Thermal Scanning Rheometric Analysis of Curing Kinetic of an Epoxy Resin. I. An Anhydride as Curing Agent

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ABSTRACT: The curing reaction of the system diglycidyl ether of bisphenol A (DGEBA), an organic anhydride (HMTPA), as curing agent and a tertiary amine (DMP 30) as initiator has been studied by Thermal Scanning Rheometry (TSR) under isothermal conditions. The gel time, which is defined by several different criteria, has been found to be a good parameter to determine the activation energy of this curing process; on the other hand, the gel time depends on the concentration of the initiator. An empirical model has been used to predict the change in viscosity (η^*) of the system with time until the gelation is reached; the first-order kinetics, the apparent kinetic constant (k'), and the activation energy before gelation have been determined. Furthermore, these results are reported together with the reaction mechanism proposed by another authors. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1239–1245, 1999

Key words: epoxy resin; curing kinetic; gel time; rheology; viscosity

INTRODUCTION

In recent years, the range of potential applications of thermosetting resins, and especially epoxy resins, is rapidly expanding from classical applications as a cover for surfaces and electronic components, powder moldings where only the resin is processing, to recent applications as composites where the resin acts as a matrix for advanced materials in the automobile and aeronautic industries.¹

Traditionally, a chemical approach has been carried out in the studies of the crosslinking process of reactive resins. This approach takes into account the degree of conversion of the reactive groups by methods such as chemical analysis, infrared spectroscopy, and calorimetry.² Although these analysis are useful for studying kinetic of curing reactions and, therefore, for deducing details of molecular arquitecture, they reveal little about bulk properties of curing polymers. Furthermore, the sensitivity and capabilities of the techniques used decrease sharply during the late stage of the curing process, which usually determines the optimal properties of a crosslinked polymer.³

Another approach consists on monitoring physical behaviour by measurement changes in density, viscosity, refractive index and dynamical, mechanical and electrical properties. Nevertheless, the total range of cure is difficult to monitor mechanically by a single experiment. This is due to the important rheological changes occuring during conversion of the liquid resin to the solid crosslinked polymer.³

Dynamic mechanical techniques more commonly used³ are: Torsional Braid Analysis (TBA),

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Properties	Unit	Rütapox LB64	MTHPA	DMP 30
Supply form	_	Liquid	Liquid	Liquid
Density at 20°C	g/cm ³	$1,17 \pm 0,01$	$1,21 \pm 0,02$	$0,98 \pm 0,01$
Viscosity at 25°C	mPa s	11000 ± 2000	60 ± 10	250 ± 150
Equivalent	g/equiv	188 ± 2	166	_
Hydrol. cholorine content	%	$<\!\!2$	_	_
Anhydride content	%		$\geq 99,5$	_
Refraction index	_		_	$1,516 \pm 0.002$
Shelf life at 20–25°C in sealed containers	months	12	12	12

 Table I
 Material Characteristics

Flexural Braid Analysis (FBA), Rheometric Dynamic Spectrometry (RDS), Dynamic Mechanical Thermal Analysis (DMTA), and the technique that has been used in this work, Thermal Scanning Rheometry (TSR).

The objective of this work was to analyze the rheological behavior and the kinetics of the system epoxy/organic anhydride/tertiary amine under isothermal conditions. Moreover, this work focuses on the relation existing between the gel time, with variables such as temperature and amine concentration.

EXPERIMENTAL

Materials

The resin used is a commercial liquid epoxy resin of diglycidyl ether of bisphenol A (DGEBA) supplied as Rütapox 064. The organic anhydride is a methyl tetrahydrophthalic anhydride (HMTPA) supplied as Hardener Hx, and the initiator is a tertiary amine, tri(dimethylaminoethyl) phenol named DMP 30. All these materials were supplied by Bakelite AG, and the technical characteristics are shown in Table I.

Epoxy resin and the HMTPA have been mixed stoichiometrically (88 wt % of the anhydride) and saturated in N₂. Afterwards, different amine concentrations were added using an automatic pipette. The final blend was homogenized by agitation.

