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Curing kinetics of a new benzoxazine-based phenolic resin by differential scanning calorimetry

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The curing reactions of benzoxazine precursors based on bisphenol A and aniline are studied to determine the feasibility of processing them into final phenolic parts. Benzoxazine precursors are able to overcome most of the shortcomings of traditional phenolic resins, and retain the excellent heat resistance and fire and smoke properties of these resins. This new type of phenolic material cures via a ring-opening mechanism that does not produce any condensation or other reaction by-products. Phenol is not used as raw material, which reduces considerably the environmental and health risks. According to differential scanning calorimetry (d.s.c.), the curing of benzoxazine precursors is an autocatalysed reaction until vitrification is reached, and diffusion begins to control the curing process afterwards. Isothermal and non-isothermal d.s.c. tests are performed. Calculations of the activation energy and the overall reaction order are made by various procedures. The vitrification times and the kinetic rate constants are also calculated.

(Keywords: polybenzoxazine; curing; kinetics)

INTRODUCTION

In recent years, processing of thermosetting resins has received strong attention from the automotive, aerospace and construction industries because of the great potential of these materials. The processing of these materials is complicated because of the involvement of chemical reactions. In addition, reinforcements, fillers, pigments and other additives are commonly added. Thus, the understanding of curing is fundamental in the analysis, control and design of any processing operation.

This kinetic study will deal with a new type of phenolic resin obtained via ring-opening polymerization. These new materials are supposed to solve the problems related to traditional phenolic resins, such as brittleness, release of water and ammonia during the condensation curing reactions, toxicity of raw materials (especially phenol), high viscosity of the precursors, strong acid compounds as catalysts, and a narrow processability window.

These novel phenolic resins are based on benzoxazine structures, which were first synthesized by Holly and Cope[1]. These structures were not recognized as phenolic resin precursors until Schreiber[2] reported in 1973 that a hard and brittle phenolic material was formed from benzoxazine precursors. No further details about structures and properties were included.

More recently, Riess *et al.*[3] studied the synthesis and reactions of monofunctional heterocyclic compounds of this kind. They found that only oligomeric phenolic structures could be obtained because the thermodissociation of the monomer was always competing with the chain propagation. Polyfunctional benzoxazine monomers have been used as modifiers for coating and encapsulation[4].

Ning and Ishida[5] synthesized bifunctional benzoxazine precursors to overcome the low degree of cure of the compounds prepared by Riess *et al.*[3]. Samples with high mechanical integrity were obtained. The synthetic method consists of a few simple steps and can easily provide different phenolic structures with a wide design flexibility.

The curing mechanism of benzoxazine resins is poorly understood. Therefore, a phenomenological approach will be taken in this study in order to understand the reaction kinetics and as a way of achieving successful processing.

EXPERIMENTAL

A benzoxazine precursor based on bisphenol A, formaldehyde, and aniline, was synthesized. All chemicals were used as received. The bisphenol A was supplied by the Shell Chemical Co. The formaldehyde (37% by weight in water), aniline and dioxane were purchased from Aldrich Chemical Co.

The synthesis of the precursor was done using a procedure explained by Ning and Ishida[5]. The reaction follows the general scheme outlined in *Scheme 1*.

The precursor obtained is a mixture of the monomer shown in *Scheme 1*, dimers and other oligomers formed in subsequent reactions during the synthesis. Thus, to

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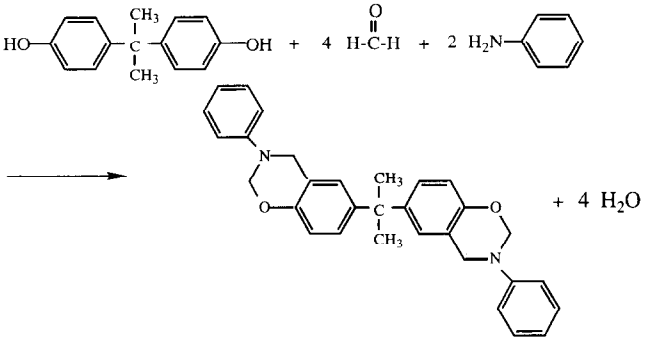

Scheme 1

perform controlled kinetic experiments, the monomeric fraction was separated from the precursor mixture. To purify the monomer, the reaction product was redissolved in ethyl ether, the solids were filtered out, and the solution was washed three times with a 3 N NaOH aqueous solution in a separatory funnel, and three times with a 2 N HCl aqueous solution; water was used for the final wash. The ether phase was dried over sodium sulfate and the solvent evaporated in a rotary evaporator. A very fine white powder was obtained. Caution was taken to store the synthesis and purification products in a dry and cold environment (ca. −4°C).

^{1}H n.m.r. spectra were taken to check the effectiveness of the separation process described above. The instrument used was a Varian XL-200, operating at 200 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane (TMS) was used as an internal standard.

