

# Effects of Chemical Structure of Hardener on Curing Evolution and on the Dynamic Mechanical Behavior of Epoxy Resins

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## SYNOPSIS

A diglycidyl ether of bisphenol-A-type difunctional epoxy resin was cured with different amine-type curing agents at stoichiometric ratios. The crosslink process was followed by viscosimetry and differential scanning calorimetry. The gelation time and the apparent activation energy were found to be strongly dependent on the structure of the hardener. The heat of reaction did not vary significantly when the hardener was changed. An interpretation based on structural aspects such as amine reactivity, steric hindrance, and chain rigidity is proposed for the variations corresponding to the curing process. Master viscosity curves have been built up for all mixtures. The effect of the hardener on the glass transition temperatures of the different mixtures has been analyzed taking into account the crosslink density, measured by the rubber modulus obtained by dynamic mechanical studies, and the chemical structure of the hardener chains. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In the last decade numerous investigations have been carried out on the cure behavior and the relationship between structure and ultimate properties of epoxy resins.<sup>1,2</sup> This interest is a consequence of the excellent thermal and chemical resistance and the superior electrical and mechanical behavior of these resins, and therefore epoxy resins are used in a wide range of applications in the adhesive, electronic, and aerospace industry. Among the several curing agents employed to formulate these materials, the amines are undoubtedly the most extensively used. When the same epoxide monomer is selected, the chemical structure of the amine is responsible for the kinetic differences upon curing as well as for the ultimate variation on the properties of these materials. Nevertheless, other factors such as steric restrictions to the epoxy-amine addition reactions or physical interactions among different functional

groups of the constitutive components, as well as the cure extension, can also influence the cure evolution and also the final properties of epoxies.

The influence of factors mentioned above has been reported in various publications,<sup>3-6</sup> but the relationship between the chemistry of the epoxide and amine monomers during the different stages of curing, and the properties of crosslinked networks, still need to be completely understood. An interesting question is the way in which the chemical structure and existing interactions among groups can modify the chemorheology and the structure of the formed network correlating the variations experimentally obtained from these physico-chemical parameters.

The main objective of this study is to elucidate the effects of the chemical structure of the curing agent on the chemorheology of curing and the physical properties of epoxy resins cured with amines with different chain backbones. The variations throughout curing and the thermal behavior of cured systems is related to the structure of the curing agent employed. Aliphatic as well as cycloaliphatic and aromatic amines have been used.

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## EXPERIMENTAL

## Materials and Mixing

Diglycidyl ether of bisphenol A (DGEBA), Rutapox VE-3966, an epoxide monomer kindly provided by Bakelite, with an equivalent weight of epoxy groups equal to 184.5 g/equiv determined by chemical titration, was used in this study.

Various aliphatic, cycloaliphatic, and aromatic amines were used as curing agents. The chemical structures of the amines and epoxide monomer are shown in Figure 1. The reactants were used as received in stoichiometric amine-epoxy equivalent ratio. DETA, IPDA, mPDA, and DDM were Fluka quality. 3DCM, Laromin C260, was purchased from BASF. Jeffamine D230 and T403 were gently supplied by Texaco.

Product	Formula
Dyglycidyl ether of bisphenol A DGEBA Rutapox VE-3966 (Bakelite)	
Diethylene triamine DETA (Fluka)	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$
Poly(oxypropylene) diamine Jeffamine D-230 (Texaco)	$\text{H}_2\text{N}-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2 \left[ \text{O}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}} \right]_x \text{NH}_2 \quad x \approx 2.7$
Poly(oxypropylene) triamine Jeffamine T-403 (Texaco)	$\text{H}_3\text{C}-\text{H}_2\text{C}-\overset{\text{CH}_2 \left[ \text{O}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}} \right]_x \text{NH}_2}{\underset{ }{\text{C}}}-\overset{\text{CH}_2 \left[ \text{O}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}} \right]_y \text{NH}_2}{\underset{ }{\text{C}}}-\overset{\text{CH}_2 \left[ \text{O}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}} \right]_z \text{NH}_2}{\underset{ }{\text{C}}}$ $x + y + z \approx 5.3$
Isophorone diamine IPDA (Merck)	
3,3'-Dimethyl-4,4'-diaminodicyclohexylmethane 3DCM (BASF)	
m-Phenylene diamine mPDA (Fluka)	
4,4'-Diamino diphenyl methane HT 972 DDM (Ciba-Geigy)	

Figure 1 Characteristics of the different materials used.

Before mixing, the DGEBA epoxy monomer was preheated at 60°C to melt any crystals present. Stoichiometric mixtures of the epoxy prepolymer and DETA, IPDA, D230, T403, or 3DCM were cast at room temperature, and at 80°C for *m*-PDA or DDM containing mixtures, for 5 min, and subsequently degassing was made in a vacuum oven for 5 min. These times were selected in order to have the minimum possible of cure reactions between the materials mixed.

### Steady Shearing Flow Behavior

Viscosity measurements were carried out in a Rotovisco, RV 20, viscometer at several isothermal temperatures by using a coaxial-cylinder device. The weight of the samples was 60 g approximately. Mixtures were poured out into a cell previously preheated to the desired cure temperature, from 35 to 90°C. Viscosity variations were recorded at a shear rate of 0.77 s<sup>-1</sup>. The gelation time was defined as the time to reach a viscosity of 1000 Pa s. A larger bob was employed to collect accurate values of the unreacted mixtures.

### Differential Scanning Calorimetry Measurements

The enthalpy of reaction,  $\Delta H$ , and the values of the initial, maximum, and final temperatures of the exothermic peak,  $T_1$ ,  $T_p$ , and  $T_2$ , were obtained from dynamic measurements at a heating rate of 10°C/min in a Perkin-Elmer, DSC-7.

### Dynamic Mechanical Thermal Analysis

Dynamic mechanical analysis was used to determine the glass transition temperature of the stoichiometric formulations of the epoxy mixtures cured. Cure schedules for each mixture, shown in Table I, have been selected by taking a time higher than the corresponding gelation time at the earlier stage of the cure schedule, and a postcure temperature which permits attaining the maximum glass transition temperature. Studies were carried out in a Metravid viscoanalyzer using a three-point bending device. For all mixtures scans were made at 10 Hz and a

heating rate of 3°C/min from 20 to 250°C. The dimensions of specimens were 60 × 12 × 6 mm. Glass transition temperatures were identified by the temperature corresponding to the maximum value of the loss factor,  $\tan \delta$ .

