

Rheological monitoring of curing reaction of an epoxy system: effect of heating rate

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Received: 1 July 1999/Revised version: 25 October 1999/Accepted: 27 October 1999

Summary

In this work, we present a rheological study of the non-isothermal curing reaction of an epoxy resin, diglycidyl ether of bisphenol A, with aliphatic amines of different functionalities. The reaction was carried out under a linear temperature program and the epoxy-amine mixtures were prepared at different epoxy groups to amine-hydrogen ratios. The effect of vitrification on the curing reaction is analyzed as a function of the heating rate. At low heating rates, the viscous modulus, G'' , presents two peaks. The first peak is due to the vitrification-devitrification phenomenon that takes place during cure. At the second peak, the sample is completely cured and the decrement in G'' is only due to the temperature increment.

Introduction

The curing of thermosetting polymers is usually characterized by two phenomena: gelation and vitrification. Gelation corresponds to the incipient formation of an infinite network, while vitrification involves the transformation from a liquid or rubbery state to a glassy state. The progress of the polymerization reaction can be monitored by rheological measurements. Halley and Mackay (1) give an excellent review in the current trends in chemorheology of thermosets. However, there is not information on the non-isothermal cure of these materials.

One of the most important disadvantages of the epoxy systems is their poor crack propagation resistance. To overcome this problem, a second component (elastomer or engineering thermoplastic) is generally added (2). The resulting toughened material is a multiphase system. The final properties of these materials depend mainly on the morphology of the blends. The morphology might be controlled by manipulation of the polymerization reaction (3). Gelation and vitrification phenomena may play an important role on the fixation of the phase-separated structure (3).

Figure 1 shows the different phases that may appear during cure of a thermoset system. In this figure, x_{gel} is the conversion at the gel point; x_v is the conversion at which the system vitrifies at given curing temperature. Tg_0 and Tg_∞ are the glass transition temperatures for an uncured sample ($x=0$) and for a completely cured material ($x=1$) respectively. Two independent aspects affect the glass transition temperature as conversion progress: a) the degree of crosslinking, and b) the copolymer effect. Regarding the first effect, linear (5) and logarithmic (6) relationships have been proposed between $(Tg-Tg_0)$ and the crosslinking density. When the curing of a thermoset system is carried

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out isothermally for temperatures lying in the range between T_{g_0} and T_{g_∞} , the system will vitrify before reaching complete reaction.

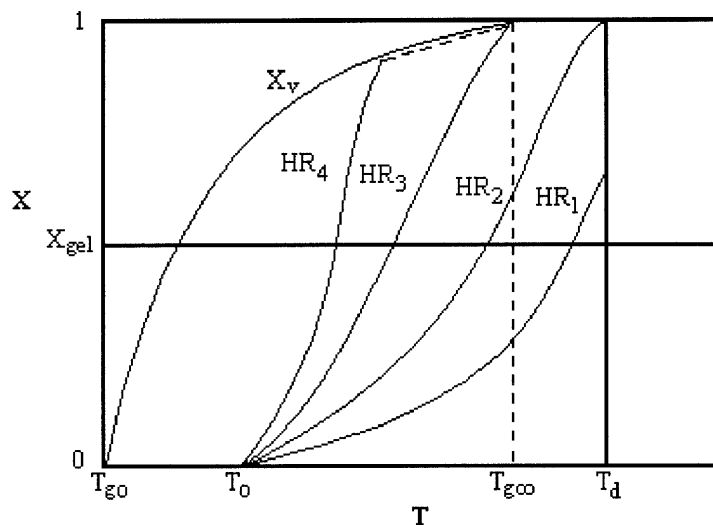


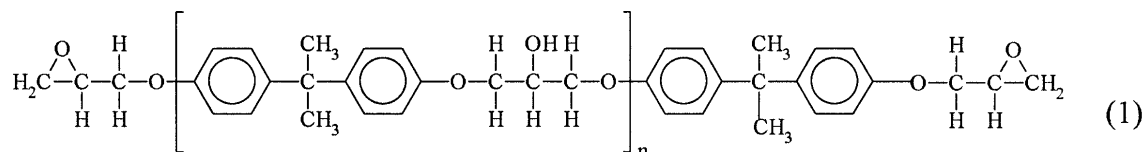
Figure 1. Vitrification diagram for a thermoset system.