A Perkin-Elmer TAS-7 differential scanning calorimeter was used to study the curing of the benzoxazine monomer. Indium was used for temperature calibration and nitrogen as the flushing gas. Temperature and power calibration were optimized for the range of 30–300°C. Standard hermetic d.s.c. pans (maximum pressure 3 atm) were used. Sample weights were between 2 and 5 mg, since small samples are necessary to ensure isothermal conditions. Isothermal and non-isothermal experiments were conducted.

For the isothermal experiments, the samples were placed in the cell at 30°C and the temperature was raised to 100°C and kept for 90 s. After thermal stability was reached, the temperature was raised again up to the selected value for each isothermal experiment. At the experimental temperature, the instrument achieved stability after 80 to 100 s. This was determined by the time that the heat readings had variations less than ±0.002 mW. The data acquisition was then initiated. After the exothermic peak when the d.s.c. curve reached the baseline level again, the sample was cooled rapidly (80°C min^{-1}) to 30°C. Further heating of the sample was done at 10°C min^{-1}, from 30 to 300°C, to determine the residual heat of reaction.

Non-isothermal experiments on uncured samples were carried out at 5, 10 and 20°C min^{-1}, from 30°C up to 300°C. A steady baseline was established before each run by using two empty sample pans with the same heating rates. As with the isothermal experiments, the reaction is considered complete when the curves levelled off to the baseline and no more drastic changes in heat are observed. Experiments were always performed below 300°C to prevent any possible degradation reactions inside the chamber. After this first heating run, the sample was cooled at 80°C min^{-1} to 30°C and a second heating was conducted at 10°C min^{-1} to check for complete cure and the glass transition temperature of the cured resin. Other non-isothermal experiments on the purified monomer were performed at different heating rates in order to determine the activation energy, E_a.

The areas under the curves were quantified by drawing a straight line extension of both sides of each exotherm. These calculations and the normalization procedures were performed by the d.s.c. software. Sample weights were taken after each isothermal and non-isothermal d.s.c. test. The weight losses, if there were any, were negligible.

RESULTS AND DISCUSSION

The ^{1}H n.m.r. spectra of the purified monomer fraction and the as-synthesized precursor are depicted in *Figure 1*. The comparison of both spectra demonstrates that separation was accomplished. The important peak assignments are indicated.

As expected, the higher the cure temperature of the isothermal d.s.c. tests, the faster the exotherm maximum and onset of curing occur (*Figure 2*). The behaviour of both parameters can be fitted to an exponential decay. From the processing point of view, it is worth noting that above 200°C the onset of the reaction occurs almost instantaneously.

Figure 3 shows the variation of the heat evolved (ΔH_{iso}) during isothermal experiments as a function of temperature. The residual heat of reaction from the subsequent scanning experiments is also drawn along with the total heat of curing, which is the sum of the two values mentioned before[6].

The heat of reaction from the isothermal experiments increases with the cure temperature since, at higher temperatures, the continuation of the curing is more favoured by reducing viscosity and delaying the vitrification process. However, at higher temperatures, the measured heat of reaction is expected to be less than the true value since the unrecorded portion of the reaction that occurs during heating of the sample and establishment of instrumental equilibrium becomes more significant. At low temperatures, the reaction tends to be very slow and it could fall within the detectability limit of the calorimeter. This also can happen at advanced stages of cure for any temperature, when the reaction becomes highly diffusion-controlled and the rate is very low.

