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Charge-recombination luminescence as a monitor of network formation during cure of epoxy resins

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Abstract

The relationship between the charge-recombination luminescence (CRL), weak light emitted after u.v.-irradiation, and the development of properties during isothermal cure of epoxy/amine thermosetting resins was investigated. The changes in CRL were compared with the transitions and changes in properties during cure as measured through dynamical mechanical analysis on separate samples cured in a rheometer. It was shown that gelation did not lead to any detectable change in CRL, whereas vitrification caused a pronounced increase in CRL. Measurements on fully cured systems at different temperatures confirmed that CRL only was observed when the system was in the glassy state. It was also found that the decay kinetics of the CRL signal were essentially independent of the temperature and of the degree of cure of the sample.

1. Introduction

Process control of thermoset materials manufacturing requires information on both the progress of the chemical cure reaction and the evolution of physical properties. While obtaining chemical information from curing thermosets in-situ was recently demonstrated by using *FT*i.r. or Raman spectroscopy and fibre-optic probes [1], monitoring the physical properties is more difficult. In general, techniques that directly measure the physical properties, such as dynamic mechanical analysis (DMA), require complex equipment to be in contact with the sample and are not suitable for in-situ use. Techniques that follow the property development in-situ indirectly, through changes in conductivity and dipole relaxation, are available [1,2]. However, these methods may suffer from electrical interference in autoclave and similar processing environments and do not provide any direct quantitative chemical information. This means that they have to be combined with spectroscopical techniques if the cure process is to be fully characterized.

The phenomenon of charge-recombination luminescence (CRL), detected as weak emission of light after u.v.-irradiation of the resin, was shown to depend on the physical properties of the material [3,4]. CRL will not provide any chemical information, but being an optical phenomenon it should be more easily combined with e.g. *FT*i.r. than the dielectric techniques.

CRL arises as the result of u.v.-irradiation. u.v.-irradiation of organic glasses causes photo-excitation of the chromophores present. Depending on the energy of the radiation, as well as the polarity of the medium, ionization may also occur. This process was first recognized for organic amines in alcohol glasses by Lewis and Lipkin [5], and they found that the resulting photo-electrons were trapped at either physical defects or chemical sites with a high electron affinity (such as a cage formed from hydroxyl groups). Several studies of the photo-ionization of amine-cured epoxy resins [3,6–9] showed that similar processes could occur and that the subsequent recombination of charges would under certain circumstances lead to emission of photons. In these studies it was believed that the photoionization process involved the tertiary amine site on either the parent epoxy resin (if it was a glycidyl amine) or the fully reacted aromatic amine (such as diamino diphenyl methane or diamino diphenyl sulphone). The trapping site in the cured epoxy resin was believed to be the hydroxyl groups formed by ring opening of the epoxy resin. These could either form a chemical trapping site or a physical cage through association of several hydroxy groups as would occur in intramolecular cyclization [10]. The recombination may occur by tunnelling of the electron or by the disruption of the cage and is of much longer duration than photoluminescent processes such as phosphorescence. It has also been

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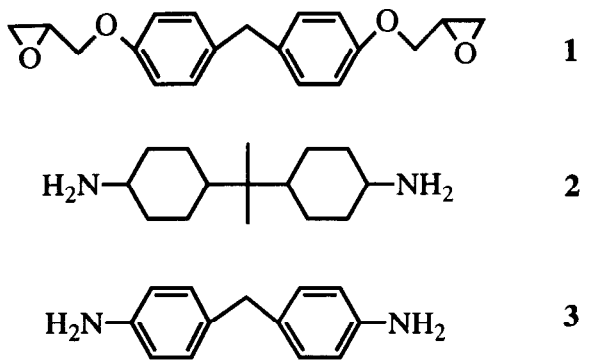


Fig. 1. Epoxy (**1**) and amine (**2** and **3**) monomers.

shown that CRL can be distinguished from chemiluminescence as it is observed in an inert atmosphere [3].

