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Charge recombination luminescence from epoxy resins
Part. 1. Correlation of luminescence with cure

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Abstract

The initial intensity of charge recombination luminescence (CRL) emitted by epoxy resins after brief periods of UV irradiation during cure has been measured for a number of resins as a function of cure time. The results are correlated with measurements of extent of reaction of the epoxy groups, using near-IR spectroscopy, and with rheological measurements. They show that the intensity of emission is directly related to the fractional conversion of the epoxy groups, irrespective of the cure temperature, but that the emission only occurs when the conversion is high enough for the resin to be glassy. Attempts to increase the emission by adding aromatic amines failed. It is proposed that, for CRL to be observed, the resin must contain enough OH groups to stabilise the electron traps by solvation and be vitreous enough to prevent immediate recombination of electron–cation pairs. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Luminescence; Cure monitoring

1. Introduction

The range of properties that can be obtained from different combinations of epoxy resins and hardeners has led to many applications in coatings, adhesives, laminates, and fibre-reinforced composites [1].

In composite manufacture, the resin, hardener and accelerator initially form a viscous liquid and are usually incorporated with the fibre into a pre-impregnated form (known as ‘prepreg’), ready for processing [2]. The prepreg is ‘laid up’ to form the desired shape and is subjected to a cycle of heat, vacuum and pressure. This first causes removal of air and water from the laminate, then consolidation, and finally cure [3,4]. During cure the resin passes from the liquid state though its gel point, where it is transformed into a rubber, then through the vitrification point, at which it is converted into a glass. The timing of the vacuum/pressure schedule is critical to the properties of the finished material. If the point of application of pressure is not correct, there may be exudation of resin or areas of delamination or void formation which will dramatically reduce the performance of the finished material.

Various in-situ monitoring techniques are used to follow the cure of resins in composites. One of the most widely used is frequency dependent electromagnetic sensing (FDEMS) [5] (also called microdielectrometry). This is based on the fact that the impedance of a capacitor with the resin as dielectric can be represented by an equivalent parallel capacitance and conductance. It is found that both conductance (ion mobility) and the dipolar relaxation time are sensitive to cure and it is possible to correlate changes with the viscosity of the resin, and hence monitor the cure [6–8]. It is also possible to find the T_g, [5,9,10] The sensor consists of interdigitated comb electrodes embedded in the resin and left in the final structure.

Although dielectric monitoring is widely used, It has some disadvantages. In particular, the very sensitive electronics suffer from interference due to the electrical noise of the industrial environment, and the sensors remain in the fully cured product where they may act as crack initiation sites. To overcome these problems, a remote technique is desirable and methods based on optical and acoustic measurements have been reported see e.g. Refs. [11–13].

In previous work [14], we reported that a short period of near-UV irradiation of a curing resin results in luminescence. The emission is barely measurable at early cure times, but increases in both intensity and lifetime as the cure proceeds, with a very sharp rise at a time dependent on the cure temperature and stoichiometry. The phenomenon is observed even in nitrogen, and we attributed it to

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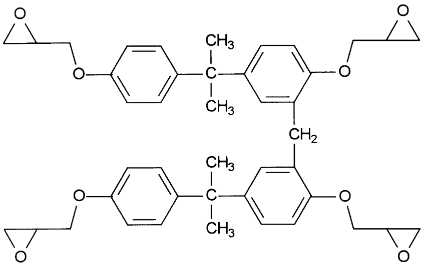
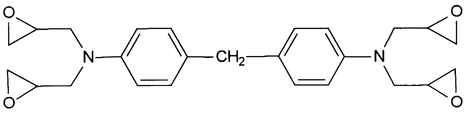
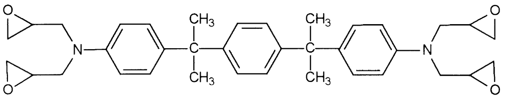
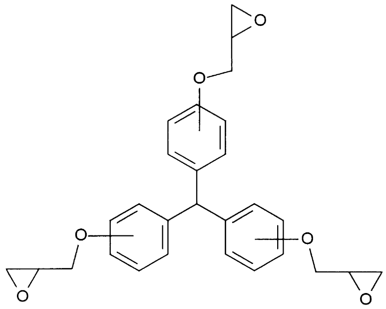
Table 1
Structures of epoxy resins used in this work

Resin structure	Trade name
	Shell 1153
	Ciba MY721
	Shell 1071
	Dow XD7342

electron–ion recombination (charge recombination luminescence, CRL), on the basis of a number of diagnostic experiments. Since the CRL measurement involves broadband irradiation and detection, the method is cheaper and simpler than fluorescence methods.

In principle, measuring the CRL from a curing epoxy is an attractive possibility for remote cure monitoring by non-invasive methods. However, it is first necessary to establish how it correlates with cure and with the mechanical properties. In this article we report studies of a number of resin/hardener systems. We have characterised the cure using DSC, FTIR and torsion rheometry. Cure and CRL data are compared, to relate the changes in luminescence activity to the physical changes during cure.

