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# The $\beta$-Relaxation in Epoxy Resins; the Temperature and Time-Dependence of Cure

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Internal friction and creep measurements have been used to reveal the mechanism of cure in epoxy resins cross-linked with diethylene triamine (DETA). The $\beta$-relaxation is associated with the main glass transition of the undercured resin network. The glass transition temperature ($T_g$) is about 40° C above the maximum temperature of cure and the curing reaction slows down about 2 h after each increase of the temperature. At 25° C the cure is only about half complete and since in this resin, when fully cross-linked, $T_g$ is at about 140° C, temperatures of 100° C or over are needed to complete cure.

## 1. Introduction

In an epoxy resin crosslinked with an aliphatic polyamine, a secondary relaxation can be observed at a temperature below that of the glass transition. This is shown by the $\beta$-peak in fig. 1, which also shows that the area under the $\beta$-peak decreases after the specimen has been subjected to higher temperatures. It is known that unreacted epoxy and amine groups are present in this resin cured below 25° C, even after long times, and that the reaction between these groups continues at elevated temperatures [1] This reaction between the epoxy molecules and the crosslinking agent is called *cure*, and the $\beta$-relaxation is clearly associated with the cure of the resin.

The nature and causes of this relaxation, its changes with temperature and time, should give valuable help in understanding the mechanism of cure. These problems are examined here using internal friction and creep measurements.

Secondary relaxations in linear polymers are often caused by side chain motion. By analogy Lewis [2] suggests that the $\beta$-relaxation in epoxy resin is due to the motion of epoxy monomer molecules attached to the network by one end only. Heating furthers the cross-linking reaction and reduces the concentration of the partially reacted monomer molecules, hence the reduction in the area under the $\beta$-peak.

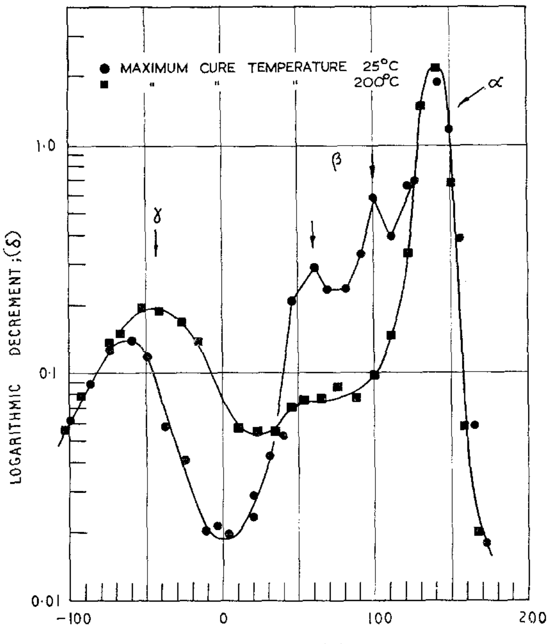

*Figure 1* Logarithmic decrement/temperature relationship for epoxy resin.

There may be, however, a different explanation for the $\beta$-relaxation. It was demonstrated in a previous paper [3] that both $T_g$ and $G_R$ (the rubbery modulus) of the resin are influenced by the degree of polymerisation and cross-linking. The resin cured below 25° C must have a network similar to that obtained by using the cross-linking agent in a non-stoichiometric concentration [3]. In this case the $\beta$-relaxation can be associated with the glass transition of the loosely cross-linked resin with a low degree of polymerisation.

A shift in $T_g$ with cure temperature for polyester resins has been suggested by Demmler [4] and for epoxy resin by Jenkins and Karre [5]. For a quantitative assessment of the network it is necessary to carry out measurements (if the resin is in the rubbery region) above the $\beta$-peak temperature. Accurate measurements, however, depend on the speed of sensitive observation relative to the speed of progressing cure. Neither of the above workers seem to have had a technique sensitive enough to detect changes in the rubbery modulus.

## 2. Experimental

The modulus $G$ and logarithmic decrement $\delta$ of the specimens were measured with a torsion pendulum in free vibration at 0.67 c/s frequency between − 180° C and + 250° C. The rigidity of the instrument was reduced by using a composite of sixteen thin wires to support the specimen and torsion arm assembly. The frequency and amplitude of the vibration could be detected virtually continuously with the aid of an optical recording instrument. Creep measurements were carried out by converting the torsion pendulum into a creep apparatus and applying a torque by an electric current put through a coil which deflected in a magnetic field. The techniques are well known and have been described in detail elsewhere [6].

