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A low resolution pulsed nuclear magnetic resonance study of epoxy resin during cure*

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Low resolution pulsed nuclear magnetic resonance, using a commercially available bench-top instrument (Bruker PC120), has been used to study the cure of an epoxy resin system (epichlorohydrin–bisphenol A resin and hardener containing a primary diamine and an amido-polyamine). Free induction decay experiments have been successfully used to observe the change from viscous liquid to crosslinked solid as the resin cured. The Carr–Purcell–Meiboom–Gill technique resolved two components in the liquid phase and indicated how the concentration and mobilities of these changed during cure. It is suggested that initially these two components are the starting materials of epoxy resin and hardener, which subsequently gave an intermediate component of an alcoholic hydroxyl and secondary amine, and finally the crosslinked solid.

(Keywords: low resolution nuclear magnetic resonance; cure profiling; cure mechanism; cure monitoring)

INTRODUCTION

The use of thermosetting epoxy resin systems has grown considerably over recent years. The main attribute of the materials is that they may be easily converted (cured) from the liquid form into a tough, hard solid without the evolution of by-products. Curing may be achieved using a curing agent that either promotes catalytic action or participates in the reaction and remains bound into the chemical chain of the product. Under appropriate conditions the epoxy ring may be reacted with at least 50 chemical groups; as a result cure may proceed at a variety of rates and temperatures depending upon the curing agent used. For example, choices are available between heat curing or room temperature curing resins, and some control over the final network structure is available through choice of curing reagent or mix of reagents. This combined with their chemical, mechanical and physical properties makes epoxy systems ideal for use in adhesive bonding. In applications of adhesive bonding it is often necessary to measure the degree of polymerization as a function of time.

In this paper it is shown that a commercially available bench-top pulsed nuclear magnetic resonance (n.m.r.) machine (Bruker PC120) can be used to follow the degree of polymerization as a function of time, since free induction decay (FID) experiments may be used to observe the change from viscous liquid to crosslinked solid as the resin cures. The Carr–Purcell–Meiboom–Gill (CPMG) technique can be used to resolve two components in the liquid phase and is able to show how the concentration and mobility of these change during cure.

EPOXY CURE REACTION

The general reaction for an epoxy resin with a primary diamine hardener is the addition reaction shown in *Figure 1*. However, when a primary amine reacts with an epoxy group, the initial reaction products are an alcoholic hydroxyl and a secondary amine. This is shown in simplified form in *Figure 2*. Studies have shown[1] that primary amines react about twice as fast as secondary amines and *Figure 3* shows how the concentrations of the primary, secondary and tertiary amines change as a function of time. Diamines and diepoxides are used to promote crosslinking in the final structure.

The reaction mechanisms of amido-polyamines are assumed to be similar to those of amines but with reduced reactivity[1].

THE N.M.R. TECHNIQUE

Relaxation n.m.r. experiments can reveal information concerning the structure of materials, since on applying an appropriate radio frequency (RF) pulse of electromagnetic radiation of frequency ν to nuclei possessing

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a spin angular momentum located in a magnetic field B_z, interaction with the RF pulse will result. This RF pulse can be considered as being applied orthogonally to the magnetic field B_z and its magnitude and duration will determine the extent of interaction, because its effect is to produce a magnetic field B_x which rotates all the resonant nuclear spins through an angle θ dependent upon the duration of the RF pulse t_p. Since $\theta = \gamma B_x t_p$, where γ is the gyromagnetic constant.

When disturbed from equilibrium, the nuclear magnetic moments precess about the applied magnetic field B_z at a rate proportional to that magnetic field. The constant of proportionality is characteristic of that particular nuclear species[2,3].

If t_p is chosen so that θ is 90°, the interaction can be represented by *Figure 4*. A detector is positioned so that it records the signal generated in the *xy*-plane after the RF pulse has been applied, and the resulting signal is seen to diminish with time. This is due to (1) a return of the nuclear spins to their equilibrium position with a net alignment along the *z*-axis (spin–lattice relaxation) and (2) by the precession spin–spin energy changes, caused by the loss of phase coherence between the spins, resulting from small differences in the local fields B_{loc} that they experience (spin–spin relaxation). The process is known as free induction decay (FID) and characterized by a time constant T_2^*.

The time taken for the generated signal to decay is a function of the physical state of the molecules containing those nuclei. For protons in the solid phase T_2^* is short, typically of the order of 10 to 20 μs. For liquids T_2^* is much longer, of the order of ms, depending upon the mobilities of the molecular species responsible for the signal. Samples containing solid and liquid constituents will yield a composite signal as shown in *Figure 5*.

The signal intensity contributing to the signal at any point on the FID is a product of two terms, one proportional to the number of magnetically active nuclei present in the sample (e.g. protons) and the second dependent upon their T_2^* values. Thus quantitative and qualitative information can be obtained by recording signal amplitudes at various times after the 90° pulse[3]. It is possible to apply a train of RF pulses subsequent to the initial excitation to record a further decay, this is the Carr–Purcell–Meiboom–Gill (CPMG) method[4]. The CPMG decay is composed of a series of echoes located between the refocusing pulses. The echo envelope is used to generate the CPMG decay, characterized by a time constant T_2. This not only compensates for inhomogeneities in the sample and magnetic field and other off-resonance effects, but also gives information about the individual components within the sample. A typical decay curve for CPMG decay is shown in *Figure 6a*, together with the FID curve.