## RESULTS

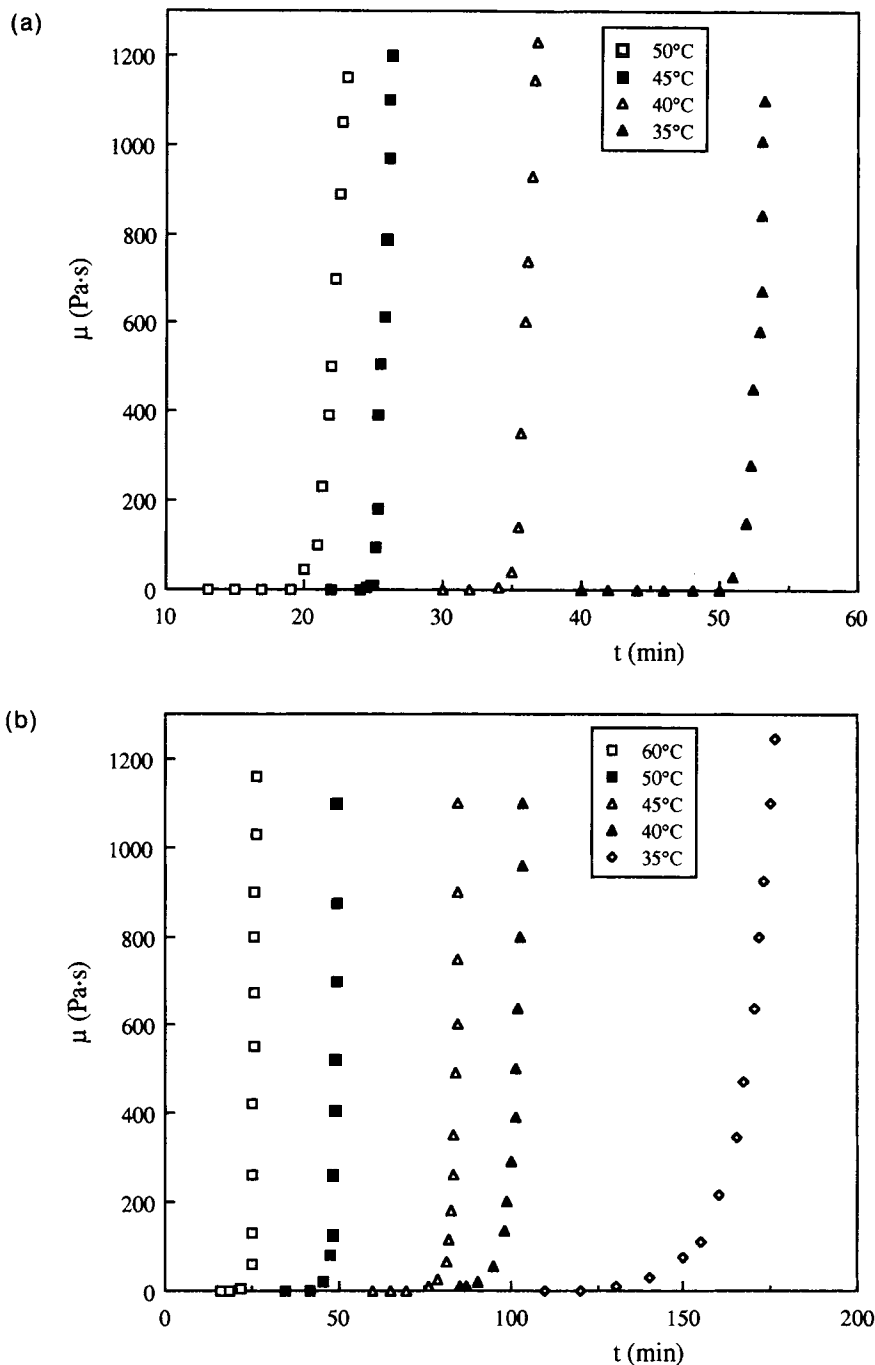
There are several ways to monitor the curing process of thermosetting resins. In this study one of the most widespread methods of investigating the initial stages of curing has been chosen to compare the curing process of epoxy resins cured with several amines. Viscosity variations during the curing process have been measured by a steady shearing technique. As it is well known,<sup>7,8</sup> curing of a thermoset resin supposes an increase of molecular weight at the earlier stages of the curing process as the initial thermoplastic epoxy material grow and branch. Thereafter, the attainment of a gel formation threshold corresponds to the formation in the curing material of a macroscopic crosslinked structure what constrains the mobility of chains, so supposing an increasing loss of fluidity until viscosity rises toward an infinite value.

As it has been shown in the literature survey,<sup>9</sup> the viscosity of these unreacted stoichiometric mixtures increased as a function of the hardener structure in the following way: IPDA < D230 = T403 < DETA < 3DCM < *m*-PDA < DDM. The surprisingly low values for mixtures containing IPDA or poly(propylene oxide) (PPO) amines is a consequence of the pendant methyl groups that hinder the intermolecular interactions among different chains, and so the strength to flow of these mixtures decreases.

The evolution of viscosity on curing for the several epoxy mixtures is shown in Figure 2(a)–(g). The bob employed to determine the gelation process did not permit accurate values of the viscosity data prior to gelation, and thus these viscosity data are shown in Figure 2(a)–(g) as a zero value despite their increase on cure time as branched molecules formed, but nevertheless viscosity remained almost constant for all mixtures at the earlier stages of curing because

**Table I** Cure Schedules Used for the Different Stoichiometric Epoxy Mixtures

Curing Agent	DETA	IPDA	3DCM	D230	T403	<i>m</i> -PDA	DDM
Cure schedule	50 (60)	50 (60)	80 (120)	60 (180)	60 (180)	80 (120)	80 (150)
$T(^{\circ}\text{C})$ [ $t(\text{min})$ ]	120 (120)	90 (120)	125 (120)	180 (120)	180 (120)	125 (120)	140 (90)
	190 (840)	190 (840)	190 (360)			190 (360)	200 (120)



**Figure 2** Viscosity profiles at the isothermal temperatures for DGEBA cured with several curing agents. (a) DETA, (b) IPDA, (c) 3DCM, (d) D230, (e) T403, (f) mPDA, (g) DDM.

the average longest linear path dominated the rheological behavior. At the onset of gelation there was an increase in viscosity which rose rapidly toward an infinite value as gelation occurred. In this work, gelation, measured by steady viscosimetry, has been taken as the time at which viscosity reached a 1000-Pa s value. Each mixture was analyzed at different

isothermal cure temperatures. In every case an increase in the cure temperature originated an increase in the rate of cure reaction. The viscosity increase around the gelation threshold was sharper at higher cure temperatures, therefore the gelation time recorded was more accurate for every mixtures when they were cured to relatively high cure temperatures.