2. Experimental

The epoxy resins used were all commercial grades. The structures and some relevant properties are given in Table 1. Epoxy concentrations were determined by titration with perchloric acid in glacial acetic acid solution [15]. Although all of the resins are known to contain impurities, they were used as supplied since the aim was to study commercial systems. They are all pale brown, and are either highly viscous liquids or glasses at room temperature.

The hardener in all cases was 4,4′-diaminodiphenylsulfone (DDS). It was reagent grade, obtained from Aldrich Chemical Co.

In typical experiments the resin and hardener were mixed at the stoichiometric ratio. The DDS was stirred into the resin as thoroughly as possible at room temperature before heating to 120°C (high enough to allow easy mixing, without significant cure) for a further 10 min of vigorous stirring to produce an opaque (indicating that the DDS had not dissolved in the resin), very pale yellow product. The material was stored in a sealed container at 5°C. It was allowed to warm to room temperature before opening, to prevent moisture condensation.

Aromatic amines assessed as viscosity-sensitive dopants were all supplied by Aldrich. The dopants tested were triphenylamine (TPA), *N*-phenylcarbazole (N-PC), *N*,*N*,*N*′,*N*′-tetraphenylenediamine (TMPD), *N*,*N*-dimethyl-*p*-toluidine (DMT), 4,4′-Methylenebis(*N*,*N*-dimethylaniline) (MBDA), and 4,4′,4″-Methylenetris(*N*,*N*-dimethylaniline) (Leuco Crystal Violet (LCV)).

The dopant denoted ‘Shell/DPA’ was synthesised with the aim of forming a compound of high viscosity sensitivity. It was produced by mixing diphenylamine in a 4:1 stoichiometric ratio with the resin Shell 1071, and heating to 180°C for 90 min to produce a brown oil. The product is a model of the epoxy network, without cross-linking.

DSC measurements were carried out in standard aluminium pans using a Perkin–Elmer DSC7, calibrated with indium and zinc standards. A modified sample chamber cover, with enlarged exhaust ports was used to allow the escape of volatiles during cure. Most of the DSC work involved three scans per sample (5–10 mg), using an empty pan as reference, and nitrogen as purge gas. First, an isothermal cure was performed, typically at 160–190°C for 60–90 min. When isothermal cure was complete, indicated by a flat baseline, the DSC was cooled by 20°C. After the instrument had stabilised, the temperature was raised, usually at 10–20°C min^{-1}, to 315°C (this temperature was chosen as it allowed the resin to reach full cure without significant decomposition). This temperature scanning run was finally repeated on the fully cured sample to give a baseline for the residual cure. The sum of the enthalpies from the isothermal and post-curing runs was taken as the total enthalpy of cure; extents of cure were calculated as fractions of this value.

For FTIR studies we used a Mettler FP84 HT heat-flux microscope hot stage, with 7 mm sapphire crucibles in conjunction with a Perkin–Elmer 2000 FTIR microscope using an InSb photovoltaic detector cooled to 77 K and a tungsten quartz halogen lamp as the radiation source, as

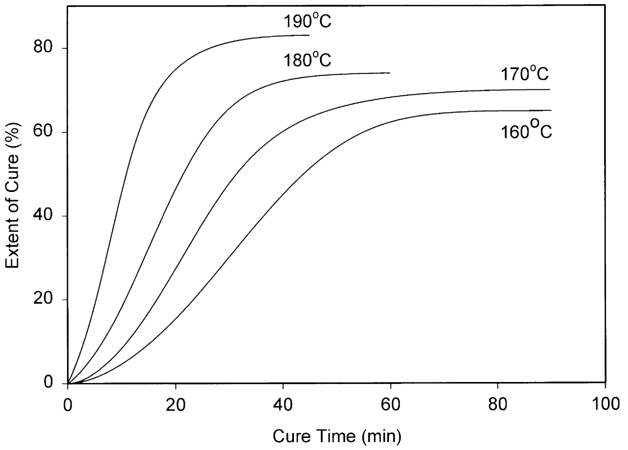


Fig. 1. Extent of cure vs. time curves for MY 721 + 36.1% DDS cured isothermally, as determined by DSC.

described elsewhere [16]. Samples were typically 20 ± 2 mg, giving a 1 mm path length, with nitrogen as purge gas.

After the resin had been placed in the crucible, it was warmed to the minimum possible amount (150°C, ca. 10 s) to allow the DDS to dissolve, before loading along with the reference into the DSC. This was necessary as alignment of the DSC on the microscope stage to optimise the energy of the IR beam required a transparent sample. When the DSC was optically aligned, the sample was heated to its isothermal cure temperature at 20°C min^{-1}. Once this temperature was reached the FTIR microscope program was begun. An average of 100 scans (taking ca. 110 s) in the NIR region (11 000 cm^{-1}–4000 cm^{-1}) was needed to give good spectra, hence they were recorded at 2 min intervals throughout the isothermal cure.