As the epoxy resin cures the physical state of the protons gradually changes from a viscous liquid to a crosslinked solid, resulting in a change in the composite

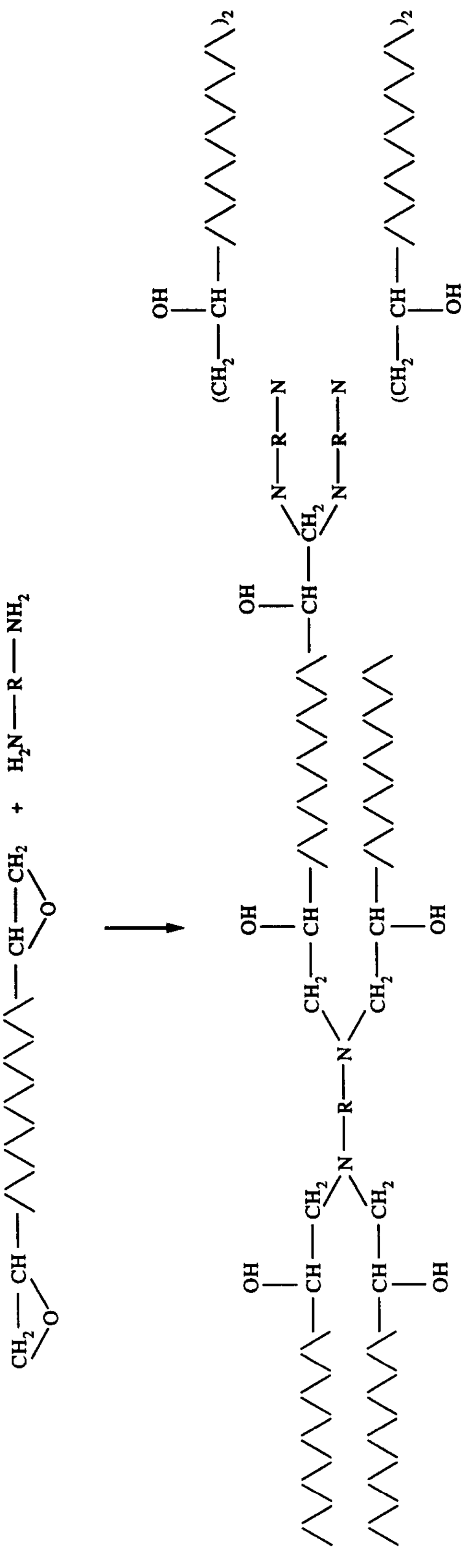
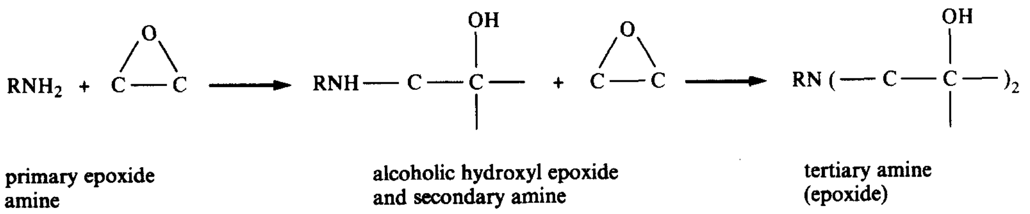


Figure 1 Reaction between an epoxy resin and primary diamine hardener



$$\mathrm{RNH_2} + \overset{\mathrm{O}}{\mathrm{C{-}C}} \longrightarrow \mathrm{RNH{-}C{-}\overset{OH}{C}{-}} + \overset{\mathrm{O}}{\mathrm{C{-}C}} \longrightarrow \mathrm{RN(-C-\overset{OH}{C}-)_2}$$

Figure 2

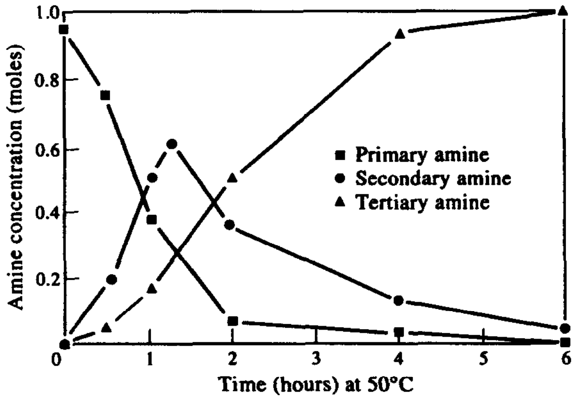


Figure 3 Graphs to show the change in concentration of primary, secondary and tertiary amine during the cure of an epoxy resin (after Ref. 1)

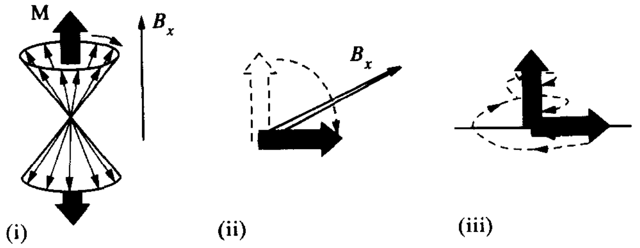


Figure 4 (i) The precessional 'cone' of a group of spinning nuclei and the resulting bulk magnetic moment vector, *M*; (ii) the application of a 90° about the *x* axis; (iii) the additional precession of *M* about the main axis, and the overall spiral motion of *M* (after Ref. 2)