For non-isothermal curing under a linear temperature program the conversion-temperature trajectory may reach the vitrification curve before it reaches complete reaction, depending on the heating rate ($HR = dT/dt$) (6-9). In figure 1, several x - T trajectories (starting at T_0) at different heating rates ($HR_1 > HR_2 > HR_3 > HR_4$) are shown. For heating rates between HR_3 and HR_2 , the curing proceeds to complete reaction. However, for heating rates lower than critical value, the vitrification curve is attained before the reaction is completed, at this point the reaction rate decreases abruptly. Since the heating continues, the reaction is again activated and the reaction proceeds until completion in a region close enough to the glassy state (6). The monitoring of the changes in rheological properties during non-isothermal curing might be helpful to study the vitrification effect on cure kinetics. For isothermal cure, some authors (10) consider the gel point when the G' (elastic or storage modulus) and G'' (viscous or loss modulus) curves crossover and the vitrification point when G'' shows a maximum (11).

In previous studies (12-13), we reported the monitoring of rheological properties during isothermal cure in epoxy-aliphatic amine systems. In this work, we have studied the non-isothermal cure of these thermoset systems. The aim of the study is to identify the heating rates at which vitrification affects the polymerization reaction and to correlate the changes in rheological properties with the vitrification-devitrification phenomenon

Experimentation

The epoxy resin used was the diglycidyl ether of bisphenol A (DGEBA). It was provided by Ciba-Geigy (Araldite GY-6010) with a functionality of 2.0 and a molecular weight $M_w=376.65$ ($n=0.125$)



As curing agents, we used four different aliphatic amines (Table 1) from Aldrich Co.

Name	Chemical structure	Functionality
Ethylenediamine (EDA)	$\text{NH}_2\text{-(CH}_2\text{)}_2\text{-NH}_2$	4
Diethylenetriamine (DETA)	$\text{NH}_2\text{-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH}_2$	5
Triethylenetetramine (TETA)	$\text{NH}_2\text{-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH}_2$	6
Tetraethylenepentamine (TEPA)	$\text{NH}_2\text{-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH}_2$	7

Table 1. Name and functionality of the aliphatic amines used in this work

The samples were prepared at 5°C in order to avoid that reaction the takes place before the sample was properly loaded in the equipment. The experiment was carried out at different epoxy groups to amine-hydrogen ratio (r) according to

$$r = \frac{gE_g}{fA_f} \quad (2)$$

where g is the functionality of epoxy resin, E_g is the number of moles of epoxy resin, f is the functionality of the amine, and A_f is the number of moles of the amine.

A dynamic rheometer (Rheometrics RDS-II), with parallel plate geometry, was used to monitor the rheological properties during cure. The operational conditions were 5% of initial strain (auto strain mode was used) and a frequency of 5 rad/s. The gap between plates was 0.5 mm. The experiments were carried out under a linear temperature program from 30 to 210 °C at different heating rates (1,2,3 and 5 °C/min). The conversion and the glass transition temperature were measured in a calorimeter Perkin-Elmer DSC-VII.

Results and Discussion

The curves for G' and G'' for the DGEBA-TETA systems ($r=1$) at different heating rates are shown in figure 2. In this figure, it can be observed that the elastic modulus increases until a constant value. On the other hand, the viscous modulus presents two maxima (denoted as peak I and peak II). When the heating rate is increased, the peak I shifts toward the peak II until only one peak appears. Beyond the second peak G'' reaches a constant value. The same curing behavior was observed for all the amines ($r=1$).

Systems with an excess amine-hydrogen ($r<1$, Figure 3) exhibit a similar behavior to the one described for the stoichiometrically balanced systems. However, for systems with an excess of epoxy groups ($r>1$, Figure 4), the G'' curves do not show any peak. Due to the excess of epoxy groups, $T_{g\infty}$ for these samples is lower than the values for the mixtures with $r \leq 1$ and the vitrification effect does not take place. In addition for these systems, there is an increment in the values of G' and G'' at a given temperature when the heating rate is increased, which indicates a different network formation.

