Thermokinetics and Chemorheology of the Cure Reactions of the Tetraglycidyl Diamino Diphenyl Methane–Diamino Diphenyl Sulfone Epoxy Systems

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Synopsis

The cure behavior of commercial grade TGDDM–DDS mixtures of compositions ranging from 10 to 100 phr of hardener and the thermal polymerization of the epoxy component are analyzed by means of differential scanning calorimetry. The kinetic parameters and heats of reaction determined in isothermal and dynamic scans suggest that DDS primary amine addition and epoxide etherification dominate the cure reactions. The primary amine epoxide addition is characterized by overall heat of reaction (referred to the weight of the epoxy component) of 255 cal/g and by an activation energy of 16.6 kcal/mol. The corresponding values for the etherification reaction are, respectively, 170 cal/g and 41 kcal/mol. A method of derivation of the epoxide conversion from the heat evolved in DSC thermal scans of these systems is presented. The results are in good agreement with independent IR determinations. The steady shear and oscillatory viscosity measurements and the calorimetric analysis of the isothermal cure at 140°C, 160°C, and 180°C of a TGDDM–DDS mixture containing 35 phr of hardener indicate that gelation is principally governed by the primary amine addition. The gelation limits calculated in isothermal tests by combining the calorimetric analysis and the theory describing the nonlinear copolymerization of the tetrafunctional TGDDM with an essentially difunctional DDS were in good agreement with the values experimentally determined through rheological measurements.

INTRODUCTION

Carbon-fiber-reinforced composites are currently made from preimpregnated materials containing high performance epoxy polymers and aromatic amines. The chemical structure, purity, functionality, and composition of the constituent compounds, as well as the extent of reaction, influence the final network structure and hence the bulk properties of the cured thermoset.[1–5]

Prepregs are generally slowly heated at constant rate up to the final cure temperature in order to remove the excess resin and to produce a void-free composite. The magnitude and shape of the viscosity–temperature–time profiles of the reacting system are, therefore, crucial in the early stage of cure where adequate flow properties of the resin are requested before the gelation (which marks the transition of the system from a viscous to a rubbery material) occurs. A proper design of the cure cycle depends on the understanding of the critical phenomena associated with the thermokinetics of polymerization, chemorheology of cure, and flow of resin during the phases of the polymerization preceding the gelation. The TGDDM–DDS system, which is widely utilized as a matrix for high per-

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formance composites is characterized by differently activated cure reactions.[2–6] In particular, three principal reactions dominate the cure, namely, the primary amine–epoxide addition, the secondary amine–epoxide addition, and the epoxide etherification. The main reaction involves an epoxide ring opening following electrophillic attack by the primary amine to form an amino alcohol, while the secondary reactions, which are characterized by lower rate constants,[5,6] are the etherification reaction between the epoxide and the hydroxyls, initially present as α-glycol impurities of the TGDDM[7] or generated in the main reaction, and the secondary amine addition.

Usually, gelation occurs at a fixed extent of conversion,[1] independent of temperature, as long as the reaction mechanism is temperature independent, which might not be the case in the complex TGDDM–DDS system. However, gelation in a structure generated from a series of reactions where the main primary amine addition is kinetically favored may be governed by a single mechanism, independent of the temperature, while the secondary reactions are principally responsible for crosslinking.[8]

Models describing the network formation, glass transition, and rheological behavior as a function of the cure time and temperature[9–12] should, in principle, consider that the morphology of the resulting homogeneous but not unique network structure is characterized by at least two different crosslinking densities arising from the two different reactions governing the gelation and crosslinking.

The influence of an hetherogeneous network on the durability in aggressive environments of these TGDDM–DDS-based composites has been extensively reported in the literature.[13–20] Moreover, the cure of these high performance matrices can only be driven to completion at high temperatures, where chemical degradation or inhomogeneous networks formation are also favored both by diffusion constrains, due to the vitrification of the system,[17] and by the presence of differently activated cure reactions.

It becomes then difficult to establish close relationships between the chemical composition, processing variables, and the optimum characteristics in real life without accounting for the influence of the time–temperature path on the molecular network structures generated during the early stages of cure, when gelation occurs, and in the final postcure of these materials.

The scope of the present work is to analyze the cure reaction mechanism of the TGDDM–DDS systems by means of rheological as well as calorimetric tests in order to separate its influence on the final network structure in the different phases of the cure process. Dusek et al.[1,11] have already successfully applied the crosslinking theory to the cure of the epoxies in order to predict the network morphology. The gelation theory[9] will be applied to describe the relationships between extent of reaction and viscosity for this nonlinear polymerization, while a kinetic analysis of isothermal and dynamic DSC thermograms will be used to derive the parameters of the reactions involved in the cure process.