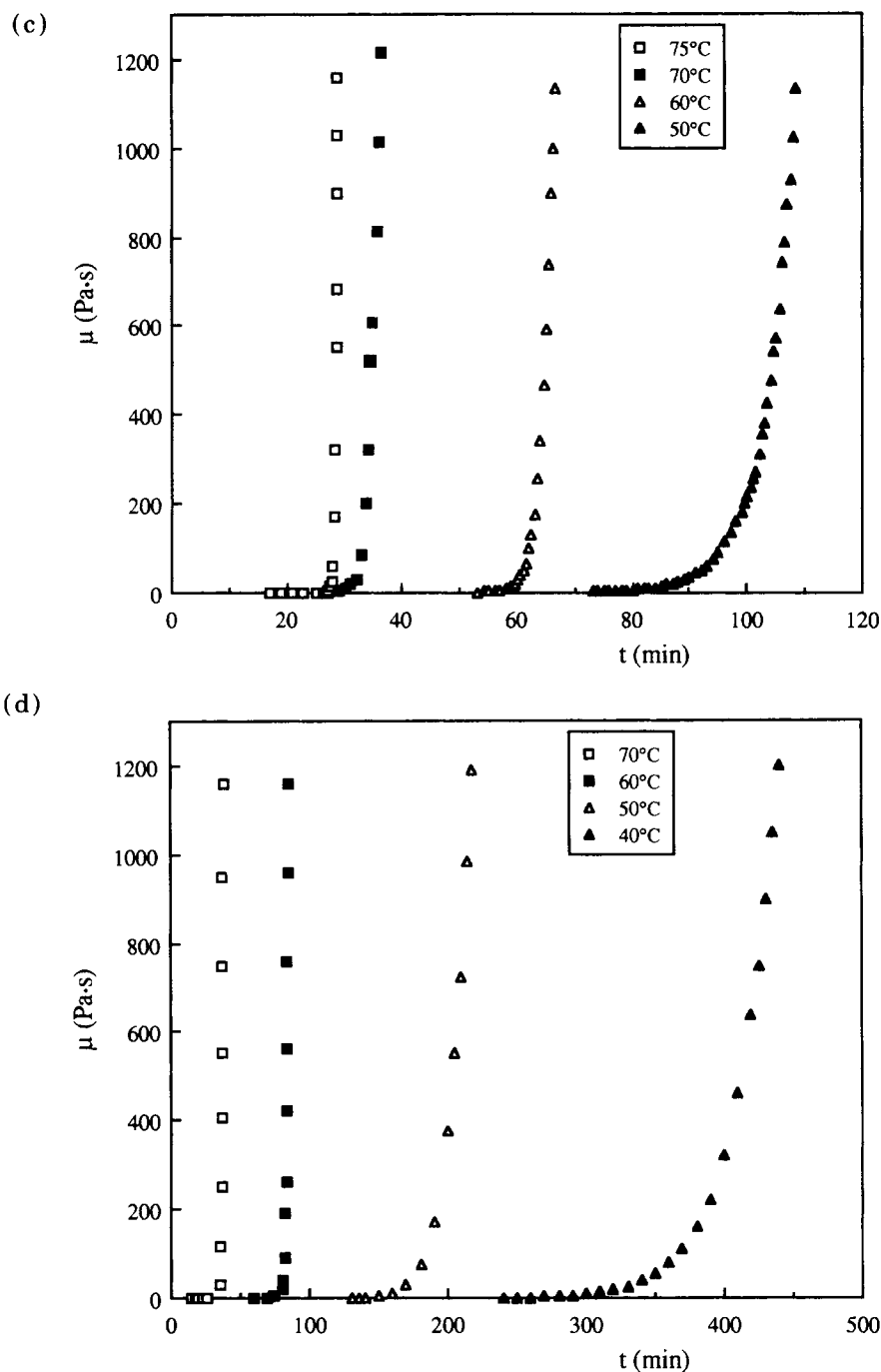


Figure 2 (Continued from the previous page)

For each temperature, gelation took place at different times as a function of the chemical structure of the curing agent employed. Gelation times for all blends at some of the several cure temperatures are given in Table II. For all mixtures, an increase in the cure temperature produced a reduction in the gelation time. This variation is a consequence of the

increase in the kinetic constant of the nucleophilic reaction between the epoxy and the primary amine groups upon the temperature.

As it is well known,<sup>10-15</sup> amine-cured epoxy networks generally form exclusively from epoxide-amine nucleophilic addition reactions, above all at low cure temperatures. Although either the primary

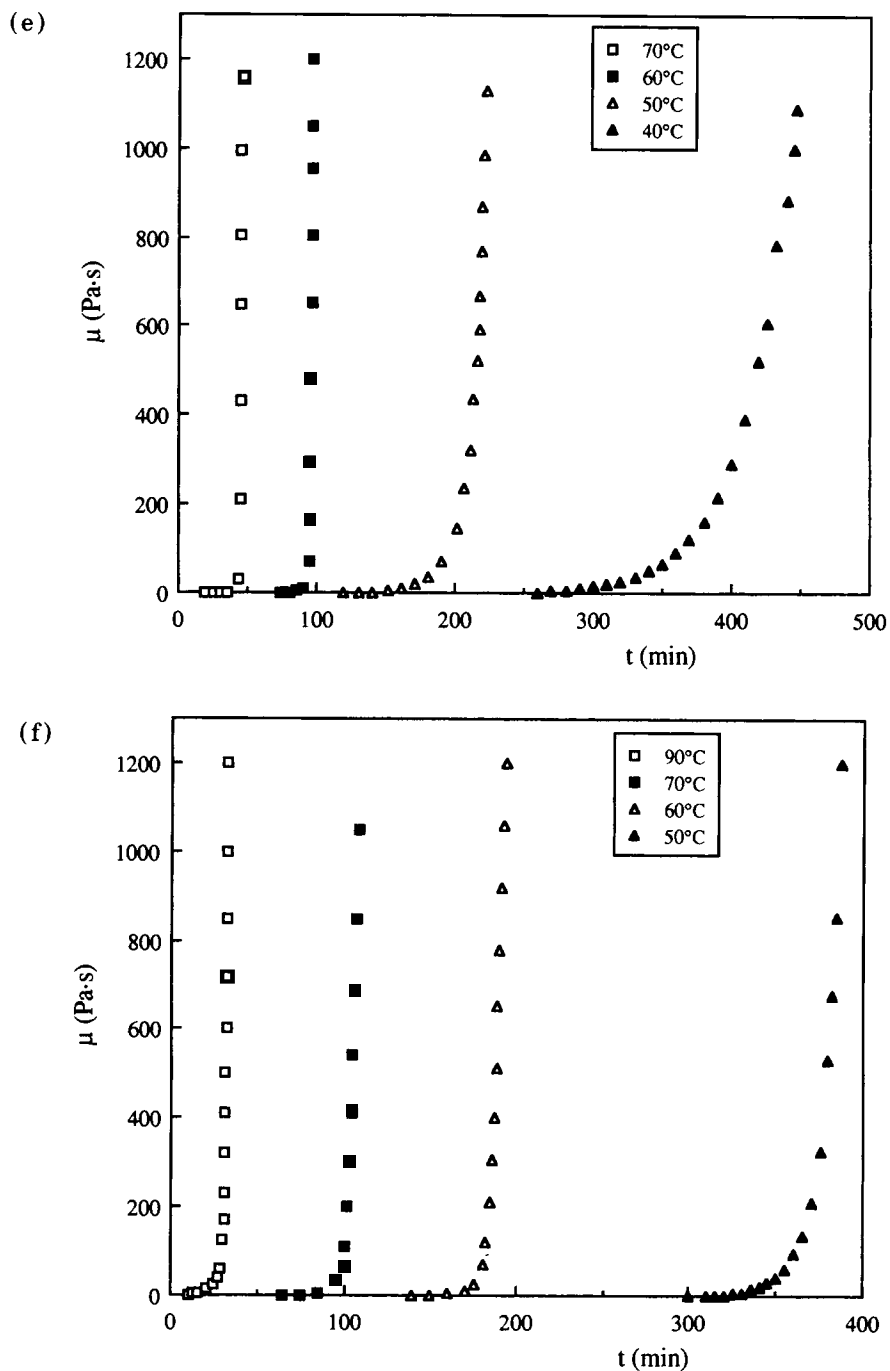


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and secondary amine-epoxide reactions occur simultaneously, the faster primary amine-epoxide reaction predominates in the earlier stages of curing which conducts to the gelation threshold. Therefore, the variations on gelation times, along with the relative viscosity values of the unreacted mixtures, can be employed to compare the reactivities of the primary amines for the different curing agents.

The dependence of the viscosity variation during curing at 50°C with the chemical structure of the curing agent is shown in Figure 3. Gelation times so obtained for these epoxy mixtures are also shown in Table II.