Rheological Measurements.

Under isothermal conditions dynamic mechanical measurements were carried out by means of a Thermal Scanning Rheometer, TSR (Rheometric Scientific Ltd). The complex viscosity of the system has been measured by the vertical oscillation of the probe below the liquid surface. The oscillatory motion of the probe is progressively damped by viscous drag, which allows the monitoring of viscoelastic properties during the curing process, as the complex viscosity and its components, the storage module (G'), the loss module (G''), and the loss tangent (tan δ).⁴

The temperatures used in this work were 70, 80, 90, and 100°C, and the amine concentrations added 1, 2, 3, 4 parts per 100 of resin. A vertical oscillation frequency of 2 Hz was used.

Other tests were carried out using a Dynamical Mechanical Thermal Analyzer (DMTA) at temperatures from -50 to 180° C. The rheological behavior of the resin and the system were measured at an oscillation frequency of 2 Hz, with the purpose of determining T_{go} , the T_g of uncured resin, and $T_{g\infty}$, the T_g of a fully cured system.

RESULTS AND DISCUSSION

The test carried out by means of DMTA gave us the T_{go} of uncured resin, $-16 \pm 1^{\circ}$ C, and the $T_{g\infty}$ of the system, $140 \pm 1^{\circ}$ C. These results allowed us to choose the isothermal cure temperature below $T_{g\infty}$. At each isothermal cure temperature below $T_{g\infty}$, the reaction proceeds normally until the molecular weight or crosslinking increases to the extent that the glass transition reaches the cure temperature.^{2,5-7}

Figure 1 shows the typical changes in storage (G') and loss (G'') moduli vs. time under isothermal conditions for the system studied. Three different regions have been appreciated from this figure. At the first region, the moduli are parallel to the time axis, which corresponds to the region



Figure 1 Storage modulus (G') and loss modulus (G') vs. time for the reaction DGEBA/MHTPA/DMP 30, under isothermal conditions.

where the moduli are below the sensitivity of the instrument; for this reason the results have not considered. In the second region, the G' and G'' values increase exponentially vs. time, where the gelation and, therefore, the crosslinking occur. Finally, in the last region, the moduli increase more rapidly, generating an increase in the background noise as a result of the higher crosslinking density of the resin.

According to P. Babayevsky and J. K. Gillham,³ the cure of reactive thermosetting resins usually involves transformation of low molecular weight monomers or oligomers from the liquid into solid state as a result of the formation of a polymer network by chemical reactions of the reactive groups in the system. This variation in the physical state, known as the gel time, is easily distinguished by viscosity measurements.

Prior to the gelation, the growth and branching of the polymer chains take place in the liquid state where the reactive system is soluble and fusible. After the gel point, an infinite network of polymer chains appears and develops, converting into a rubbery and flexible material as they lose the solubility and fusibility. The final reactions take place in the solid state, where the molecules are nearly motionless at the glass state.

Parameters such as the gel time, the dynamic mechanical moduli, and the complex viscosity can be used^{3,8} as kinetic parameters of the thermosetting systems because their changes are directly proportional to the extent of cure.

Gel Time Measurements

The gel time has been determined according to the more commonly used criteria⁹ as: (a) first criterion, the gel time has been taken as the point that corresponds to the crossing between the baseline and the tangent drawn at the yield point in the modulus G' curve. At that moment, it can be said that the material exhibits an elastic behavior. (b) Second criterion, the gel time has been taken at the point corresponding to the crossover between the G' and the G'' curves; in other words, where G' = G'' (the lost energy is equal to the stored energy). This fact shows that the behavior is not only viscous, but also elastic.

According to these criteria the gel time has been calculated as shown in Table II. From the analysis of this table it has been deduced that the different criteria give similar results. The variation of the gel time obtained vs. temperature or amine concentration is similar, independently of the criterion used for its determination.