EXPERIMENTAL

Materials. Commercial grade tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM, Ciba-Geigy MY 720) and 4,4′-diaminodiphenylsulfone (DDS, Ciba-Geigy) have been used without any further purification to prepare 10 mixtures

of composition ranging from 10 to 100 phr of hardener. The two-components were mixed at 80°C to avoid any reaction. The DDS purity was calorimetrically determined by DSC (97%) while the TGDDM, MY 720, was reported[7] to have 130 epoxy equivalents.

Apparatus and Procedures. A computerized differential scanning calorimeter, Perkin–Elmer DSC-2, has been used to characterize the glass transition temperatures and heats of reaction of the unreacted and partially cured samples. Heating rates of 10°C/min and 20°C/min were used to scan 5–10 mg of resin from −30°C to 300°C in sealed steel pans. A Perkin–Elmer IR spectrometer, Model 599, was used to monitor the intensity of the epoxide band at 906 cm^{-1} of partially cured samples. A steady shear cone and plate viscometer, Ferranti-Shirley, and a dynamic viscosity spectrometer, Rheometrics, with parallel plates and operating at 1.0 Hz, were utilized to determine the isothermal rheological behavior of the TGDDM–DDS system at 140°C, 160°C, and 180°C.

RESULTS AND DISCUSSION

On a molecular level, the cure of thermosetting systems is characterized by a gelation occurring at a constant chemical conversion, and by a progressive reduction of molecular mobility caused by the increase of the molecular weight and crosslinking density. Both processes lead to the vitrification of the material and hence to the quenching of all reactions. Gillham et al.[17,21] treated the cure behavior of several thermosetting systems by using time–temperature–transformation diagrams which correlate the molecular characteristics to the processing variables. However, the occurrence in the TGDDM–DDS system of differently activated and kinetically distinct reactions suggests further considering the chemorheology of the cure, gelation, and vitrification processes with respect to the prepolymer composition and temperature cure path. In fact, the gelation and vitrification phenomena, which usually occur in two phases of the material processing such as the initial polymerization and final postcure, may strongly influence the thermoset molecular morphology and hence the material properties.[13-20]

Thermokinetic

Differential scanning calorimetry (DSC) is often used for the indirect determination of the advancement of the cure for prepregs, with the assumption that the heat evolved is proportional to the extent of reaction. Several kinetic methods of determination of the activation energies and rate constants of the cure reactions are based on the same assumptions.[22,23] Although simple nth-order kinetics with the temperature-dependent rate constant given by an Arrhenius expression could be too simplified to express the entire cure reactions in these systems, these methods assume that a single reaction with a single rate constant is being considered.[1-6] In the case of multiple reactions characterized by different values of the kinetic parameters and heats of reaction[6,8] the previous models are, in fact, invalid. DSC analysis, however, could be also applied to complex systems in order to know the extent of reaction as a function of time if the kinetics of the single reactions are independently determined.

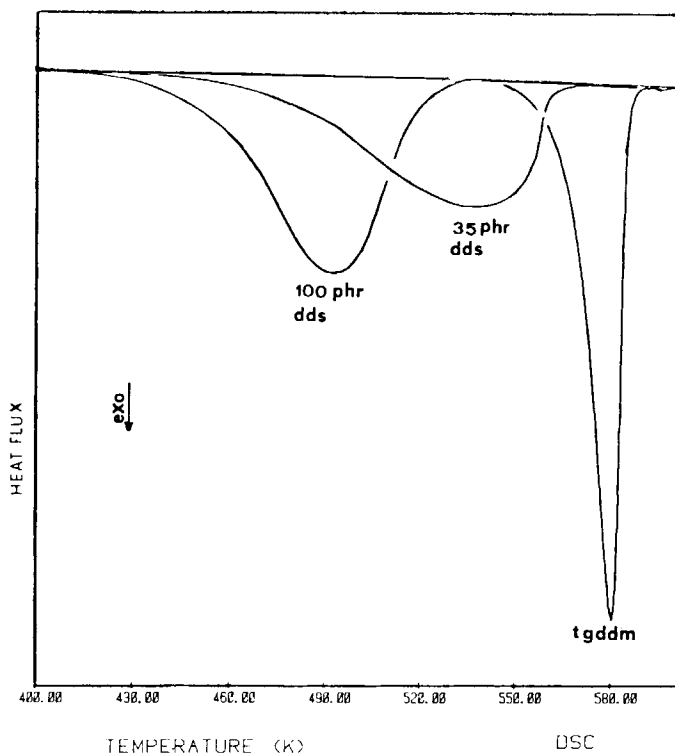Previous investigations[2-6] agreed with the conclusion that three reactions

Fig. 1. DSC thermograms of: (a) TGDDM–DDS 100 phr; (b) TGDDM–DDS 35 phr; (c) TGDDM. Heating rate 10°C/min.