Let us analyze the different times to gelation for these amine-cured epoxy resins. At a constant cure temperature, it becomes evident that gelation time

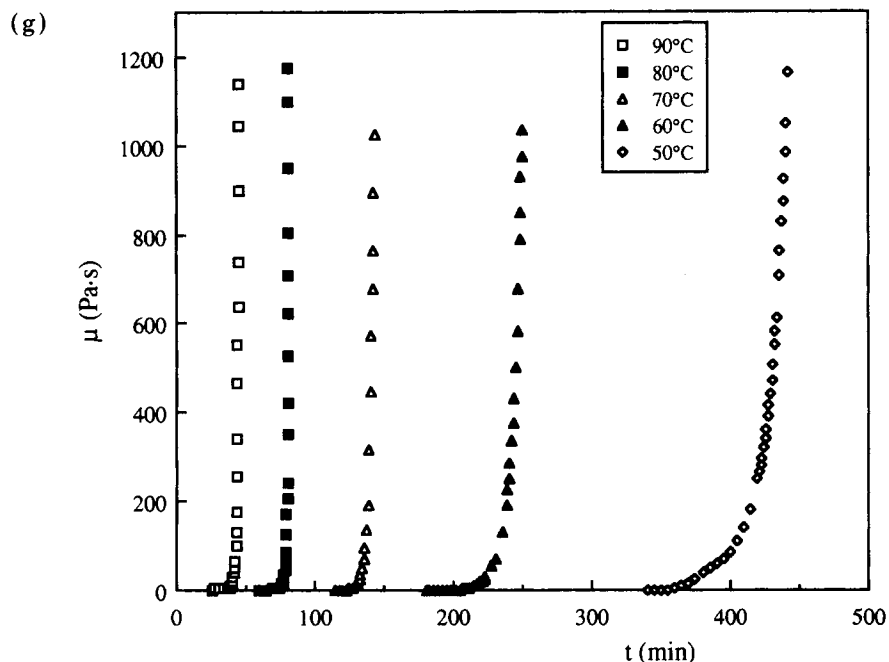


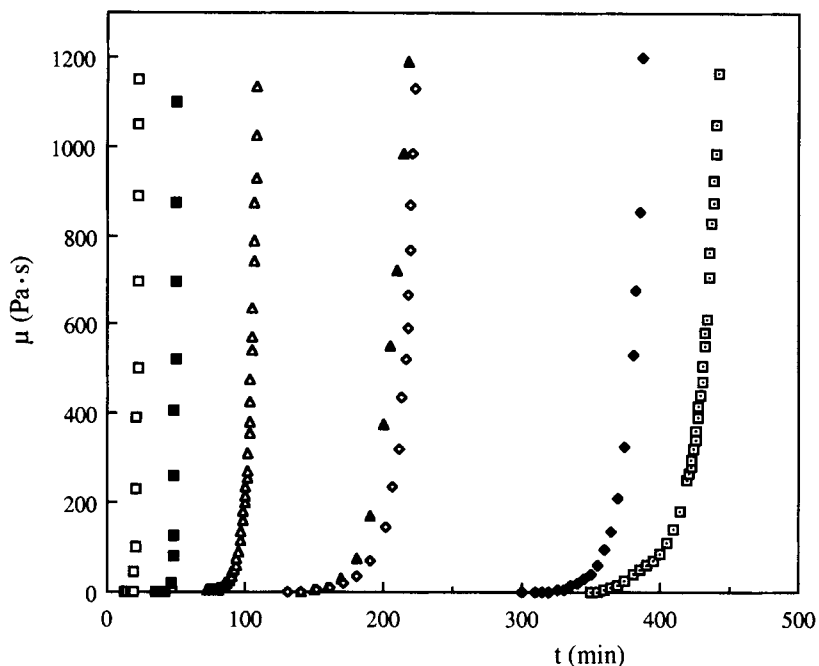
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is a function of the curing agent employed or, in other words, of the chemical structure of the components, which are reacting, as well as of the viscosity of the mixture. Indeed, when comparing gelation times of systems based on DETA and IPDA, a variation from aliphatic to cycloaliphatic framework supposed an important delay in the gelation threshold as a consequence of the loss on chain flexibility introduced by the cycloaliphatic cycle. This behavior becomes more evident when the rigidity of the cycloaliphatic amine was increased, as it was for the 3DCM. Nevertheless, it is worth noting that for the IPDA containing mixture, the different reactivities of the amine groups, because of that attached

to the methylene unit is more hindered than that attached to the aliphatic cycle, can lead to mistakes in the interpretation of results since viscosity increasing at low cure temperatures could occur as a consequence of vitrification more than gelation (the conversion of the epoxy group was not high at this stage of curing, and therefore the real gelation should happen at higher cure times). Thus, as stiffness of the amine chain increased (when mixtures cured with cycloaliphatic, IPDA and 3DCM, and aromatic *m*-PDA and DDM, amines were compared), gelation appeared at longer times for the aromatic ones. In this latter comparison, besides the stiffness of the hardener, in which the side chains or groups have

Table II Gelation Times (min) at Different Cure Temperatures

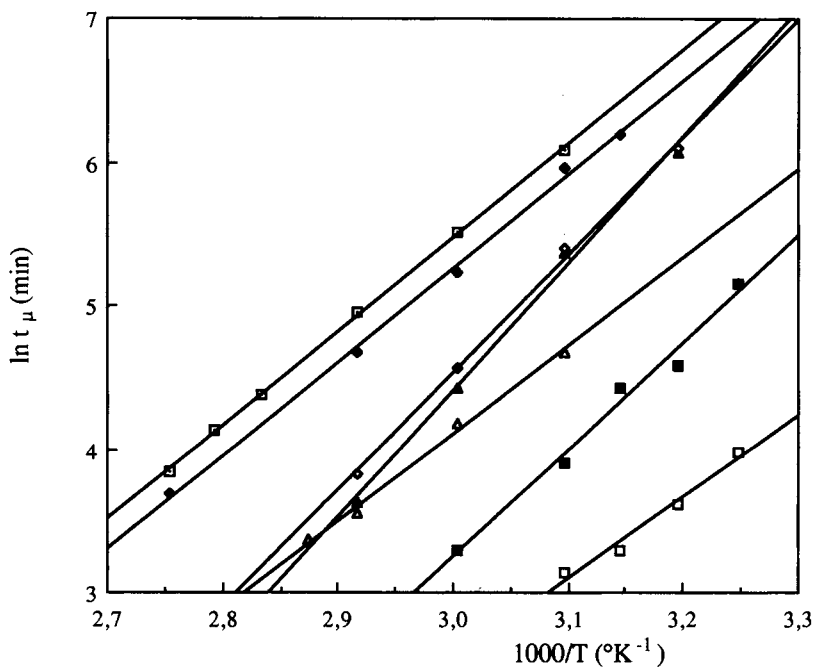
T (°C)	Curing Agent						
	DETA	IPDA	3DCM	D230	T403	<i>m</i> -PDA	DDM
35	53	175	—	—	—	—	—
40	36	103	—	435	445	—	—
45	26	85	—	—	—	—	—
50	22	50	108	216	221	386	441
60	—	26	66	85	96	192	250
70	—	—	36	38	46	108	143
75	—	—	28	—	—	—	—
80	—	—	—	—	—	—	81
90	—	—	—	—	—	35	47



**Figure 3** Viscosity profiles for the epoxy mixtures cured at 50°C. (□) DETA, (■) IPDA, (△) 3DCM, (▲) D230, (◇) T403, (◆) mPDA, (◻) DDM.

to be considered, it must be taken into account that in aromatic amines the nucleophilicity lowers with respect to that for cycloaliphatic amines. Consequently, the chain stiffness and the amine reactivity of the curing agent are the main features whenever

the gelation behavior has to be analyzed. Nevertheless, undoubtedly other factors have to be considered as well. Indeed, as shown in Figure 3, gelation times corresponding to the aliphatic PPO-based curing agents were conducted in a very different way since



**Figure 4** Arrhenius plots for gelation times. Symbols as in Figure 3.



for these amine-cured mixtures gelation occurred at very long times. Therefore, the variation of cure behavior on the polyether di- or triamine based formulations must be connected with other structural features than chain rigidity.

According to Dusek and Matejka,<sup>16</sup> the different reactivities of the terminal primary amino groups of these PPO-based amines differ from that of NH<sub>2</sub> groups of aliphatic amines because of competition between the epoxy and ether groups of the polymer backbone in an interaction with proton donors; besides, the methyl substitution effect in the amine group reactivity is more negative than in aliphatic amines.