As shown in the table, as the temperature raises the gel time decreases at any amine concentration used. This fact can be explained at microscopic level as an increase in chain mobility as a result of the increase in temperature. The rate equation for this process can be expressed as:

Table	II Gel	Times	and k'	Values	Obtained
under	Isother	rmal Co	onditio	ns	

			$t_{\rm gel}$		
	T	wt %			k'
Sample	(°C)	Amine	aª	bb	(\min^{-1})
E.70.1	70	1	343	358	0.0459
E.70.2		2	224	c	0.0588
E.70.3		3	150	c	0.0922
E.70.4		4	114	c	0.117
E.80.1	80	1	161	152	0.154
E.80.2		2	96.3	87.5	0.188
E.80.3		3	68.3	68.0	0.230
E.80.4		4	55.7	49.4	0.263
E.90.1	90	1	91.1	81.4	0.240
E.90.2		2	57.2	50.8	0.321
E.90.3		3	35.9	33.5	0.512
E.90.4		4	25.5	24.6	0.593
E.100.1	100	1	58.8	52.4	0.414
E.100.2		2	26.4	24.6	0.837
E.100.3		3	17.6	15.9	1.28
E.100.4		4	12.2	12.0	2.09

^a First criterion;

^b Second criterion.

^c The gel time cannot be obtained from these tests.



Figure 2 Determination of the activation energy by the first criterion.

$$- \frac{dX}{dt} = k' X'' \tag{1}$$

where X is the concentration of reactive groups, k' is an apparent kinetic constant, and n is the reaction order.

The difference $(X_o - X_g)$ at the gel point is a constant for a given system.³ The integral of eq. (1) has limits from t_o to the gel time, t_{gel} , where the reactive concentrations are X_o and X_g respectively, leading to the following equation:

$$t_{gel} = cte \; \frac{1}{k'} \tag{2}$$

Expressing k' as function of the temperature according to the Arrhenius relationship, the final equation reached is:

$$\operatorname{Ln} t_{gel} = cte + \frac{Ea}{R} \frac{1}{T}$$
(3)

Figure 2 shows the relationship between the Ln $t_{\rm gel}$ and T^{-1} for all the amine concentrations used, and in Table III the apparent activation energy (E_a) values obtained from both criteria are shown. As it can be observed, the results show a similarity for the energy values independently of the criterion used for their calculation. For this reason, from now on, the gel times chosen are those calculated by the first criterion.

In Tables II and III an interesting effect of the amine concentration on the gel time and the apparent activation energy can be observed. As the amine concentration increases, the gel time decreases as a result of an increase in the number of

Table III	Apparent Activation Energy
Obtained	by Different Criteria

wt % Amine	E_a (kJ/mol)		
	a^{a}	b^{b}	
1	62.97	62.41	
2	70.64	73.97	
3	73.88	74.85	
4	77.86	79.74	

^a First criterion; ^bsecond criterion.

activated epoxy groups. The crosslinking of the resin occurs at an earlier stage, leading to a more rapid cure reaction and, therefore, to a lower gel time and higher viscosity. As the viscosity increases, the chains feel restricted to move. Consequently, the system requires an extra energy to favor not only the chain mobility but the cure reaction as well. Figure 3 shows this amine concentration–gel time dependency where $t_{\rm gel}^{-1}$ is plotted vs. wt % of amine. As we can see in the figure, linear plots have been obtained, where the intercepts are very close to zero, and the slope increases with the increase in temperature. The linear behavior observed is related to the reaction mechanism, which will be explained later.

The E_a values are in concordance with those values reported by S. Montserrat et al.⁸ (73 kJ/mol) for a similar system, and also similar to those previously reported by Zukas et al.¹⁰ (75.6 kJ/mol) and Fava et al.¹¹ (74.6 kJ/mol).