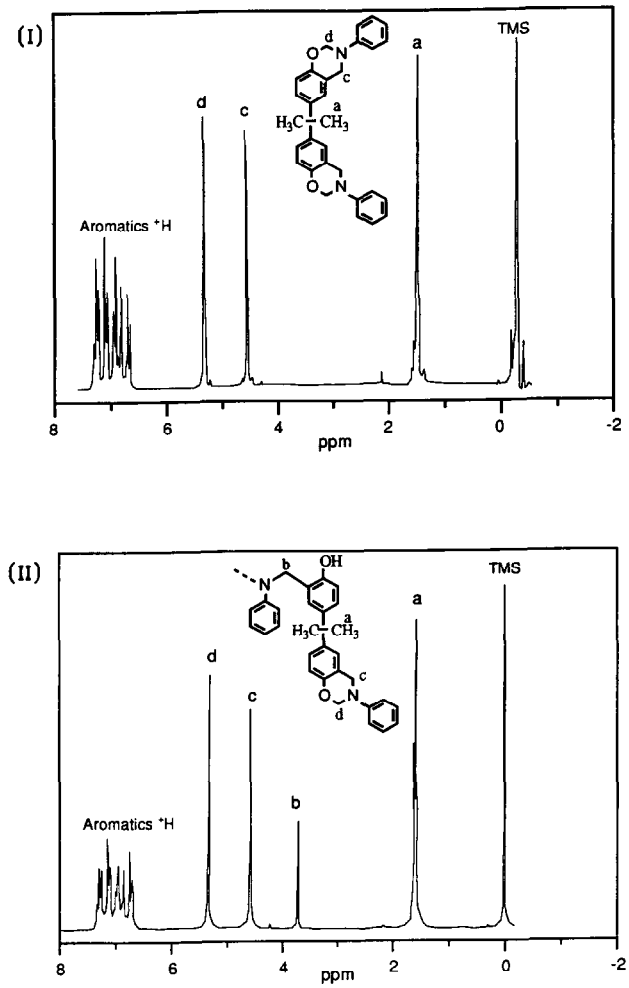

Figure 1 Proton n.m.r. spectra of the monomer fraction (I) and the as-synthesized precursor (II)

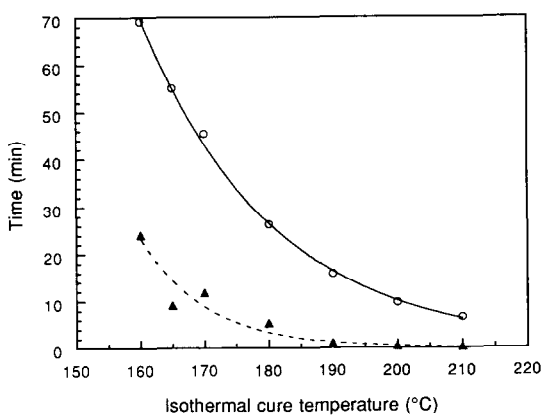

Figure 2 Peak (○) and onset (▲) of the curing exotherm for monomer at different isothermal cure temperatures

There can also be unrecorded heat during the cooling cycle between the isothermal heating and the subsequent non-isothermal test.

Obviously, the residual heat from the scanning experiments made immediately after the isothermal tests (ΔH_{resid}) follows the opposite tendency to ΔH_{iso} (ref. 6). At 210°C, no exotherm was observed, indicating that the reaction was completed during the isothermal cure or the heat generation rate fell below the detection

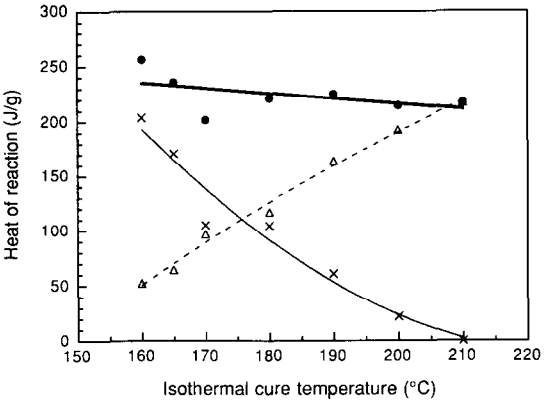

Figure 3 Heat generated by the curing reaction at different isothermal cure temperatures: heat from the isothermal reaction (△); residual heat of reaction (×); and total heat of reaction (●)

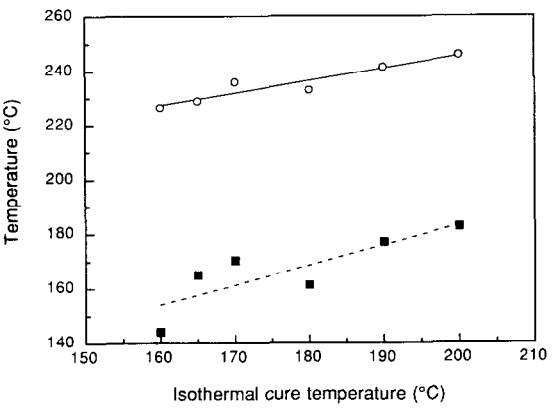

Figure 4 Peak (○) and onset (■) of the residual curing exotherm from the scanning experiments on the isothermally cured monomer samples as a function of the cure temperature

limit of the calorimeter. In general, when the heat of reaction is completely evolved at a certain isothermal cure temperature, the curing temperature is close to or above the glass transition of the fully cured sample ($T_{g\infty}$), implying that vitrification did not occur.

The total heat of reaction (ΔH_{RXN}) can be obtained by adding the ΔH_{resid} values from the non-isothermal tests to the isothermal heat values. Theoretically, ΔH_{RXN} is the total heat liberated for a material when it is taken from an uncured state to a complete cure; thus, it is expected to be constant for each thermoset. According to *Figure 3*, those values are quite constant within the range of temperatures studied.

Figure 4 shows the values of the exothermic peak and the onset of the residual reaction as a function of the cure temperature. Both temperature values increase with the cure temperature. The onset of the exotherm is approximately the temperature at which the previous isothermal cure was performed. Several authors[7-9] consider this onset temperature as the glass transition temperature of the isothermally (partially) cured sample. Ideally, a curing process at a temperature below $T_{g\infty}$ should lead to a material with a T_g that is equal to the isothermal cure temperature.

