Thermochimica Acta, 126 (1988) 339–354
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DYNAMIC, ISOTHERMAL AND RESIDUAL HEATS OF CURING OF AN UNSATURATED POLYESTER RESIN

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(Received 13 July 1987)

ABSTRACT

The polymerization of unsaturated polyester resins can be highly exothermic. The released heat tends to raise the temperature and accelerates the curing reaction. In this work, dynamic and isothermal heats were obtained at different scanning rates, temperatures and setting times, using DSC techniques. Residual heats were also obtained after each isothermal run. The results show the importance of the specific heat of the samples in relating dynamic and isothermal experimental data. The calorimetric techniques and the lack of instrument sensitivity can considerably affect the applicability of the data obtained to determine time–temperature–degree of conversion curves. A method is proposed to determine corrected isothermal curves as well as adiabatic reaction temperature from dynamic experimental data, using the energy analysis of the reaction process.

INTRODUCTION

Two general methods are commonly used for the polymerization of unsaturated polyester resin. Both methods, thermal-catalytic and promoted catalytic cure, result in free radical-initiated polymerization. The selection of a particular process will depend on its specific application. [1–3]

The polymerization of unsaturated polyester resin can be highly exothermic. The released heat tends to raise the temperature and accelerates the curing reaction. The process depends on the temperature of the environment, the particular grade of resin and the concentration of initiator–promoter [4]. Variations in the amount of catalyst can affect both the rate of polymerization and ultimate extent of cure.

In general, thermal analysis techniques have proved to be valuable tools in studying heat generation and reaction kinetics of such systems. However, the interpretation of the data thus obtained has been the source of considerable discussion [5].

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0040-6031/88/$03.50

In commercial applications, thermosets are cured via a non-isothermal process. The exothermic heat and the exothermic peak temperature obtained in a dynamic procedure are more interesting than the heat evolved in an isothermal scanning. Nevertheless, in curing processes at room temperature or in applications in which the high surface/volume ratio facilitates heat removal, little temperature rise is observed and the process may be considered as isothermal. On the other hand, when the curing is highly activated due to the elevated rate of heat generation, as well as bad thermal conductivity of the material, the temperature rises considerably; this can produce high shrinkage and cracks [6]. For a given polyester formulation, in this type of application, it is useful to know the maximum temperature to which the system could rise (the adiabatic reaction temperature).

The present work focused on the reaction exothermic heats determined by DSC for an unsaturated polyester resin activated with a promoted catalytic system. Dynamic and isothermal heats were obtained at different scanning rates, temperatures and setting times. Residual isothermal reactivities of the samples were obtained after each isothermal run. The relation between the experimental dynamic and isothermal data, the effect of specific heat samples in the calorimetric measurements and the applicability of the data obtained to determine accurate time–temperature–degree of conversion curves have also been investigated. A method is proposed to determine corrected isothermal curves as well as adiabatic reaction temperature from dynamic experimental results.

THEORETICAL ASPECTS

Energy analysis of the reaction process

When a system undergoes a chemical reaction at constant pressure, the energy conservation equation can be applied; then

$$\Delta H_R = H_2 - H_1 \tag{1}$$

where ΔH_R is the heat exchanged by the system with its environment during the process and H_2 and H_1 are the enthalpies of the final state of the products and the initial state of the reactants, respectively.

In a non-isothermal process, the temperature of the products T_2 will be much higher than the initial temperature T_1 of the reactants. Equation (1) can be rewritten as a function of two terms

$$\Delta H_R = H_2 - H_1 = H_2(T_1) - H_1(T_1) + H_2(T_2) - H_2(T_1) \tag{2}$$

The first term represents the exothermic heat obtained in an isothermal process (with the temperature of the products equal to the initial temperature of the reactants T_1 and the reaction carried to the same degree of completion as in the actual process)

$$\Delta H_{\mathrm{iso}} = H_2(T_1) - H_1(T_1) \tag{3}$$

The second term is the change in enthalpy of the products due to the change in temperature

$$H_2(T_2) - H_2(T_1) = \int_{T_1}^{T_2} C_{\mathrm{p}}(T)\,\mathrm{d}T \tag{4}$$

$C_{\mathrm{p}}(T)$ is the specific heat associated with the products' mass.

For the same degree of extension, eqn. (2) can be used to compare exothermic heats obtained in isothermal calorimetric experiments with those obtained in a dynamic way.

If it is supposed that the chemical reaction takes place with a negligible amount of energy supplied or in such a way that no heat is exchanged with the surroundings, the following equation can be written

$$H_2 = H_1$$

or

$$\Delta H_{\mathrm{iso}} + \int_{T_1}^{T_2} C_{\mathrm{p}}(T)\,\mathrm{d}T = 0 \tag{5}$$

The final temperature T_2 obtained in such conditions is called the adiabatic reaction temperature; it represents the maximum temperature attainable by the system due to exothermic effect. Equation (5) can be used to solve T_2 as a function of ΔH_{iso} and $C_{\mathrm{p}}(T)$.