Kinetic Model and Apparent Activation Energy

Various quantitative interpretations of viscosity data during curing reactions have been report-



Figure 3 Influence of wt % of amine in t_{gel} at different temperatures by the first criterion.

ed.^{12–16} Models do not have easy applications in many occasions. In this work, as other authors¹⁶ have used, isothermal data have been correlated using empirical expressions as:

$$\eta(T, \alpha) = \eta(T)\eta(\alpha) \tag{4}$$

where the viscosity has been divided in two components, one depending on the temperature $\eta(T)$, and the other depending on the time or on the conversion (α), ($\eta(\alpha)$.

In an isothermal curing process $\eta(T)$ can be taken as constant for a temperature:

$$\eta(T) = \eta_o \tag{5}$$

where η_0 is the zero-time viscosity.

Until states near to the gel time, a first-order reaction¹ can be assumed; thus:

$$\frac{d\alpha}{dt} = k' \ (1 - \alpha) \tag{6}$$

where k' is an apparent kinetic constant. If the variation of the conversion determines the changes in the viscosity of the system, the integration of the previous equation gives:

$$\eta(T) = e^{k' \cdot t} \tag{7}$$

Substituting these two expressions (5) and (7) into eq. (4), eq. (8) is obtained:

$$\eta(\alpha, T) = \eta_o e^{k' \cdot t} \text{ or } Ln \ \eta = Ln \ \eta_o + k't \quad (8)$$

where $\eta(\alpha, T)$ depends on the conversion and temperature, and η_0 only depends on temperature.

Roller¹⁷ extends eq. (8) to take into account the temperature by assuming the Arrhenius-type relationship:

$$\eta_o = \eta_\infty e^{E_{\eta}/RT}$$

$$k' = k'_\infty e^{-E_{k}/RT}$$
(9)

where $\eta_{\infty} y k'_{\infty}$ are the zero-time viscosity and apparent kinetic constants at $T = \infty$, and E_{η} and E_k are the associated activation energies.

Substituting these expressions into eq. (8):

$$Ln \ \eta(t) = Ln \ \eta_{\infty} + \frac{E_{\eta}}{RT} + (k_{\infty} e^{-E_{k}/RT})t \quad (10)$$



Figure 4 Plot of the empirical model given by the eq. (8).

As the TSR supplies viscosity data η^* vs. time, it is possible to apply eq. (8) to this study. Figure 4 shows this plot for three different formulations. In all cases, linear plots have been obtained until times close to the gel time. After the gel time, a deviation from linearity takes place (this part of the curve is not presented in Fig. 4) due to the material vitrification. The apparent rate constant, k', was determined at each temperature, and an interesting temperature and amine concentration dependency was observed. This dependency is related to the mechanism of the reaction.

Trappe¹⁸ and Matejka¹⁹ have proposed the following mechanism for epoxy resins cured by using an anhydride as curing agent and a tertiary amine as initiator:

(1)
$$I + M \xrightarrow{k_i} P_1^*$$

(2) $P_1^* + A \xrightarrow{k_1} P_2^*$
(3) $P_{n-1}^* + M \xrightarrow{k_2} P_n^*$

In the first reaction, the amine (I) will react with the resin (M) to promote active chains that afterwards will react either with a molecule of anhydride (A) or a molecule of resin, through reactions 2 and 3. The curing process may also take place by the reaction of an anhydride and the resin through the OH groups of the latest, opening in this way the rings of the epoxy groups.²⁰

The fact that k' and E_a are dependent on the amine concentration leads one to think that the curing process of the formulations studied follows



Figure 5 Influence of the amine concentration on k' under isothermal conditions.

the reactions described above and does not occur by a direct reaction with the anhydride, especially up to times close to the gel time.

From the above mechanism:

$$-\frac{d[A]}{dt} = k_1 [P_1^*][A]$$
(11)

$$-\frac{d[M]}{dt} = k_i[M][I] + k_2[P_{n-1}^*][M]$$
(12)

The time-determining step is the opening of the epoxy ring, as the created alcoholate anion (reaction 1) reacts virtually immediately with the anhydride (reaction 2). Under such conditions $k_1 \gg k_2$. Equation (12) describes the rate of the reaction until the gel time is reached.