When the cure was complete, spectral accumulation was stopped, and the DSC was cooled by 20°C. As with the regular DSC experiments, the temperature was then scanned to 315°C to allow the remainder of the cure to take place. Concentration profiles for each of the functional groups were extracted from the spectra using a method based on Beer's Law [17–19].

Luminescence measurements were made using equipment designed to allow the sample to be heated, irradiated and monitored automatically. The apparatus consists of a light tight cell with a photomultiplier tube (PMT) (EMI, 9813QB) mounted vertically above a sample platen. Intensity measurement uses single photon counting electronics designed in our laboratory. The platen temperature is controlled to ±0.1°C. A combination of shutters and a mirror allows the sample to be irradiated by light from a 150 W Xe lamp, fitted with a heat filter. Nitrogen was fed through the chamber at about 20 ml min^{-1} to prevent luminescence from oxidation of the resin [20]. An Archimedes 410 computer was used to control the apparatus and to record luminescence and temperature data. Light intensity was measured as a series of data points representing the integrated photon count over consecutive 0.5 s periods. Samples were typically 30–35 mg, contained in standard DSC pans.

Rheometric experiments were conducted using a Polymer Laboratories Torsion Rheometer System (TRS) using parallel aluminium torsion plates. The top plate was smaller in diameter (30 mm), and therefore determined the effective cross-sectional area (707 mm^2) of the sample. For a typical run about 0.5 g of resin was placed between the plates which were set to a gap of 500 μm, with an applied force of 0.5 N. A slow heating rate ($\leq$ 5°C min^{-1}) was used to allow the apparatus to heat uniformly. The most reliable temperature data were recorded separately by using a thermocouple attached to the underside of the lower torsion plate.

The large thermal mass of the TRS made rapid heat-up impossible, the instrument taking about 30 min to attain the required temperature and stabilise. As fast loading of preheated apparatus was not practical, a combined TRS/DSC method was devised for finding the gel point of the resin. The apparatus was set up as normal, but a few DSC pans, each containing 5–10 mg of resin, were placed on the upper side of the top plate, shielded from the direct heat of the oven elements by aluminium foil. The experiment was then conducted as normal, with the TRS set to give tan δ and log G' readings. At the onset of gelation, indicated by a small peak in the tan δ curve, and an extremely rapid increase in the log G' curve, the oven was opened, and the DSC pans removed and quickly cooled. The residual heats of cure were later measured by isothermal DSC at the same temperature. By comparison with curves from uncured resin, it was possible to estimate the conversion at gelation.

In some experiments we also used the chemiluminescence method for monitoring gelation, as described elsewhere [20].

3. Results

Although we have used several resins in this work, the results for all were very similar. For this reason, we mainly present results for the TGDDM/DDS system, with discussion of the others where relevant.

3.1. Resin cure

The simplest method of monitoring resin cure is by isothermal DSC [21], which depends on the assumption that the extent of cure is proportional to the fraction of the total heat of cure evolved at any stage, i.e. that the different reactions taking place at different points during cure have similar enthalpies. For illustration we consider stoichiometric mixtures of TGDDM and DDS, cured isothermally at 160, 170, 180 and 190°C. Fig. 1 shows typical extent of cure vs. time plots derived from partial area analysis of the isothermal DSC data. The total heat of reaction is taken as the sum of that for the isothermal cure and a subsequent ramped experiment to complete reaction.

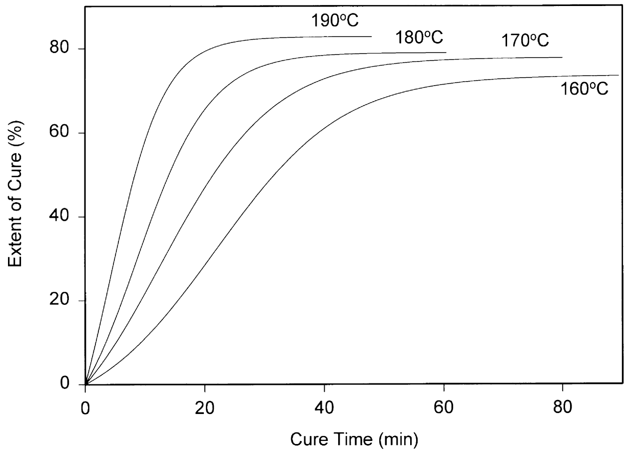


Fig. 2. Extent of cure vs. time curves for MY 721 + 36.1% DDS obtained from the change in epoxy concentration measured by FTIR.