Regarding the relation between CRL and the development of physical properties during cure, it is useful to first review the changes that occur during the cure process at different cure temperatures [11,12]. The two main events that may occur are gelation, i.e. the liquid-to-rubber transition, and vitrification, i.e. liquid or rubber-to-glass transition. Gelation corresponds to the formation of an infinite network, whereas vitrification occurs when the glass transition temperature (T_g) of the reacting system reaches the cure temperature. There are two main temperature regimes for isothermal cure. On curing above the ultimate glass transition temperature ($T_g\infty$) of the polymer, only gelation will occur. The system will then vitrify upon cooling. If the cure temperature is below $T_g\infty$ the system will first gel and then vitrify. Previous studies attempting to link CRL with the transitions encountered during cure were performed on materials cured below $T_g\infty$ [3,6–8]. In general, CRL was only detected as the materials vitrified, but in some cases the onset of CRL was found to coincide with gelation [6,8]. Since no studies with samples undergoing only gelation were performed, the direct influence of gelation on CRL was not investigated. In addition, vitrification was measured indirectly, through DSC scans on partially cured samples, and reported only as a point, while it is well-known that it is a gradual process.

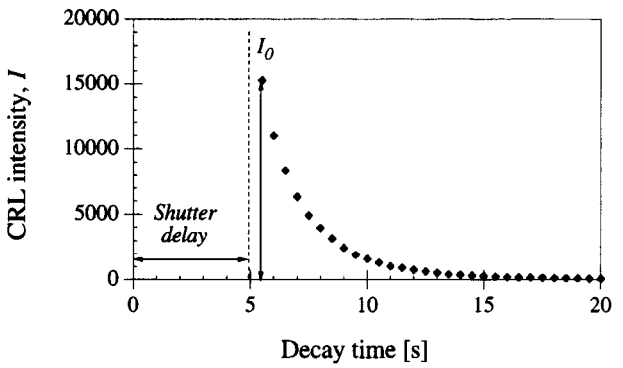


Fig. 2. Typical decay curve for the charge-recombination luminescence from the intensity measured 5 s after ceasing UV irradiation.

In this work the CRL during isothermal cure at different temperatures of an epoxy resin reacted with two different amines is investigated. The changes in CRL are compared with detailed dynamic mechanical data obtained from samples cured in a rheometer.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol F (**1**), and 2,2,-di(4-aminocyclohexane)propane (**2**), were received from Ciba Geigy. 4,4″-diaminodiphenylmethane (**3**), was obtained from Aldrich. All chemicals were used without further purification. The monomers are presented in Fig. 1.

2.2. Methods

Dynamic mechanical analysis was performed in a RDS 2, using parallel plates of 8 mm diameter and samples of approximately 4 mm diameter and 1.5 mm thickness. The samples, stoichiometric mixtures of **1** + **2** or **1** + **3**, were placed in the instrument at ambient temperature, and brought to the cure temperature at 15°C min^{-1}. The complex modulus was measured at regular intervals throughout the cure process using a multiwave technique involving superposition and decomposition of the signal, which permitted data at several frequencies to be collected simultaneously. The strain was 0.3% and the frequencies 0.2, 1 and 5 Hz. After the cure was completed, temperature scans at a cooling rate of about 5°C min^{-1} were run. The sample dimensions were checked after cure, and the modulus data re-calculated accordingly.

Charge recombination luminescence was measured in a set-up composed of a sample hot-stage, covered by a quartz window, and placed in a light-tight box with a Thorn EMI 9816B photomultiplier tube mounted in the lid. Photon counting was carried out by a SR400 2-channel photon counter (Stanford Research Systems), connected to a PC for data acquisition. Stoichiometric mixtures of **1** + **2** or **1** + **3** in aluminium pans were placed in the hot-stage and allowed to equilibrate for 5 min at room temperature. The sample compartment was continuously flushed with nitrogen. The sample was then brought to the cure temperature at 15°C min^{-1} and the CRL measured by repeatedly irradiating the sample with a Kulzer Duralex u.v.-300 fibre optic wand for 60 s. After each irradiation the shutter of the photomultiplier was opened with a delay of 5 s, and the intensity of the emitted light recorded for 120 s. The light intensity was measured as the number of photons emitted over 0.5 s. The initial intensity of emitted light, I_0, was taken as the first data point. An example of a typical decay curve with the definition of I_0 is shown in Fig. 2.