The experimental procedure used to perform isothermal experiments can influence the data obtained. In one

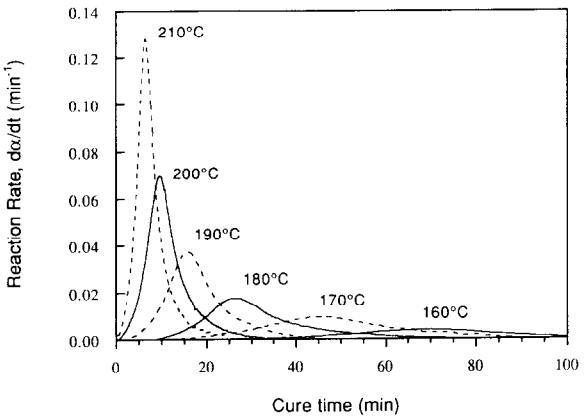

Figure 5 Reaction rate as a function of time for the benzoxazine monomer at different cure temperatures

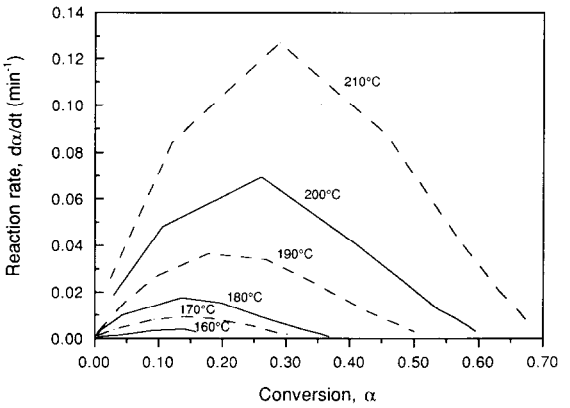

Figure 7 Reaction rate as a function of conversion for the benzoxazine monomer at different cure temperatures

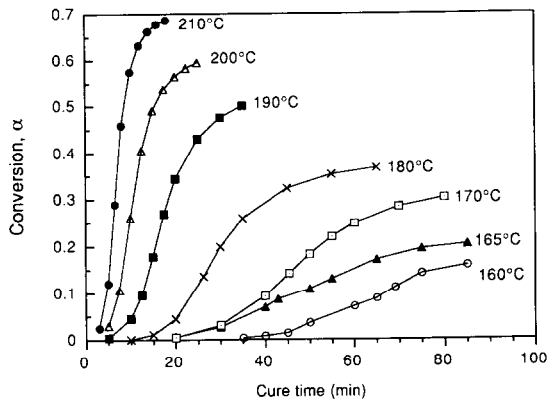

Figure 6 Conversion as a function of cure time for the benzoxazine monomer at different isothermal cure temperatures

method, the calorimeter could be preheated to a preset reaction temperature before placing the sample in the chamber; in another case, the sample is placed in the calorimeter at a temperature at which no reaction occurs, the temperature is rapidly increased to the desired reaction temperature, and the test starts when a certain degree of equilibrium is reached. The latter method was used since the placement of the sample may cause problems with heat transfer when the chamber is between 150 and 210°C. According to Miller and Oebser[10], these methods produce quite similar results even though the time to establish equilibrium is shorter for the first method.

A single peak is observed in all the d.s.c. curves, and it is assumed that the curing originates from a single chemical process as a first approximation. However, an overall process formed by two or more simultaneous or very close chemical reactions cannot be ruled out. In addition, it has to be assumed that all the heat generated is a result of the curing reaction, which is irreversible ring-opening and formation of the methylene bridge (indicated as 'b' on *Figure 1*). It is further assumed that no reaction takes place before the experiments started, and there is no volatilization in sample pans that can affect the reaction kinetics or the reaction exotherm. Thus, it is feasible to relate the area under the exotherm curves to the heat of reaction.

The following general expression is used for the rate of reaction:

$$d\alpha/dt = kf(\alpha) \quad (1)$$

where k is the reaction rate constant, and $f(\alpha)$ is a function of conversion that has to be determined in order to study the rate of reaction. For this purpose, it has to be established whether the reaction follows an nth-order kinetics or is autocatalysed.

The rate of reaction does not have a maximum at time zero in *Figure 5*, where the rate of reaction of the benzoxazine monomer is plotted as a function of time. In addition, the conversion curves have an inflection point when plotted against cure time (*Figure 6*). Thus, the curing of benzoxazine resin is not an nth-order reaction.

According to other authors, the ring-opening reactions generate free phenol groups that can actually accelerate further ring opening[3,5]. This argument can explain the autocatalytic nature of the reaction kinetics. Furthermore, the plot of reaction rate as a function of conversion (*Figure 7*) shows that the maximum reaction rate occurs between 15 and 30% conversion depending upon the isothermal cure temperature. These conversions are fairly close to what is typically found for autocatalysed reactions, where the maximum reaction rate is obtained between 20 and 40% conversion[11-13]. However, the fact that the maximum reaction rate shifts to higher conversions when the temperature increases may be indicating that certain structural rearrangements are occurring at higher temperature, probably after 180°C, when the changes in reaction rate maxima are more pronounced.

