Polymer Networks Derived from the Anhydride Curing of Tetraepoxides

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ABSTRACT: The cure of a technical-grade TGDDM ($N,N,N'N'$-tetraglycidyl-4,4′-diaminodiphenylmethane) with two different anhydride hardeners (hexahydrophthalic anhydride [HHPA] and tetrahydrophthalic anhydride [THPA]) is reported. The reaction was followed by differential scanning calorimetry (DSC), *in situ* infrared spectroscopy (FTIR), and viscosity measurements at constant temperature. Onset values of the glass transition temperatures of fully reacted networks under stoichiometric conditions were 206°C with HHPA and 184°C with THPA. THPA was more reactive than was HHPA but it was necessary to heat the mixture above its melting point to generate a homogeneous solution (HHPA remained in solution at room temperature). A first-order kinetics was observed after an induction period necessary to establish a pseudo-steady-state concentration of OH and COOH groups. A catalytic effect of the KBr used in the FTIR measurements was found, in agreement with other authors. Formulations containing an epoxy excess exhibited a higher reactivity due to the increase in the hydroxyl concentration introduced by the epoxy monomer. An increase in the heat of reaction expressed per anhydride equivalent was ascribed to the presence of the epoxy homopolymerization as a side reaction. It was estimated that about 38% of excess epoxy groups over the anhydride groups are homopolymerized in the case of HHPA and 17% in the case of THPA. Full conversions of both epoxy and anhydride groups are obtained for formulations with stoichiometric ratios, r (anhydride/epoxy groups) = 0.72 in the case of HHPA and 0.85 in the case of THPA. These values are in the range where the maximum glass transition temperature has been reported for epoxy–anhydride formulations. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 157–166, 1997

Key words: epoxies; epoxy–anhydride reaction; tetrafunctional epoxies

INTRODUCTION

Polyfunctional epoxy monomers are used in applications requiring a relatively high thermal resistance. Examples are the manufacture of high-performance epoxy/carbon prepregs for the aerospace industry and the production of insulating materials for electronic devices. A well-known type of these epoxy monomers is technical N,N,N',N'-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM).

The cure of TGDDM with aromatic diamines has been extensively studied because the resulting network constitutes the basis of the usual matrix of advanced composites. However, only a few reports deal with the anhydride curing of TGDDM. Raghava[1,2] studied the thermal and me-
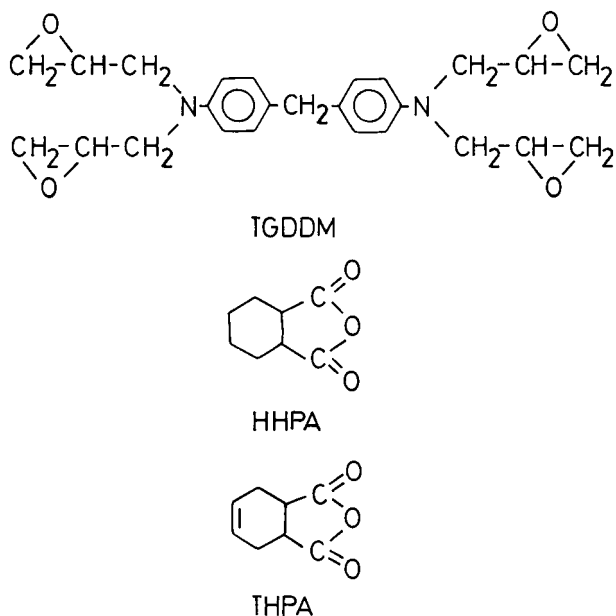
Figure 1 Chemical structures of the epoxy monomer and cyclic anhydrides.

chanical properties of TGDDM–aromatic anhydride matrices modified by polyethersulfones. In particular, the glass transition temperature (T_g) of the matrix was about 200°C, measured from the drop of the storage modulus. Therefore, the thermal resistance of TGDDM/anhydride polymer networks may be of the same order than the one of materials based on TGDDM–aromatic diamines.

The aim of this article was to present and discuss experimental results related to the cure of a technical-grade TGDDM with two different anhydrides, using variable stoichiometric ratios (r = anhydride groups/epoxy groups). The effect of r on the reaction scheme, heat of reaction, cure kinetics, and vitrification region is addressed.

EXPERIMENTAL

Materials

Chemical structures of the technical-grade epoxy and anhydride monomers are shown in Figure 1. The epoxy monomer was a commercial product (Ciba-Geigy MY-9512), consisting mainly of N,N,N',N'-tetraglycidyl-4,4′-diaminodiphenyl-methane (TGDDM). The mass per epoxy group was 120.1 g, as determined by titration with perchloric acid. The theoretical value for pure TGDDM is 105.5 g, meaning that an important

amount of impurities is present in the commercial product. These have been identified as chlorohydrins, glycols, dimers, trimers, and higher oligomers.[3,4] The presence of a broad band at 3500 cm^{-1} in the FTIR spectra showed that the commercial product contains a significant concentration of OH groups. This has a bearing on the cure kinetics, as will be shown later.

The epoxy group is bifunctional in the reaction with anhydrides. Therefore, the mass per epoxy equivalent of the commercial TGDDM is 60.05 g/ee. Before mixing with an anhydride, the epoxy monomer was degassed under vacuum for about 10 min at 50°C.