The resin was cast from the purified diglycidyl ether of bisphenol A with the stoichiometric amount of diethylene triamine (DETA) curing agent. After one week's cure at 25° C, specimens of 10 × 1 × 0.15 cm were machined out of the block. The fully cured resin has its glass transition temperature, as measured by the damping peak, at 140° C.

### 2.1. The Cause of the $\beta$-Relaxation

Two experiments were carried out in order to find the cause of the $\beta$-relaxation. To minimise chemical changes during the first experiment the temperature of the specimens immersed in an oil bath was quickly raised, by heating the bath at the rate of 5° C/min. The specimens' modulus $G$ and logarithmic decrement $\delta$ were continuously monitored in the torsion pendulum and fig. 2 shows the plot of $G$ and $\delta$ against the temperature.

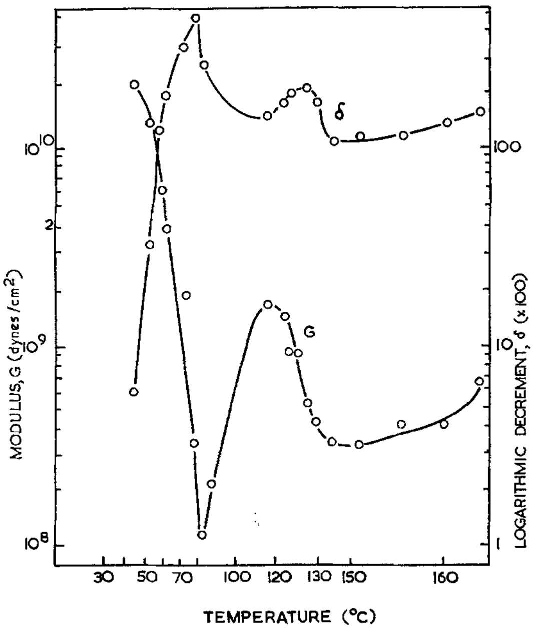

*Figure 2* Changes in the logarithmic decrement and modulus of an undercured resin during rapid heating.

When the temperature of the bath reached 50° C, the modulus of the resin started to drop until at 80° C it reached the very low value of $1.14 \times 10^8$ dyn/cm$^2$. This value is lower than the rubbery modulus of the same resin (fully cross-linked [3]) extrapolated to this temperature. On further heating, finally, the modulus approached the value it has in the fully cured state at the test temperature.

A small drop in $G$ only is expected to coincide with a true $\beta$-relaxation, but the resin should remain in the glassy state until it is heated above its glass transition temperature. This experiment therefore suggests that the $\beta$-relaxation, as observed in fig. 1, is a result of a glass-rubber transition of the whole resin network, which is in an undercured state.

The second experiment was designed to investigate the reproducibility of the damping peak on cooling. If heating causes the peak to reduce in size but to remain at the same temperature, $\delta$ should increase on cooling from a temperature above the peak. If heating causes the peak to move to higher temperatures, $\delta$ should continue to decrease on cooling from a temperature above the peak. Indeed the only safe way of telling whether a peak is stable or not is to see if it can be reproduced on cooling.

The temperature of another specimen was quickly raised and its $G$ and $\delta$ continuously monitored (fig. 3). Immediately after a drop in $\delta$ was observed, heating was stopped and the specimen was cooled. After a low value of $\delta$ was reached, heating was started again. The procedure of heating and cooling was repeated and a "new" peak was found several times, always at higher temperatures. In no instance did $\delta$ increase again on cooling, except when the peak moved to its final temperature.

The changes in the modulus, $G$, of the specimen during the experiment are also shown in fig. 3. A trough corresponds to each peak of $\delta$, except in the last case, when the peak was reproduced on cooling. If the apparent damping peak represents a true relaxation $G$ should reach a low value at the high temperature end of the peak. This is not the case, however, except above 150° C when a value of $2.7 \times 10^8$ is reached just above the peak temperature.

The results of this second experiment support the hypothesis that the observed peaks are not real, that is, they represent a change in the state of the resin resulting in a continuous shift of the main glass transition with progress of cure.

### 2.2. Time Effects

The temperature-dependence of cure has been demonstrated above, but not the rate at which cure progresses. The activation energy of the curing reaction, calculated from measurements taken before the resin reached its gel point, is known [2, 5, 7]. The gel point in a polycondensation reaction is reached when an infinite network develops.

According to Flory [8] the probability of a polyfunctional unit A being linked to a chain which at its other end is connected to another polyfunctional unit B is:

$$\alpha = P_A P_B = P^2$$

where $P_A$ and $P_B$ are the extent of reaction for groups A and B.