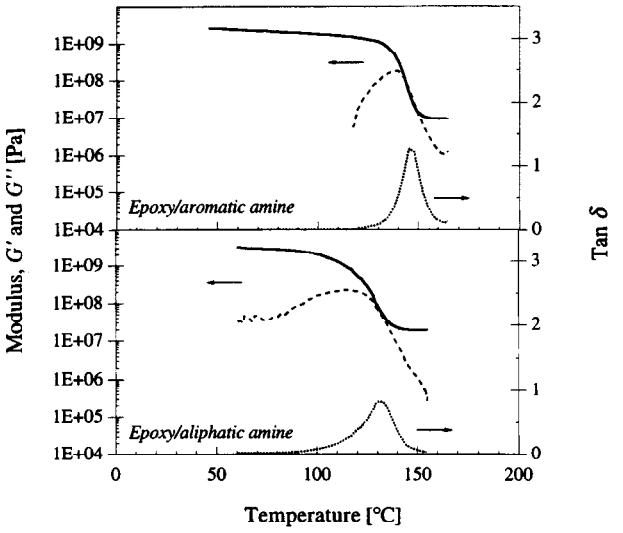


Fig. 3. G' (solid line), G'' (dashed line) and tanδ (dotted line) at 1 Hz obtained on cooling of fully cured epoxy/amine systems.

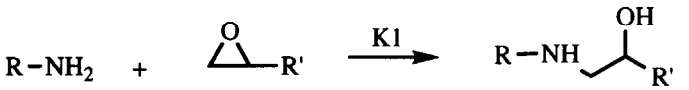
3. Results and Discussion

3.1. Dynamic-mechanical characterization

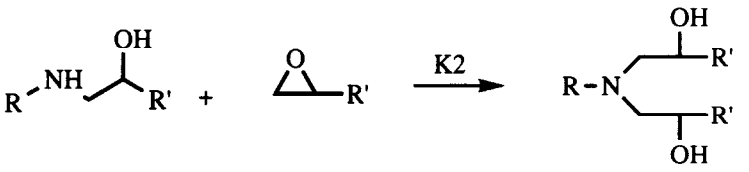
Two different amines, one aromatic and one cycloaliphatic, were used (see Fig. 1). Fig. 3 shows the dynamic-mechanical behaviour of the fully cured epoxy–amine systems as a function of temperature. The behaviour of the two materials is quite similar, except that the epoxy/aliphatic amine system shows a lower T_g and a wider glass transition than the epoxy/aromatic amine system, as indicated by the differences in shape and position of the tanδ and G'' curves. The T_g and the rubbery and glassy moduli of the cured systems are presented in Table 1. The lower T_g of the aliphatic system is to be expected from the lower stiffness of the cycloaliphatic moiety compared to its aromatic counterpart. However, the higher rubbery modulus of the aliphatic amine system shows that it has a somewhat higher crosslink density than the aromatic system. This is further indicated by the wider transition and lower peak value of tanδ in the aliphatic system. The crosslink density is equal to the inverse of the molecular weight between crosslinks, i.e. the molecular weight of the monomers, which is similar for the two amines. The fact that there is a difference in crosslink density between the systems means that the two amines must react in different manners, producing networks with different structures. The epoxy–amine reaction proceeds primarily through addition of the epoxy groups to primary amine (Scheme 1) and secondary amine Scheme 2). Under certain conditions addition of epoxy groups to hydroxyl groups (Scheme 3) will occur. This

Table 1
Properties of the cured resins measured by DMA

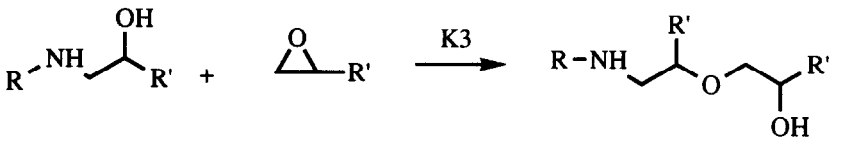
Amine	T_g [°C] (tanδ peak)	Rubbery modulus [MPa]	Glassy modulus [MPa]
Aromatic	150	10	2600
Aliphatic	130	20	3300