At all temperatures analysed, the isothermal cure showed auto-acceleration in the initial stages, indicated by the slight positive curvature. Barton [21] showed similar auto-acceleration for bisphenol-A diglycidyl ether cured with DDS. Most other resins have their greatest rate of reaction at the beginning of the cure [22,23], as might be expected. It is believed that curing is in part catalysed by OH groups, which are present in considerably lower concentrations in the relatively pure MY 721 than in other resins. Therefore, the point at which the rate of cure is greatest is determined by the balance between increased concentration of catalytically-active products and consumption of reactive groups.

Cure vs. time curves were also generated from the concentration of unreacted epoxy groups measured by FTIR, and these are shown in Fig. 2 for the same resin. The FTIR method should be a more precise indicator of extent of cure than DSC as it directly measures the chemistry taking place, rather than the heat evolved. Fig. 3 shows the correlation of the results from the two methods. It shows that the extent of cure from EP conversion is considerably greater than that from heat evolution for any given cure time.

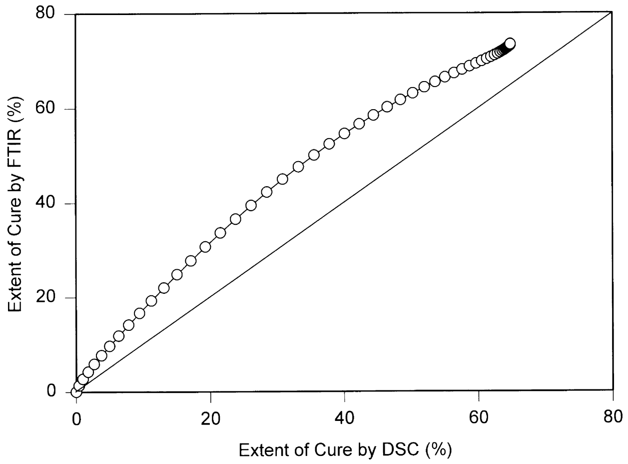


Fig. 3. Plot of extent of cure by heat evolution against extent of cure by epoxide conversion for MY 721 + 36.1% DDS at 160°C. The solid line indicates the function $y = x$.

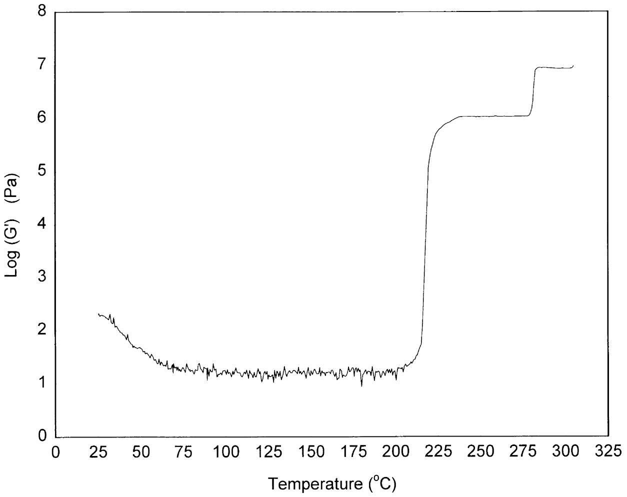


Fig. 4. Change in log G′ of MY 721 + 36.1% DDS cured in a temperature scanning experiment at 5°C min^{-1}.

After an isothermal cure at 160°C about 73% of the EP groups have been converted, but only about 65% of the total available heat of cure has been evolved. This must arise from the failure of the assumption that all of the cure reactions have equal enthalpies. We observed this deviation with other resins and associate it with variations in enthalpy for the different components of the cure reaction.

The gel point for a cross-linking system is usually taken as the point at which the storage modulus (G′) and the loss modulus (G″) become equal [24], ($\tan \delta = 1$), with the constraint that the temperature must be above the minimum gel forming temperature, so that vitrification does not precede gelation. For our resin, gelation and vitrification are both very apparent in the plots of G′ and are taken as the onsets of the two large increases which occur during cure. Fig. 4 is a typical plot of $\log G'$ for a 5°C min^{-1} temperature ramping experiment, clearly showing gelation at 223°C and vitrification at 275°C.

In the basic theory of gelation [25], the fractional conversion at gelation (γ_g) is a constant, independent of cure temperature. In principle, it can be calculated from an appropriate DSC measurement on resin at the gel point. However, the validity is limited both due to the failure of the assumption that all of the cure reactions are of the same enthalpy, and to the change in importance of the cure reactions with temperature. Using the combined TR/DSC

Table 2
Fractional conversion at gelation in TGDDM/DDS resin

Cure temperature/°C	γ_g/% (DSC)	γ_g/% (FTIR)	Gel time (min)
160	54 ± 3	66 ± 2	47 ± 3
180	39 ± 1	60 ± 1	17.5 ± 0.5