Therefore, one significant reason for the delay in gelation for mixtures based on PPO amines must arise from the inter- and intramolecular interactions by means of hydrogen bonding, in addition to those existent for other epoxy-amine systems.<sup>17</sup> In fact, the presence of the ether group, the oxygen atom is a strong H-acceptor, in the PPO-based polyamines appears to be responsible for the decrease on the cure rate by the occurring intramolecular bonding, but also by intermolecular interactions which slow down the reactivity of the active hydrogens of the amine groups, and so their nucleophilicity. Therefore, despite the chain flexibility of these PPO-based polyamines, the gelation threshold appeared at very long times. Indeed, when the curing agent reactivity must be analyzed, besides the nucleophilicity of the reacting group, factors such as chain rigidity, inter- and intramolecular interactions, steric hindrance, and others have to be considered as well.

Morgan et al.<sup>11</sup> have suggested that the methyl group adjacent to the amine group in PPO-based polyamines would sterically interfere, especially in the rate of secondary amine reactions, and thus the methyl groups should not influence enough the gelation time with respect to that for aliphatic amines since before gelation reactions with primary amines occur preferentially to those with secondary amines.<sup>15,16</sup> Nevertheless, these methyl groups contained in the PPO-based polyamines structurally obstruct the nearest-neighbor amines and so the intermolecular interactions, therefore decreasing the viscosity of the mixtures and consequently improv-

ing the accessibility of other reactive groups like epoxy with respect to that existing in mixtures with aliphatic amines unsubstituted. Indeed, the high gelation times for mixtures cured with PPO-based polyamines seem to be basically due to the decreasing amine reactivity due to the presence of the ether group.

On the other hand, the slight longer gelation times of T403 cured mixtures with respect to that for D230 containing ones, especially at low cure temperatures [figs. 2(d) and 2(e)] possibly is due to the higher oxygen-active hydrogen atoms ratio in the T403 triamine, which would increase the hydrogen bonding between oxygen and amine groups in the T403 rather than for the D230 amine.

The influence of cure temperature on the gelation time has been also studied for each epoxy mixture [figs. 2(a)-(g)]. As it is well known, the dependence of gelation time on the cure temperature can be well fitted with an Arrhenius-type equation.<sup>5,18,19</sup> Thus, the time required to reach a viscosity of 1000 Pa s,  $t_{\mu}$ , can be written:

$$t_{\mu} = t_0 e^{E_a/RT} \quad (1)$$

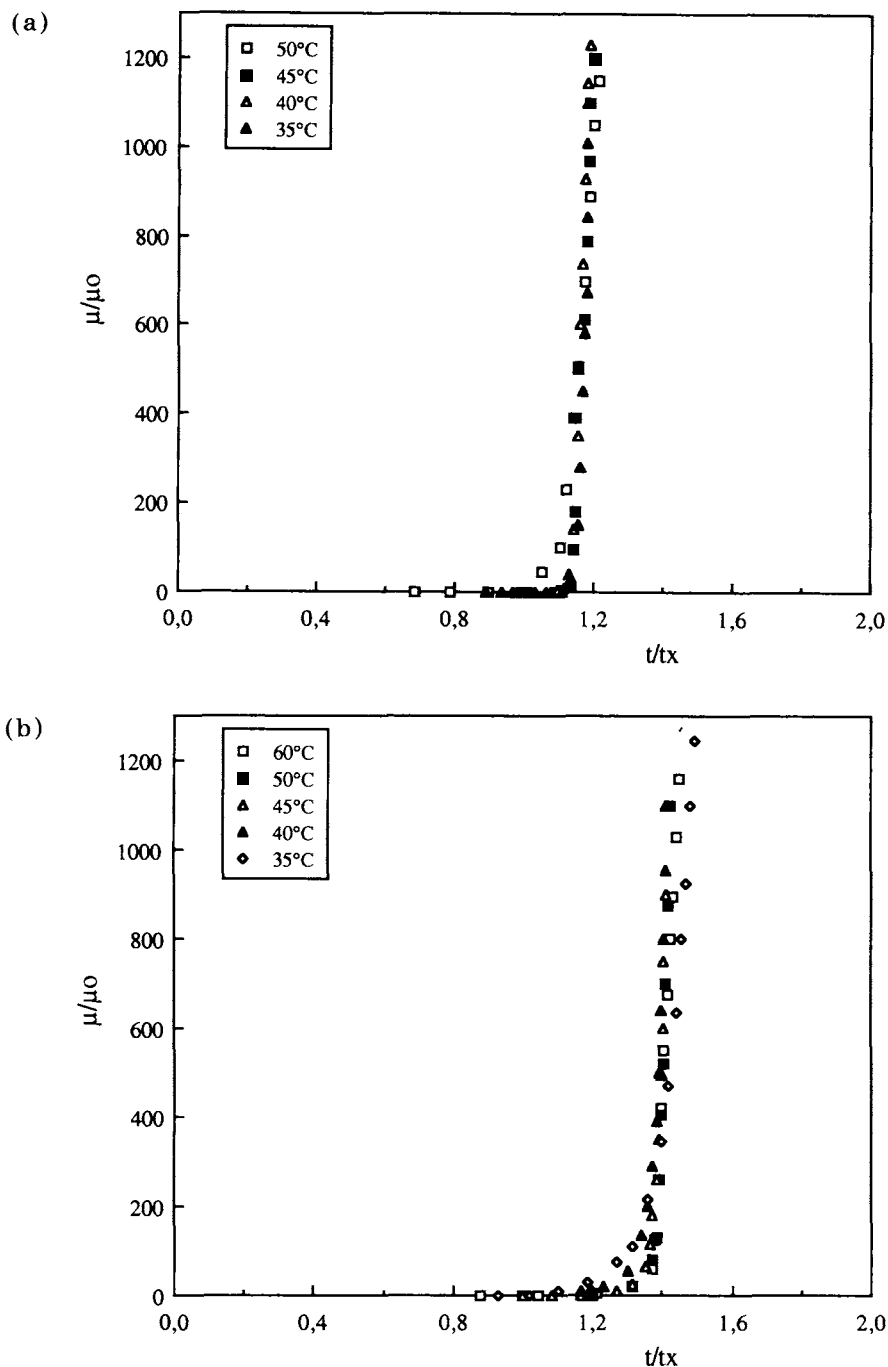
where  $t_0$  is a constant for each mixture,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature expressed in K.

Indeed, Figure 4 shows a linear dependence of the logarithm of gelation time on the inverse cure temperature for all epoxy mixtures analyzed. The apparent activation energies for gelation determined from the slopes of these straight lines are shown in Table III. The values obtained are similar to those reported in the literature survey [for instance, Grillet et al.<sup>5</sup> using a Contraves viscosimeter obtained an activation energy of 53 kJ mol<sup>-1</sup> for a DGEBA (DER 332)/DDM mixture].

