EFFECT OF CURE ON THE IMPACT BEHAVIOUR OF AN EPOXY RESIN

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Impact tests have been conducted on an epoxy resin mixed with DDM hardener and cured at either 100°C or cured at 100°C followed by postcure at 180°C. The impact fracture energy G_c decreased with increasing time of cure and postcure. The extent of cure was determined by assay of the epoxy groups using near infrared spectroscopy. In order to specify the structure of the resins two parameters have been identified, the glass transition temperature T_g^i and the area of the viscoelastic tanδ loss peak. There were linear relationships between G_c and these parameters for both cure and postcure. In addition the glassy Young's modulus E_g was a linear function of T_g^i.

INTRODUCTION

In recent years there has been a significant increase in the use of polymers for structural applications. Frequently the limiting selection criterion is the response of the material to impact. Despite the developments in fracture mechanics conventional impact tests are still widely used for comparing different materials and for quality control purposes since they are useful to assess their relationships with other structural and mechanical parameters. For epoxy resins there are major changes in their properties with cure which are related to increase in their glass transition temperatures.

Extent of cure is a term used ubiquitously to qualitatively represent the concept of the relative progress of the processes that occur when a thermosetting resin is the subject of a thermal treatment, that is a cure temperature T_c and a cure time t_c. However, a method of quantitative specification of the extent of cure has been elusive. An unambiguous operational definition of the "state of cure" is required. The effects of cure on mechanical properties have been discussed by Ellis (1) who recognised that the T_gTP diagram introduced by Wang and Gillham (2) provides a framework for

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correlating the physical properties of thermosetting resins. Kim et al (3) undertook a general survey of cure on mechanical properties by varying the epoxy/hardener ratio. Our recent work (4) indicates that the extent of cure is not a monotonic function of the extent of the consumption of epoxy groups. Hence for analysis of the chemical kinetics of cure it is essential that the concentration of functional groups is assayed as a function of cure treatment. This is best achieved by studying an epoxy of constant composition and monitoring the effects of cure T_c, t_c and postcure T_{pc}, t_{pc}.. In the present paper systematic studies of the effects of cure treatment for a constant composition of an epoxy resin have been evaluated in terms of the impact behaviour relative to the glass transition temperature and the glassy Young's modulus.

EXPERIMENTAL

Epoxy resin, Shell 828, was mixed with 27 phr (parts per hundred of resin) DDM hardener at 100°C and cast into slabs using sheet moulds. The moulds were placed in an oven for curing at T_c = 100°C for times t_c = ½ to 24 h (•) or for curing at T_c = 100°C for t_c = ½ h followed by postcuring at T_{pc} = 180°C for times t_{pc} = ½ to 7 h. Two postcure routes were used : route A - the resin was postcured immediately following cure at T_c = 100°C for t_c = ½ h(O); route B - the sheets were allowed to cool to room temperature, "rested" for three days at 22°C and then postcured at T_{pc} = 180°C (⊕). Rectangular specimens containing a sharp pre-crack were loaded in four-point bending in a Hounsfield Plastic Impact Tester. The glassy Young's modulus E_g of the resins were determined from flexural testing of rectangular specimens using four-point bending in a Mayes servo-electric testing machine under a constant displacement of 0.5 mm/min.

The complex Young's modulus E* of the cured resins were measured using a Polymer Laboratories dynamic mechanical thermal analyser (DMTA) over the temperature range 20 to 220°C in an air environment with constant displacement. Measurements were at a fixed frequency of 1 Hz with a temperature scan of 4°C/min. The glass transition temperature T_g^i was determined from the intercept of the glass plateau with the transition slope of the storage modulus log E' versus temperature curve as defined in Ref. (4). In addition the loss peak tanδ was determined. The concentration of epoxy groups at different cure times were measured in order to determine the extent of reaction X_e. A Perkins-Elmer 300 uv-visible spectrophotometer was used in the near infrared spectral region in the absorbance recording mode at a scanning speed of 450 nm/min. (4).

RESULTS AND DISCUSSION

In Figure 1 the extent of reaction is plotted against equivalent cure time $t_c^{'} (= t_c - ½ h)$ and postcure time t_{pc} which allows both the results of resins cured at 100°C and also postcured to be presented on a common time axis. Direct assay of the consumption of epoxy groups is necessary but not sufficient to specify the structure of the cured resin since structural changes occur after the consumption of all epoxy groups as the graph of increasing glass transition temperature T_g^i with cure and postcure demonstrates in

Figure 2. We have previously (4) suggested operational definitions of the glass transition temperature of the cured resin and indicated that T_g^i appears to be most appropriate if a single parameter is to be used and that it is necessary to specify the frequency and scanning rate of the DMTA. Since the assay of the concentration of epoxy groups becomes increasingly inaccurate at $X_e \rightarrow 1$ it can be appreciated from comparison of Figures 1 and 2 that the glass transition temperature continues to increase with prolonged cure and especially with higher temperature postcures (4).