Scheme 1



Scheme 2



Scheme 3

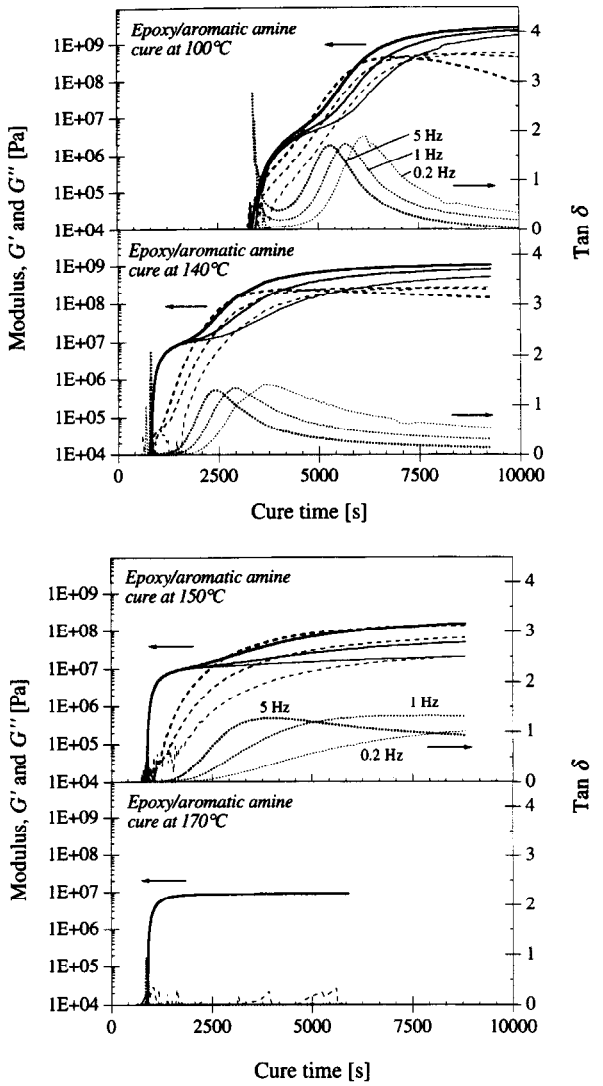


Fig. 4. G' (solid lines), G'' (dashed lines) and tanδ (dotted lines) measured at 0.2 Hz (fine lines), 1 Hz (medium lines) and 5 Hz (heavy lines) during cure of the epoxy/aromatic amine system at different temperatures.

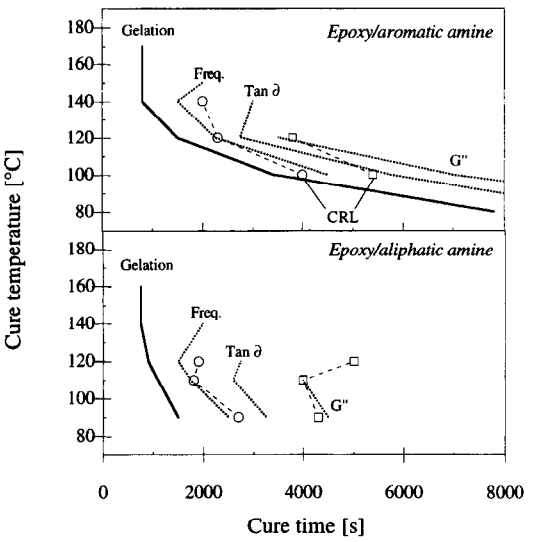


Fig. 5. Gelation times (solid lines) and vitrification times (dotted lines) for cure at different temperatures of the two systems. The vitrification times were defined as onset of frequency dependence of G', peak in tanδ and peak in G''. Also shown are the times at which the CRL signal starts to increase (circles) and levels out (squares).

etherification side reaction adversely affects the network formation, and is much more prevalent in aromatic amine systems than in aliphatic amine systems [13]. One reason for this is the lower basicity of aromatic amines which makes them less reactive towards epoxy groups. Another reason is the higher cure temperatures employed with aromatic amines. The etherification reaction has a higher activation energy than the amine–epoxy addition [14], and thus competes more with the secondary amine reaction at higher cure temperatures.