Two commercial anhydrides were used as hardeners (Fig. 1). Hexahydrophthalic anhydride (HHPA, Fluka) had a melting point of 30–32°C and a theoretical mass per anhydride equivalent equal to 77 g/equiv. *cis*-1,2,3,6-Tetrahydrophthalic anhydride (THPA, Fluka) had a melting point of 98–100°C and a theoretical mass per anhydride equivalent equal to 76 g/equiv.

The stoichiometric ratio was defined as

$$r = \text{anhydride equiv/epoxy equiv}$$
$$= \text{anhydride groups/epoxy groups}$$

Both stoichiometric samples ($r = 1$) and samples containing an epoxy excess over stoichiometry ($r < 1$) were analyzed. TGDDM–HHPA samples were prepared by mixing both components for about 10 min at 50°C. The solution remained homogeneous at room temperature, meaning that HHPA crystallization was inhibited upon cooling. From the constancy of the reaction heat measured by differential scanning calorimetry, it was verified that the reaction was not advanced during the mixing period in the 0–10 min range. TGDDM–THPA samples were mixed at 100°C for about 10 min. For samples with $r > 0.3$, a dispersion of THPA crystals was obtained upon cooling to room temperature.

Techniques

Differential scanning calorimetry (DSC) was performed using two different devices (DSC-7 Perkin-Elmer and Shimadzu TA 501), calibrated by standard procedures. Runs were carried out under a nitrogen atmosphere, using isothermal or dynamic conditions at different heating rates (5–30°C/min). In the standard use of both devices,
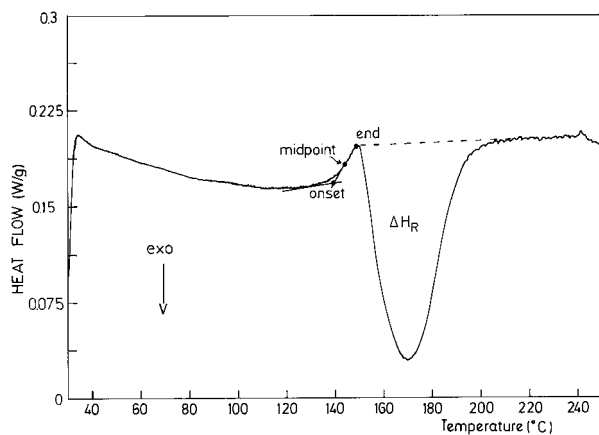
Figure 2 DSC scan at 10°C/min for a partially reacted TGDDM–HHPA sample, showing onset, midpoint, and end values of the glass transition temperature (T_g), followed by the residual exotherm.

exothermic peaks appeared below the base line in the Perkin-Elmer and above the base line in the Shimadzu. The *exo* direction is thus indicated in every DSC thermogram.

Three different definitions of the glass transition temperature (T_g) will be used: the onset, midpoint, and end values, as shown in Figure 2 for a partially reacted TGDDM–HHPA sample. The conversion attained after keeping the sample for a certain time at a constant temperature is calculated from the DSC scan as

$$x = 1 - \Delta H_R/\Delta H_T \qquad (1)$$

where ΔH_R is the residual reaction heat and ΔH_T is the reaction heat evolved by the unreacted sample in a dynamic DSC scan. The determination of conversions from isothermal DSC thermograms was not reliable due to the uncertainty in the base line definition.

Dynamic DSC scans were processed using Barrett's method,[5] assuming a n-th order reaction kinetics:

$$dx/dt = A \exp(-E/RT)(1 - x)^n \qquad (2)$$

Taking $x = \Delta H/\Delta H_T$ (ratio of partial and total reaction heats), the following relationship may be written:

$$\ln\{(dH/dt)/[\Delta H_T(1 - \Delta H/\Delta H_T)^n]\}$$
$$= \ln A - E/RT \qquad (3)$$

A plot of the left-hand side as a function of $1/T$

enables one to determine the reaction order, from the best linear plot, and the activation energy (E), from the slope.

Fourier-transformed infrared spectra (FTIR) were obtained using a Perkin-Elmer 16PC FTIR device. A drop of the epoxy–anhydride mixture was placed between two KBr pellets and the ensemble was located in a thermal chamber where cure was carried out at a constant temperature. A temperature calibration was previously performed by placing a thermocouple between the two KBr pellets. Spectra were obtained at different times, using 40 scans in the 400–4000 cm^{-1} range with a resolution of 4 cm^{-1}. The anhydride consumption was monitored by the decrease of the absorbance at 1858 cm^{-1}, measured with respect to the absorbance of the peak at 1610 cm^{-1} (phenyl ring), taken as a reference. It was not possible to follow the consumption of epoxy groups by this technique, due to the superposition of bands characteristic of the epoxy group with bands arising from the anhydride structure.

The viscosity of the reactive mixture was followed at a constant cure temperature, using a Rotovisco RV-20 (Haake), with a concentric-cylinders geometry and a strain rate of 1.035 s^{-1}. The system was preheated to the desired temperature before loading the sample (about 60 g). The gel time was taken at a viscosity level of 10^3 Pa-s.