Calorimetric approach

The different calorimetric measurements to study the curing process involve the generation of accurate time–temperature–degree of conversion curves. This is the first step to determine the kinetic constants. It also provides a valuable practical information for establishing optimum environmental curing conditions.

Isothermal and dynamic methods require an accurate value of ΔH_{R}, the exothermic heat associated with the overall heat reaction process, and values of $\Delta H_{\mathrm{R}}(t)$, the evolution of exothermic heat, as a function of time or temperature. Accurate experimental values of ΔH_{R} and $\Delta H_{\mathrm{R}}(t)$ are not easy. In isothermal measurements, part of the initial reaction and final reaction steps were unrecorded due to the lack of instrument sensitivity. The same can happen in dynamic evaluation at slow heating rates. At fast heating rates, the exothermic cure heat may be altered or masked by competitive thermal events, such as vaporization of solvent or thermal decomposition in the later stages of curing. The exothermic heat obtained in isothermal experiments conducted at room temperature is not the overall reaction heat, ΔH_R, as conversion is not completed because the system becomes glassy and restricts species from reacting. Dynamic scans are performed to check the presence of additional curing and to determine the residual heat of reaction, ΔH_{res}. Some authors take $\Delta H_R(t)$ together with ΔH_{res} to obtain the degree of conversion. From a practical point of view, ΔH_{res} can be related to the ultimate extent of curing at temperature T and setting time t.

Degree of conversion from heat reaction

Providing the exothermic heat reaction is the only thermal event, the degree of cure α, can be defined as the ratio of the heat generated at a particular time t at an isothermal curing temperature T to the overall exothermic heat evolved in the complete reaction process

$$\alpha = \Delta H_R(t)/\Delta H_R \tag{6}$$

In calorimetric techniques it is assumed that the reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ is directly proportional to the rate of heat generation $\mathrm{d}(\Delta H_R(t))/\mathrm{d}t$ (the ordinate of the DSC trace)

$$\mathrm{d}\alpha/\mathrm{d}t = (\mathrm{d}\Delta H_R(t))/\mathrm{d}t)/\Delta H_R \tag{7}$$

When different simultaneous events can coexist in the reaction process, or the reaction does not reach completion, eqns. (6) and (7) can be ambiguous in order to define the degree of curing and the reaction rate [5].

EXPERIMENTAL

Materials

Polyester resin

A general purpose polyester resin (commercial name: A228) was selected and used; it was supplied by Rio Rodano (Spain). The base polyester resin was prepared using phthalic anhydride, maleic anhydride and propylene glycol, with a mole ratio of 2 : 1 : 3 obtained by NMR. As a crosslinking agent, styrene monomer had been added to the resin by the supplier. The styrene content was determined as 35% using the method reported in ref. 7.

Initiator/accelerator

A 50% solution of methyl ethyl ketone peroxide (MEKP) in dibutyl phthalate was used as initiator, and a 6% cobalt octoate solution in xylene was added as accelerator.

Calorimetric measurements

The calorimetric measurements were conducted in a Mettler differential scanning calorimeter, equipped with a control and programming unit (microprocessor TC 10) and a calorimetric cell (DSC20) arranged to permit temperature scans from −10 to 600 °C.

A standard resin sample was catalysed by mixing it with MEK peroxide (1% by weight) and the cobalt octoate solution (0.1% by weight) for about 1 min. The required amount of sample (20.0 ± 0.2 mg) was weighed into a previously weighed sample pan for each measurement. The weight of the specimen was also measured after the run to check whether there was any loss of mass.

RESULTS AND DISCUSSION

Isothermal experiments and residual curing reactions

The DSC thermograms for isothermal experiments performed at 10, 20, 30, 40, 50 and 60 °C and setting times of 240 and 800 min are shown in Figs. 1 and 2. As can be seen, isothermal experiments performed at 20, 30 and 40 °C exhibit a quantitative induction time. The appearance of a maximum