The introduction of methyl substituents in the carbon atom located in the  $\beta$  position with respect to the reactive groups, 3DCM or IPDA cases, gives rise to shielding and steric hindrance of the reactive groups. Indeed, as it has been recently shown,<sup>6</sup> the introduction of alkyl substituents in carbon atoms near to the reactive groups leads to an increase of the activation energy of the chain segments implied,

**Table III** Apparent Activation Energies and  $_{\text{gel}}T_g$ 's for the Epoxy Mixtures

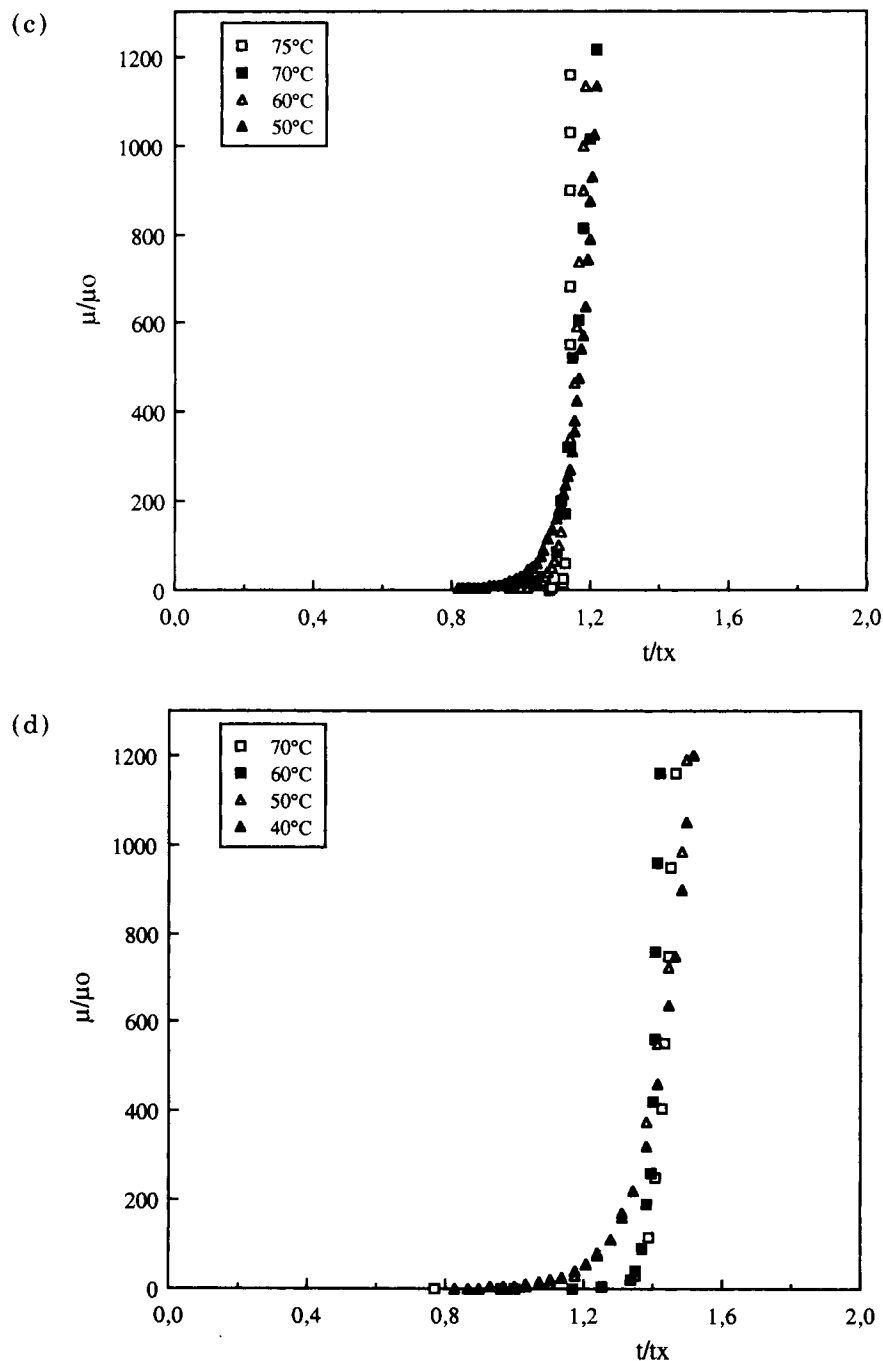
Curing Agent	DETA	IPDA	3DCM	D230	T403	<i>m</i> -PDA	DDM
Activation Energy (kJ/mol)	47.7	62.3	50.9	73.4	68.1	54.5	54.1
$_{\text{gel}}T_g$ (°C)	—	32	47	42	43	40	47



**Figure 5** Master curing curves of viscosity for epoxy mixtures cured under isothermal conditions for the different curing agents used. (a) DETA, (b) IPDA, (c) 3DCM, (d) D230, (e) T403, (f) mPDA, (g) DDM.

and so the similarity of activation energies for mixtures cured with alkyl-substituted cycloaliphatic amines or with aromatic amines arises from the comparable increase on chain rigidity introduced either by the alkyl substituents or by the aromatic rings. Moreover, the high activation energy for IPDA containing mixture is possibly due to the lowering

on mobility of the hydrocarbon cycle introduced by the methyl groups located far away from the reactive sites. The surprising activation energy values for mixtures with PPO-based amines must be a consequence of both the steric hindrance of the methyl group and the intramolecular interactions between the hydrogens of the amine groups and the ether



**Figure 5** (Continued from the previous page)

groups of the amine backbone. Intramolecular interactions between hydrogen and nitrogen atoms of the amine groups are also possibly responsible of the relatively high activation energy for the DGEBA-DETA mixture.

On the other hand, it was noted that the curing curves of viscosity under various isothermal conditions had similar shapes for the different mixtures analyzed. Attempts have been made to shift the cur-

ing curves by using a time shift factor,  $a(t)$ . In order to do that, cure times have been divided by an arbitrary time,  $t_x$ , taken as time to which the viscosity of the mixture steadied. As shown in Figure 5, for each mixture a single generalized curve described the viscosity evolution during isothermal curing, thus indicating that the reaction mechanisms did not change for the intervals of cure temperatures studied. However, at the early stage of the sharp