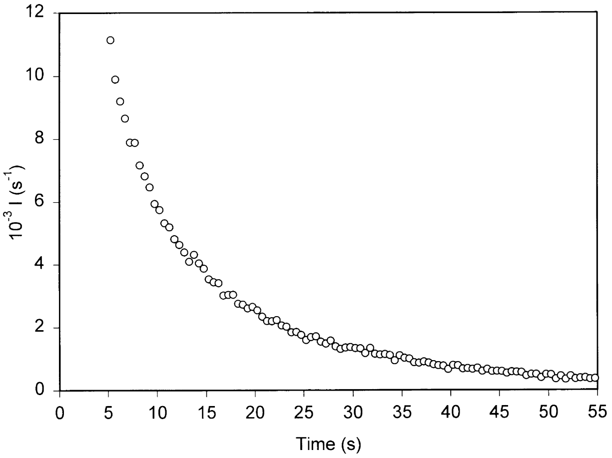


Fig. 5. A typical CRL decay curve for MY 721 + 36% DDS irradiated 30 min into cure at 180°C.

technique we found that the variation of γ_g with cure temperature (Table 2) was considerable.

The variation is much smaller when γ_g is computed from the FTIR data, though it is still significant. As stated above, the TGDDM/DDS system is not ideal and different reactions, particularly ether formation by reaction of hydroxy groups with the epoxy ring, are favoured at higher temperatures meaning that alternative network structures are formed which will have different gel points [17,18].

3.2. CRL from curing resin

3.2.1. The CRL phenomenon

We have previously shown [14] that UV irradiation of an epoxy resin during cure in an inert atmosphere is followed by measurable CRL. The intensity is a maximum immediately after irradiation is stopped, and decays to the pre-irradiation background level over several minutes. A typical decay curve is shown in Fig. 5.

Two properties of the CRL curve are potentially interesting, the initial intensity, I_0, and the decay rate. For the moment, we focus on the value of I_0, since this does not depend on any kinetic model for its interpretation and is the most easily measured parameter.

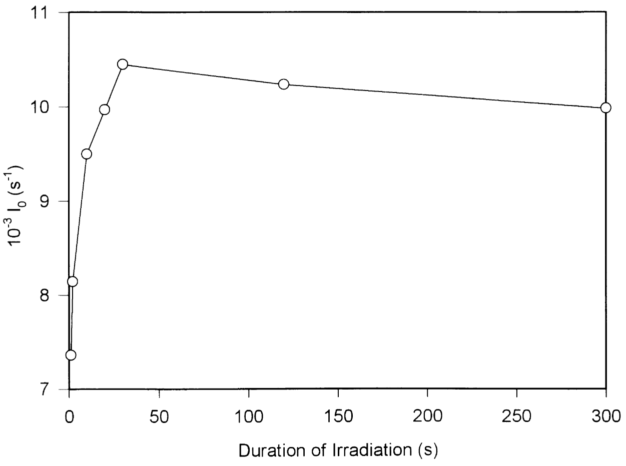


Fig. 6. Variation of I_0 with irradiation time for a sample of MY 721 + 36.1% DDS 45 min into cure at 180°C.

Since I is the photon count integrated over a 0.5 s period, I_0 should be taken as the photon count over the first 0.5 s period after cessation of irradiation. True I_0 values cannot be measured because the emission immediately after irradiation contains a significant, rapidly-decaying, phosphorescence component. We therefore take I_0 as the first measurement, made 5 s after cessation of irradiation (i.e. the integrated count from 5–5.5 s).

CRL is induced because irradiation of the resin produces electron–cation pairs, whose recombination leads to light emission. The concentration of pairs must depend upon the rates of their formation and decay and should achieve a steady state during irradiation. For reproducible results it is important to determine what irradiation time is needed to achieve the steady state. A series of resin samples was therefore cured at 180°C, and each irradiated once. The duration of irradiation was varied and each experiment was carried out so that the first reading was taken at 45 min cure time. Fig. 6 shows that the effect of irradiation time on I_0 is small as long as the irradiation time is more than 30 s. Irradiation times of 1 min were used in this work. At longer irradiation times I_0 decreases by about 3–4% from its maximum value. This is almost within experimental error, though it may be due to damage to the polymer by the large dose of UV.

Since curing samples are subjected to multiple irradiations during experiments, a control experiment was run to determine whether there is any effect of irradiation history on subsequent measurements. Two samples of resin were cured at 180°C—one was irradiated at 5 min intervals for 60 min, as in a typical experiment, and the other was irradiated only once, at 60 min. The values of I_0 for the irradiation at 60 min were found to be identical for the two samples, and so it was concluded that the irradiation history of a curing resin is of no consequence to latter irradiations.

3.2.2. Correlation of CRL intensity with cure

Fig. 7 shows some typical plots of I_0 against cure time, obtained in an experiment in which a resin sample was periodically irradiated during cure in nitrogen. The position of the data points in relation to the time axis represents the point at which irradiation ceased (e.g. if a 1 min irradiation was initiated at 5 min, the data point is plotted at 6 min).