In this process, the concentration of growing chains does not remain constant at the beginning of the reaction, but afterwards, no change in the number of growing chains is assumed during the course of the reaction, in other words, the growing chains are constant when all the initiator has reacted.

Because the number of growing chains is just the number of already reacted initiator molecules at a given time, $[P_1^*] = [I]_o - [I]$, and substituting in eq. (12) gives:

$$\frac{d[M]}{dt} = -k_2[I]_o[M] + (k_2 - k_i) [I][M] \quad (13)$$

and assuming that during the initiation step the resin concertation does not change:

$$\frac{d[I]}{dt} = -k_i[I][M] \simeq -k_i[I][M]_o \qquad (14)$$

integrating:

$$[I] = [I]_o \ e^{(-k_i[M]_o t)} \tag{15}$$

Substitution in eq. (13), gives:

$$\frac{d[M]}{dt} = -k_2[I]_o [M] + (k_2 - k_i) [I]_o e^{(-k_i[M]_o t)} [M] \quad (16)$$

and integration of this equation gives finally:

$$Ln(1 - \alpha) = -k_2[I]_o t + \frac{k_2 - k_i}{k_i} \frac{[I]_o}{[M]_o} (1 - e^{-k_i[M]_o t}) \quad (17)$$

The second part of this equation becomes important only at the beginning of the reactions where the conversion is very low. Moreover, the instrument is not able to detect viscosity changes at the beginning of the curing process. Therefore, in this system, the equation can be reduced to:

$$Ln \ (1 - \alpha) = -k_2 [I]_o t \tag{18}$$

If this equation is compared with eq. (6), it can be deduced that:

$$k' = k_2[I]_o$$
 (19)

This equation explains the effect of the amine concentration on the k' and the gel time at any temperature. Furthermore, eq. (19) predicts a linear relation, as shown in Figure 5, for all formulations.

Besides, this linear dependency implies that the treatment of curing process used by means of



Figure 6 Determination of k_{∞} and E_a .

Temperature (°C)	$k_2 \; (M^{-1} \; \min^{-1})$
70	1.022
80	1.518
90	5.167
100	17.75

Table IV	k_2	Values	Obtained	for	Different
Tempera	ature	es			

the dynamic mechanical test is correct for the system studied.

The global kinetic constant values, k_2 , are shown in Table IV, and assuming an Arrhenius type relationship of k_2 with the temperature (Fig. 6):

$$Ln \ k_2 = Ln \ k_\infty - \frac{E_k}{RT} \tag{20}$$

the following values of k_{∞} and E_k have been obtained:

$$k_{\infty} = 4,90.10^{15} \, M^{-1} \, {
m min}^{-1}$$
 $E_{\scriptscriptstyle h} = 103.8 \ {
m kJ} \ {
m mol}^{-1}$

This activation energy value is higher than that determined by the gel times. This difference is a result of the influence of the stages after the gel point supported by this second method. This fact was observed by M. E. Ryan and A. Dutta²¹ for a DGEBA (DER-332), using *m*-phenylene diamine as a curing agent.

CONCLUSIONS

The TSR measurements have confirmed that the TSR is a good technique to monitor the curing process of this system. It is possible to record the η^* , G^* changes, and their components, which are important during the processing of this resin. It has been proved that the gel time determined by different criteria is a good parameter to calculate the apparent activation energy involved in the process despite the different chain mobility restriction. In this system the "average" value among all the formulations could be considered as $E_a = 72.23$ kJ/mol. These results show a great

concordance with those reported by other authors.

An empirical model has been applied for the change in viscosity with the time, and an apparent first-order kinetic constant has been obtained that depends on the amine concentration.That dependence has been explained by applying the mechanism proposed by Trappe¹⁸ and Matejka¹⁹ up to the gel time.

It is important to emphasize that this model is not appropriate for posterior stages to the gel time due to the influence of the vitrification process on the reaction kinetics.

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