dominate the cure behavior of the TGDDM–DDS systems, namely, epoxide–primary amine addition, epoxide etherification with the hydroxyls, and the epoxide–secondary amine addition. The kinetic constant of the former reaction in the range of temperature between 177°C and 200°C has been reported to be at least 1 order of magnitude higher than the other two values.[5]

DSC has been applied to particular conditions of temperature and composition in order to isolate the single reactions. Due to its high rate constant, primary amine addition will principally occur in TGDDM–DDS mixtures containing more than an equimolar content of DDS primary amines and epoxy groups, i.e., a DDS–TGDDM molar ratio higher than 1.8 or, in a weight base, more than 90 phr of DDS. The reaction of etherification, conversely, characterizes the thermal polymerization of a TGDDM sample containing some initial concentration of hydroxyls (i.e., isopropyl alcohol). These two limiting systems and 10 intermediate mixtures of molar ratios ranging from 0.207 to 1.245 (10–60 phr of hardener on a weight base) were tested for comparison.

The DSC thermograms of the two limiting mixtures, TGDDM–100 phr DDS and TGDDM–isopropyl alcohol, are compared in Figure 1 with the scan of the mixture of DDS–TGDDM molar ratio 0.726 (35 phr of DDS). The three thermograms show well-distinct characteristics associated with the different reactions. Typically, the etherification due to the thermal polymerization of the TGDDM occurs over a narrow range of high temperatures and has a sharp exotherm[7] while, in comparison, that of the primary amine addition, which princi-

Type of reaction	DDS (phr)	ΔH (cal/g TGDDM)	E_a (kcal/mol)	ln K_0
Etherification	0	170	41.0	33.0
PA addition	>90	255	16.6	13.9

pally occurs in the mixture containing 100 phr of DDS, is broadly distributed over a wide range of lower temperatures. The thermogram of the mixture containing 35 phr of DDS shows an intermediate behavior which resumes the characteristics of the previous two limiting cases. The shape of this thermogram suggests that, as already reported in literature,[5,8] the early stages of cure are governed by the primary amine addition, while the etherification principally occurs once all the primary amines are exhausted.

In order to assign characteristic heats of reaction to the epoxide ring opening in the two different reactions, the values determined in the DSC tests were not referred in this work to the overall weight of the mixture but only to the weight of the TGDDM.

The kinetic analysis of the dynamic DSC scans has been carried out according to the method proposed by Prime.[22] The activiation energy, E_a, the frequency factor, K_0, and the overall heat of reaction for the two limiting systems are reported in Table I. The overall heat of reaction of the primary amine addition is significatively higher than that of the etherification, i.e., 255 and 170 cal/g of TGDDM, respectively, while the heat of reaction of the mixture containing 35 phr of DDS has an intermediate value, 213 cal/g of TGDDM.

Considering that in the two limiting cases only a single reaction is occurring (hence the cumulative heat may be considered proportional to the advancement of the reaction), the kinetic analysis method[22] may be properly applied and the results considered valid. The values found for the activation energy of the primary amine addition and etherification were, respectively, 16.6 and 41.0 kcal/mol. These two reactions are principally governing the cure behavior of the TGDDM–DDS systems. Electron spin trap[5,8] techniques have demonstrated that the addition of primary alcohols to the epoxide always generate another primary alcohol, keeping constant the active hydroxyl concentration, while an independent FT–IR analysis[5,8] has shown that the hydroxyl concentration is almost constant once all the primary amines are exhausted. These facts suggest that the secondary amine addition, at least at temperatures below 200°C,[6] does not play a relevant role in the cure reactions.

In the simplified hypothesis that only these two limiting reactions are occurring and that all the primary amines are first consumed, the overall heat of reaction, referred to the weight of TGDDM, for the mixtures containing different concentrations of Hardener could be theoretically calculated. The relationship between the heat developed during the cure and the corresponding value of the epoxy conversion for TGDDM–DDS mixtures of different composition may be derived considering that the DDS molecule is essentially acting as a bifunctional curing agent while the TGDDM is tetrafunctional. The heat developed in the

TABLE II
Experimental and Theoretical Heats of Reaction for the TGDDM–DDS Mixtures (cal/g TGDDM)

DDS (phr)	0	10	20	25	30	35	40	45	49	60	>90
ΔH_{expt}	170	184	194	201	205	213	215	226	218	230	255
ΔH_{theor}	—	179	188	192	197	201	206	210	214	224	—

early stages of the cure or scan, where only the primary amine addition is assumed to occur, is proportional to the heat of reaction of the epoxide with the primary amines, $\Delta H(t) = \beta(t)\Delta H_a$, up to threshold values,

$$\Delta\overline{H} = (m_{a0}/m_{e0})\Delta H_a \tag{1}$$

corresponding to an epoxy conversion

$$\overline{\beta}_e = \Delta\overline{H}/\Delta H_a = m_{a0}/m_{e0} \tag{2}$$

where $m_{a0} = 2m_{D0}$ and $m_{e0} = 4m_{T0}$ and m_{D0} and m_{T0} are the initial moles of DDS and TGDDM. Obviously, expressions (1) and (2) are valid up to an equimolar amine–epoxide ratio, $m_{a0}/m_{e0} = 1$, corresponding in our case to a DDS–TGDDM mole ratio of 1.8 (90 phr of DDS).

