ is independent of the initial isothermal curing temperature. Since k_p only depends on temperature, the common trend in reduced rate, shown by the systems in Fig. 8, suggests that the concentration of active radicals (as distinct from trapped radicals) is the same in each system.

Table 1 reveals that summation of the isothermal photocure exotherm with the corresponding temperature ramping residual exotherm tends to produce approximately the same overall heat of polymerization and a similar total conversion (average 90%) for all isothermal curing temperatures. This suggests that the topological limit is independent of cure temperature. This conclusion supports findings by Ziaee and Palmese [34] that the final conversion of both methacrylate and vinyl double bonds after postcure was the same in samples which had previously been cured isothermally at either 30 or 90 °C. The constancy of the final conversion also indicates that the radicals frozen in the vitrified matrix during isothermal cure were able

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[1] Unpublished ESR studies show that there is no evidence of peroxy radicals arising from dissolved O_2, but styryl and methacrylyl radicals are observed.

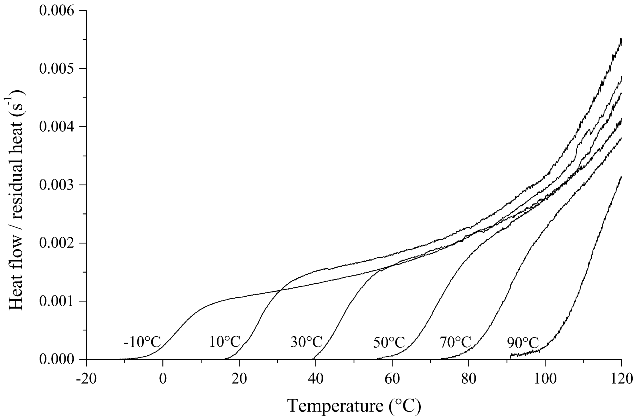

Fig. 8. Reduced rate, calculated from heat flow divided by the residual heat, during temperature ramping DSC measurements of Derakane 470-300 which had been previously photocured isothermally at the temperatures indicated.

to complete the curing reaction for all isothermal curing temperatures.

The temperature at which the polymerization recommences (Fig. 9), denoted here as the onset temperature (T_{onset}), increases when the isothermal cure temperature (T_{cure}) is raised. As discussed above, the T_g of the isothermally photocured polymers should be closely related to the isothermal curing temperature, T_{cure} (provided the isothermal curing temperature does not exceed the maximally attainable T_g of the resin) because the resin had vitrified during the isothermal photocuring experiment. In turn, during the subsequent temperature-ramping experiment, T_{onset} should correspond closely to this T_g because once devitrification occurs, the polymerization is free to recommence [29,30,32,33]. As a result, a 1:1 correlation between T_{onset} and T_{cure} is observed as shown in Fig. 9. The difference between T_{onset} and T_{cure} for Derakane 470-300 is approximately 4 °C, and similar observations have been reported in previous studies for vinyl ester [29] and epoxy [30,32] resins.

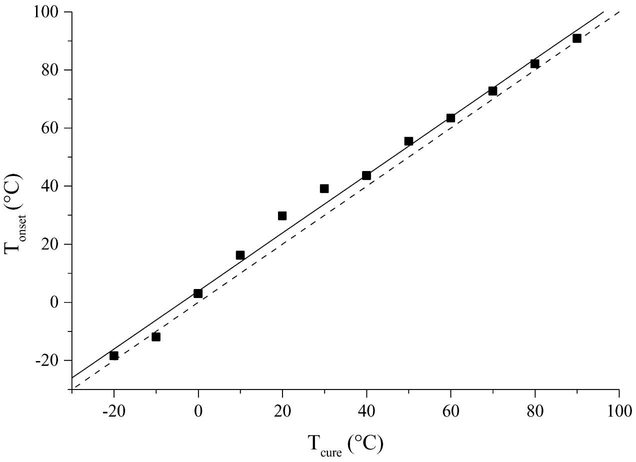

Fig. 9. T_{onset} versus T_{cure} for photocured Derakane 470-300. The dashed line shows a one-to-one relationship.