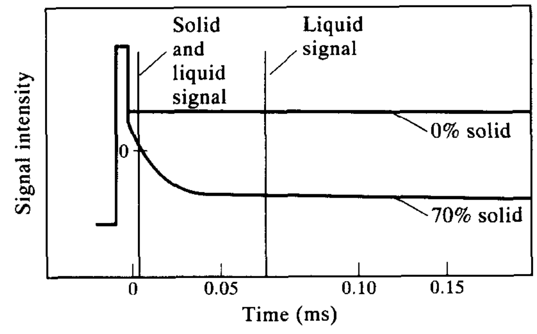


Figure 5 FID curves observed for liquid sample and a 70% solid sample (after Ref. 3)

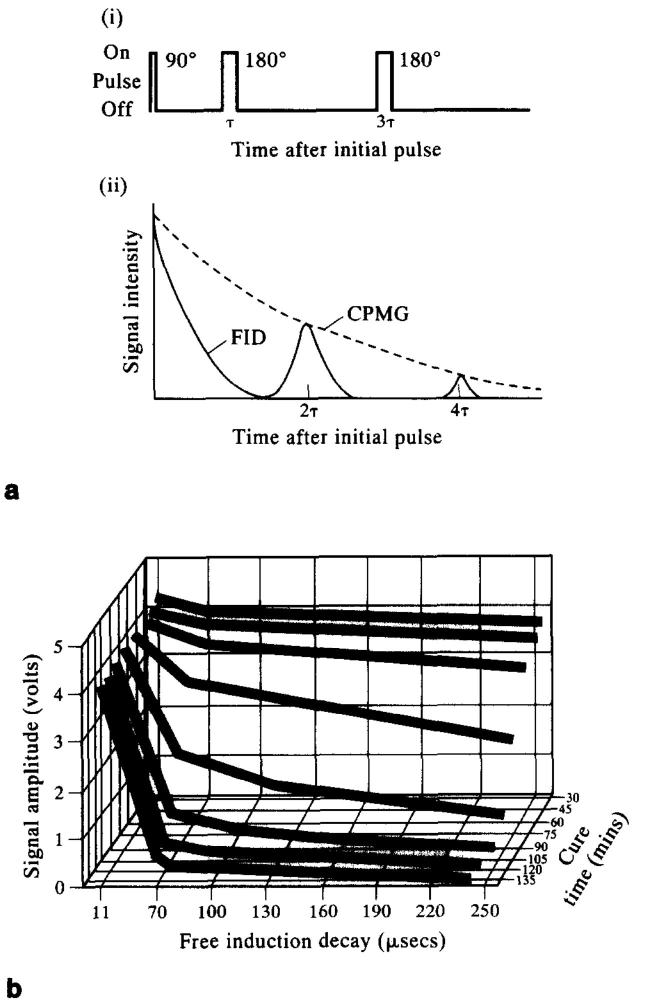


Figure 6 (a) (i) The pulse timing of a 90°-τ-180° sequence, and (ii) the resultant spin echoes (after Ref. 2). (b) Graph to show the change in FID signal amplitude at time intervals between 30 and 150 min during the cure of an epoxy resin

decay curve. Therefore, after allowing the protons sufficient time to recover, the pulse sequence may be repeated to produce a further composite decay curve at time *t* later. This process can be continued over long periods (20 h in this case), producing an updated composite decay curve at intervals (3 min) during the cure process. Examples of curves produced from the FID data are shown in *Figure 6b*. These decay curves show the change in concentration of the liquid protons as the physical state of the mixture changes from a liquid to a solid.

Interpretation of the n.m.r. relaxation is direct, the decay times (T_2^* and T_2) are considered as proportional to the rate of motion of the molecular species containing the resonant nuclei and the zero-time amplitudes (A) to their concentrations.

EXPERIMENTAL METHOD

The resin used was AY-105, an unmodified bisphenol-A epoxy resin, and the hardener was HY-4076GB, a modified aliphatic polyamine with at least four active sites per molecule and containing dioxadodecane diamine; both were supplied by Ciba Polymers, Duxford, UK.

Samples of the resin and hardener were warmed in an oven at 40°C for approximately 30 min to ensure that they matched the operating temperature of the n.m.r. equipment. They were subsequently mixed in a ratio of 100:46.6 (w/w), respectively, this being the recommended ratio as given by the manufacturer. The time at which mixing began was taken as time zero. A portion of the sample was then transferred to an n.m.r. sample tube, inserted into the Bruker PC120 Minispec (having a permanent magnet of 4.7 kG ± 10 G and an operating frequency of 20 MHz) and allowed to equilibrate for 5 min. Data files, consisting of the voltage of the demodulated and filtered RF signal after the initial pulse at 11, 70, 100, 130, 160, 190, 220, 250 μs for the composite FID decay curve as determined by the response time of the instrument of 30 μs and at 512, 1024, 1536 ... 81 920 μs ($\tau = 256$ μs) for the CPMG decay curve, were collected at intervals of 3 min for a total of 20 h.