After the depletion of the primary amines, the heat developed is proportional to the etherification heat of reaction, ΔH_e, while the cumulative heat is

$$\Delta H(t) = \Delta\overline{H} + [\beta_e(t) - \overline{\beta}_e]\Delta H_e \tag{3}$$

Finally, the overall heat evolved is

$$\Delta H_T = \beta_e\Delta H_a + (1 - \overline{\beta}_e)\Delta H_e \tag{4}$$

The values of the overall heats of reaction for the TGDDM–DDS mixtures of composition, ranging from 10 to 60 phr of hardener calculated according to expressions (4), favorably compare in Table II with those experimentally determined in the DSC scans. The data reported in Table II show a maximum discrepancy of the order of 6%. However, the theoretical values of the heats of reactions are always lower than the experimental ones. This systematic variation may be attributed to the fact that the occurrence of some secondary amine addition cannot be excluded a priori in the scans carried out up to 580 K.[6] In a recent publication,[8] Gupta and co-workers reported a value of the overall heat of reaction for a mixture containing 28 phr of DDS that if referred to the weight of TGDDM, agrees with our analysis. Nevertheless, it could be questioned that secondary amine addition may be characterized by a heat of reaction of the same magnitude of that of the etherification, leading to the same good agreement. The low reactivity observed for the secondary amine, however, could be attributed to its position in the chain, strongly hindered by the DDS aromatic ring which further limits its mobility as compared to that of the primary alcohols. Thus, it seems reasonable that such constrains should only increase the activation energy of the reaction not altering its heat of reaction. In the case when only primary and secondary amine addition occurs, the overall heat of reaction referred to the weight of TGDDM should be independent of the DDS content, a fact which is not experimentally observed in Table II.

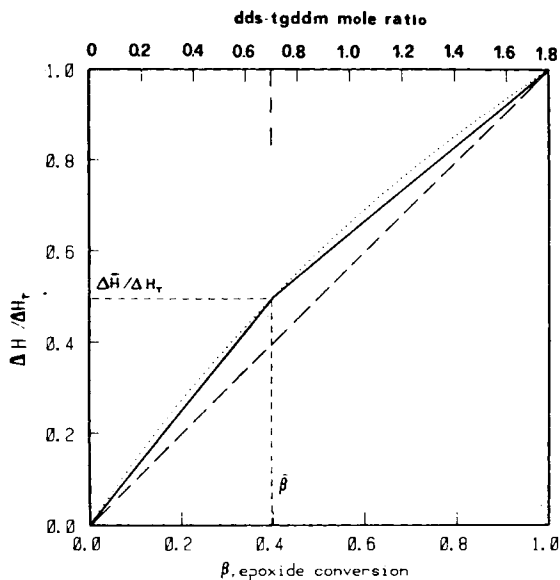The relationships between DDS content, fractional cumulative heat,

Fig. 2. Fractional heats of reaction vs. epoxy conversion for the TGDDM–DDS systems. The full lines refer to the 35 phr composition while the pointed line is the locus of the couples of values of epoxy conversion and fractional heat for DDS primary amine exhaustion in mixtures of different TGDDM–DDS mole ratios (top of the figure).

$\Delta H(t)/\Delta H_T$, and the epoxide conversion, β_e, expressed by eqs. (1)–(4), are reported in Figure 2. The pointed line represents the locus of the couples of threshold values of fractional cumulative heat, $\Delta \overline{H}/\Delta H_T$, and epoxy conversions, $\overline{\beta}_e$, corresponding to the complete depletion of the primary amines in mixtures of different composition. The two full lines refer to the same relationship between the heat developed and the epoxy conversion for a mixture of fixed composition, i.e., 35 phr of DDS in Figure 2, before and after the primary amine exhaustion, while the dotted line represents the assumption that the advancement of the reaction is proportional to the fractional heat evolved during the cure. In this case, the estimates of the epoxy conversion are higher than those calculated from eqs. (1)–(4). The validity of the proposed mechanism of cure and method of determination of the epoxide conversion has been tested by comparing calorimetric and IR spectroscopy data. The decrease in intensity at 906 cm^{-1} of the epoxide adsorbance and the residual heats of reaction were determined for

TABLE III
Epoxy Conversions, β_e, Calculated from the Cumulative Heats (Fig. 2) and IR in Samples of Different Composition and Degree of Cure