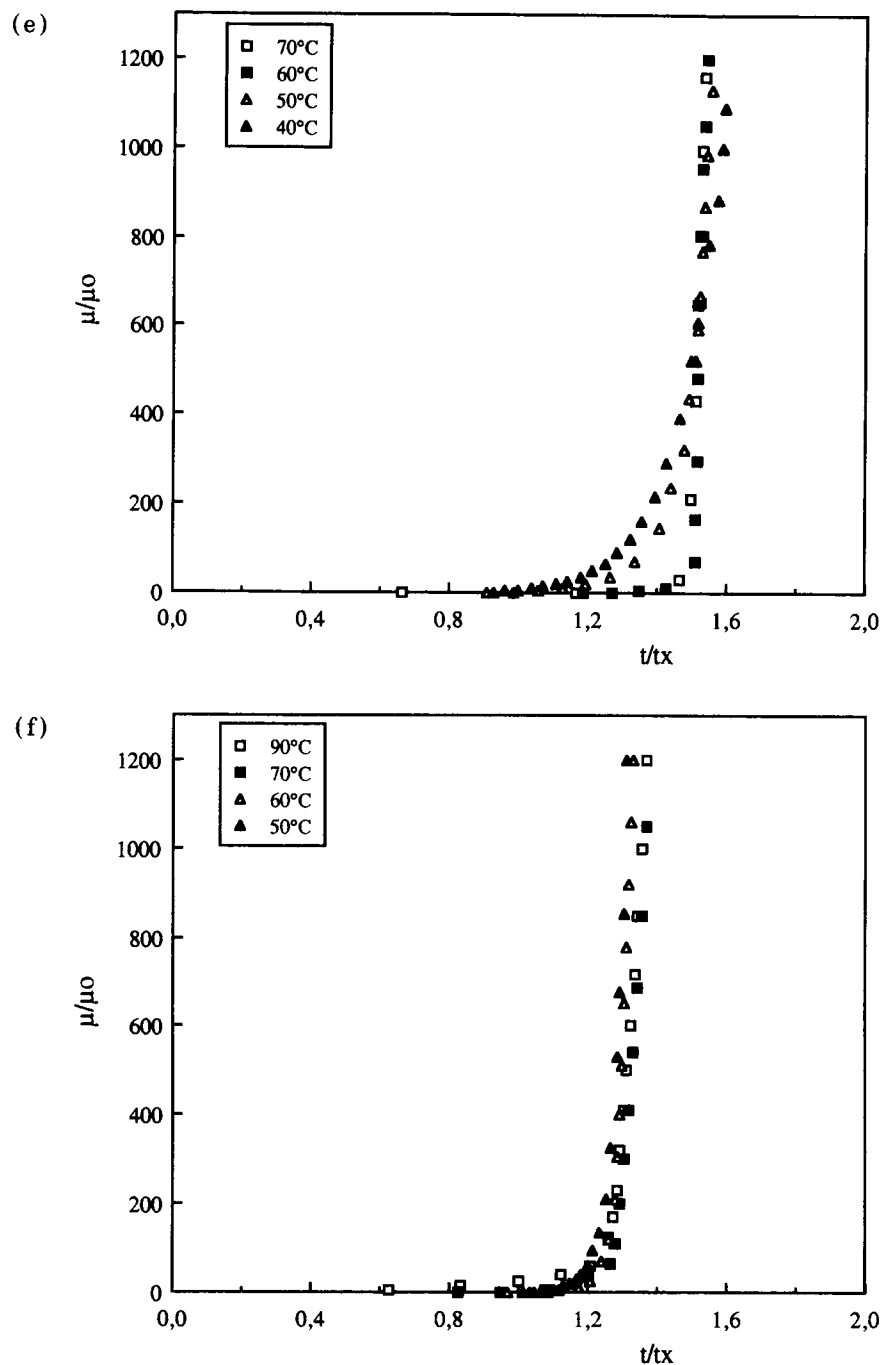


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variation on viscosity some deviation in the curves corresponding to the higher cure temperatures was observed, especially for PPO-based amine mixtures, possibly as a consequence of competitiveness between gelation and vitrification at low cure temperatures.

The linear dependence of the time shift factor upon the inverse temperature for the different mix-

tures indicated Arrhenius-like relationships from which the apparent activation energies were calculated. The values so obtained, though not shown, are equal to those shown in Table III.

Furthermore, the temperature at which gelation and vitrification take place simultaneously,  $_{gel}T_g$ , has been calculated for all mixtures studied. The values of the slopes on the viscosity versus time curves cor-

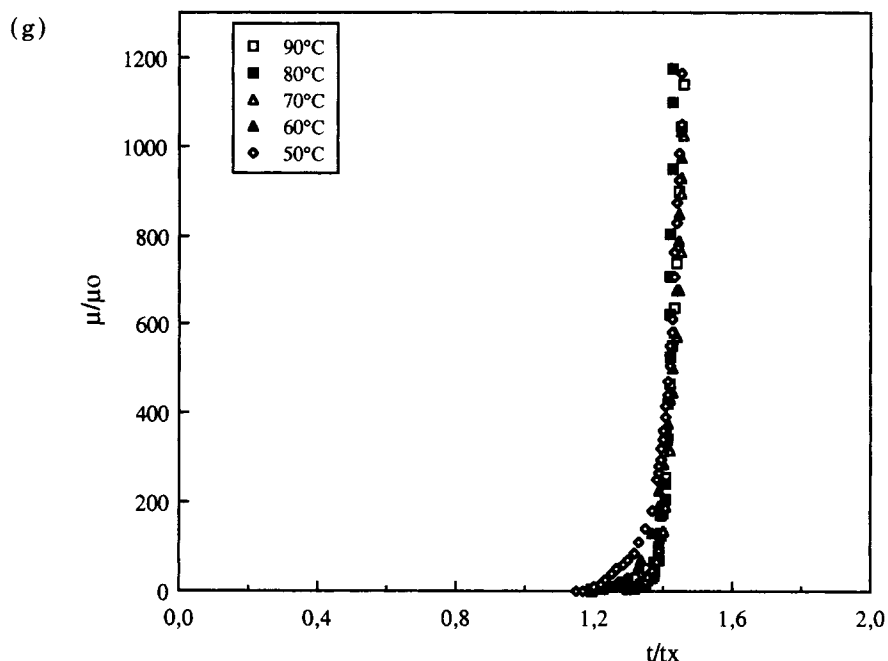


Figure 5 (Continued from the previous page)

responding to both regions before and after the sharp rising on viscosity during curing have been measured and plotted against reciprocal absolute cure temperatures. For every mixtures all experimental values were well fitted by straight lines, which means that, within the experimental error, the method was adequate to obtain the  $_{gel}T_g$  values of the studied mixtures. Data so obtained are shown in Table III, and they are similar to those shown in the literature survey.<sup>15</sup> Despite the evident dependence on the structure of hardener, at this time we do not have an interpretation of the values obtained. More investigations with other hardeners and epoxy monomers with different molecular weights are necessary in order to understand this behavior.

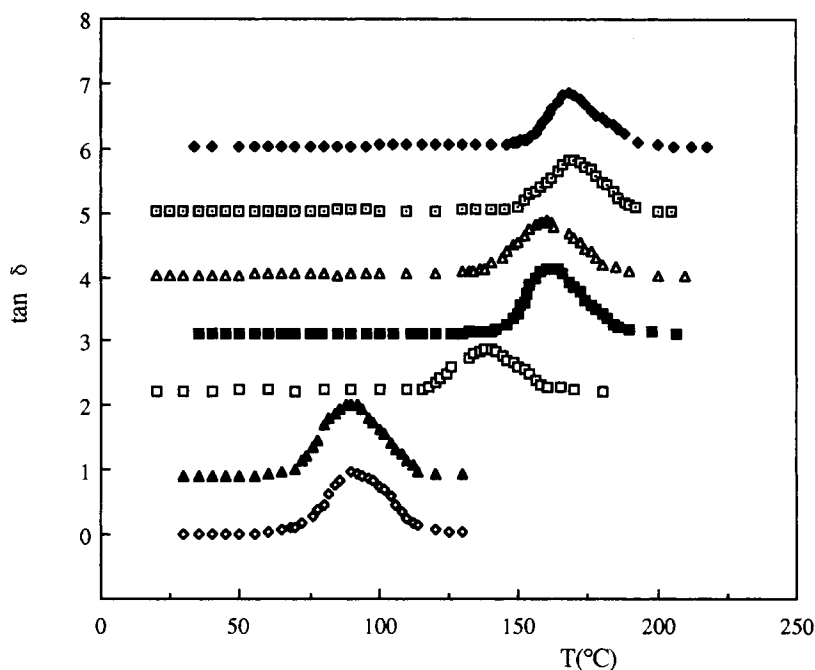
Dynamic differential scanning calorimetry (DSC) scans have also been carried out for all epoxy mixtures studied. Results are reported in Table IV.  $T_1$ ,  $T_p$ , and  $T_2$  are the temperatures corresponding to the initial, the peak, and the final temperatures of the cure exotherm through the dynamic scan, respectively. The value of  $T_p$  is strongly dependent on the structure of the curing agent. Thus, aromatic amines like *m*-PDA or DDM are less reactive than the aliphatic and cycloaliphatic. Besides, the steric hindrance existing in D230 and T403, as well as in the cycloaliphatic amines, IPDA and 3DCM, also increases  $T_p$ . Consequently it indicates a lower reactivity in the corresponding epoxy mixtures. The

overall heats of reaction to epoxy equivalent were quite the same for all epoxy-amine mixtures analyzed, thus indicating the similarity in the mechanisms of the reactions for these systems.