RESULTS AND DISCUSSION

General Characteristics of the Cure of Both Systems

The reaction scheme for the cure of epoxides with anhydrides in the presence of OH groups is shown in Figure 3.[6–9] The polymerization is started by
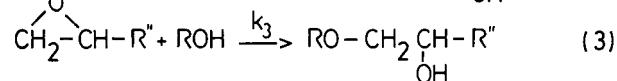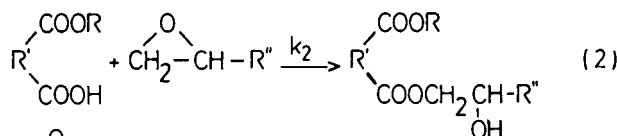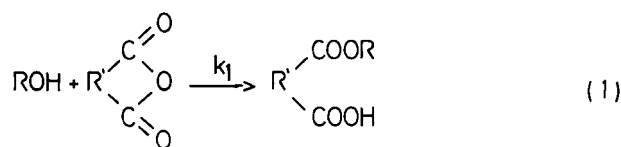

Figure 3 Reaction scheme for the cure of epoxides with anhydrides in the presence of OH groups.
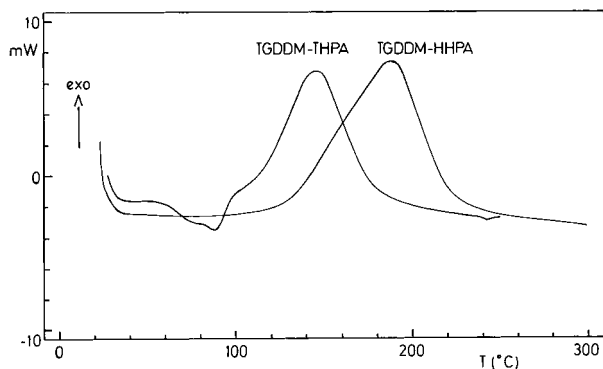
Figure 4 DSC scans at 10°C/min for both anhydride–epoxy systems in stoichiometric ratios ($r = 1$).

OH groups which are present in the technical-grade epoxy and proceeds by the formation of a monoester intermediate. The epoxy group reacts then with the carboxylic acid to regenerate an OH group. The reaction continues as an alternating copolymerization leading to a crosslinked polyester network. The third reaction in Figure 3 is the polyetherification of epoxides through reaction with OH groups. It is normally a side reaction which becomes significant in the presence of an epoxy excess over stoichiometry ($r < 1$).

Neglecting the epoxy consumption through the third reaction, the following kinetic scheme may be written:

$$-d[\text{Anh}]/dt = k_1[\text{Anh}][\text{OH}] \quad (4)$$

$$-d[\text{Ep}]/dt = k_2[\text{Ep}][\text{COOH}] \quad (5)$$

$$-d[\text{OH}]/dt = d[\text{COOH}]/dt$$
$$= k_1[\text{Anh}][\text{OH}] - k_2[\text{Ep}][\text{COOH}] \quad (6)$$

As $k_1 \gg k_2$,[10,11] a pseudo-steady-state may be reached where both [OH] and [COOH] become constant, i.e., $k_1[\text{Anh}][\text{OH}] = k_2[\text{Ep}][\text{COOH}]$. From this time on, the kinetics of anhydride and epoxide consumption follows a first-order kinetics.[8–12] Steinmann[13] proved that using a relatively high initial OH concentration led to a first-order kinetics from the beginning of the reaction.

The overall behavior of both epoxy–anhydride systems at stoichiometric ratios ($r = 1$) is now analyzed. From the DSC scans shown in Figure 4, it is observed that THPA reacts with TGDDM at a faster rate (i.e., lower-temperature range) than does HHPA. In the case of THPA, melting of the anhydride precedes the reaction peak.

Values of the peak temperatures, reaction

heats, and glass transition temperatures of the cured products are shown in Table I. Reaction heats are in the range of values reported for other epoxy–anhydride systems.[14] Glass transition temperatures are very high, particularly for the case of HHPA. This confirms the possibility of using the anhydride cure of TGDDM to obtain high-T_g polymer networks. Dynamic mechanical analysis of a stoichiometric TGDDM–THPA system showed a maximum in tan δ at 228°C, operating at 10 Hz and a heating rate of 3°C/min.[15] As expected, T_g values arising from the maxima in damping peaks are higher than are values obtained from the DSC scans. However, part of the difference may be due to the prolonged cure cycle employed for the samples characterized by dynamic mechanical analysis, i.e., 2 h at 120°C, 2 h at 170°C, and 2 h at 200°C.[15] Some particular characteristics of the cure of both systems are analyzed separately in what follows.