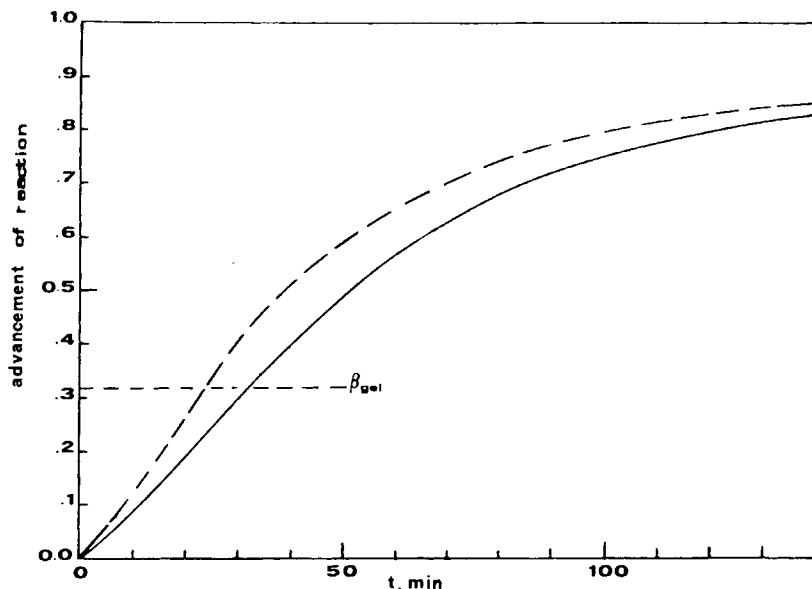| 20 phr			30 phr			50 phr		
$\Delta H/\Delta H_T$ (%)	Fig. 2 (%)	IR (%)	$\Delta H/\Delta H_T$ (%)	Fig. 2 (%)	IR (%)	$\Delta H/\Delta H_T$ (%)	Fig. 2 (%)	IR (%)
15	11	9	27	19	23	48	36	32
36	24	22	71	64	57	—	—	—
41	33	37	77	72	72	86	82	82
49	42	42	80	75	72	86	82	85

Fig. 3. Comparison between the DSC cumulative heat and the epoxy conversions calculated from Figure 2 during the isothermal cure at 180°C of a TGDDM–DDS mixture containing 35 phr of hardener.

samples of different composition and degree of cure. The values of the epoxy conversion reported in Table III and directly calculated from the residual heat of reaction are higher than those, almost coincident, obtained from the IR spectra and Figure 2. This result agrees with our hypothesis that the primary amine addition and the etherification are kinetically well distinct and govern the cure of the TGDDM–DDS systems.

As a consequence, the estimates of the cure reaction kinetic parameters for the TGDDM–DDS system where more than one reaction occurs are not valid if obtained from DSC analysis methods[22,23] based on the assumption that the heat evolved is proportional to the extent of reaction and/or using nth-order kinetic expressions governed by a single rate constant. The isothermal cure, however, may be analyzed by models using more than a single rate constant and order of reaction.[24-26]

The calorimetric analysis of the isothermal cure of the TGDDM–DDS mixture containing 35 phr of hardener has been performed at temperatures ranging from 140 K to 205 K. The scans showed a maximum in the reaction rate, characteristic of the autocatalytic reactions, while an increase in temperature increased the value of the reaction rate at the maximum and decreased the time required to reach the peak. The cumulative heat generated during the cure was obtained by integrating the reaction rate data while the corresponding advancement of the reaction was calculated by using the full lines reported in Figure 2. According to the previous discussion, the use of the cumulative heat as a measure of the advancement of the reaction, leads to an overestimate of the reaction rate of the system, as shown in Figure 3 for the test relative to 180 K.