At the beginning of cure, I_0 is close to background and it increases sharply with cure. As the cure temperature is raised, the increase in I_0 occurs sooner, but the maximum intensity is lower. The lower values of I_0 at higher cure temperatures may be due to increased self-absorption in the resin, which darkens more quickly. It may also be due to a lower initial concentration of luminescence producing species, and possibly a lower quantum efficiency for the

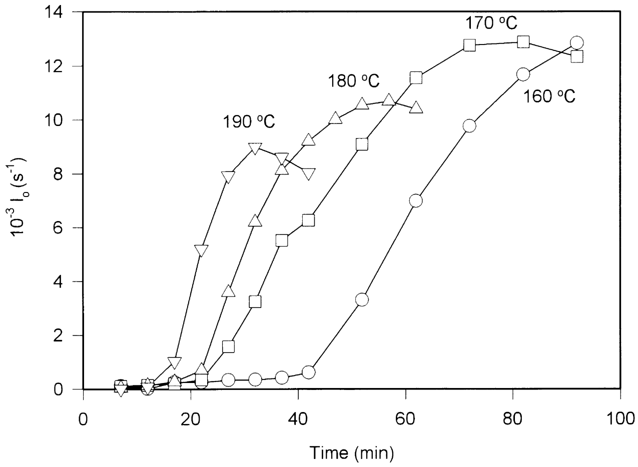


Fig. 7. The variation of I_0 with increasing cure time of MY 721 + 36.1% DDS.

recombination. The darkening is also the reason for the eventual declining of I_0 at extended cure times.

Using cure data, it is possible to convert the I_0 vs. cure time plots (Fig. 7) to plots of I_0 against extent of cure (Figs. 8 and 9). At the same time, gelation and vitrification data from rheometric or chemiluminescence [20] measurements can be superimposed.

Fig. 8 shows the plot of the data in Fig. 7 when the time axis is converted to a conversion axis, using cure data from DSC. It can be seen that the plots become relatively closer together and that the sharp rise in I_0 occurs somewhat after gelation. Therefore this parameter cannot be used as an indicator of the onset of gelation in this system.

In Fig. 9 the same data are plotted using the epoxy group conversion as measured by FTIR as the ordinate. In this case, the data collapse very close to a common curve, again with the sharp rise occurring after gelation. For this system the data do not allow us to distinguish gelation and vitrification completely.

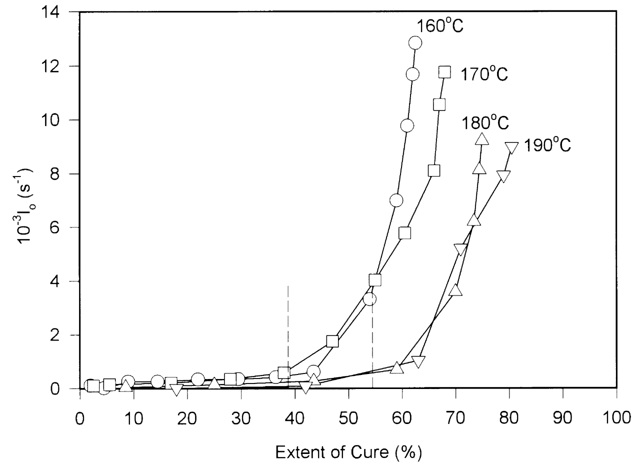


Fig. 8. Plot of I_0 vs. extent of cure by DSC for MY 721 + 36.1% DDS. The vertical dashed lines indicate the conversions measured by DSC at gelation, for cure at 160°C (0.54) and 180°C (0.39), respectively.

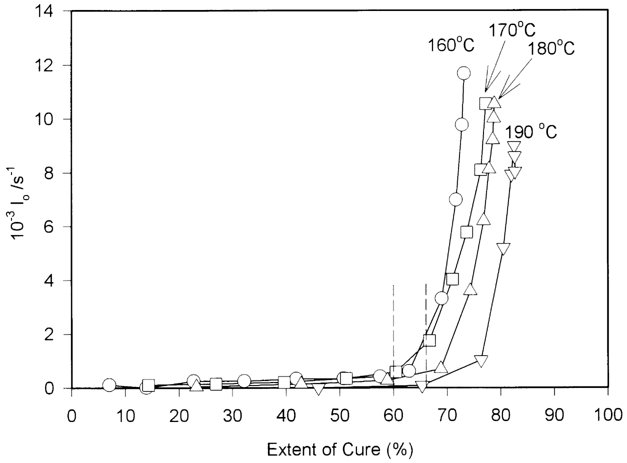


Fig. 9. Plot of I_0 vs. extent of cure by FTIR for MY 721 + 36.1% DDS. The vertical dashed lines indicate the conversions measured at gelation by FTIR, for at 160°C (0.66) and 180°C (0.60), respectively.