TGDDM–HHPA System

The polymerization of a stoichiometric system ($r = 1$) was followed *in situ* by FTIR at three different temperatures: 80, 100, and 120°C. The anhydride conversion was defined as

$$x_{\text{anh}} = 1$$
$$- \{[A_{1858}(t)/A_{1610}(t)]/[A_{1858}(0)/A_{1610}(0)]\} \quad (7)$$

Figure 5 shows a first-order kinetic regression at the three temperatures. The first-order kinetic law gives a good correlation of experimental results from a conversion close to 0.1 (induction period) to a maximum conversion that depends on temperature: $x_{\text{max}} = 0.55$, 0.70, and 0.94 for $T = 80$, 100, and 120°C, respectively. For $x > x_{\text{max}}$, there is a significant drop in the experimental re-

Table I   Characteristics of the Cure of Both Epoxy–Anhydride Systems at Stoichiometric Ratios ($r = 1$): Reaction Heat ($-\Delta H$), Temperature at the Maximum of the Exothermic Peak in a Scan at 10°C/min (T_{peak}), and Glass Transition Temperatures of the Cured Products

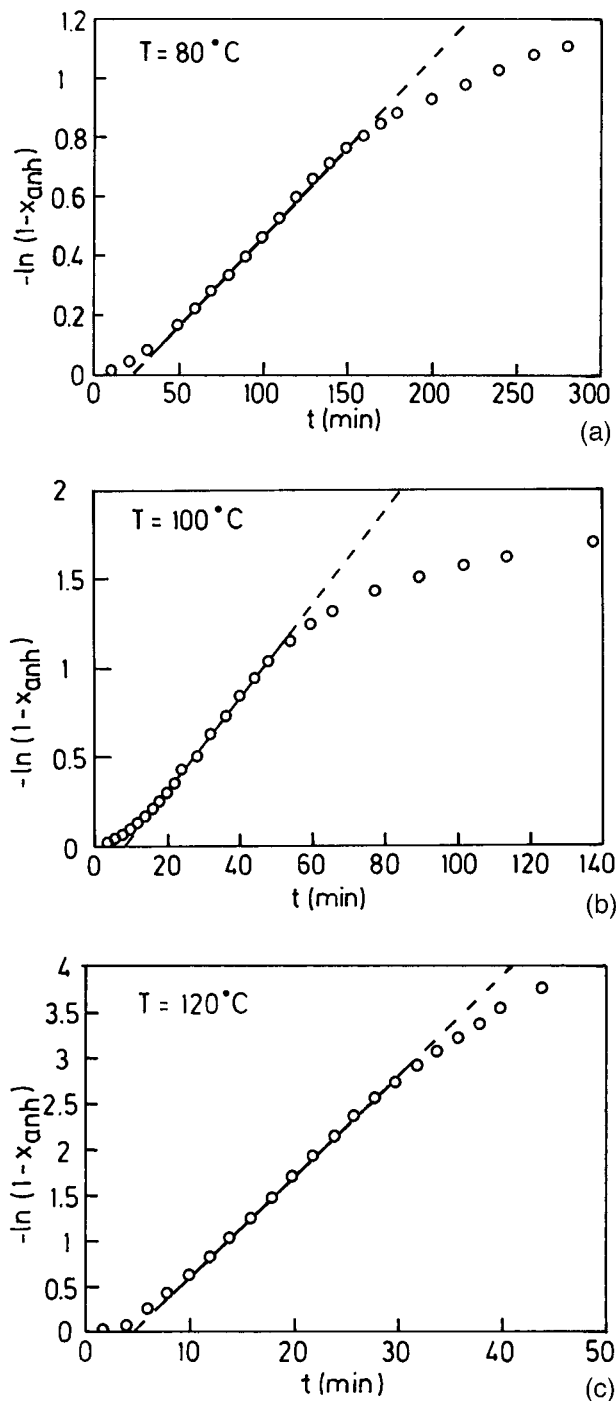| System	$(-\Delta H)$ (kJ/ee)	T_{peak} (°C)	$T_{g,\text{onset}}$ (°C)
TGDDM–HHPA	52.5	187.5	206
TGDDM–THPA	53	144.5	184

Figure 5 First-order kinetic regression of the anhydride conversion in a TGDDM–HHPA system ($r = 1$), followed by FTIR, as a function of time: (a) $T = 80°C$; (b) $T = 100°C$; (c) $T = 120°C$.

mined as in Figure 2. Results are shown in Figure 6, where the vitrification region composed between $T_{g,onset}$ and $T_{g,end}$ was plotted in a conversion–temperature–transformation diagram.[16,17] Circles indicate the value of x_{max} for each isothermal cure temperature. Clearly, vitrification is the origin of the significant drop in the polymerization rate at $x > x_{max}$. For $T = 80$ and $100°C$, x_{max} is located at the beginning of the vitrification region, as expected. However, for $T = 120°C$, the effect becomes evident only when the sample was fully vitrified.

An Arrhenius plot of the first-order reaction rate constants determined by FTIR is shown in Figure 7. The activation energy is $E = 82$ kJ/mol.