Note that the values for the reaction rate, $d\alpha/dt$, were obtained from the expression:

$$d\alpha/dt = (dH/dt)_{iso}/\Delta H_{RXN} \quad (2)$$

where dH/dt is the trace of isothermal d.s.c. curves, and ΔH_{RXN} is the total heat of reaction averaged from non-isothermal experiments at different heating rates. The reaction rate values can also be obtained by differentiating the isothermal conversion curves. The results from both procedures are very similar.

The degree of conversion, α, was calculated from the partial areas in the d.s.c. trace divided by ΔH_{RXN}. In *Figure 8*, the final conversion is plotted as a function of the isothermal cure temperatures. The differences in

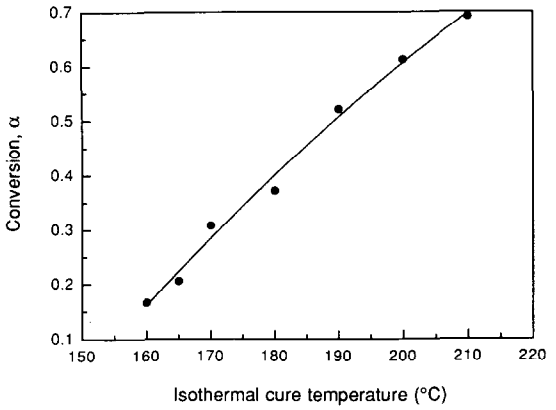

Figure 8 Conversion obtained after isothermal tests as a function of the isothermal cure temperature for the purified monomer

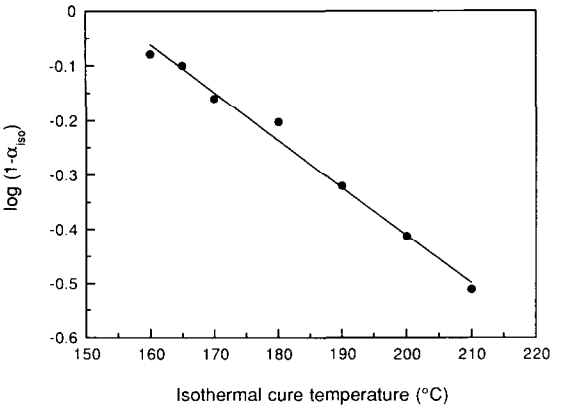

Figure 9 Unreacted fraction of the benzoxazine monomer after isothermal experiments as a function of isothermal cure temperature

conversion rate, induction time (*Figure 6*) and final conversion (*Figure 8*) are quite large between 160 and 210°C; nevertheless, this trend is expected.

It is important to mention here that the accuracy of the kinetic information obtained through isothermal and non-isothermal d.s.c. depends on the reliability of the value of the total heat of reaction. It is recommended that this value be calculated from non-isothermal experiments at different heating rates, preferably 2 to 20°C min^{-1} (refs. 12,14). For isothermal experiments there is the risk of unrecorded heat evolving at the beginning of the tests. Accurate measurements of ΔH by scanning tests require that a baseline can be drawn between a discernible onset and end of the cure reaction, which is the case for these experiments.

By curve fitting the experimental data for the isothermal heat of reaction, on *Figure 3*, the following quadratic equation is obtained:

$$\Delta H_{iso} = -0.013T^2 + 8.25T - 932 \qquad (3)$$

Kamal *et al.*[15] and Han *et al.*[16] found the same type of relationship for unsaturated polyester and epoxy systems. Complete conversion is expected at 257°C for isothermal conditions by inserting the value of ΔH_{RXN} in equation (3). This temperature seems very high, considering that the residual heat of reaction is zero at 210°C. However, this inconsistency must come from experimental errors during the performance of the isothermal tests and also due to the detection limit of the instrument. Nevertheless, these two values are defining a range within which the isothermal curing can apparently go to 100% conversion, and the information is important from the processing point of view.

If ΔH_{RXN} cannot be confirmed by another complementary technique, it is uncertain that the actual ultimate heat of reaction is being measured[8]. Even with post-cure resulting in no residual exotherm, some systems never reach 100% conversion. This is because a certain mobility in the network is required to obtain total conversion, and the system cannot achieve full conversion in spite of the increased temperature[9]. Sourour and Kamal[6] showed that, by extrapolation of a semilogarithmic plot of $(1 - \alpha_{iso})$ against isothermal cure temperature, the temperature below which unreacted resin exists in the glassy state, T_{c0}, can be obtained. *Figure 9* shows the determined $(1 - \alpha_{iso})$ values with the fitted straight line. By extrapolating this line to an isothermal conversion (α_{iso}) equal to unity, the value obtained for T_{c0} is 153°C. Since no significant reaction will occur below this temperature, T_{c0} is an important value for storage and processing purposes[6,12].