Figs. 10 and 11 show similar data for other resins. In all cases the same pattern is observed. When epoxy conversion by FTIR is used as the ordinate, all of the data collapse very close to a common curve, again with the sharp rise occurring after gelation. With 1153 resin it is especially clear that the sharp rise is actually better correlated with vitrification than with gelation. It is noticeable that the maximum values of I_0 are about ten times lower for these two glycidyl ether resins than for the Shell and Ciba glycidyl amine resins.

These results suggest that the appearance of measurable CRL is dependent on a critical EP conversion, as well as upon the physical state of the resin.

3.2.3. Attempted enhancement of CRL

It is believed that the pairs responsible for CRL in UV-irradiated epoxy resins consist of a cationic nitrogen site, with limited mobility in the cured resin, with a photo-ejected electron as the mobile species [19]. If the light

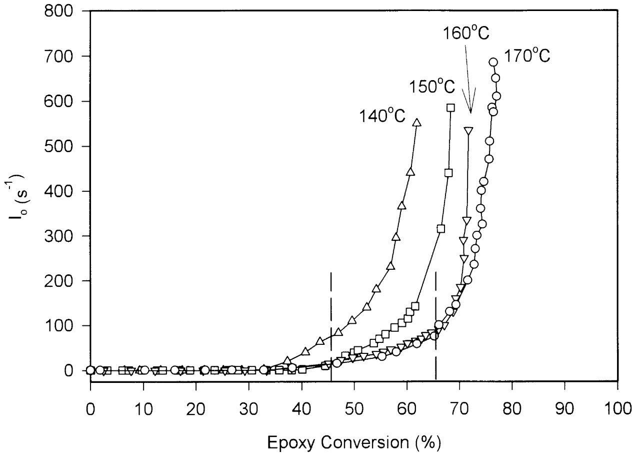


Fig. 10. Plot of I_0 vs. extent of cure by FTIR for Dow resin + DDS. The vertical dashed lines indicate the conversions measured by FTIR at gelation (0.46) and vitrification (0.66) for cure at 160°C.

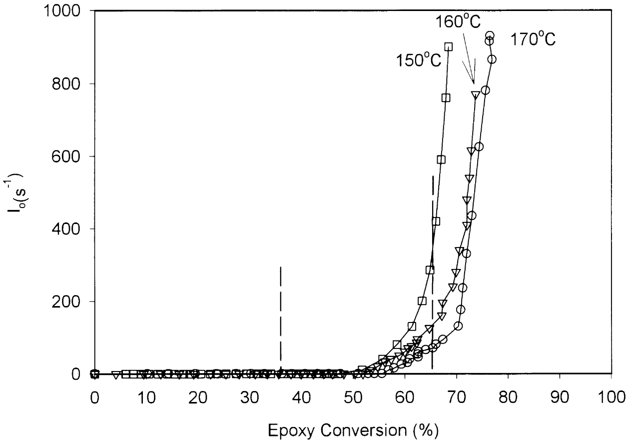


Fig. 11. Plot of I_0 vs. extent of cure by FTIR for Shell 1153 resin + DDS. The vertical dashed lines indicate the conversions measured by FTIR at gelation (0.37) and vitrification (0.65) for cure at 160°C.

emission is related to the concentration of tertiary aromatic amine groups then it may be possible to increase the sensitivity of the measurement and to induce a signal at lower conversions by artificially increasing the concentration of ion pairs by doping the resin before cure with a suitable compound.

Compounds were selected as potential dopants on the basis of mimicry of the fully cured resin structure and resistance to chemical reactions during cure.

The dopants tested were triphenylamine (TPA), *N*-phenylcarbazole (N-PC), N,N,N',N'-tetraphenylenediamine (TMPD), N,N-dimethyl-*p*-toluidine (DMT), 4,4′-Methylenebis(N,N-dimethylaniline) (MBDA), and 4,4′,4″-Methylenetris(N,N-dimethylaniline) (Leuco Crystal Violet (LCV)). The dopant denoted 'Shell/DPA' was synthesised by reacting diphenylamine in a 4:1 stoichiometric ratio with the Shell 1071 resin to produce a high molecular weight species which is a model of the epoxy network, without cross-linking.

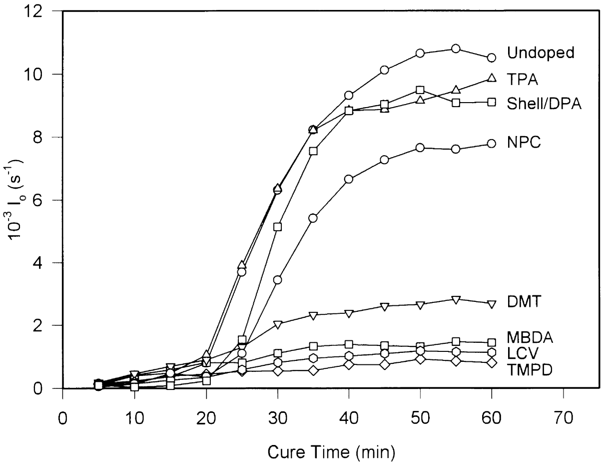


Fig. 12. The effect of dopants on I_0 for MY 721 + 36.1% DDS cured at 180°C.

