Effect of crosslinking density on $\Delta C_p(T_g)$ in an epoxy network

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The difference in heat capacity of the liquid state and that of the glassy state at the glass transition temperature, $\Delta C_p(T_g) = C_{p(l)} - C_{p(g)}$, has been determined in samples of epoxy resin with different extents of cure. The epoxy was a diglycidyl ether of bisphenol A cured isothermally by phthalic anhydride as hardener in a temperature range between 30 and 130°C for various periods of time. As crosslinking density increases, the $\Delta C_p(T_g)$ decreases. This result has been interpreted within the framework of 'strong' and 'fragile' behaviour of glass-forming systems. The decrease of $\Delta C_p(T_g)$ with increased crosslinking suggests a resistance of the glassy structure to the breakdown due to a 'strengthening' effect of the crosslinked structure.

(Keywords: crosslinking density; epoxy resin; glass transition)

Introduction

It is well known that one of the factors that affects the glass transition temperature, T_g, is the crosslinking introduced into the polymer to form a network. An increase of the crosslinking density reduces the chain mobility and, consequently, increases the T_g. This effect can be understood within the framework of the free volume concept, and by the Gibbs–DiMarzio theory[1].

In amorphous and semicrystalline polymers, the difference in heat capacity of the liquid state and that of the glassy state at T_g, $\Delta C_p(T_g) = C_{p(l)} - C_{p(g)}$, has been observed to decrease as the T_g increases. A review by Mathot[2] summarizes about 40 non-crosslinked polymeric systems showing this dependence of $\Delta C_p(T_g)$ on T_g.

This effect has also been observed in polymeric networks where an increase of the crosslinking density produces not only an increase of T_g, but a diminishing of $\Delta C_p(T_g)$. Ellis *et al.*[3] observed this effect in polystyrene/divinylbenzene networks. More recently, Chang[4] has shown that increasing T_g in diglycidyl ether of bisphenol A (DGEBA) homopolymerized by a catalyst using different thermal histories causes $\Delta C_p(T_g)$ to decrease. However, Lee and McKenna[5] observed no significant changes in $\Delta C_p(T_g)$ when crosslinking density was increased in a polypropylene oxide/DGEBA network.

Recently, the $\Delta C_p(T_g)$ has been discussed by Angell[6] in terms of 'strength' and 'fragility' of glass-forming liquids. 'Strong' liquids show a network structure of the glass which is resistant to breakdown well above T_g. These systems, such as silica, show a typically Arrhenius dependence of viscosity and small values of $\Delta C_p(T_g)$. On the other hand, 'fragile' liquids present a structure that breaks down easily with temperature, which suggests an apparent absence of glassy structure above T_g. These systems show a non-Arrhenius behaviour, and large values of $\Delta C_p(T_g)$ where the discontinuities in liquid/glass behaviour are clearly visible.

This classification has been widely applied in inorganic and organic non-polymeric substances and it can be extrapolated to polymeric systems assuming that the liquid state above the glass transition region corresponds to the molten state.

In this paper, the effect of crosslinking on $\Delta C_p(T_g)$ in an anhydride cured epoxy resin based on DGEBA has been studied. The decrease of $\Delta C_p(T_g)$ when the extent of cure increases suggests a 'strengthening' effect due to the crosslinking of the epoxy network.

Experimental

The epoxy resin was a modified DGEBA (Ciba-Geigy Araldite CY225) crosslinked by hardener derived from phthalic anhydride (PA) with catalyst (Ciba-Geigy HY225) as described in refs 7 and 8. To obtain different extents of cure, the samples were isothermally cured in a temperature range between 30 and 130°C for various periods of time.

Calorimetric measurements were performed with a Mettler Thermoanalyser TA 4000 equipped with a low temperature range DSC 30 differential scanning calorimetry module. The calorimeter had previously been calibrated with indium standard. The samples weighed about 10 mg. The d.s.c. traces were obtained at a heating rate of 10 K min^{-1} from -80 to 280°C, under nitrogen atmosphere.

The extent of cure, α, was calculated by the residual enthalpy of curing method[7,8]. The ΔC_p value was obtained extrapolating both the C_p liquid line and the C_p glassy line. The extrapolation of $C_{p(g)}$ was carried out at a temperature well below the T_g, where the dependence of $C_{p(g)}$ on temperature was nearly linear. Above the T_g, the dependence of $C_{p(l)}$ on temperature was practically linear, showing a lower slope than in $C_{p(g)}$. The estimated uncertainty of ΔC_p was about 5%.