Dynamic DSC runs carried out at different heating rates (from 5 to 30°C/min) were processed using Barrett's method [eq. (3)], assuming a first-order kinetic behavior. Results are also shown in Figure 7 for a conversion range composed between 0.1 and 0.9. A first-order kinetic behavior is again observed but the rate constant is considerably lower than the one measured with FTIR. The origin of this significant difference is the catalytic effect of KBr, as reported by several authors.[10,18–20] The activation energy arising from the DSC runs is $E = 67.5$ kJ/mol, i.e., in the range reported by other authors for the uncatalyzed epoxy–anhydride reaction.[13] However, this value reflects an average behavior in a broad temperature range. In the low-temperature range, i.e., the range cov-
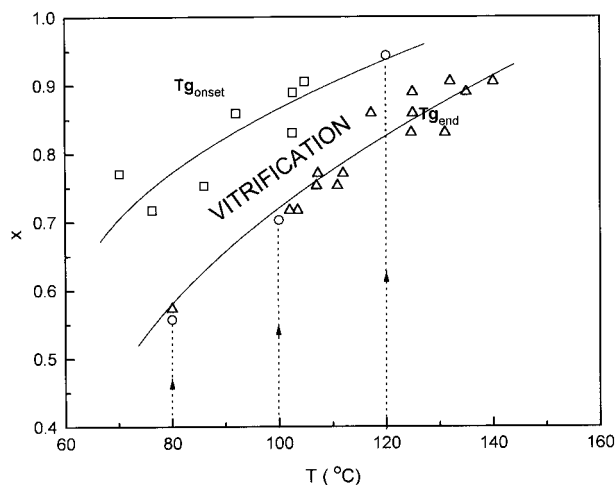

Figure 6 Vitrification region of a TGDDM–HHPA system ($r = 1$), plotted in a conversion–temperature–transformation diagram; circles indicate the maximum conversion, at each isothermal cure temperature, for which a first-order kinetic regression was observed.
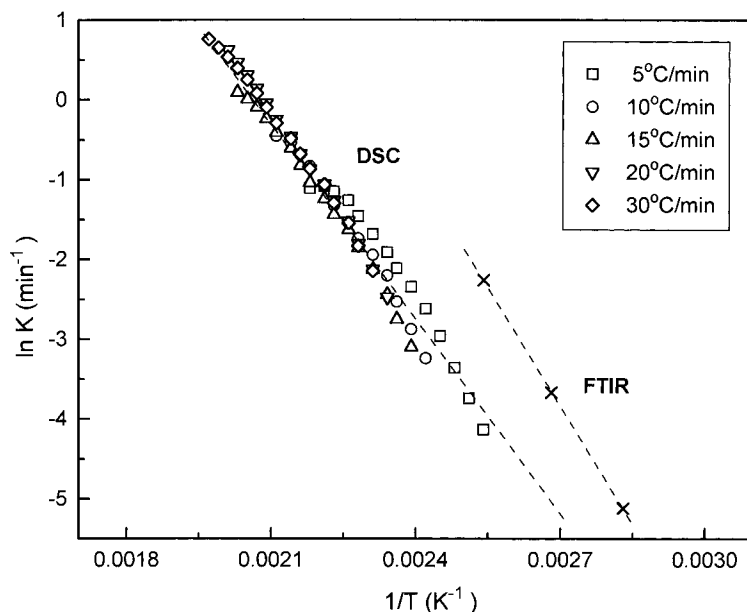
action rate. This may be explained by diffusional restrictions associated to vitrification. To prove this, conversions and glass transition temperatures of partially reacted samples were deter-

Figure 7 First-order reaction rate constants for a TGDDM–HHPA system ($r = 1$) determined from DSC (dynamic runs carried out at different heating rates from 5–30°C/min, processed using Barrett's method[5]) and from FTIR (isothermal runs).

ered by FTIR runs, the value of the activation energy is significantly higher.

The effect of using an epoxy excess ($r < 1$) in the TGDDM–HHPA formulations is now addressed. Figure 8 shows the reaction heat (expressed per anhydride equivalent), as a function of the stoichiometric ratio. Increasing the amount of epoxy in the formulation (i.e., decreasing r) leads to an increase in the reaction heat, up to a
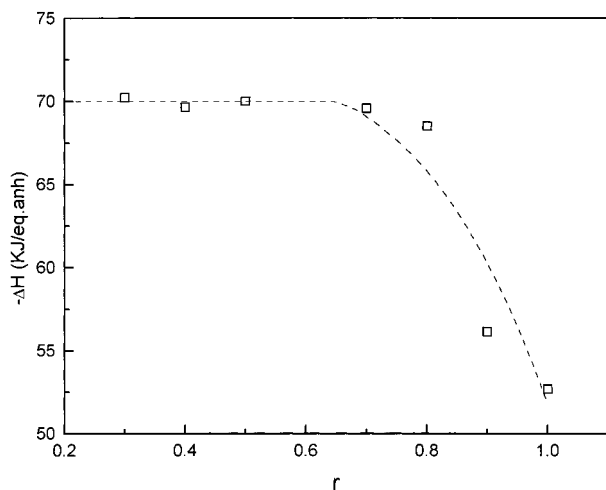

Figure 8 Reaction heat for a TGDDM–HHPA system as a function of the stoichiometric ratio, r = anhydride groups/epoxy groups.

maximum value equal to ($-\Delta H$) = 70 kJ/equiv. This is a clear indication that the epoxy homopolymerization (third reaction in Fig. 3) is taking place in formulations containing an epoxy excess. However, this side reaction does not go to completion when r is decreased below 0.7 (the reaction heat expressed per equivalent of the reactant in the defect remains constant, meaning that the epoxy excess below $r = 0.7$ does not react). This may explain the fact that the maximum T_g for epoxy–anhydride formulations is usually reported for $r < 1$.[14,15]

The maximum r value at which a reaction heat equal to ($-\Delta H$) = 70 kJ/equiv is obtained may be associated to a formulation where both the epoxy and anhydride groups have reacted to completion. As the reaction heat evolved in the epoxy homopolymerization is 92 kJ/epoxy group, as reported by Klute and Viehmann,[21] the excess of epoxy groups per anhydride equivalent necessary to increase the reaction heat from 52.5 to 70 kJ/equiv anhydride is (70 − 52.5)/92 = 0.19. As there are 2 equiv per epoxy group, the predicted r value at which the maximum reaction heat is obtained at full completion is $r = 1/1.38 = 0.72$, in rough agreement with the experimental result.