Each of these molecules was added to the MY721/DDS resin at concentrations of 0.5 wt.%, and cure monitoring carried out at 160 and 180°C. The results were almost identical and the data obtained at 180°C are shown in Fig. 12. At best, the dopants had little effect on I_0, as with TPA and Shell/DPA, and in most cases they acted as a luminescence sink, with dopants such as TMPD,[1] MBDA and LCV completely quenching the CRL.

Although it was not possible to force a useful shift in the rise of the I_0 during cure, the results do give some information. The four dopants (DMT, TMPD, MBDA, LCV) which suppressed the CRL signal considerably all contain relatively unhindered tertiary amine groups bearing only one large substituent and two methyl groups, i.e. of the form $R{-}N(CH_3)_2$. The remaining three dopants, which suppressed the CRL much less, contain more heavily substituted tertiary amine groups. It is notable that the signal for NPC is significantly lower than that for the structurally very similar TPA, but this can be attributed to the fact that the constraints placed on the substituent rings in NPC lead to its central N atom being more exposed. This suggests that only the most sterically shielded tertiary amine atoms in the curing system, i.e. those on the heavily cross-linked parts of the forming network, are stable enough to support the ion pairs produced on irradiation for any length of time. Introduction of inert dopants may interfere with the density and orientation of the matrix and upset this shielding, which may explain the suppression of the CRL signal. Also, since gelation is the point at which an infinite network is first formed, we would expect areas of high cross-link density to appear shortly after this. The fact that I_0 rises shortly after gelation supports this idea.

4. Discussion

It is well known see e.g. Refs. [26,27] that UV irradiation of tertiary aromatic amines trapped in frozen organic glasses leads to photoionisation, producing a matrix-trapped electron and the corresponding delocalised nitrogen cation (Wurster's blue). The existence of the trapped electron has been demonstrated both indirectly and by ESR spectroscopy [28]. In a mobile matrix, photoionisation leads to electrical conductivity during irradiation, but recombination is so fast that there is no storage of energy. In a matrix which is rigid enough to trap both the cation and the electron the effect is storage of energy which can be released slowly and leads to CRL.

Whilst the cation is trapped by the viscosity of the medium, the nature of the electron trap is less clear. In non-polar glasses, the electron energy may be localised in sites created by density fluctuations in the matrix. However,

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[1] It was observed that samples doped with TMPD took on a slight blue coloration a few days after the experiment. Exposure to the fluorescent strip lighting in the room was evidently enough to produce a stable concentration of the Wurster's blue cation.

there is considerable evidence that glassy matrices which contain OH groups can solvate electrons and provide stable trapping sites see e.g. Refs. [29,30]. George et al. [31], showed that a model compound, the product of hydrolytic ring opening of the glycidyl groups of MY721, gives CRL when below its T_g, but not above. They proposed that the electron trapping site in epoxy resins is a cavity surrounded by a sufficient number of hydroxyl groups to stabilise the electron charge.

CRL emission from any material must depend on there being enough trapped electrons to allow a measurable signal and upon their decay occurring on the time scale of the measurement. On this basis, it is possible to propose that the CRL from an epoxy requires two conditions: (i) there must be enough OH groups to solvate and stabilise the electron and (ii) the matrix must be rigid enough to prevent decay of CRL before it can be observed.

In our experiments, the rapid increase of CRL always occurs at essentially the same fractional conversion, irrespective of the temperature of the cure reaction. Thus we can have the same intensity of light from resins at quite different temperatures (and quite different mobilities) as long as they are at the same conversion and the resin is below T_g. At the same time, addition of significant amounts of aromatic tertiary amines (analogues of the cation site) has no activating effect on the CRL (indeed it is often deleterious). These results suggest that the CRL is dominated by the production of OH groups which stabilise the trapped electron, although the requirement for a rigid matrix is also clear, and the differences between amine and ether resins show that aromatic nitrogen sites are advantageous.

5. Conclusions

We have shown that the CRL from a group of epoxy resins irradiated in nitrogen with UV light during cure is directly related to the extent of cure, to the extent that the plot of CRL intensity against fractional conversion of epoxy groups is essentially a master curve for any given resin type. Since addition of tertiary amines produced no significant increase in CRL, it is concluded that the hydroxyl groups, rather than the tertiary amines are more important in determining the stability of electron–cation pairs in the irradiated resin and that CRL arises as the concentration of OH groups builds up to the point where photo-electrons can be solvated, and the resin becomes sufficiently immobile to make the time scale of recombination long enough for the emission to be detected.

Future articles will examine how detailed analysis of the CRL decay kinetics can give further information on the CRL process.

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