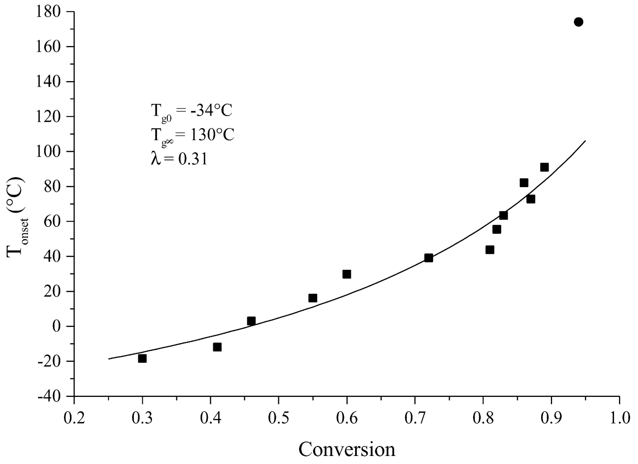

Fig. 10. T_{onset} versus conversion for photocured Derakane 470-300. The circle is a data point for the fully cured material taken from Ref. [11].

Fig. 10 shows T_{onset} versus conversion for Derakane 470-300. Since T_{onset} is closely related to T_g, the onset temperature rises with increasing conversion due to the more extensive crosslinking and the loss of plasticizing species. Several studies have investigated the glass transition temperature of a thermosetting resin as a function of conversion [29,30,32,35,36] and have generally found that the T_g increases more rapidly with conversion at higher levels of conversion as is observed in Fig. 10. Pascault and Williams [35] have proposed a semi-empirical equation to describe this behaviour, as given by the expression

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \qquad (2)$$

where x is the conversion, T_g is the glass transition temperature at conversion x, T_{g0} and $T_{g\infty}$ are the T_gs of the uncured and fully cured resin, respectively, and λ is the ratio of the heat capacity step (ΔC_p) of the fully cured and uncured resin. The fit of Eq. (2) to the experimental data (but omitting the data point for the fully cured resin) is shown in Fig. 10. The fitted values of T_{g0} and λ are reasonable, however, the value of $T_{g\infty}$ is 44 °C lower than that found experimentally [11]. This may be explained by compositional drift during the copolymerization of the VER. At low conversions, the styrene and methacrylate groups enter into the copolymer at similar rates [11,37,38] but at high conversions the mobility of the methacrylate is reduced and so the styrene is more readily incorporated into the network. This styrene has a much greater plasticizing effect on the network and so its consumption causes a marked increase in T_g. As a result, the T_g rises with conversion much faster than predicted towards the end of the polymerization.

4. Conclusions

As part of a larger study of the photocuring of glass fibre reinforced composites, isothermal DSC was used to investigate the photopolymerization kinetics of a commercial VER employing the camphorquinone/amine redox pair as the photoinitiator system.

The rate of photopolymerization of Derakane 470-300 increased tenfold as the isothermal cure temperature was varied from −30 to 90 °C but did not obey the Arrhenius relation. The maximum in the cure rate occurred at lower conversions as the isothermal cure temperature decreased and this may occur because the transition from segmental/chain diffusion to reaction diffusion occurs at lower conversions at lower temperatures and/or because the initiation efficiency drops more rapidly as the temperature is lowered. The extent of cure increased as the temperature was raised due to a delay in vitrification of the resin. After cessation of the isothermal photopolymerization, the samples were temperature ramped in the DSC and the reduced rate was found to be independent of the prior isothermal cure temperature, suggesting that the radical concentrations were equal. Summation of the isothermal and residual polymerization heats indicated that the final degree of cure after postcure was independent of the isothermal cure temperature.

A linear relationship was observed between the isothermal curing temperature and the onset temperature for recommencement of cure. This correlation occurred because cure was stopped by vitrification at the isothermal cure temperature and recommenced when the temperature was ramped above the isothermal temperature. The variation of the onset temperature (which is approximately equal to the T_g) was determined as a function of conversion.

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