Thermal conductivity studies on the curing process of diol-modified epoxy systems

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Diglycidyl ether of bisphenol A was cured with aliphatic diols of different chain length. The time to gelation and the end curing time or time to vitrification were determined at different curing temperatures and concentrations of diol, by means of thermal conductivity measurements. From these results Arrhenius activation energies can be obtained.

(Keywords: epoxy curing; thermal conductivity; gel point)

Introduction

Monitoring the cure of resin products is very important for quality control in reactive polymer processing industries. While curing, dramatic changes take place in the properties of the systems owing to the chemical crosslinking reaction. In a previous paper[1] we described a simple device to monitor the cure of thermosetting resins by means of thermal conductivity measurements. The method involves the determination of thermal diffusivity with a pulse arrangement from which the thermal conductivity can be calculated. We now report the results of a study on diol-modified epoxy systems by this method.

Experimental

All chemical products are commercially available and were used without further purification. Diglycidyl ether of bisphenol A (DGEBA) was reacted with α,ω-diols of different chain length (HO–$[CH_2]_n$–OH; $n = 2, 4, 6, 8$ and 10) in a molar ratio DGEBA:diol of 1:0.25. Magnesium perchlorate (3 mol%) was added each time as a catalyst. The system with 1,4-butanediol was also prepared with molar ratios DGEBA:diol of 1:0.5, 1:0.75 and 1:1, achieving systems with different concentrations of diol.

The purpose of using diols in the systems was to render flexible, in a controlled way, the otherwise hard and brittle basis resin according to studies of Tänzer, Fedtke and co-workers[2–5]. We used magnesium perchlorate as a catalyst because it is known to be more selective than tertiary amines or other common epoxy catalysts[5]. Curing experiments were carried out in a temperature range of 90–120°C for all investigated systems. All thermal conductivity measurements during the curing process were made in a device described in a previous paper[1].

Results and discussion

The experimental curves of thermal conductivity *versus* cure time show the qualitative behaviour expected for thermoset resins for all studied systems. The time to gelation (t_{gel}) and the time to the end of cure (t_{end}) or time to vitrification (t_{glass}) can be obtained from these curves[1]. At the end of a curing process the developing network structure does not change appreciably. The result is a constant value of the thermal conductivity, since this parameter is related to the structure of a polymer[6]. On the other hand, it is well known that for epoxy systems, depending on the curing temperature vitrification can take place, resulting in a freezing of the developing network structure[7,8]. This will also lead to a constant value of the thermal conductivity. Therefore with a single thermal conductivity experiment, in addition to t_{gel}, only t_{end} or t_{glass} can be obtained.

Figure 1 shows the obtained times to gelation plotted *versus* the diol chain length for different curing temperatures. With increasing curing temperature t_{gel} drops as expected for thermoset epoxy systems. For all curing temperatures the time to gelation also drops with increasing diol chain length. This behaviour is more pronounced at relatively low curing temperatures. At higher curing temperatures, such as 120°C, the dependence on diol chain length seems to vanish. Two effects may account for such behaviour. First, increasing the curing temperature results in a decrease of viscosity and therefore the mobility of the reactants increases, and second, the greater reactivity of the larger chain diols in the curing system results in a decrease of t_{gel}. Similar plots for the t_{end}/t_{glass} (not shown here) gave qualitatively the same behaviour as t_{gel} for different diols and different curing temperatures.

Figure 2 shows the plots of both t_{gel} and t_{end}/t_{glass} *versus* the molar ratio DGEBA:diol for the systems with different concentrations of 1,4-butanediol. There is a minimum for all curing temperatures for the system with a molar ratio DGEBA:diol of 1:0.5. We find an explanation for this unexpected behaviour in the preparation of the system mixtures before curing. Since magnesium perchlorate is not soluble in the basis resin

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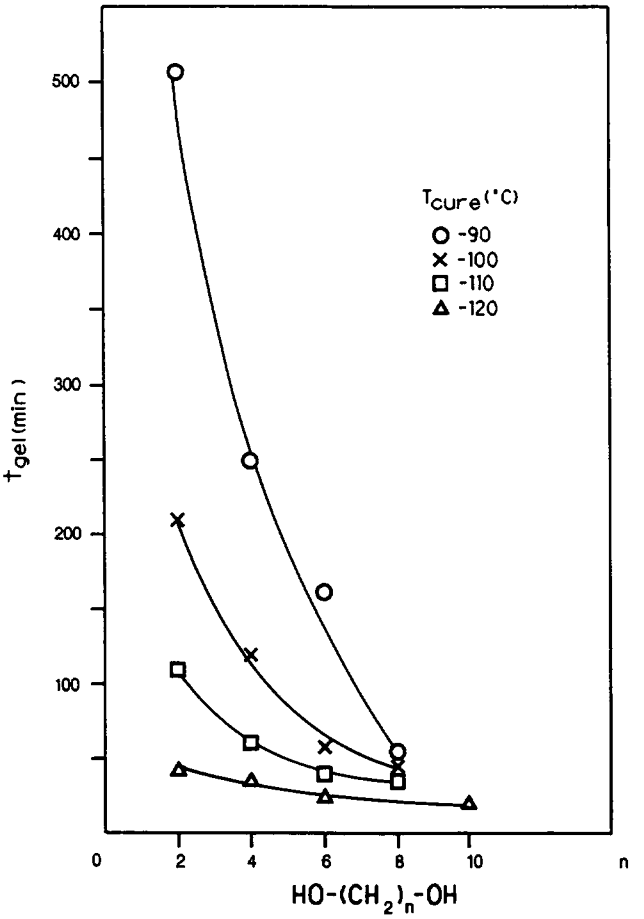