On the other hand, the maximum glass transition temperature of these epoxy mixtures, obtained for each mixture with the cure schedules shown in Table I, has been measured by dynamic mechanical studies as the temperature corresponding to the maximum value of the  $\alpha$  relaxation,  $T_\alpha$ . Results are shown in Figure 6 and Table V. Instead the rheological behavior, the mixtures containing PPO di- or triamines presented the lower glass transition temperatures

Table IV Initial, Peak, Final Temperatures, and Heats of Reaction Obtained from DSC Analysis for Stoichiometric Mixtures

Curing Agent	$T_1$ (°C)	$T_p$ (°C)	$T_2$ (°C)	$\Delta H$ (kJ/equiv)
DETA	34	98	200	100
IPDA	40	114	210	104
3DCM	50	131	215	106
D230	45	108	176	94
T403	44	113	222	97
<i>m</i> -DPA	85	159	240	104
DDM	80	168	240	104



**Figure 6** Variation of loss factor as a function of temperature. Symbols as in Figure 3. The scale is correct for T403. For the rest of the hardeners, the scale is offset vertically from that of its immediate neighbors by 1.0.

of all systems analyzed. As is well known, for an epoxy network the maximum  $T_g$  is reached when the cure is complete. However, as previously shown for different epoxy mixtures,<sup>20-23</sup> despite using the optimum cure schedule some epoxy groups still remain unreacted. The storage moduli,  $E'$ , for these stoichiometric DGEBA-hardener mixtures are plotted against temperature in Figure 7.  $E'$  conducted in a relatively similar way for all mixtures since at temperatures lower than the  $T_g$   $E'$  values were high, showing a sharp decrease in the glass transition region corresponding to each mixture. Afterward, the storage modulus reached a near constant value because all materials became like a rubber.

The average molecular weight between strands of the different crosslinked networks can be theoretically calculated by assuming a full conversion of epoxy resin in the curing process and afterward its value can be compared with the experimental one

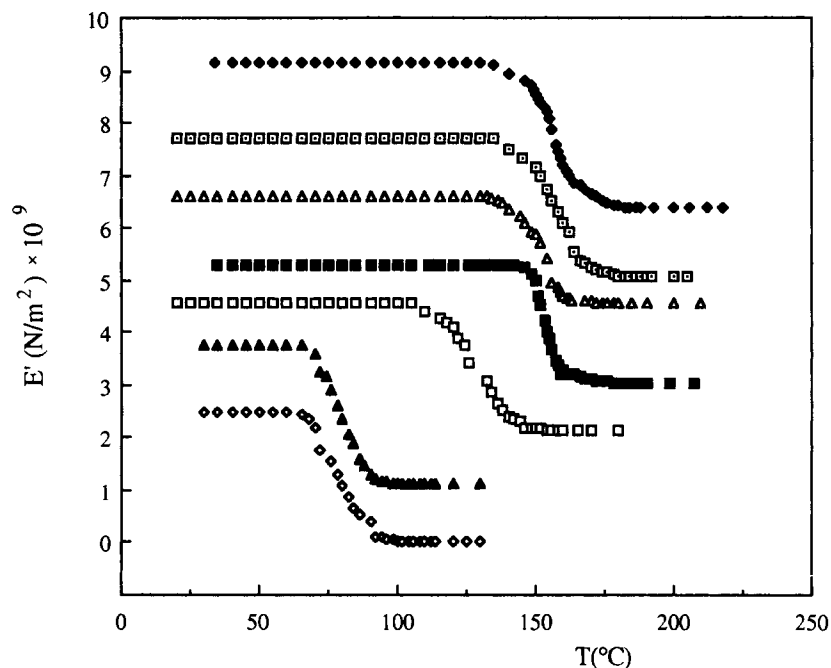
to know the crosslink density of the formed network. Therefore, in order to know the crosslinking density of the epoxy mixtures, most authors<sup>24-28</sup> use an approximation of the simple rubber elasticity theory, along with the experimental equilibrium rubber modulus,  $E_r$ , taken as elastic modulus at  $T_g + 30^\circ\text{C}$ . Thus, the average molecular weight between crosslinks can be approximated through the following relationship<sup>29</sup>:

$$M_c = \frac{\phi \rho R T}{3 E_r} \quad (2)$$

where  $\phi$  is the front factor,  $\rho$  the density at absolute temperature  $T$ ,  $R$  the gas constant, and  $E_r$  the equilibrium elastic modulus. Although  $E_r$  is usually taken as the tensile modulus (or shear modulus,  $G_r$ ), values of flexural rubber modulus, shown in Table V, can be used in order to compare the physical rigidity of the several mixtures studied.

**Table V** Glass Transition Temperatures and Rubber Moduli for the Different Epoxy Mixtures

Curing Agent	DETA	IPDA	3DCM	D230	T403	m-PDA	DDM
$T_g$ ( $^\circ\text{C}$ )	138	161	160	90	91	169	170
$E_r$ ( $10^{-7}$ ) ( $\text{N/m}^2$ )	6.0	5.0	2.3	2.8	5.0	6.0	6.0



**Figure 7** Storage modulus variation upon temperature. Symbols as in Figure 3. The scale is correct for T403. For the rest of the hardeners, the scale is offset vertically from that of its immediate neighbors by 1.0 (for mPDA the offset is 1.5).

Although the crosslink density of the cured network is the main factor to determine the glass transition behavior for an epoxy resin crosslinked with a given hardener and cured at different conditions,<sup>6,11</sup> other factors such as chemical structure of the hardener backbone must be considered to compare different amine-cured epoxy mixtures. With the exception of PPO-amine based mixtures, while rubber modulus values did not show significant changes for the mixtures cured with the different hardeners, the glass transition temperatures of the fully cured mixtures showed evident variations from one mixture to another. Therefore, the variation on  $T_g$ 's between the different mixtures did not have a clear relation with their crosslink density or rubber modulus, as shown in Table V. Instead, the chemical structure of the amine explained the differences in the glass transitions of these mixtures in spite of other factors such as packing density<sup>30</sup> or that variations on the free volume<sup>23,31-33</sup> could vary slightly the reported values. Thus, the networks constructed with aliphatic amines showed the lower glass transition temperatures because of the flexibility of their chains, higher for the PPO di- and triamines than for DETA-cured mixtures since the higher aliphatic segment-amine nitrogen ratio in the PPO di- and triamines with respect to that for DETA, rigidized by the central amine group after its reaction, in spite

of the steric restrictions to motion between chains led by the bulky methyl groups in the PPO polyamines based mixtures have been seen to increase the  $T_g$  in other epoxy blends.<sup>34</sup> The T430-cured system showed a slightly higher  $T_g$  than that for the D230 containing mixture; this change is certainly related to the more complicated network formed for the T430-cured mixture.<sup>11</sup> On the other hand, the glass transition temperatures for mixtures cured with cyclic amines increased as rigidity of amine cyclic chains did, i.e.,  $T_g$ 's were higher for the mixtures cured with aromatic amines than those for cycloaliphatic amines containing mixtures, that despite the high  $T_g$  of the latter mixtures because of the steric restrictions to chain motions of the pendant methyl groups.

## CONCLUSIONS

The cure behavior of epoxy mixtures cured with hardeners with different backbone stiffness and pendant methyl groups has been investigated by rheological techniques. Gelation times and apparent activation energies of the several mixtures have been related to the different characteristics of the curing agent such as amine nucleophilicity, backbone stiffness, steric hindrance, and inter and intramolecular interactions between different groups.

DSC dynamic analysis has shown the relationships between the reactivity in the mixtures as a function of the chain stiffness of the curing agent and the pendant groups of the amines.

The glass transition temperatures of cured epoxy mixtures, dependent on the crosslink density for a given formulation, are a function of the chemical structure of the curing agent employed. The analysis of the rubber modulus in stoichiometric epoxy mixtures, obtained with various curing agents, has shown that for a similar crosslink density the  $T_g$  varies upon the chemical backbone structure between crosslink sites.

This study has been concerned with the analysis of the relationships between cure evolution and ultimate properties of epoxy systems and the chemical structure of the amine-type hardener employed. Such studies can be used to control the network formation and to develop structure-property relations for thermosetting mixtures.

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