More evidence of the presence of the epoxy homopolymerization as a side reaction in formulations containing an epoxy excess is given in Figure
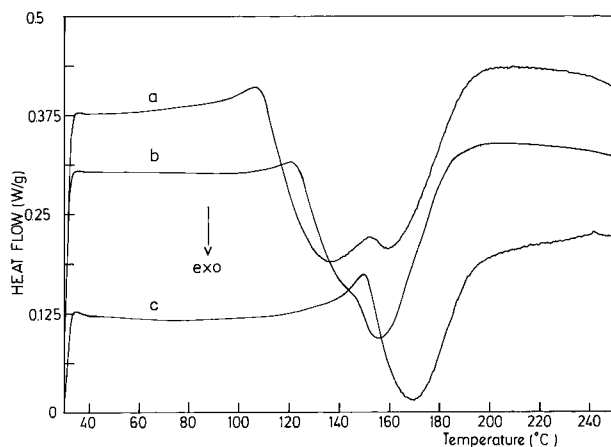
Figure 9 Residual reaction heat for a TGDDM–HHPA system ($r = 0.5$) previously reacted at a constant temperature up to the return to the base line: (a) $T = 80°C$; (b) $T = 100°C$; (c) $T = 120°C$.

Figure 10 DSC scans for TGDDM–HHPA systems containing different stoichiometric ratios: (a) $r = 0.3$; (b) $r = 0.7$.

9. This represents residual reaction heats obtained in dynamic DSC scans after isothermal cures at different temperatures (TGDDM–HHPA formulation with $r = 0.5$). In the DSC scan following the cure at 80°C, two exothermic peaks are present. The peak at lower temperatures is assigned to the continuation of the epoxy–anhydride reaction, interrupted by vitrification in the previous isothermal run. The peak at higher temperatures is assigned to the homopolymerization of part of the epoxy excess. When the isothermal cure is carried out at 100°C, the epoxy–anhydride reaction is advanced to a higher extent and only a shoulder is observed in the residual reaction heat. When the polymerization is performed at 120°C, the epoxy–anhydride reaction proceeds to completion and only the peak assigned to the epoxy homopolymerization is present in the subsequent DSC scan.

Another effect of using an epoxy excess over stoichiometry is the significant increase in the reaction rate, as shown by Figure 10. This may be explained by the increase in the initial concentration of OH groups present in the commercial epoxy monomer. This, in turn, increases the pseudo-steady-state concentration of OH and COOH groups and the apparent first-order rate constant.

To separate the epoxy–anhydride reaction from the epoxy homopolymerization, the cure at low temperatures must be analyzed. Times to gel were measured in the 60–100°C range for formulations containing different stoichiometric ratios. Results are shown in Figure 11 as ln t_{gel} vs. $1/T$. The slope of such a plot is proportional to the
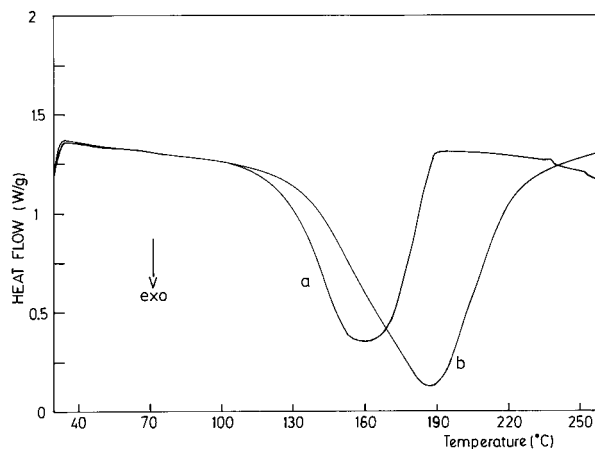
activation energy of the reaction provided that the gel conversion does not change with temperature.[16] Table II shows the activation energies found for the different stoichiometric ratios. They increase from 60 to 70 kJ/mol when increasing r from 0.3 to 0.7, i.e., formulations curing at higher rates exhibit lower values of the activation energy.