Gelation and vitrification during isothermal cure can be detected through changes in the dynamic mechanical properties. Extensive work on gelation has established that it is most precisely detected as the point at which tanδ becomes independent of measurement frequency [15,16], although a number of criteria were used in the literature [17]. For vitrification there is no generally accepted criterion, but the peak in G'' or tanδ was used [18]. It should be noted that it is difficult with dynamic mechanical analysis to accurately measure properties through the whole cure process (liquid–gel–glass) using one single geometry, since the stiffness typically changes by seven orders of magnitude. In the present work the geometry was chosen to give reliable data in the part of the process following gelation, which means that the readings before and during gelation show significant scatter. The evolution of G', G'' and tanδ at three frequencies during cure of the epoxy/aromatic amine mixture at different temperatures is depicted in Fig. 4. The curves for the epoxy/aliphatic amine are similar, and are not shown. Initially the same behaviour is observed at all temperatures. Before gelation, the system is liquid, and the stiffness too low to be detected. As the sample then gels there is a rapid increase in stiffness, and G' becomes independent of frequency. From this point onwards the behaviour depends on the cure temperature. At temperatures below $T_g\infty$, i.e. 100, 120 and 140°C, the system vitrifies, as indicated by the continuing rise in G', G'' and tanδ, beginning at high frequencies, and the onset of frequency dependence of G'. At 100°C vitrification goes to completion, as evidenced by the decrease in tanδ and G'' and decrease in frequency dependence of G'towards the end of cure. On cure at $T_g\infty$, vitrification is no longer complete and the sample is still in the transition zone at the end of cure. At temperatures above $T_g\infty$, i.e. 170°C, only gelation is observed; tanδ and G'' remain low and there is no frequency dependence in G'.

By applying criteria for gelation and vitrification to the dynamic-mechanical data, and plotting the corresponding times versus cure temperature, a time–temperature-transformation diagram can be constructed [11]. In the

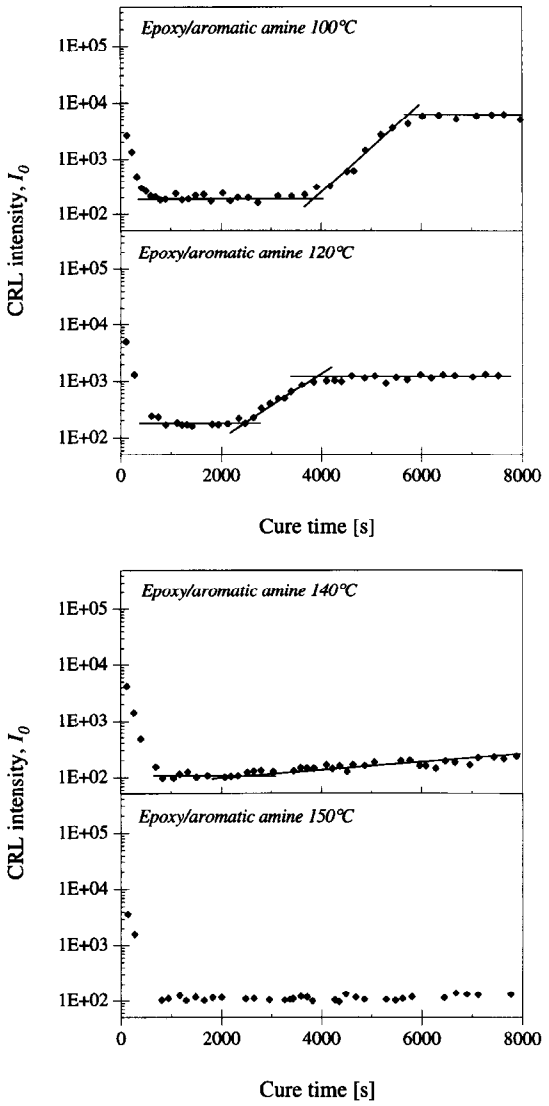


Fig. 6. Charge-recombination luminescence intensity as a function of cure time during cure of the epoxy/aromatic amine system at different temperatures. The lines have been added to define the transition points.