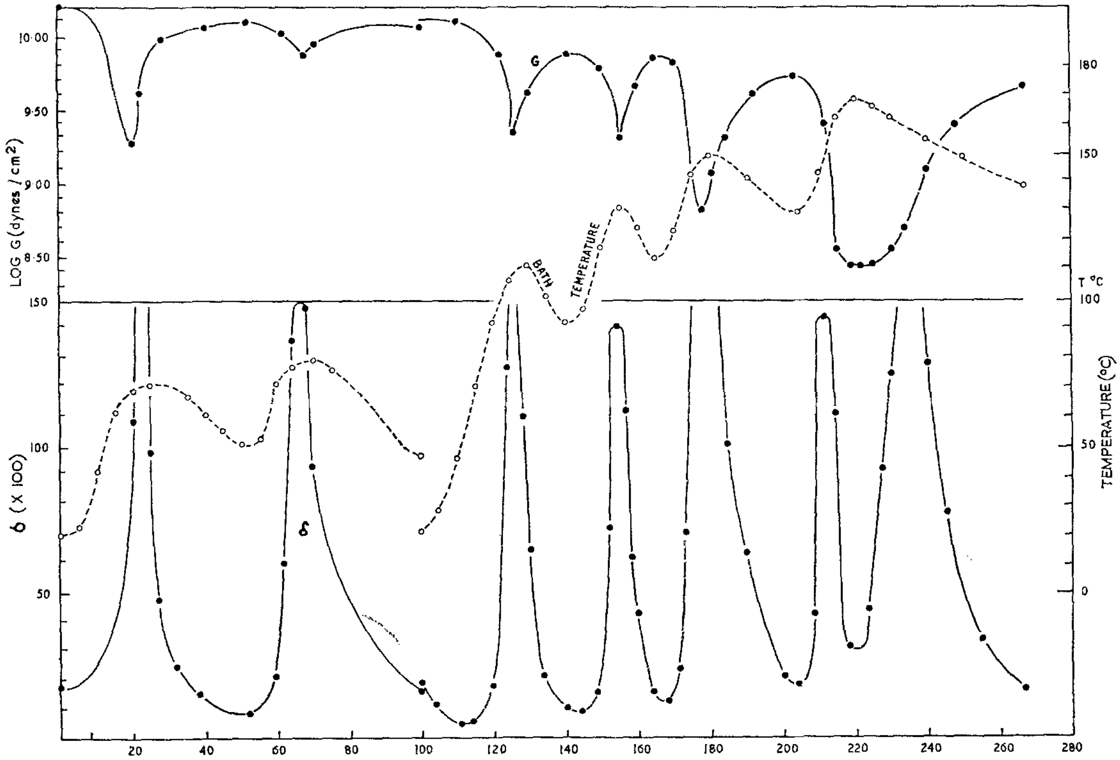

*Figure 3* Changes in the logarithmic decrement and modulus of an undercured resin during rapid heating and cooling cycles.

The critical value of $\alpha$ where an infinite network develops, causing gelation, is related to the functionality* of group A by the relationship

$$\alpha_{\text{crit}} = \frac{1}{f-1} \cdot$$

In the resin cast from the diglycidyl ether of bisphenol A and DETA, $f = 5$ and $\alpha_{\text{crit}} = \frac{1}{4}$. Consequently $P = \frac{1}{2}$. This is to say that the extent of reaction (i.e. the fraction of the functional groups initially present that have undergone reaction) at the gel point is approximately 50%, and little is known of the times necessary to complete cure after this stage.

Flory pointed out that during a linear polycondensation reaction, the reactivity of a group is not affected by the size of the molecule to which this group is attached. He found the rate constants to be unchanged up to 90% conversion, during which the viscosity of the mixture increased 2000-fold. Batzer and Fisch [9] found the same to be true in an acid anhydride-cured epoxy resin, where the velocity of the reaction remained constant whilst passing through the gel point and up to 80% conversion.

In epoxy resin the increase in viscosity during cure is much greater than 2000-fold. The viscosity of the mixture (a few thousand poise) increases to an ultimate value of $10^{13}$ poise, which is reputed to be the viscosity of a glass. At these very high viscosities it is most unlikely that further reaction can take place at any measurable speed. Tanaka and Kakiuchi [10] have indeed shown that the rate of cure slows down at the gel point. It is also clear from their figs. 13 and 14 that the rate of cure above the gel point is practically independent of the temperature. Similar conclusions can be drawn from a paper by Peerman *et al* [11].

However, Haran, Gringras and Katz [12], on the basis of dielectric measurements, suggest that 6 h at 30° C is enough to reach the final state of cure. Kwei [13] cured two resins, one cross-linked with DETA, the other with diamino hexane, at 70° C for 17 h, and reports their $T_g$ as 76° C and 52° C respectively. These values are much below those found by others [12, 14], indicating insufficient cure. It is clearly necessary to investigate how cure progresses with time at different temperatures.