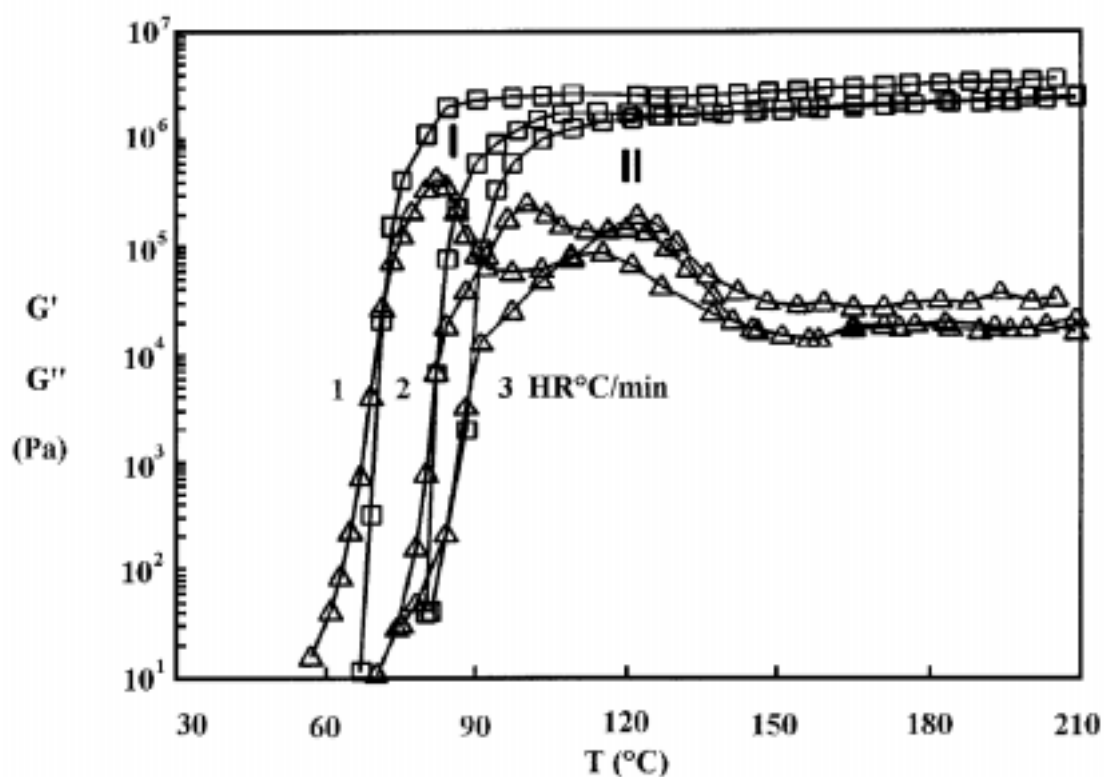


Figure 2. Rheological monitoring of the non-isothermal cure for the DGEBA-TETA system ($r=1$). Key: \square G' , Δ G''