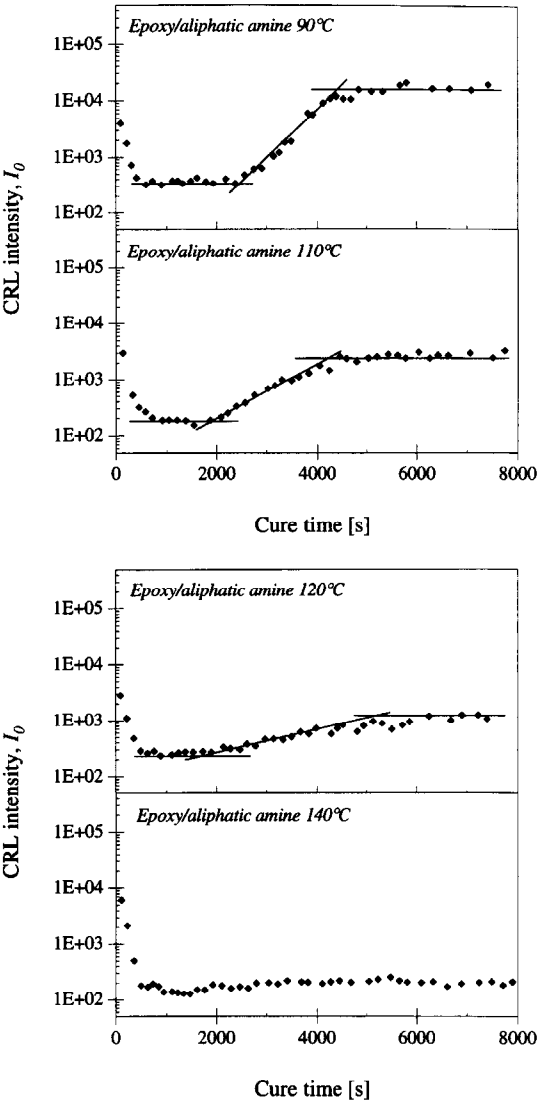


Fig. 7. Charge-recombination luminescence intensity as a function of cure time during cure of the epoxy/aliphatic amine system at different temperatures. The lines have been added to define the transition points.

present work one criterion for gelation and three criteria for vitrification were used. The criteria selected were tanδ crossover for gelation, and (1) onset of frequency dependence in G', (2) peak in tanδ at 1 Hz and (3) peak in G'' at 1 Hz for vitrification. All criteria except the onset of frequency dependence in G' have been previously used in the literature [17,18]. As long as vitrification is preceded by gelation, the emergence of a frequency-dependence in G' can also be taken as a sign of vitrification [12,19]. The gel- and vitrification times for both the aromatic and the aliphatic amine cured systems are presented in Fig. 5. As can be expected, the gel times increase with decreasing cure temperatures, whereas the vitrification times show the characteristic minimum at intermediate cure temperatures [11]. It is also evident that vitrification is not a point but a process that extends over a large part of the cure.

3.2. Charge-recombination luminescence

The initial intensity, I_0, of CRL as a function of isothermal cure time at different cure temperatures is shown for the two systems in Figs. 6 and 7. During the initial heating up, high levels of light are observed, but as the samples reach their cure temperature the signal decreases to the background level of about 100 counts. As the cure then proceeds, there is an increase in CRL to a higher plateau at lower cure temperatures. The level of this plateau depends on the cure temperature as well as on the system. At temperatures close to the T_g^∞, only a small, gradual increase in CRL is observed and no second plateau is seen. Finally, cure above T_g^∞ does not produce any CRL after the initial burst related to the heating up. From this it may be concluded that gelation does not, by itself, cause any change in the CRL signal. Regarding the relationship between change in CRL and vitrification, it is useful to compare the CRL

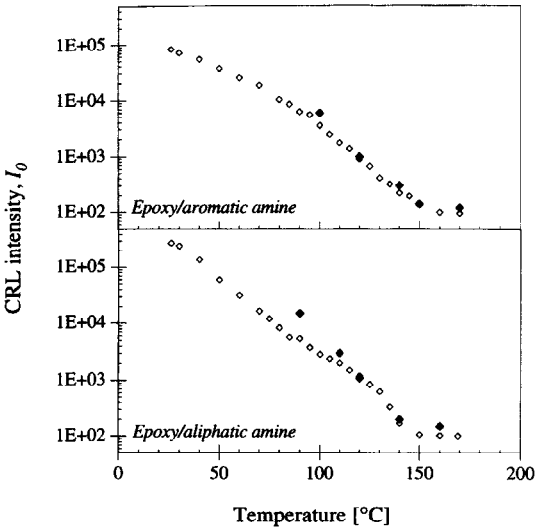


Fig. 8. Charge-recombination luminescence intensity as a function of temperature during cooling of the fully cured systems (unfilled diamonds). Also shown are the final values of CRL obtained during isothermal cure at different temperatures (filled diamonds).