ANALYSIS OF DATA

The analysis of the decaying radio frequency amplitude signals is based on the assumption that the signal is composed of a number of real exponential or Gaussian functions, thus

$$y(t) = \sum_{n=1}^{N} A_n \mathrm{e}^{(-t/T_{2_n})^x} \tag{1}$$

where A_n is the amplitude of the nth component, T_{2_n} the associated decay time, t the time after the initial pulse and x is 1 for an exponential fit or 2 for a Gaussian fit. The basis of the analysis was the Newton–Raphson method to fit exponentials of the form $A\exp(-t/T_2)^x$ to the measured data in a least-squared error protocol. Some modification was required since no usable signal was available for 11 μs after the n.m.r. excitation pulse due to saturation of the detector radio frequency preamplifier. The analysis of the FID data was based on a Gaussian fit for two components [$N = 2$ in equation (1)], one short time constant component corresponding to a signal representing nuclear resonance relaxation in the solid constituents of the sample and a single long time constant component corresponding to signals from a number of liquid constituents combined together. We assume that these signal components are

$$y(t_{\mathrm{FID}}) = y_1(t_{\mathrm{FID}}) + y_2(t_{\mathrm{FID}})$$

$$y_1(t_{\mathrm{FID}}) = A_1 \mathrm{e}^{(-t/T_{2_1}{}^*)^2} \qquad \text{(solid)} \tag{2a}$$

and

$$y_2(t_{\mathrm{FID}}) = A_2 \mathrm{e}^{(-t/T_{2_2}{}^*)^2} \qquad \text{(liquid)} \tag{2b}$$

The analysis routine first fits a Gaussian function corresponding to $y_2(t_{\mathrm{FID}})$ to the raw data in the time interval 70 μs $< t >$ 250 μs, providing estimates of A_2 and T_2^*. The short time constant component [$y_1(t_{\mathrm{FID}})$] was expected to have decayed considerably during the 11 μs dead time, so no attempt was made to formally fit A_1 and $T_{2_1}^*$. Instead, its value at 11 μs was calculated by subtracting the fitted $y_2(t_{\mathrm{FID}})$ signal from the raw data at $t = 11$ μs to give an indication of the strength of the short time constant component, $y_1(t_{x_{\mathrm{FID}}})$, say. Thus

$$y_1(t_{x_{\mathrm{FID}}}) = y(t_{x_{\mathrm{FID}}}) - A_2 \mathrm{e}^{(-t_x/T_{2_2}^*)^2} \tag{3}$$

where $t_{x_{\mathrm{FID}}}$ is 11 μs in this case.

In order to track the changing proportions of the solid and liquid in the sample, $y(t_{\mathrm{FID}})$ was recorded every 3 min and $A_1(t_{x_{\mathrm{FID}}})$, A_2 and $T_{2_2}^*$ were estimated as described above. This provided $y_1(t_{x_{\mathrm{FID}}})$, corresponding to the solid constituent amplitude $A_1(t_{x_{\mathrm{FID}}})$, and A_2, corresponding to the liquid constituent amplitude, both recorded every 3 min.

Radio frequency decay data obtained from the CPMG pulse sequence were initially analysed for one component [$N = 1$ in equation (1)]. These data were less distorted by sample and equipment characteristics, such as inhomogeneities in the magnetic field, than were the FID data, and corresponded to the composite liquid component only. The analysis routine in this case fits the exponential function corresponding to $y(t_{\mathrm{CPMG}})$ to the raw data in the time interval 512 μs $< t >$ 81 920 μs, yielding estimates of $A_{l'}$ and $T_{2_{l'}}$ by the same curve fitting procedure as before. Further analysis of these decay data resolved the composite liquid signal into two liquid components [$N = 2$ in equation (1)], one component corresponding to a short liquid decay time and the other a long liquid decay time, thus

$$y_{1\mathrm{s}'}(t_{\mathrm{CPMG}}) = A_{1\mathrm{s}'} \mathrm{e}^{(-t/T_{2_{1\mathrm{s}'}})} \qquad \text{(short liquid)} \tag{4}$$

and

$$y_{21'}(t_{\mathrm{CPMG}}) = A_{21'} \mathrm{e}^{(-t/T_{2_{21'}})} \qquad \text{(long liquid)} \tag{5}$$

The results of the analysis were samples every 3 min of $A_{1'}$, $A_{1\mathrm{s}'}$, $A_{21'}$ and the corresponding $T_{2_{1'}}$, $T_{2_{1\mathrm{s}'}}$ and $T_{2_{21'}}$. The way in which these change during adhesive cure, together with $A_1(t_{x_{\mathrm{FID}}})$ and A_2 for the FID analysis, can give information on mobility and concentration of the solid and liquid components.

RESULTS

Figures 7, *8* and *9* show the calculated parameter A_n plotted *versus* adhesive cure time for the FID and CPMG decay curves. *Figures 7a* and *b* show that, at an elapsed time of between 1 and 2 h, there is a distinct rise in solid signal amplitude and a corresponding fall in the liquid signal amplitude. This is confirmed by the 1 (one) component CPMG liquid signal amplitude as shown in *Figures 8a* and *b*. Resolution of the CPMG 1 component liquid signal amplitude into two component liquid amplitudes is shown in *Figures 9a–d*. These show an overall fall similar to the liquid signal amplitudes of the FID and CPMG 1 component curves, but also show a shoulder on both curves.