Whilst internal friction measurements provide an excellent qualitative measure of cure they are difficult to use for a quantitative investigation. Another parameter related to changes in the logarithmic decrement $\delta$ is the creep compliance $J_{(t)}$ measured at time $t$, and the relationship between these parameters according to Zener [15] is:

$$\delta_{(\omega)} = \frac{\pi^2}{2}\left(\frac{\mathrm{d}\log J_{(t)}}{\mathrm{d}\log t}\right)_{\omega\,=\,1/t}$$

where $\omega$ is the frequency used in the experiment.

Measurements of the creep compliance for a fixed time interval (10 sec) after applying the stress can be used as a measure of changes in $\delta$. This provides a more sensitive and exact way of following changes during cure after the gel point is reached than any other method known today.

A new specimen was heated in steps for the first time and at each temperature the creep compliances between 1 and 10 sec were intermittently measured. In this way the specimen was under stress for 10 sec only once in every 5 min or more. Zero time was taken as 15 min after the bath reached the new temperature, since in previous experiments this time was found to be enough for equilibrating the temperature in the specimen. The resultant curves in fig. 4 show the dependence of the 10 sec compliance on time at each temperature.

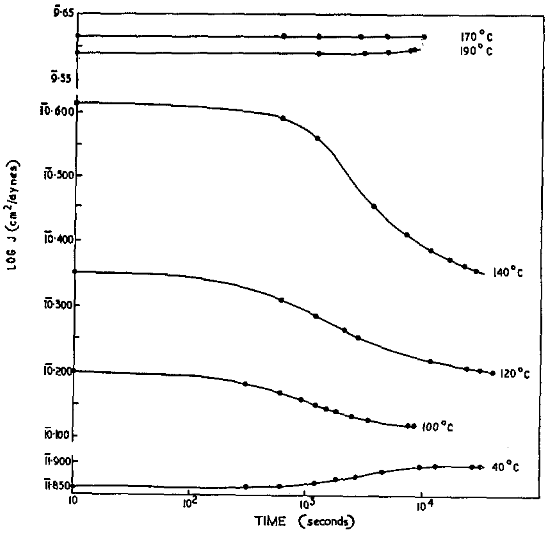

*Figure 4* Changes in the 10 sec creep compliance of epoxy resin with time at different cure temperatures.

The 10 sec compliance values increase with time at 40° C and decrease with time at and above

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*The number of other monomers with which a monomer may join when fully polymerised.

100° C. The increase below 50° C is due to the development of a flexible segment

$$(\text{—CH}_2\text{—CHOH—CH}_2\text{—O—})$$

causing the $\gamma$-relaxation, as will be discussed in a later publication [16]. The decrease in the 10 sec compliance with time, at temperatures at and above 100° C is due to further cross-linking, which shifts the glass transition to higher temperatures. The compliance at each new temperature follows a sigmoidal curve and reaches a new equilibrium, corresponding to a new equilibrium of $J$ ($t$ = 10 sec). The inflexion point of these curves is at about 3000 sec, irrespective of the temperature. There is no change in the creep compliance with time after the resin has been heated to above its permanent glass transition temperature.

It is reasonable to assume that, on heating, cure progresses in the following stages: 1. increased temperature reduces viscosity, which increases chain mobility; 2. increased mobility results in further cross-linking; 3. further cross-linking results in increased viscosity and reduced mobility. Thus $T_g$ of the resin appears to be about 40° C above that of the maximum cure temperature.

At the inflexion points in fig. 4, the resin is probably in an iso-viscous state and the rate of further cure at all temperatures is identical. The apparent activation energy of cure, as long as the resin is beyond the gel point, appears to be zero. In fact the term "activation energy" cannot be used because of the different initial degree of cross-linking in each case.

This experiment confirms the results of Tanaka and Kakiuchi [10], and clearly indicates that Haran *et al* [12] and Kwei [13] did not realise that their resin was undercured.

It can be concluded, therefore, that the purified diglycidyl ether of bisphenol A cured with the stoichiometric amount of DETA at room temperature, gels at about 50% conversion, and probably solidifies and reaches an equilibrium at about 65% conversion [15]. After 100° C only this equilibrium progresses to near completion. For many applications a 100% conversion is not required and resin manufacturers may correctly suggest in their literature that the 100° C postcure can be replaced by two weeks at 25° C. Sensitive mechanical, thermal or (probably) electrical measurements can detect undercure in these resins, and such undercured resin may be unsuitable for certain applications.

## Acknowledgement

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