Figure 1 Time to gelation *versus* diol chain length for different curing temperatures

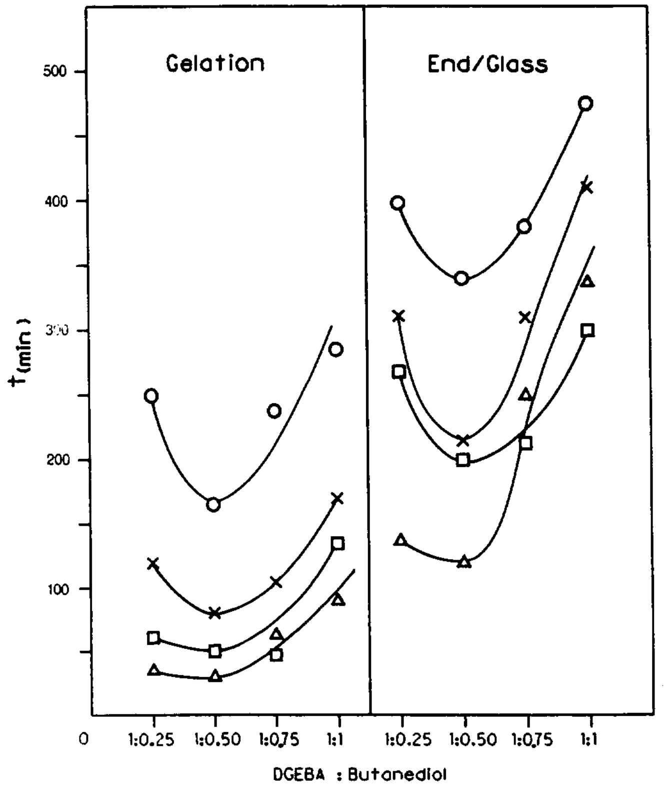

Figure 2 Time to gelation and time to end of cure/time to vitrification *versus* amount of diol for different curing temperatures: ○, 90°C; ×, 100°C; □, 110°C; △, 120°C

Table 1 Arrhenius activation energies

	E_a at t_{gel} (kJ mol^{-1})	E_a at t_{end}/t_{glass} (kJ mol^{-1})	E_a at t_{gel} / E_a at t_{end}/t_{glass}
Diol			
1,2-Ethanediol	88	37	2.4
1,4-Butanediol	78	40	2.0
1,6-Hexanediol	76	36	1.8
1,8-Octanediol	26	38	0.7
Molar ratio DGEBA:diol			
1:0.25	78	40	2.0
1:0.50	68	42	1.6
1:0.75	53	21	2.5
1:1	46	15	3.1

alone, the diol assisted in the dissolution of the catalyst and generated homogeneous mixtures. According to the reaction mechanism proposed by Nikitina and Rosolovskii[9] for this kind of catalyst in epoxy systems, undissociated catalyst would be unreactive. Therefore we postulate that at concentrations of diol lower than in the molar ratio of 1:0.5, part of the catalyst is not dissociated. The result is a slower curing reaction than in the system with a molar ratio of 1:0.5. With even higher concentrations of diol, when the catalyst is already completely dissociated, a dilution effect on the active centres takes place resulting again in a slower curing process.

The temperature dependence of a curing reaction near t_{gel} shows Arrhenius behaviour[10], therefore the times to gelation can be plotted and the activation energies can be obtained using a modified Arrhenius equation[11]:

$$\ln(t_{gel}) = \ln(K/A) + E_a/RT$$

Table 1 shows the results of these calculations. As expected, the activation energies were systematically higher for the systems with smaller diol chain length, owing to the lower reactivity of these diols. For comparison, the reported[12] activation energies for the reaction of the basis resin with alcohols of different chain length is 59–63 kJ mol^{-1}. These reported values are in the same range as the values found for our systems. The values of the activation energies of the systems with different concentrations of diol are in the same range but not in accordance with the expected trend, since for the slower curing systems we expected higher activation energies. In some publications[5,12] we find the same kind of plots for the time to the end of cure as for the time to gelation in order to obtain the activation energies of the entire curing process. For the explanation of these unexpected results we also tried these plots and calculations. The obtained activation energies at t_{end}/t_{glass} are shown in *Table 1*. *Table 1* also shows the ratio of the activation energies at t_{gel} to the activation energies at t_{end}/t_{glass}. Finally, we find the expected trend of values with a minimum for the system with a molar ratio resin:diol of 1:0.5. This means that the activation energies to gelation alone do not explain the experimental values of gel point measurements. It seems that we need to take into account the process until the end of cure and make a correlation between the activation energies of both events.

Conclusions

Thermal conductivity measurements proved to be a suitable method for cure monitoring of diol-modified epoxies. With this method it was clearly shown that the use of different diols in epoxy systems not only results in a different network density and final properties of the resins[13,14] but also in a different curing behaviour.

The longer the diol, the faster the curing process at a given temperature within the studied temperature range. The higher the concentration of diol, the slower the curing process if the catalyst is completely dissolved in the system. Otherwise a minimum in the characteristic curing times with diol concentration is observed.

From these measurements, activation energies at two different stages of the curing process can be obtained and a better understanding of this process can be achieved.

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