Figure 4(a) reports the epoxy conversion kinetics at 140°C, 160°C, and 180°C. Ryan and Dutta[27] proposed a rapid procedure to estimate the kinetic parameters,
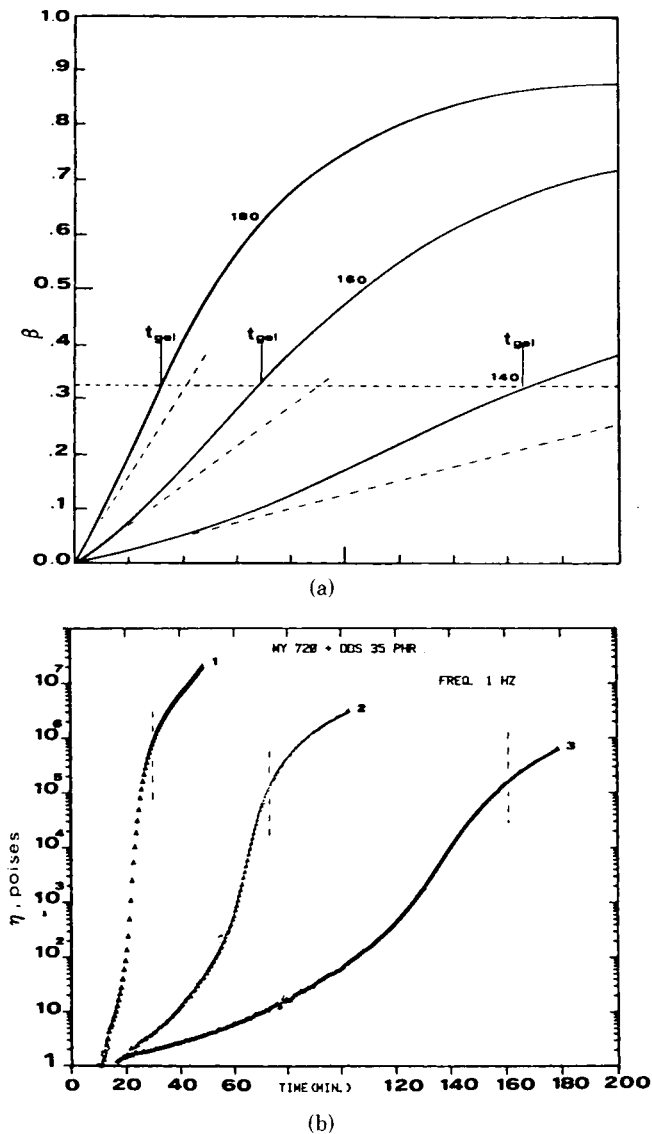
Fig. 4. (a) Autocatalytic behavior of the cure reaction at 140°C, 160°C, and 180°C of the TGDDM–DDS system. Dotted lines are the initial reaction rates. The theoretical epoxy conversion for gelation is indicated in the figure. (b) Complex viscosity profiles during the isothermal cure at (1) 180°C, (2) 160°C, and (3) 140°C of the TGDDM–DDS system. The marks refer to the minimum in tan δ.

k_i, describing the early stages of the cure. The values of the kinetic constants isothermally determined in the range of temperatures between 160°C and 205°C favorably compare in Table IV with those, k_d, determined for the primary amine addition using the kinetic method of analysis of the dynamic DSC thermogram. The good agreement between the two independent determinations of the rate data further indicates that the primary amine principally dominates the early stages of the cure reactions, probably up to the gelation.

TABLE IV
Comparison between the DSC Isothermal, k_i, and Dynamic, k_d, Estimates of the Kinetic Rate
Constants for Primary Amine Addition

T (°C)	$k_i \times 10^3$ (min^{-1})	$k_d \times 10^3$ (min^{-1})
140	0.9	1.4
160	3.3	3.6
165	7.0	4.5
180	7.9	8.5
205	18.0	23.0

Chemorheology

The rheological behavior is particularly sensitive to the molecular modification of a reacting melt. The time dependency of the viscosity of a TGDDM—DDS mixture containing 35 phr of hardener has been characterized in oscillatory and steady shear tests at 140°, 160°C, and 180°C.

Whereas the steady state shearing flow measurements characterize only the rheological properties of the material in the liquid state, the oscillatory shearing may be used to characterize the rheological properties of the material entering the gelation stages. Some authors[28] identified the gel point when the two components G' and G'' of the complex viscosity crossover (tan $\delta = 1$). Recently, Han et al.[29,30] indicated that in the isothermal cure of an insaturated polyesters the time needed to reach the maximum G'' was coincident with the gel time independently determined in a steady shearing flow measurement, while the tan δ was unity in shorter times when the system was still a viscous liquid.

The isothermal gel times for our system were estimated from the viscosity vs. time plots of steady state and oscillatory flow characterizations. Figure 5 reports the complex viscosity and tan δ relative to the isothermal cure at 160°C of the TGDDM–DDS mixture. At the beginning of the cure, the viscosity slowly increases with time up to a critical point, where tan δ is approximately unity while the system is liquid. In this stage, extensive branching and/or entanglement are probably occurring, leading to a very rapid increase of the viscosity which approaches very large values. The vertical portion of the curve in the constant shear rate tests and the inflection point of the G'' (corresponding in our case to a minimum in tan δ) have been used to estimate the gel times. This behavior is the same at the three temperatures investigated, although the values of the critical times and viscosities were obviously influenced by the test temperature. Figure 4(b) compares the dynamic viscosity profiles obtained at the three temperatures in the oscillatory shearing measurements with the calorimetrically determined conversion kinetics [Fig. 4(a)]: the time corresponding to the minimum in tan δ is marked on the figure.