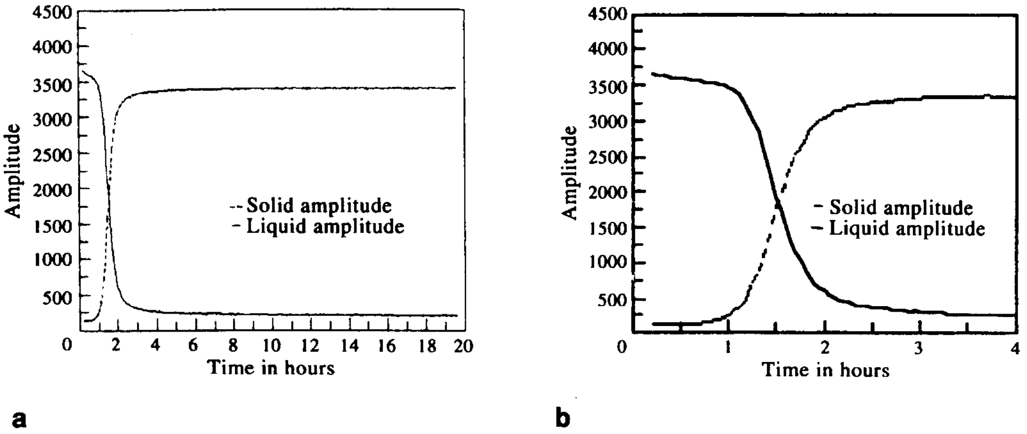


Figure 7 Graphs to show the rise in solid and fall in liquid FID signal amplitudes, $A_1(t_{xFID})$ and A_2, during cure (a) up to 20 h and (b) in detail during the first 4 h

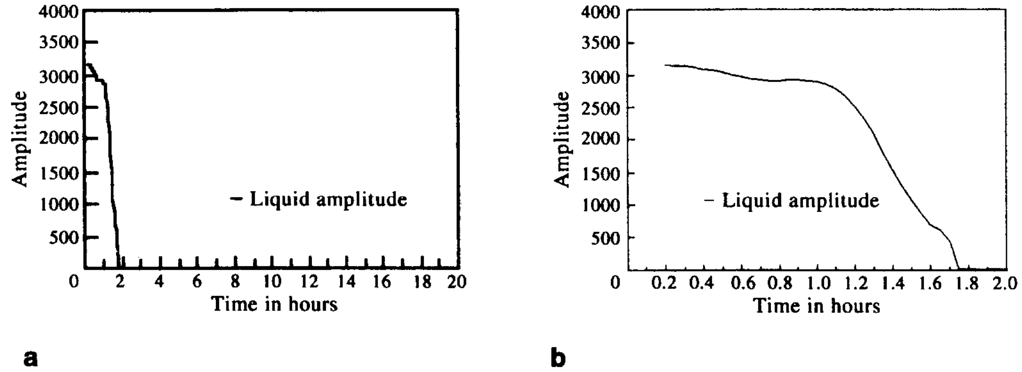


Figure 8 Graphs to show the fall in the 1 component CPMG liquid signal amplitude, A_1, during cure (a) up to 20 h and (b) in detail during the first 2 h

Figures 10a–c show the corresponding decay times for the component *n* in the samples. *Figure 10a* shows a fall in the composite liquid decay time T_{2_l}, until a time of 1.7 h. The component with the shorter liquid decay time, *Figure 10b*, shows that $T_{2_{1s}}$, falls until a time of 1.5 h, while the component with the longer liquid decay time, *Figure 10c*, shows $T_{2_{2l}}$, to fall until a time of 1.2 h.

DISCUSSION

Figures 7a and *b* show the resolved FID signal amplitudes for the solid and liquid components. It can be seen that the liquid signal amplitude falls and the solid signal amplitude increases as adhesive cure proceeds, reflecting the reduced mobility of the nuclei as the matrix forms.

The reaction appears to proceed slowly at first, with little reduction in proton mobility. After 1 h the liquid content begins to decrease rapidly and the solid content increases rapidly, reflecting an increase in the reaction rate. At about 1.75 h the rate of change starts to slow, with the bulk of the reaction being over in 4 h. However, the signal amplitudes continue to change for up to 20 h indicating that some reaction is still taking place with some conversion of the remaining liquid signal to solid signal and a further reduction in the mobility of the nuclei.

These results agree with the reaction mechanism suggested earlier. Initially the epoxy reacts with the amines to produce an alcoholic hydroxyl and a secondary amine, and little reduction in the liquid signal or increase in the solid signal is observed. As the concentration of alcoholic hydroxyl and secondary amine increases then so does their rate of reaction; network formation begins and is indicated by the decrease in mobility of the nuclei and the corresponding decrease in the liquid signal amplitude and increase in the solid signal amplitude (between 1 and 1.75 h). As the concentration of the reactants decreases then so does the rate of reaction, as indicated by the decrease in magnitude of the gradients of both the solid and liquid curves (between 1.75 and 4 h). These measurements agree with the manufacturer's data which give a lap shear strength of >1 MPa at 1.3 h, indicating gelation to have occurred prior to this increase in mechanical strength, and 'handling strength' (lap shear strength >10 MPa) to have developed at 2 h. A slight increase in the solid and decrease in the liquid signal amplitudes then continues for up to 20 h. This again agrees with the manufacturer's data, which suggests that full