Most of the methods to quantify kinetic parameters require a prior knowledge of the reaction kinetics[15-19], but few papers exist on benzoxazine resin. Nevertheless, there are some methods that can be used to calculate kinetic parameters, such as activation energy, without involving any mechanistic knowledge of the system.

By considering that the activation energy, E_a, is a time–temperature shift factor[12], we can estimate its value from the plots of conversion as a function of time for different isothermal cure temperatures as previously shown in *Figure 6*.

The following expression can be used to obtain the activation energy:

$$t_2/t_1 = \exp[E_a(T_1 - T_2)/RT_1T_2] \qquad (4)$$

where (t_1, T_1) and (t_2, T_2) are the time–temperature pairs that have reached the same conversion and R is the gas constant. The average value of E_a obtained for the monomer was 102 kJ mol^{-1}.

The implication here is that polymers obtained by curing at different temperatures can have the same conversion as long as the total heat generated from the reaction is the same. Some differences might exist due to branching and other irregularities during the network growth, but the assumption is plausible as a first approximation[16].

As was indicated before for the system studied, the conversion is not constant at the exothermic peak for all isothermal curves. If that were the case, the activation energy could be calculated by plotting the time to reach the maximum conversion, t_{max}, against the inverse of the isothermal cure temperature[12]. This relationship can be understood by integrating equation (1):

$$\int_0^{\alpha_{max}} \frac{d\alpha}{f(\alpha)} = \text{constant} = k\int_0^{t_{max}} dt = kt_{max} \qquad (5)$$

and by assuming that the dependence of the kinetic rate constant with temperature follows an Arrhenius-type

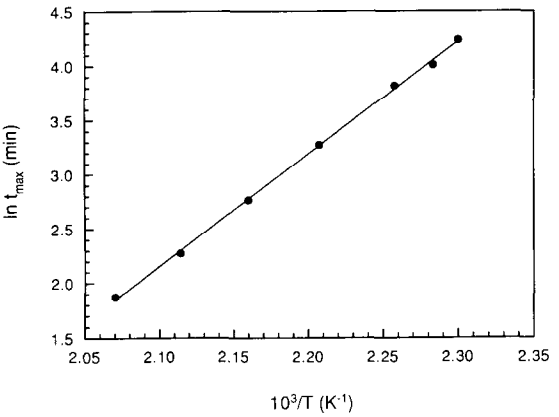

Figure 10 Time to reach maximum conversion rate as a function of the isothermal cure temperature for the benzoxazine monomer

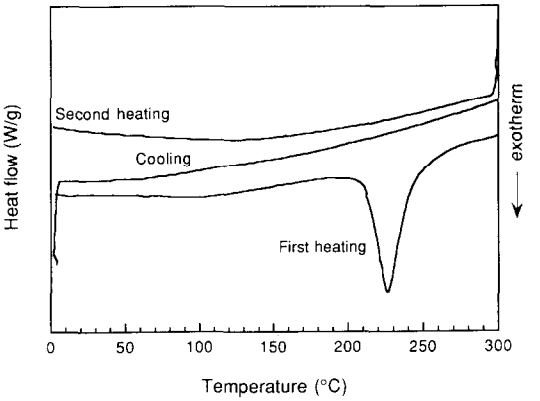

Figure 11 Typical non-isothermal d.s.c. curves for the benzoxazine monomer (first heating rate: 5°C min^{-1})

Table 1 Results obtained from non-isothermal d.s.c. experiments on the benzoxazine monomer

Scanning rate (°C min^{-1})	Exotherm peak (°C)	Onset exotherm (°C)	ΔH (J g^{-1})
5	226	188	313
10	241	176	321
20	255	209	313

relationship:

$$k = A\exp(-E_a/RT) = \text{constant}/t_{max} \quad (6)$$

Thus,

$$\ln t_{max} = \text{constant} - E_a/RT \quad (7)$$

In a semilogarithmic plot, shown in *Figure 10*, the fitted straight line for equation (7) has a correlation coefficient of 0.999. However, the value of the activation energy obtained, 86 kJ mol^{-1}, differs significantly from the one calculated from conversion curves. This may indicate the existence of other processes with higher activation energy barriers that are not considered under the assumptions of equation (7).

A typical non-isothermal d.s.c. experiment is depicted in *Figure 11*. During the first heating a well defined exotherm is observed. For the cooling and the second heating, no special features appeared. Notice that during the second heating there is no exotherm, which indicates that the maximum conversion possible has been achieved. The determination of T_g is very difficult owing to the crosslinking, since the instrument is probably not sensitive enough to record the heat absorption during this transition. However, for experiments that did not reach a high degree of conversion, the characteristic shape that indicates T_g on d.s.c. curves was observed during the second heating. In these cases, the minimum value obtained was approximately 163°C.