Figure 3 shows that the glassy Young's modulus E_g decreases linearly with T_g^i. The glassy modulus was measured at 22°C which is well below their glass transition temperatures. There are conflicting reports on the effect of network structure on the glassy moduli with Morel et al (5) listing cases where these moduli either increase, decrease or are independent of the crosslink density and Vakil and Martin (6) report that the Young's modulus measured in flexure at 25°C is not a function of the average molecular weight of network chains. There does not appear to be a universal relationship between E_g and T_g (7).

The measured impact fracture energies G_c, based on the analysis of Plati and Williams (8), decrease with cure/postcure time as shown in Figure 4. These impact energies of a cured epoxy resin are higher than those of Kinloch et al (9) but lower than those of Low and Mai (10). Both their measurements were made using nominally very similar cured epoxy resins, with 5 phr piperidine cured for 16 h at 120°C so it is somewhat surprising that their results are divergent. However, from our measurements it is clear that for relatively small changes in cure treatment there may be very significant changes in impact energy, for instance, with a postcure time of $t_{pc} = 1\frac{1}{2}$ h G_c decreases from 1.4 to 1.1 kJm^{-2}. Low and Mai (10) show that the impact fracture energy is rate dependent increasing from $G_c = 2.43$ to 3.5 kJm^{-2} when the strain rate is increased from 18 to 113 s^{-1}. The rate of strain for our impact tests was 100 s^{-1}. For a SENB test with a strain rate of 6.5×10^{-4} s^{-1} Low and Mai found that $G_c = 1.2$ kJm^{-2}. We have also measured the strain energy release rate G_{ICi} for our resins with a double-torsion test geometry and obtained values of 0.14 to 0.16 kJm^{-2} for samples cured at 100°C and 0.18 to 0.28 kJm^{-2} depending on the cure or postcure times (11). From study of Figure 4 it can be appreciated that there are structural changes in an epoxy resin with extended cures/postcures with the greater effects with postcure at 180°C which occur even after all the epoxy groups have been consumed, as observed when comparing Figures 1 and 4. Such structural changes that occur after all the epoxy groups have been consumed produce very significant changes in the glass transition temperature of these resins, as shown in Figure 2, with most of the increase in T_g^i with postcure after all the epoxy groups have reacted.

The relationships between impact energy G_c and the glass transition temperature are shown in Figure 5. The observation of the two separate linear relationships is a direct consequence of Figures 4 and 2 which show that there are two relations for both G_c and T_g^i with $t_c^{'}/t_{pc}$. Whilst T_g^i is a sensitive measure of the extent of cure it is not

sufficient for the specification of the structure of these cured epoxy resins. It is important to consider viscoelastic effects on the fracture of polymeric materials (12). For a viscoelastic material there are energy absorbing processes associated with the bending and vibrations of the Charpy specimen and also time dependent strains at the crack tip. Wada and Kasahara (13) considered the fracture energy in terms of a Maxwell viscoelastic model. Thus, following the implications of Wada and Kasahara there should be a dependence of the impact fracture energy on the area of the tanδ viscoelastic loss peak. This is confirmed by our data shown in Figure 6, where it is seen that there is a linear relation between G_c and the area of the tanδ loss peak for the resins cured at $T_c = 100°C$. Further research is required in order to determine the exact relationship for the postcured resins. There are in fact two linear relationships between the area of the loss peak and T_g^i depending on the cure or postcure temperatures as shown in Figure 7. It should be noted that the tanδ loss peak was measured at a frequency of 1 Hz so it must be that this is an additional parameter to T_g^i which is required for the specification of the structure of a cured epoxy resin. It is these changes in structure which affect the impact fracture energy of these epoxy resins. With prolonged postcure the loss peak is appreciably narrowed as discussed previously (4). This relatively small loss peak is associated with the lowest measured impact energy.

CONCLUSIONS

1. For epoxy resin systems it is necessary to specify : detailed composition, full cure treatment, and other relevant variables.

2. For cured epoxy resins T_g^i is a primary parameter of their structure. However the area of the viscoelastic tanδ loss peak is also required to specify their structure more completely.

3. The glassy Young's modulus for these resins is a linear function of T_g^i.

4. The impact fracture energy G_c decreases with t_c' / t_{pc} for DDM cured resin ($T_c = 100°C$, $T_{pc} = 180°C$).

5. There are two linear relations for G_c versus T_g^i for $T_c = 100°C$ and $T_{pc} = 180°C$ and also for G_c versus $\int \tan \delta \, dT$.