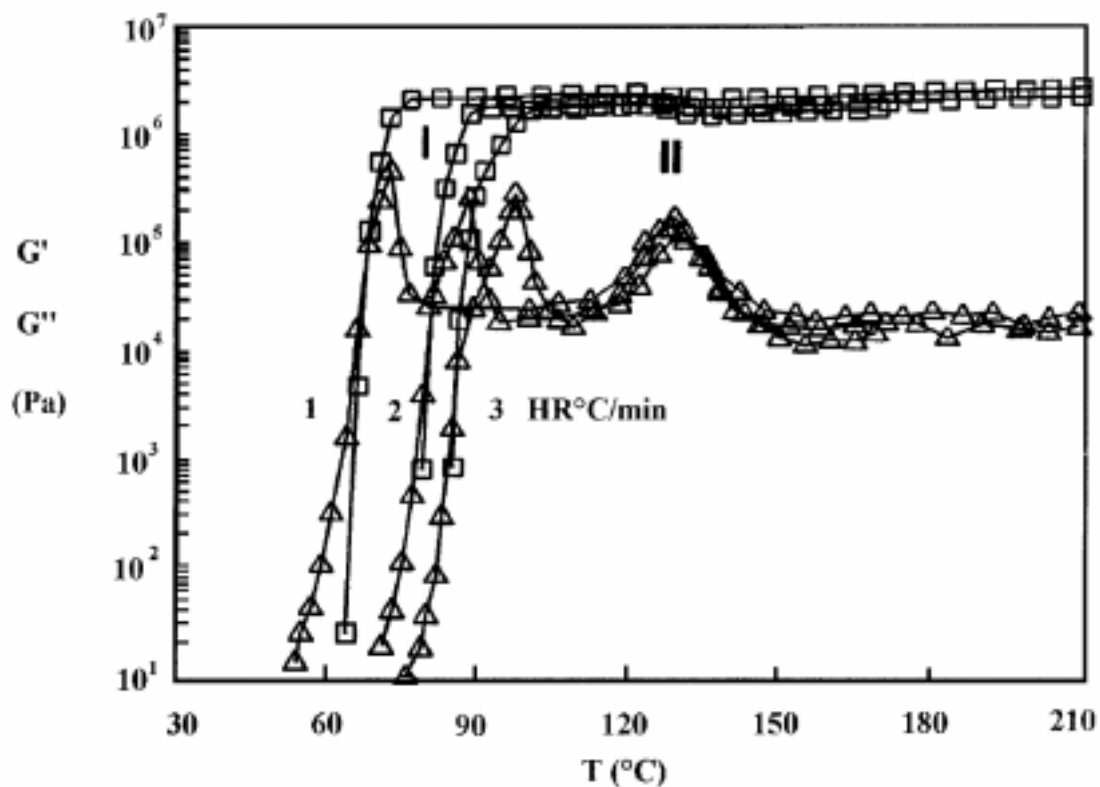


Figure 3 Rheological monitoring of the non-isothermal cure for the DGEBA-TEPA system ($r=0.62$). Key: \square G' , Δ G''