Table 1 shows the total heat of reaction calculated from non-isothermal experiments at different heating rates. As mentioned before, ΔH_{RXN} should ideally be constant for a given thermoset. However, at slow heating rates some of the heat generated at the beginning or at the end of the reaction is not recorded because of lack of calorimeter sensitivity. At fast heating rates, degradation or other kinds of secondary reactions could also interfere in the determination of ΔH_{RXN}. Another problem is that less than 100% conversion takes place in some cases. Several authors[10,18] have found that ΔH_{RXN} tends to be constant between heating rates of 2 and 20°C min^{-1}. This assertion agrees well with our results. Thus, it is assumed that complete conversion is achieved and the value of the total heat of reaction is the average of the total heat generated from experiments at 5, 10 and 20°C min^{-1}. That average is 316 J g^{-1}.

It is important to mention that the ΔH_{RXN} from non-isothermal studies should be the same as the heat of reaction obtained after adding the ΔH from isothermal tests and the residual ΔH from the subsequent scanning experiments. This sum leads to an average value of 225 J g^{-1}, which is considerably smaller than the 316 J g^{-1} obtained from the non-isothermal tests. That can be due to all the problems described previously, and also to unrecorded heat during the process of the first heating, equilibration of the instrument, sensitivity of the calorimeter at slow reaction rates, rapid cooling, and the rate of temperature scanning. This difference may also suggest the existence of further structural rearrangements at higher temperatures, since the exotherm of reaction proceeds up to relatively very high temperatures in the scanning experiments. The same phenomenon has been found on systems where high-temperature reactions are known to occur.[13]

Owing to the autocatalytic character of the system under study, it was assumed that the reaction can be described by the following general expression for autocatalysed systems:

$$d\alpha/dt = k(1-\alpha)^n\alpha^m \quad (8)$$

where α is the fractional conversion, k is the kinetic rate constant, and $m+n$ is the overall reaction order. In general, it can be assumed that the specific heat is constant or that it has a linear variation with the scanning temperature in order to generate kinetic data from non-isothermal experiments[17]. In addition, the reaction rate was considered to have an Arrhenius temperature dependence. Thus, the following expression can be written:

$$d\alpha/dt = A\exp(-E_a/RT)(1-\alpha)^n\alpha^m \quad (9)$$

where A is the pre-exponential or frequency factor. By expressing the scanning rate as $\beta = dT/dt$ and taking the

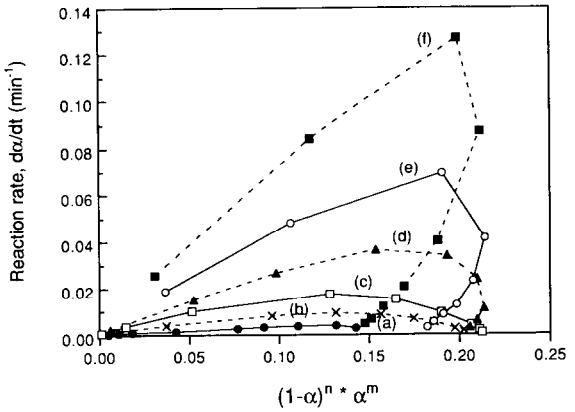

Figure 12 Plots of $d\alpha/dt$ as a function of $(1-\alpha)^n\alpha^m$ at different isothermal temperatures: (a) 160°C, (b) 170°C, (c) 180°C, (d) 190°C, (e) 200°C and (f) 210°C

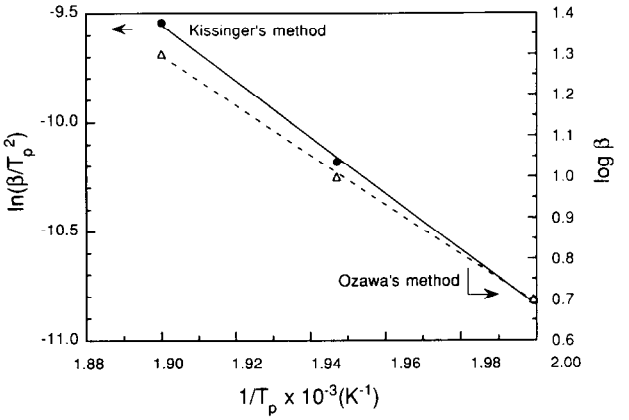

Figure 13 Representation of (Δ) Ozawa's[20] and (●) Kissinger's[21] methods to calculate activation energy from non-isothermal data of the benzoxazine monomer (T_p = temperature at maximum reaction rate; β = scanning rate)

Table 2 Values obtained from multilinear regression with non-isothermal data

Scanning rate (°C min^{-1})	Activation energy (kJ mol^{-1})	n	m
5	93	1.6	1.0
10	80	1.2	0.8
20	57	1.3	1.1