TGDDM–THPA System

For this particular system, the analysis will be restricted to the influence of the epoxy excess on some characteristics of the cure. Figure 12 shows
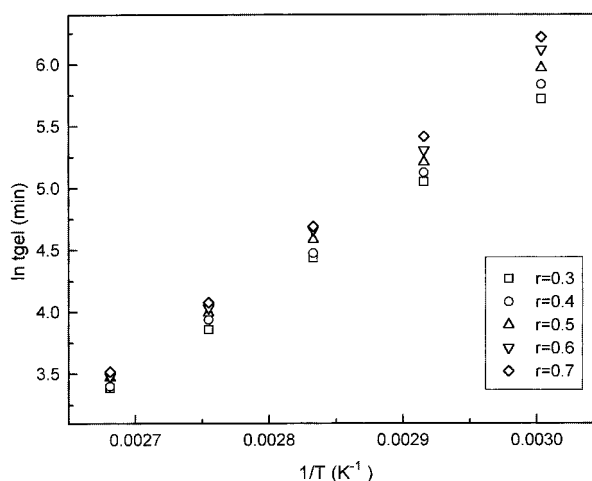

Figure 11 Times to gel as a function of the inverse of temperature for TGDDM–HHPA systems containing different stoichiometric ratios; $r = 0.3–0.7$ anhydride groups/epoxy groups.

Table II Activation Energies for the Epoxy–Anhydride Reaction in TGDDM–HHPA Systems Containing Different Stoichiometric Ratios (r = Anhydride Groups/Epoxy Groups)

E (kJ/mol)	r
60.6	0.3
62.7	0.4
64.2	0.5
67.7	0.6
69.7	0.7

the reaction heat expressed per anhydride equivalent, as a function of the stoichiometric ratio. Now, the reaction heat increases from 53 kJ/equiv (Table I) to about 61 kJ/equiv, due to the homopolymerization of part of the epoxy excess. Thus, this side reaction occurs to a lesser extent when replacing HHPA by THPA. The fraction of epoxy groups involved in the homopolymerization reaction is $(61 - 53)/92 = 0.087$ epoxy groups/equiv anhydride. This gives a stoichiometric ratio, $r = 1/1.17 = 0.85$, where full conversion of both epoxy and anhydride groups may be obtained. As a reference, the maximum glass transition temperature for a TGDDM–THPA system is obtained for formulations with r values composed between 0.8 and 0.9.[15]

The cure kinetics for samples containing different stoichiometric ratios was followed by measuring the residual reaction heat in DSC scans after a certain time at 80°C. Results are shown in Fig-
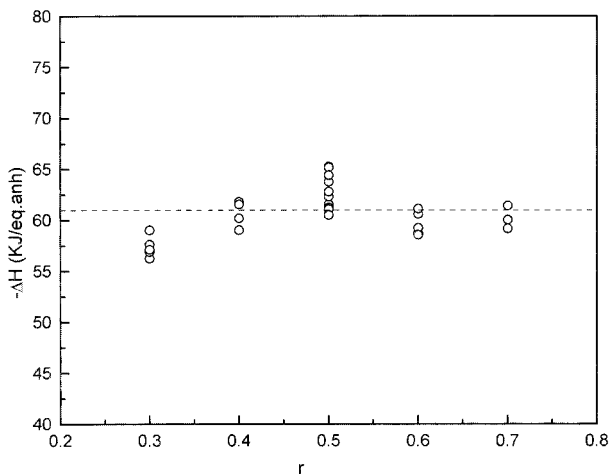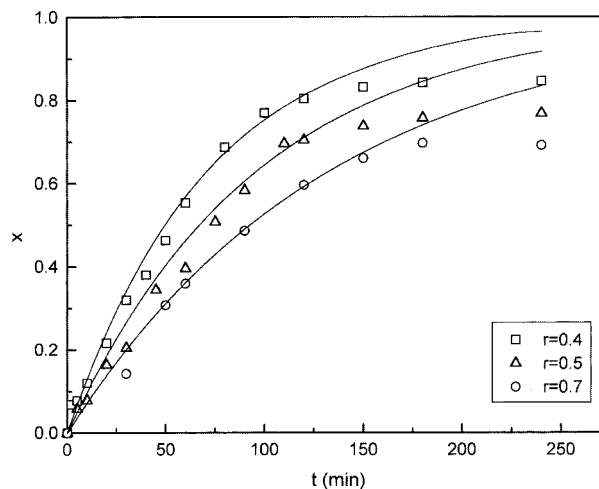

Figure 13 Conversion vs. time for TGDDM–THPA systems with different stoichiometric ratios (r = anhydride groups/epoxy groups), polymerized at 80°C. (Conversion was defined from the residual reaction heat in the DSC.)

ure 13 for three selected formulations. Kinetic curves could be fitted by a first-order kinetics (full curves), up to a conversion where diffusional restrictions associated to vitrification become significant. The higher the epoxy excess (i.e., the lower the r value), the higher are both the specific rate constant and the maximum attained conversion. While the former effect is associated to the increase in the OH concentration introduced by the epoxy monomer, the latter is due to the decrease in the glass transition temperature with a decrease of r in the explored range (the conversion must be increased to attain vitrification when r is decreased).

To follow the viscosity increase at low temperatures (to avoid exothermic effects in the course of the reaction), it was necessary to use homogeneous samples at room temperature. Therefore, only formulations with $r = 0.3$ could be used for this purpose. Figure 14 shows gelation times as a function of the inverse of temperature, giving an activation energy of 67.9 kJ/mol, i.e., in the range of values reported for the TGDDM–HHPA system.