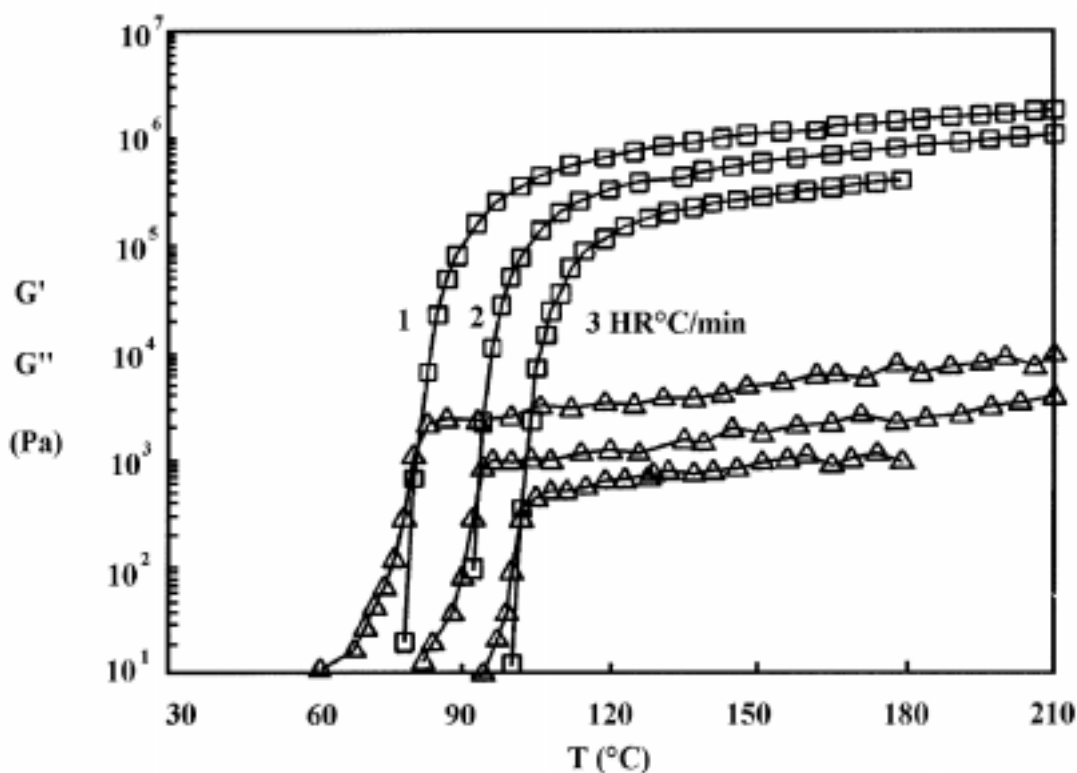


Figure 4. Rheological monitoring of the non-isothermal cure for the DGEBA-TEPA system ($r=2$). Key: \square G' , Δ G''

The final storage modulus can be related to the crosslinking density of the networks. Comparing the G' values at high temperature (at this point the samples are fully cured) for different reactive group ratios, it can be observed that the values for the system with $r > 1$ are smaller than the values for other ratios. As it is well known, an excess of either of the reactive groups lead to a smaller crosslinking density. However, Arellano et al. (12) reported that under isothermal curing, the decrease in the final G' value is more significant when an excess of epoxy groups is used for the same aliphatic amines studied in this work.

In order to investigate the nature of the two peaks in G'' , samples were cured in a calorimeter at the same conditions as the rheological experiments. The curing continues until the temperature at which the peaks were observed is reached. The samples then were cooled down to 30 °C and a temperature sweep was carried out to determine the glass transition temperature and conversion of the epoxy groups in those points. Figure 5 presents the thermograms for the temperature sweeps for the DGEBA-TETA system after the curing at 1 °C/min. The following results were observed:

- 1) When the sample was cured until the temperature at which the first peak in G'' appears. Residual heat was detected and the glass transition temperature coincided with that of the first peak.
- 2) When the sample was cured up to the temperature of the second peak of G'' , residual heat was not detected and the glass transition temperature coincided with the value for a completely cured sample.

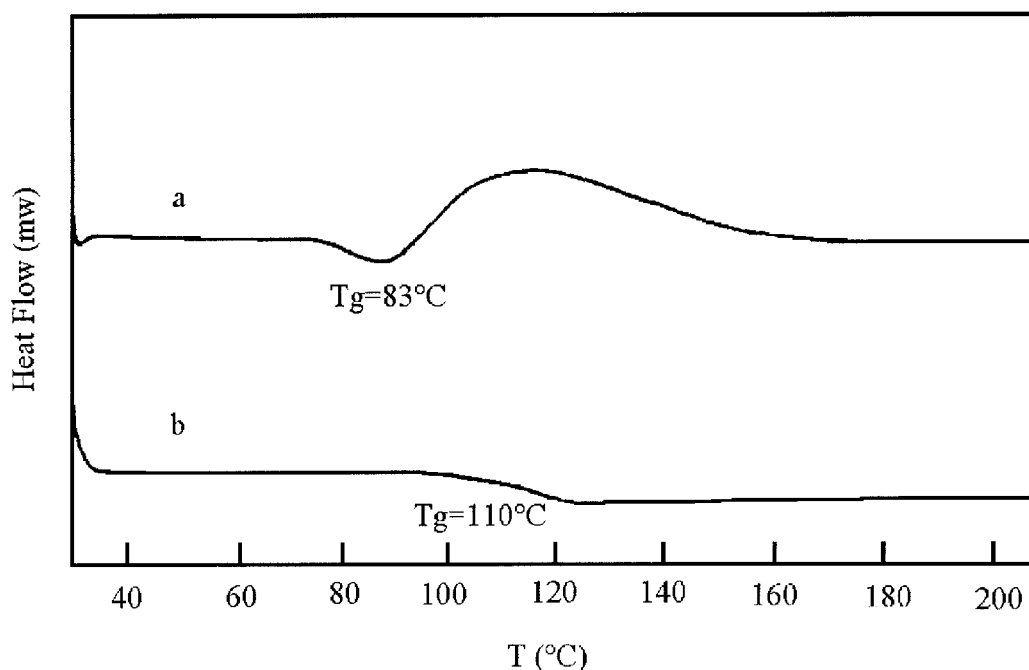


Figure 5. DSC thermograms for the DGEBA-TETA system: (a) sample cured until peak I and (b) sample cured until peak II.