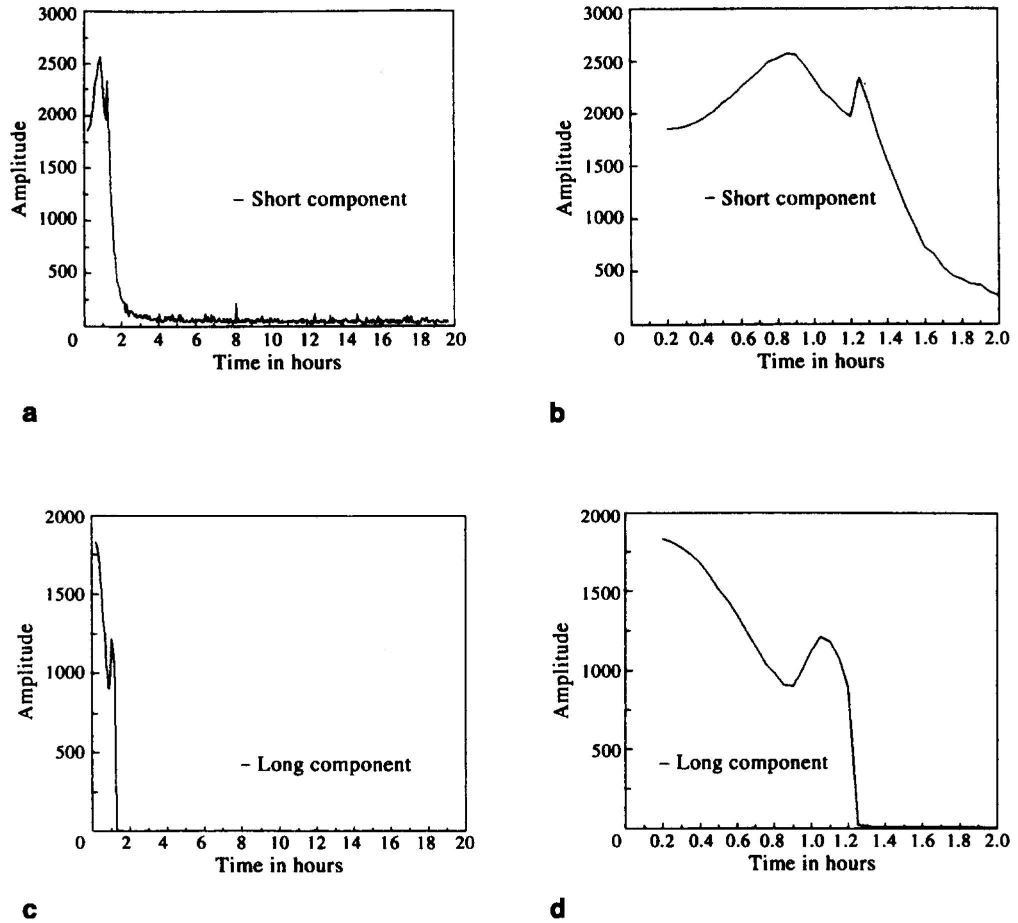


Figure 9 Graphs to show the fall in 2 Component CPMG liquid signal amplitude, $A_{1s'}$, for the short decay time component during cure (a) up to 20 h and (b) in detail up to 2 h. Graphs to show the fall in 2 component CPMG liquid signal amplitude, $A_{2l'}$, for the long decay time component during cure (c) up to 20 h and (d) in detail up to 2 h

strength for the adhesive may take up to 48 h to develop.

The CPMG results for the one component liquid signal, *Figures 8a* and *b*, also indicate a slow rate of change in amplitude with respect to adhesive cure time for up to 1 h before a sharp change in rate until 1.6 h, when the rate slows slightly. After 1.75 h the composite liquid component no longer gives a signal and is thought to have reacted to produce a significantly less mobile product, the decay time of which is too short to be detected using this pulse sequence. The corresponding decay times, *Figure 10a*, confirm this composite component to have changed mobility, losing the resolvable signal at 1.7 h. This therefore suggests that the liquid-like components react within 1.75 h to form a reaction product with reduced mobility and, together with the FID results, suggests this product consists of a solid matrix.

The CPMG liquid signal amplitude may be resolved to show the presence of a short decay time component and a long decay time component, the initial decay times being 12.5 and 76 ms, respectively (*Figures 10b* and *c*). These are thought to be attributable to the starting components, i.e. resin and hardener, since the decay times of these separate components were found to be 13.02 and 141.5 ms, respectively (the discrepancy being the result of (1) the change in viscosity upon adding the hardener to the more viscous resin and (2) the initial reaction between them).

Assuming this to be the case, from *Figures 9b* and *d* it appears that the hardener reacts with the resin to form a longer chain intermediate with less mobility, since the amplitude of the longer decay time component falls in proportion to the increase seen for the shorter decay time component (longer chain length), up to a time of 0.9 h. This is consistent with the formation of an alcoholic hydroxyl and secondary amine (*Figure 11*), since the increase in overall proton concentration for this longer chain intermediate could cause the increase in signal amplitude for the shorter decay time component and corresponding decrease for the longer decay time component.

At this point the longer decay time component's signal amplitude increases as the shorter decay time component's signal amplitude decreases until 1.1 and 1.2 h respectively, reflecting a change in the concentration and mobility of the protons. This is probably due to hydrogen exchange between the alcoholic hydroxyl and secondary amine groups, since this would produce a more mobile proton, the signal of which may contribute to the longer decay time