In a previous work,[31] it has been indicated how the influence of the temperature on viscosity during the cure of the TGDDM–DDS system may be resolved into effects arising from kinetic and rheological aspects. A single viscosity vs. cure-time curve describing the rheological behavior at different temperatures was obtained by normalizing the experimental data to the characteristic critical viscosities and times. In fact, the overall mechanism of reaction, at least up to the gel point, was not significantly influenced by the test temperature, and therefore the gel times were derived from kinetic considerations.
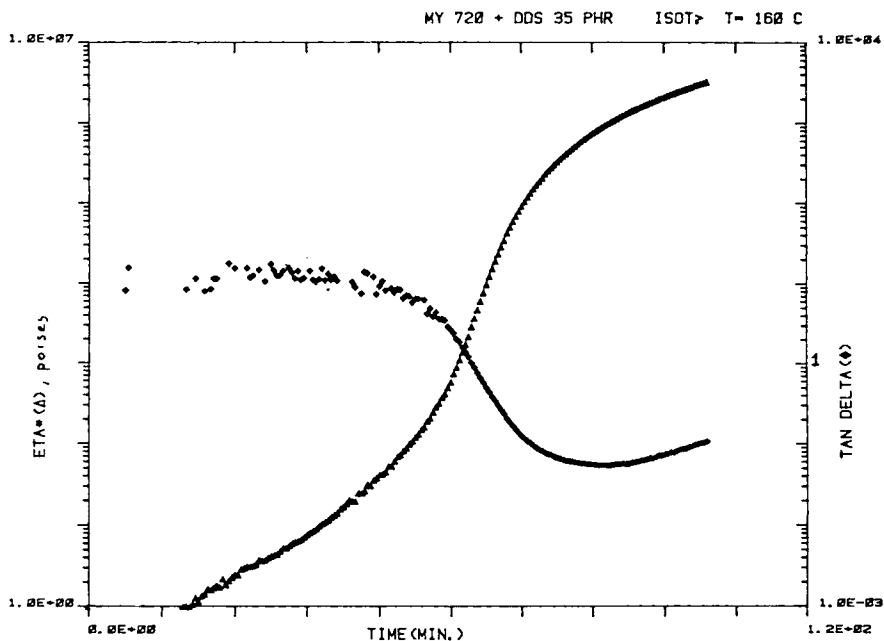
Fig. 5. Complex viscosity and tan δ vs. time during the isothermal cure at 160°C of the TGDDM–DDS system.

In addition to the rheological tests, a calorimetric determination of the gel time of the system during the cure is then possible using the gelation theory once the epoxy conversion kinetic is determined.

The basic relationships between the extent of reaction and molecular structure in nonlinear polymerization have been introduced by Flory in the case of equal reactivity of the functional groups and the hypothesis of the absence of intra-molecular reactions.[9]   Models were developed[9] in order to correlate the conversion of one of the reacting species to the corresponding average molecular characteristics, functionalities, and initial composition.

Gelation will occur at a constant value of the epoxy conversion, β_g, function of the mixture stoichiometric imbalance, $r = m_{e0}/m_{a0} = 4m_{T0}/2m_{D0}$, when the system develops an infinite network:

$$\beta_g = \sqrt{1/(1 - f)(1 - g)r} \tag{5}$$

where f and g are the functionalities of the TGDDM and DDS, in our case, respectively, 4 and 2.

In the previous discussion it has been pointed out that the early stages of the cure are mainly dominated by the addition of the primary amines which leads to the formation of a homogeneous structure described by the gelation theory. It is clear that this condition is no longer valid when limiting values of the epoxy conversion, corresponding to a change in the reaction mechanism, are reached. For instance, after the complete depletion of the primary amines when $\beta_a = 1$ and $\beta_e = 1/r$ (since $\beta_a = r\beta_e$[9]), epoxides will continue to react by homopolymerization, leading to a change of the reagent functionalities and hence of the gelation limits.   In the commercial TGDDM used in this work the limiting lower

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TABLE V
Isothermal Gel Times from Steady and Dynamic Viscosity Measurements and from the DSC
Determined Epoxy Conversions [$\beta(t)$ and $\Delta H/\Delta H_T$]

T (°C)	Gel times (min)			
	Steady	Dynamic	$\beta(t)$	$\Delta H/\Delta H_T$
140	>170	170	165	130
160	> 54	70	64	44
180	> 30	30	32	23

composition corresponding to a gelation process completely governed by the single primary amine addition is 33 phr of DDS, a lower value than the composition investigated (35 phr).