The summary of the DSC results is shown in table 2. Plotting T_g versus conversion at peak I (at two heating rates) in a vitrification diagram for the DGEBA-TETA system (reported in reference (13)), it was found that the points fall very close to the vitrification curve (figure 6). These results lead us to conclude that the peak I in G'' is related to the vitrification-devitrification phenomenon that takes place during the cure of these systems.

HR (°C/min)	T peak I (°C)	x	T _g (°C)	T peak II (°C)	x	T _g (°C)
DGEBA-EDA						
1	76	0.918	-	135	1.0	126
DGEBA-DETA						
1	74	0.917	75	141	1.0	122
2	93	0.962	92	132	1.0	123
3	102	0.965	-	132	1.0	120
5	-	-	-	119	1.0	122
DGEBA-TETA						
1	82	0.889	83	122	1.0	110
2	100	0.950	96	120	1.0	108
3	-	-	-	112	1.0	100
5	-	-	-	120	1.0	106

Table 2. Summary of the DSC results for systems with $r=1$.

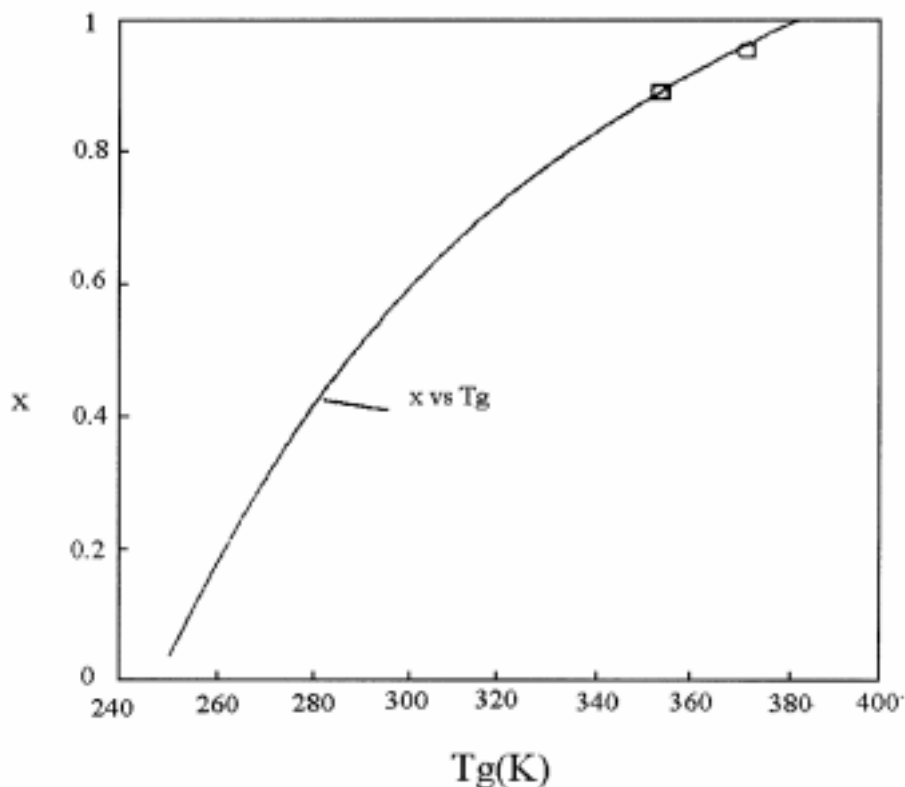


Figure 6. Vitrification diagram for the DGEBA-TETA system ($r=1$). Vitrification diagram from reference (13).

Conclusions

In this work, it was shown that rheological experiments could be used to study the vitrification-devitrification phenomenon that takes place during the non-isothermal cure of epoxy systems. The rheological and calorimetric results show that the first peak observed in the viscous modulus curve is due to this phenomenon; and the second peak is a consequence of the change in G'' with temperature for a completely cured sample. In addition, as the heating rate increases peak I approach peak II until only one peak is observed.

Acknowledgments

This research was supported by Mexico's National Council for Science and Technology (CONACyT 25478-A) and the Universidad de Guadalajara.

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