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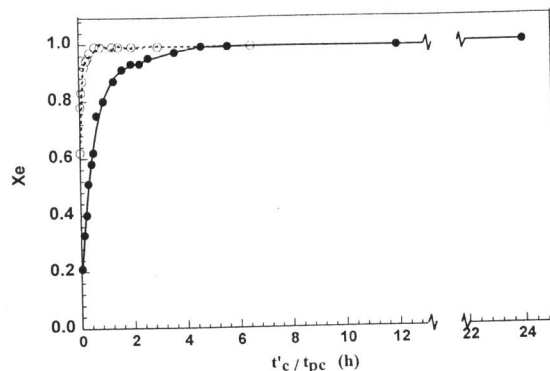
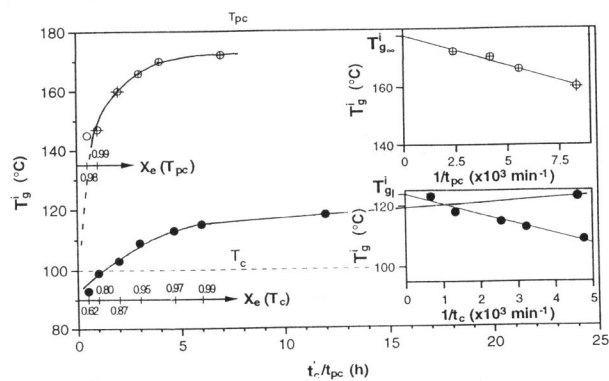Figure 1   Extent of reaction (X_e) v cure/postcure time $\left(t'_c / t_{pc} \right)$.

Figure 2   Glass transition temperature T_g^i v cure/postcure time $\left(t'_c / t_{pc} \right)$.
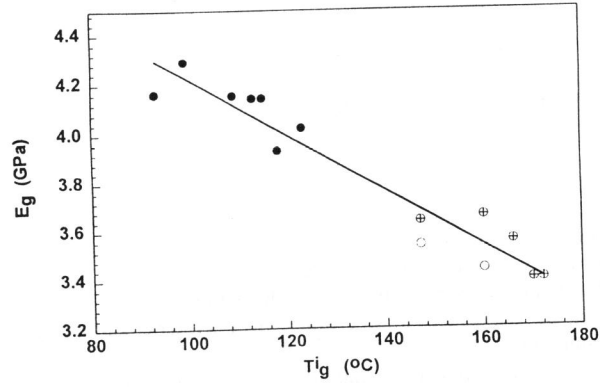
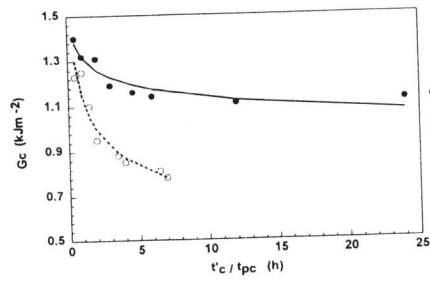Figure 3   Glassy Young's modulus (E_g) v glass transition temperature $\left(T_g^i\right)$.

Figure 4   Impact fracture energy G_c v cure/ postcure time $\left(t_c^{'} / t_{pc}\right)$.
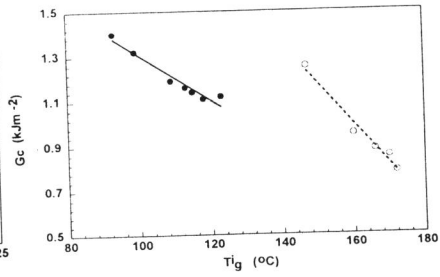
Figure 5   Impact fracture energy G_c v glass transition temperature $\left(T_g^i\right)$.
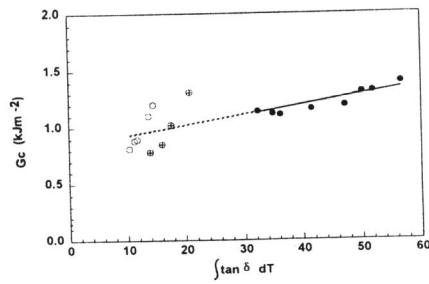

Figure 6.   Impact fracture energy G_c v loss peak area ($\int \tan \delta \, dT$).
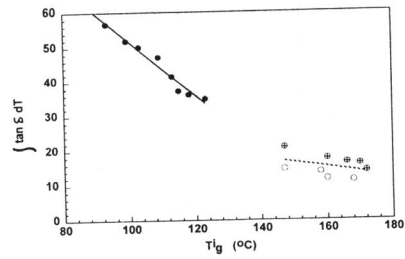
Figure 7   Loss peak area ($\int \tan \delta \, dT$) v glass transition temperature $\left(T_g^i\right)$.