The calorimetric estimates of the gel times were obtained using the reaction kinetics reported in Figure 4(a). The time necessary to reach the theoretical value of the epoxy conversion at the gel point, $\beta_g = 0.315$ for a mixture containing 35 phr of DDS (stoichiometric imbalance $r = 0.32$) was considered the gel time. The gel times estimated from the epoxy conversions kinetics, $\beta(t)$, favorably compare in Table V with those obtained from both steady and dynamic viscosity measurements. Estimates of the gel times were also calculated in the simplified hypothesis that the conversion of the epoxy groups are proportional to the fractional heat evolved, $\Delta H(t)/\Delta H_T$, but, as already discussed in the previous section, the use of the cumulative heat fraction leads to an overestimate of the actual rate of reaction, and therefore to lower estimates of the gel times, as indeed observed in the fourth column of Table V.

The relationship between the glass transition temperature and the advancement of the cure reported in Figure 6 was determined from the residual heats of reaction of samples cured at 180°C for times ranging from 1 to 45 min. The glass transition temperatures of the system completely cured, uncured, and isothermally cured at 140°C, 165°C, 180°C, and 205°C up to vitrification are also reported in Figure 6. The plot shows a change in the slope at the value of the epoxy conversion corresponding to the exhaustion of the DDS primary amines, $\beta_a = 1$ and $\beta_e = 0.308$, which can be intuitively rationalized as a change in the reaction mechanism. The system investigated, however, presents almost the same theoretical value for the gelation, i.e., 0.315, which may also explain the observed behavior.

The shifts in the glass transition with conversion is made up of two nearly independent effects, namely, degree of crosslinking and copolymer effect. Crosslinking always increases T_g while the copolymerization can either increase or decrease T_g, depending upon the chemical nature of the hardener. The relation between crosslinking and conversion, which has been described by linear and logarithmic expressions,[32] should apply in the range of conversions above the gel point and should correlate the variations of the glass transition temperature of the uncrosslinked polymerized material near gelation to its final value when completely cured (approximately 60°C and 220°C in our case). Although the T_g vs. β curve is not expected to be described by a simple linear relation over the entire range of conversions; since in our case different types of chemical reactions are possible, it is not surprising that a linear relation may be observed before and after gelation, when only a single type of reaction may occur.
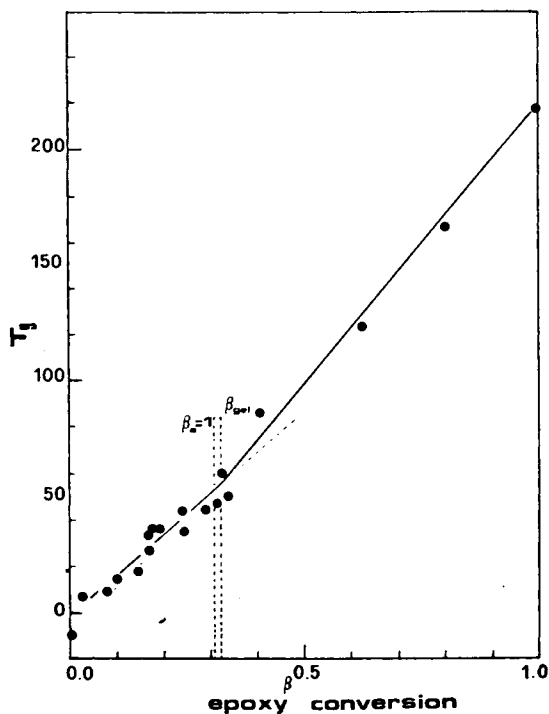
Fig. 6. Glass transition temperatures vs. epoxy conversions for the TGDDM–DDS system.

CONCLUSIONS

The cure behavior of a widely utilized epoxy system has been analyzed by calorimetric, IR spectroscopy, and rheological techniques in order to establish the actual mechanisms of molecular interactions leading the system to gelation and vitrification.

The evaluation of the kinetic parameters from isothermal and dynamic DSC analyses[22,23] of TGDDM–DDS mixtures of compositions ranging from 0 to 100 phr of hardener indicated that primary amine addition and etherification of the epoxides, which are characterized by different heat of reaction and activation energies, principally drive the cure reactions.

Gelation, which is principally governed by the addition of the primary amines to the epoxides of the TGDDM for DDS contents higher than 33 phr, may be theoretically described by models considering the nonlinear copolymerization of tetrafunctional (TGGDM) and bifunctional (DDS) monomers. The calorimetric determination of the gel times obtained by using the extent of reaction favorably compares to the rheological measurements only if the epoxy conversions are estimated considering that the primary amine are reacted first.

The variations of the glass transition temperature of the system during the cure was also considered. An empirical linear relationship adequately describes the change of the T_g up to gelation where a change in the behavior is observed. The commercial formulation of the TGDDM–DDS systems, which have been described to contain several types of impurities and higher oligomers,[7] may be

also theoretically analyzed if the relative functionalities, molecular weight, and concentrations are determined.[33]

The influence of the prepolymer composition on the kinetic and average molecular properties will be further investigated by means of dynamic-mechanical and calorimetric measurements, in order to predict the cure behavior above gelation up to the vitrification of the material.

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