The isothermal curing, the vitrification phenomenon and further physical ageing of the DGEBA–PA system have been described in previous papers[7,8]. The dependence of T_g on the thermal history has also been investigated in the same system[9].
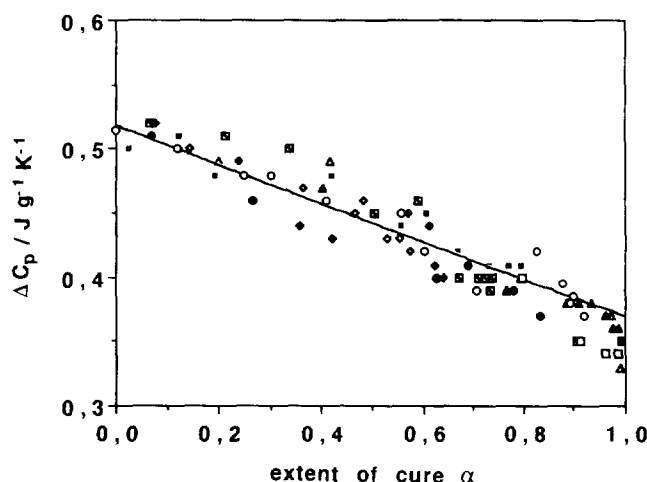
Figure 1 $\Delta C_p(T_g)$ values *versus* the extent of cure reaction, α, obtained in the epoxy resin cured at different temperatures: ($\Diamond$, 30°C; $\blacklozenge$, 40°C; $\boxminus$, 50°C; $\blacksquare$, 60°C; $\bullet$, 70°C; $\bigcirc$, 80°C; $\triangle$, 90°C; $\blacktriangle$, 100°C; $\square$, 110°C; $\boxplus$, 130°C. The solid line is calculated from equations (1) and (2)

Results and discussion

Figure 1 shows the values of $\Delta C_p(T_g)$ *versus* the extent of cure obtained at different curing temperatures. It is observed that $\Delta C_p(T_g)$ decreases as the extent of cure increases or, in other words, as the crosslinking density increases. The values of $\Delta C_p(T_g)$ in the initial mixture of resin–hardener is about 1.5 times the value for the fully cured epoxy resin. *Figure 1* also shows a line calculated from equations (1) and (2). Equation (1) shows the dependence of T_g on extent of cure according to Pascault and Williams[10] based on an equation proposed by DiBenedetto[11]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (1)$$

where λ is an adjustable parameter whose value was found to be 0.69, T_{g0} is the glass transition temperature of the reactants ($-23.2°C$), and $T_{g\infty}$ is the maximum T_g of the resin (109°C) as described in ref. 9.

Equation (2) refers to the dependence of $\Delta C_p(T_g)$ on T_g and is similar to the equation proposed by Boyer[12]:

$$\Delta C_p(T_g) = a + \frac{b}{T_g} \quad (2)$$

where a and b, estimated from our experimental results were $8.9 \times 10^{-2}\,J\,g^{-1}\,K^{-1}$ and $107.2\,J\,g^{-1}$, respectively.

According to the Gibbs–DiMarzio theory of the glass transition[13], an increase of the crosslinking density originates an increase of the chain stiffness. The stiffer the chains become the lower is the configurational entropy, and it follows from the statistical mechanics that ΔC_p should also decrease.

Additionally, the decrease of $\Delta C_p(T_g)$ with crosslinking density can be described empirically within the framework of 'strong' and 'fragile' behaviour of glass-forming liquids[6]. As pointed out above, the 'strong' liquids are observed to be those with self-reinforcing network structures, which also manifest their resistance to structural breakdown by small changes in $\Delta C_p(T_g)$. From this point of view, an increase of the crosslinking density of the epoxy network could suggest a 'strengthening' effect similar to that reported in some inorganic network glasses[6,14], leading to lower values of $\Delta C_p(T_g)$. The occurrence of this 'strengthening' effect agrees with the expected decrease of configurational entropy of the epoxy network when the crosslinking increases. This is an additional result to other studies about structural parameters obtained by enthalpy relaxation experiments, which show that the crosslinked structure strengthens the glass[15].

In short, the crosslinking process of an epoxy network originates a decrease in $\Delta C_p(T_g)$. Within the framework of the 'strong' and 'fragile' classification of glass-forming liquids, this decrease suggests a resistance to the breakdown of the glassy structure due to a 'strengthening' effect.

Acknowledgement

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