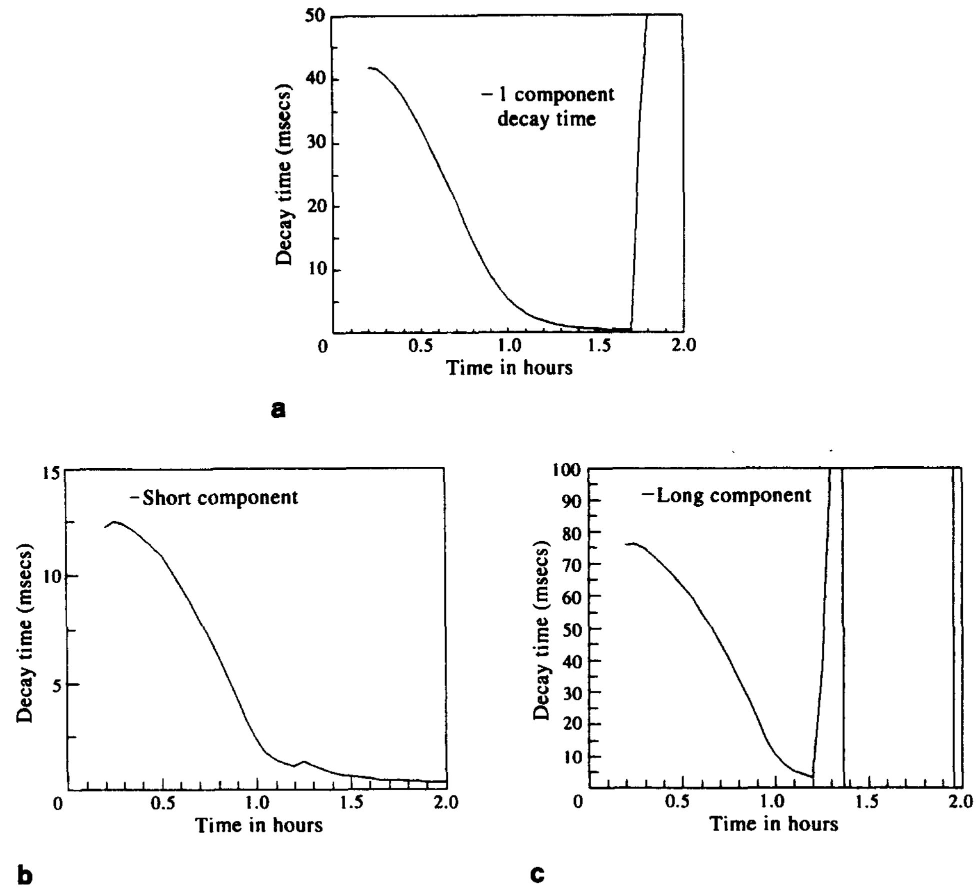


Figure 10 Graphs to show the fall in CPMG (a) 1 component decay time, $T_{2l'}$, (b) 2 component decay time for the shorter decay time component, $T_{2ls'}$ and (c) 2 component decay time for the longer decay time component, $T_{2l'}$

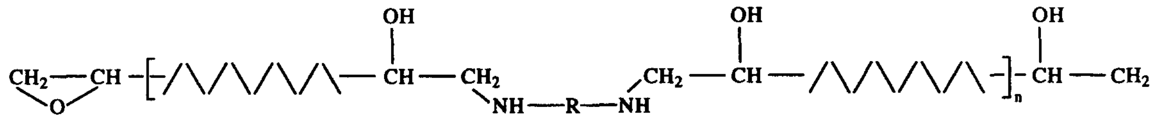


Figure 11 Alcoholic hydroxyl and secondary amine

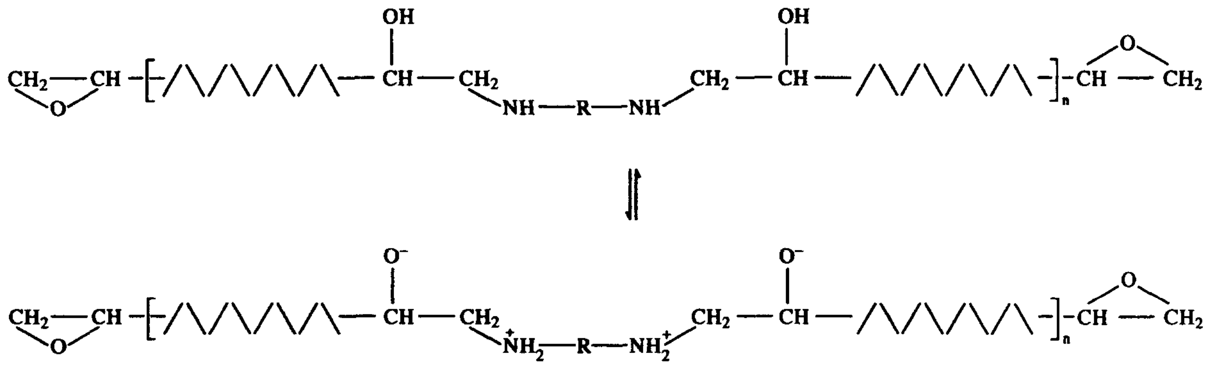


Figure 12 Hydrogen exchange of the alcoholic hydroxyl and secondary amine group

component signal amplitude instead of the shorter decay time component signal amplitude (*Figure 12*).