Table 3 Vitrification times of the monomer obtained from isothermal experiments

Temperature (°C)	Vitrification time (min)
160	75
170	46
180	26
190	18
200	10
210	7

Table 4 Kinetic rate constants of the monomer obtained from isothermal experiments

Temperature (°C)	Reaction kinetic constant, k (min^{-1})
160	0.03
170	0.07
180	0.13
190	0.23
200	0.33
210	0.60

natural logarithm of both sides of equation (9), we obtain:

$$\ln(\beta\, d\alpha/dT) = \ln A - E_a/RT + n(1-\alpha) + m\alpha \quad (10)$$

A multilinear regression can be performed to obtain the values of A, E_a, m and n. These values are presented in *Table 2*. The deviation observed for the activation energy values may be related to the high-temperature changes that were suggested before. To check the validity of the kinetic model in equation (8), one can prepare plots of $d\alpha/dt$ against $(1-\alpha)^n\alpha^m$ as shown in *Figure 12* for different isothermal temperatures. The average values of m and n obtained through non-isothermal data are used and they are assumed to be constant with temperature.

Although these plots are expected to be straight lines, with the slopes being the values of the kinetic rate constant k, there is a deviation from linearity in all cases marked by a sharp decrease of the reaction rate at a point that could be related to the onset of diffusion control of the reaction. Beyond that point the constant k must become strongly dependent on the diffusion rate of the reactants[6,12]. As the isothermal temperature increases, the deviation from linearity occurs at higher conversion since the diffusion rates are directly proportional to the temperature. The reaction time at which this deviation from linearity occurs is taken as the vitrification time, which is reported in *Table 3*.

The values of the constant k can be calculated from the slope of the linear portion of each curve (*Table 4*). Those constants follow an Arrhenius-type relationship with temperature. Thus, from these results one can say that the model proposed is valid for the early stages of cure prior to diffusion control.

By using non-isothermal data at different heating rates, we have an alternative way of calculating the activation energy without assuming any model or kinetic parameter, and without integrating the exotherm peak. That includes two different approaches by Ozawa[12,20] and by Kissinger[21]. The plots suggested by them are shown in *Figure 13* (see the respective d.s.c. curves in *Figure 14*). For our scanning experiments, the extent of cure at the peak exotherm is constant, although the temperature at which the peak exotherm occurs obviously depends on the heating rate, and that is the condition necessary to apply these methods. The calculated values of E_a obtained are 107 kJ mol^{-1} by Ozawa's method and 116 kJ mol^{-1} by Kissinger's method. They are quite close to each other and also to the earlier result of 102 kJ mol^{-1} by equation (4).

So far, similar values of activation energy and heat of reaction have been obtained from certain isothermal and non-isothermal analysis. The differences observed in some cases are not surprising since it is well known that kinetic information determined by scanning thermal analytical techniques does not usually agree with the parameters determined by isothermal tests. This is the case not only for d.s.c. or d.t.a. but also for t.g.a. for even very simple systems[22]. The causes of this discrepancy can be intuitively understood owing to the

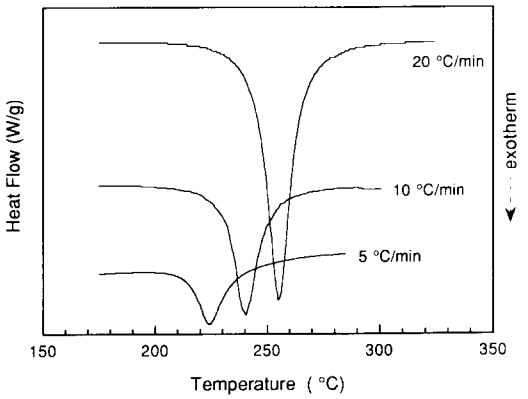

Figure 14 Non-isothermal d.s.c. curves for the benzoxazine monomer at different heating rates

already mentioned differences between these two procedures, but they have not been fully established yet[23]. On the other hand, some of those differences may be indicating that some further structural rearrangements may be possible at high temperature, which will be studied in more detail as the reaction mechanisms for benzoxazine resins are completely elucidated.

CONCLUSIONS

According to d.s.c. results, the benzoxazine precursor studied undergo an autocatalytic-type curing mechanism. The model proposed for the curing reaction is valid for the early stages of cure, prior to diffusion control. The activation energy is between 102 and 116 kJ mol^{-1}, with an overall order of reaction of approximately 2. Some evidence from isothermal and scanning experiments suggests that further structural rearrangements may be occurring at high temperatures.

From isothermal experiments, the vitrification times and the kinetic rate constants at different cure temperatures were calculated. The isothermal heat of reaction follows a quadratic relationship with the cure temperature, while the onset of curing and the exotherm maximum during the isothermal tests were found to decay exponentially with that temperature.

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