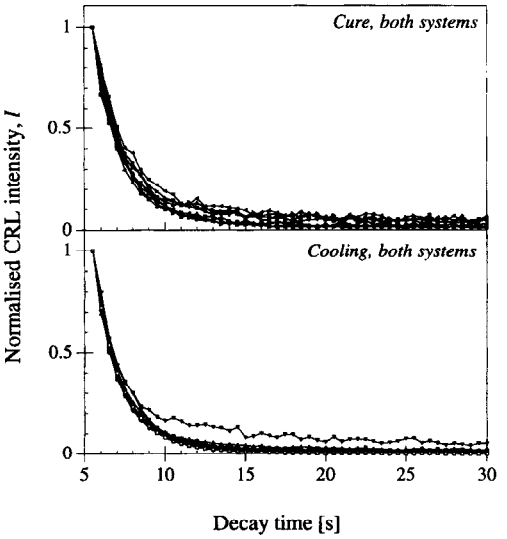


Fig. 9. Normalised (by division by I_0) CRL intensity decay curves for both systems. Data are shown for different points during isothermal cure at 110°C for the aliphatic and 120°C for the aromatic amine (cure), and for temperatures from 30 to 110°C for fully cured samples (cooling).

data with the dynamic mechanical results. The onset of increase and levelling out of CRL, taken as the intersections between the lines in Figs. 6 and 7, is shown together with the vitrification times in Fig. 5. As can be seen, there is good agreement between onset of rise in CRL and the beginning of vitrification as detected by the appearance of frequency dependence in G'. The levelling out of the CRL shows good correlation with the peak in G'', which corresponds to the later part of vitrification [18].

There appears to be a clear link between the emergence of a CRL signal and vitrification of the material. Another way of obtaining vitrification is through cooling of a cured system. CRL as a function of temperature for fully cured systems are presented in Fig. 8. At high temperatures only low light levels are detected. As the temperature is decreased there is an increase in CRL, and comparison with dynamic mechanical data (see Table 1 and Fig. 3) shows that the onset of the increase occurs at the glass transition temperature. This is thus further evidence that CRL is a feature of the glassy state in these systems. Another observation that can be made from Fig. 8 is that the CRL intensity detected at the end of isothermal cure is similar to the intensity obtained for a fully cured system at that temperature. Since the degree of cure is lower for systems cured at temperatures far below $T_g\infty$ [11], this means that the CRL intensity is not particularly sensitive to the chemical degree of conversion. The intensity of the CRL is determined both by the number of charges created by the u.v.-irradiation and by the rate at which they recombine. The rate of charge recombination is largely determined by the mobility in the system. Previous studies have shown that the decay kinetics of the CRL signal after u.v.-irradiation may change with temperature and cure time [7,8]. In Fig. 9 the decay of the CRL signal obtained at different points during isothermal cure and at various temperatures during cooling is depicted. To make the curves comparable they were normalized by division by I_0. No correction is made for the dark count, which leads to increased scatter for low values of I_0 as observed at short cure times and high temperatures. It can be seen in the top graph in Fig. 9 that the decay time is essentially independent of cure time for both systems. Moreover, it is similar for both systems. The bottom graph in Fig. 9 shows that, allowing for some scatter at high temperatures, the decay time remains the same at all temperatures. This leads to the conclusion that the decay time is largely unaffected by the state and the nature of the material, and that the differences in CRL intensity must be due exclusively to differences in the number of charges created by the u.v.-irradiation.

Regarding the influence of the amine moiety on the CRL, a comparison of the final levels obtained during isothermal cure, shown in Fig. 8, reveals that under comparable conditions (same distance from T_g), the epoxy/aliphatic amine system produces higher CRL intensities than the epoxy/aromatic amine system. This means that there should be more ionizable sites in the aliphatic amine network. Tert-amine groups have often been suggested to be involved in CRL [3,6]. It is therefore worth noting that the lower tendency for etherification (Scheme 3) in the aliphatic amine leads to a higher fraction of tert-amine groups in this system compared to the aromatic amine system, which is thus consistent with the higher CRL intensities in the aliphatic system.

4. Conclusions

The relationship between charge-recombination luminescence and the properties of epoxy/amine systems was

investigated. During isothermal cure, no influence of gelation on the CRL could be detected. However, CRL was observed when the systems were in the glassy state, which occurred both during cure and on cooling. The decay kinetics of the CRL were found to be independent of the state and nature of the system, i.e. no influence of degree of cure or temperature was observed. It is concluded that CRL is a potential technique for constructing an on-line monitoring device for vitrification during cure.

Acknowledgements

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