The longer decay time component signal amplitude then begins to decrease, initially slowly but then more rapidly until the signal can no longer be seen at 1.25 h. At this point the hardener appears to have completely reacted to the alcoholic hydroxyl and secondary amine and hydrogen exchange has ceased. It is believed that the amido-polyamine (a minor constituent of the hardener) behaves in a similar but less reactive manner to the primary diamine, but that the signal due to this component remains unresolved and forms part of the

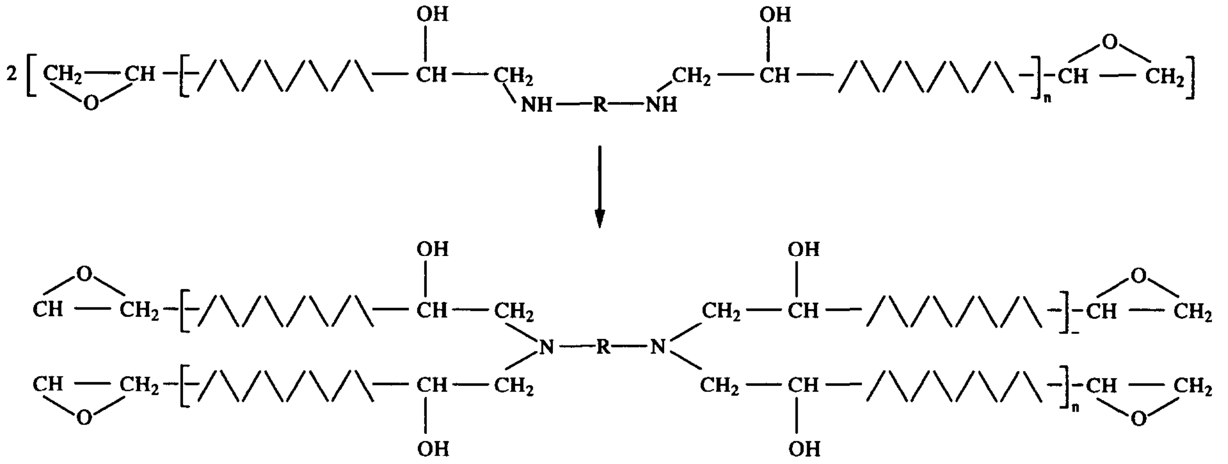


Figure 13 Reaction of alcholic hydroxyl and secondary amine to the tertiary amine

composite longer decay time liquid CPMG signal. During the same period, the shorter decay time component increased in amplitude until 1.25 h, then continued to decrease rapidly until 1.6 h and more gently until 4 h. The increase is possibly due to further reaction of the alcoholic hydroxyl and secondary amine to produce a tertiary amine (*Figure 13*). This would result in a much shorter decay time component, the amplitude of which would show an increase due to the increased number of protons.

After this maximum (*Figure 9b*), the rapid decrease in amplitude is thought to be due to the increase in chain length of the tertiary amine as the value of *n* increases. At this point the decay time becomes too short for resolution into the short decay time liquid component as shown in *Figure 10b*, where the decay time falls to approximately 1 ms at 1.3 h. The following slow amplitude decay for the shorter decay time component could be the result of hydrogen bonding between the long segments of the tertiary amine structure.

The corresponding decay times show a steady decrease for both components, the longer decay time component signal disappearing at 1.2 h (*Figure 10c*) consistent with the loss of amplitude signal (*Figure 9d*). Decay time for the shorter decay time component also drops until 1.3 h, when it becomes of the order of 1 m (*Figure 10b*).

This suggests that the cure can be divided into the following phases.

Phase 1 (from 0 to 0.9 h). During this phase the FID curve shows the adhesive to be liquid; the CPMG long decay time component is reducing in amplitude, indicating a reduction in the concentration of the mobile hydrogen nuclei as the epoxy resin and primary amine react to form short polymer chains. The CPMG short decay time component is rising, showing a corresponding increase in the concentration of bound hydrogen nuclei. All parameters are changing reasonably slowly, indicating that the cure reaction is proceeding slowly at this time.

Phase 2 (0.9 to 1.2 h). Over this phase the liquid amplitude begins to fall and the solid amplitude begins to rise as the cure reaction accelerates. The CPMG short decay time component, which reached a peak at 0.9 h, is falling in amplitude, indicating a further change in the mobility of the bound hydrogen nuclei. The CPMG long decay time component amplitude reaches a minimum at 0.9 h and then increases to a maximum at 1.1 h before falling rapidly until 1.25 h when there is no measurable signal. This peak probably indicates a hydrogen exchange reaction between an alcoholic hydroxyl group and a secondary amine.

Phase 3 (1.2 to 1.3 h). During this short period there is a sharp rise in the CPMG short decay time component, which reaches a peak at 1.25 h. The FID liquid and solid amplitudes are now rapidly changing, showing an increase in the solid content of the adhesive. The peak in the CPMG short decay time component is probably due to the further reaction of the alcoholic hydroxyl/secondary amine to form the tertiary amine. The secondary-to-tertiary amine reaction causes an increase in chain length before crosslinking between chains commences. This reaction causes an increase in the concentration of bound hydrogen in the tertiary amine.

Phase 4 (1.3 h and beyond). The FID liquid amplitude drops quickly as the adhesive solidifies, progressively flattening out until 4 h when the adhesive is largely cured. The CPMG short decay time amplitude also initially decays rapidly, flattening out as time passes. This indicates that the hydrogen nuclei are becoming progressively more tightly bound as crosslinking between polymer chains occurs.

CONCLUSIONS

1) Low resolution pulsed n.m.r. FID experiments, using a low cost, commercially available instrument,

may be used as a cure monitoring technique for epoxy resins: the change in signal amplitude of the solid and liquid components in the decay signal after the application of a 90° pulse can be monitored with respect to time in order to estimate the progress of cure.

2) The CPMG pulse sequence may be used to show the existence of at least two liquid components in the curing system, and their related properties.
3) The concentration and mobility of these components may be followed during cure using CPMG pulse sequences.
4) These changes are consistent with the formation of an alcoholic hydroxyl and secondary amine intermediate, and a long chain tertiary amine.

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