The comparison of cures performed under isothermal and dynamic conditions is shown in Figure 15. Full circles correspond to isothermal cures with specific rate constants determined by residual reaction heats, as in Figure 13. The rest of the experimental points resulted from the application of Barrett's method to dynamic DSC runs carried out at different heating rates (from 5 to 30°C/min). The full line joining dynamic values

Figure 12 Reaction heat for a TGDDM–THPA system as a function of the stoichiometric ratio, r = anhydride groups/epoxy groups.

in the moderate- to high-conversion range (high-temperature range) with isothermal values leads to an activation energy of 67.7 kJ/mol. Specific rate constants arising from dynamic runs in the low-conversion range (low-temperature range) lie below the full line. A possible explanation is that, under dynamic conditions, the pseudo-steady state is reached at higher conversions than under isothermal conditions. A complete kinetic modeling would require the analysis of the initial unsteady state as well. It must be pointed out that this effect can also be present in dynamic results reported in Figure 7. However, the difference between DSC and FTIR results is much more significant than this effect, i.e., FTIR results cannot be extrapolated to the high-temperature range of the DSC curve.

CONCLUSIONS

A technical-grade TGDDM was cured with commercial anhydrides to give high-T_g polymer networks, i.e., T_g, onset = 206°C with HHPA and 184°C with THPA, both under stoichiometric conditions. THPA was more reactive than was HHPA but it was necessary to heat above its melting point in the epoxy monomer to obtain a homogeneous solution (HHPA remained in solution at room temperature).

The epoxy–anhydride alternating copolymerization followed a first-order kinetics after an induction period necessary to establish a steady con-
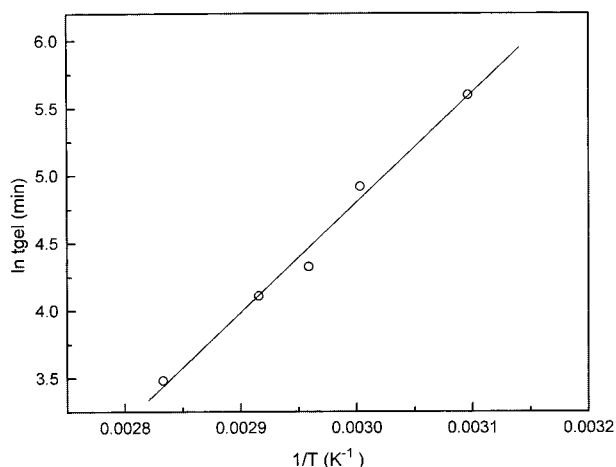

Figure 14 Times to gel as a function of the inverse of temperature for a TGDDM–THPA system with an epoxy excess ($r = 0.3$ anhydride groups/epoxy groups).
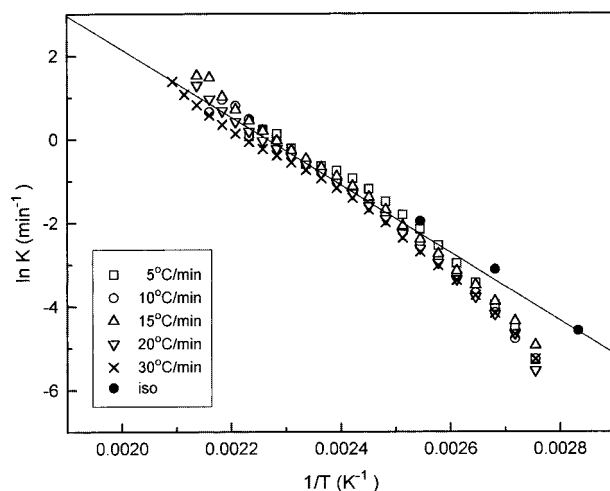

Figure 15 First-order reaction rate constants for a TGDDM–THPA system ($r = 0.5$) determined from DSC (dynamic runs carried out at different heating rates, from 5 to 30°C/min, processed using Barrett's method[5]) and from runs at constant temperature as in Figure 13 (full circles).

centration of OH and COOH groups. A significant drop of the specific rate constant was observed when the system evolved through the vitrification region. When the reaction was performed *in situ* in the FTIR device, the specific rate constant was significantly higher than the one arising from DSC measurements. The same effect was found by other authors[10,18–20] and ascribed to the catalytic effect of KBr.

Formulations containing an epoxy excess ($r < 1$) exhibited a higher reactivity due to the increase in the hydroxyl concentration introduced by the epoxy monomer. An increase in the heat of reaction expressed per anhydride equivalent was ascribed to the presence of the epoxy homopolymerization as a side reaction. It was estimated that about 38% of excess epoxy equivalents over the anhydride equivalents are homopolymerized in the case of HHPA and 17% in the case of THPA. Full conversions of both epoxy and anhydride groups are obtained for formulations with stoichiometric ratios, $r = 0.72$ in the case of HHPA and 0.85 in the case of THPA. These values are in the range where the maximum T_g is obtained for epoxy–anhydride formulations.[14,15]

Activation energies are composed in the range 60–70 kJ/mol for both systems and different stoichiometric ratios. Results obtained from dynamic DSC runs must be considered with caution as the induction period seems to extend to higher conversions than in the case of isothermal runs. A com-

plete kinetic modeling would require the analysis of the initial unsteady state.

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