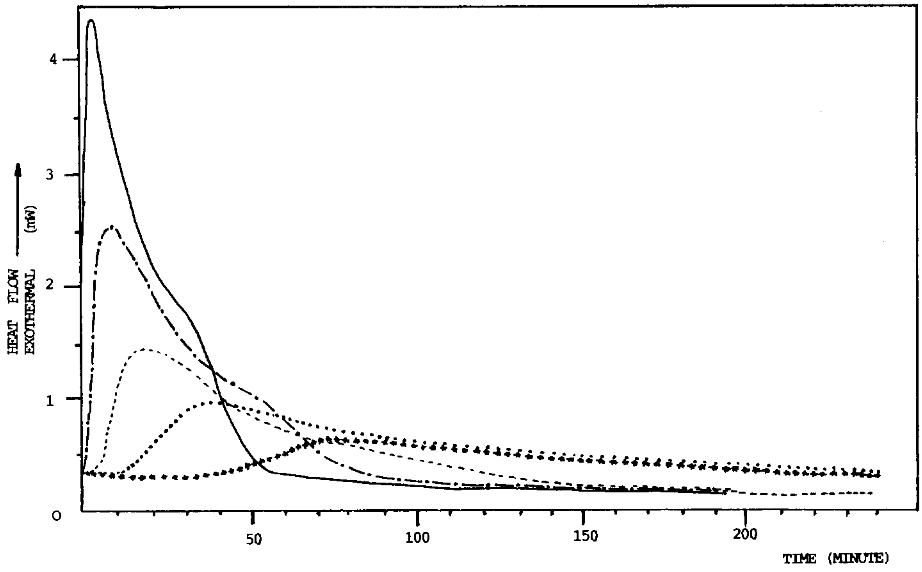

Fig. 1. DSC thermograms for the unsaturated polyester system at different temperatures: (——) 60 °C, (·–·–·) 50 °C, (- - - - -) 40 °C, (· · · · · ·) 30 °C, (* * * *) 20 °C. Cure time $t = 240$ min.

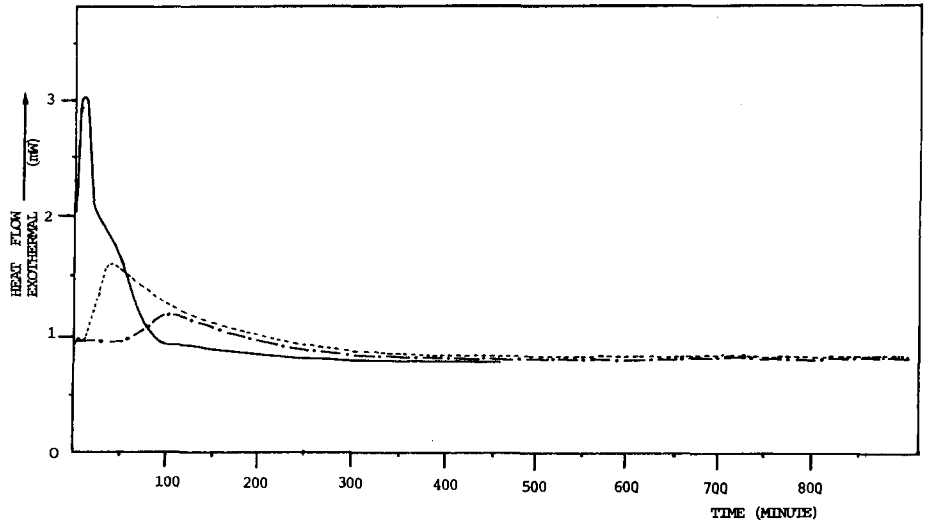

Fig. 2. DSC thermograms for the unsaturated polyester system at different temperatures: (——) 50 °C, (- - - - -) 30 °C, (·—·—·) 20 °C. Cure time, $t = 800$ min.

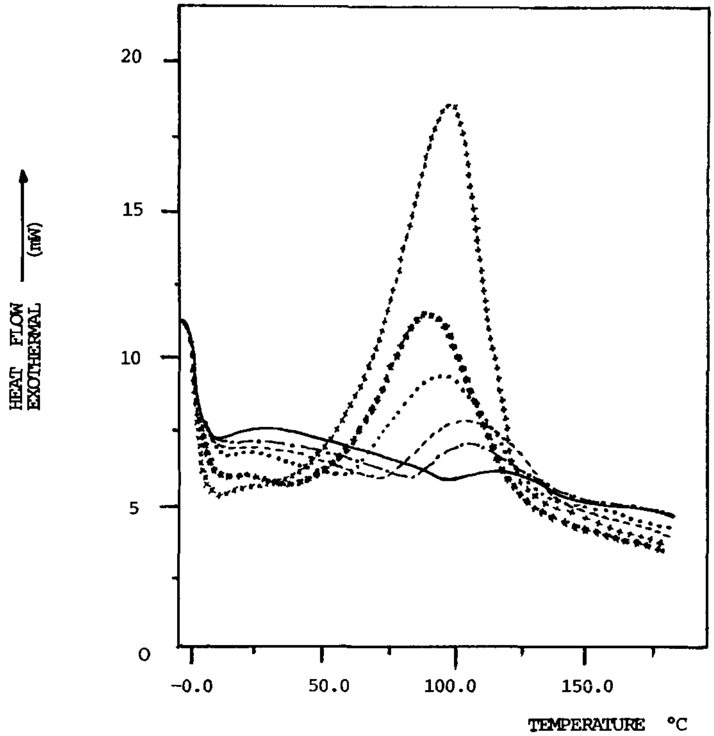

Fig. 3. Dynamic (10 °C $\min^{-1}$) DSC thermograms of the residual heat of reaction after the isothermal runs: (+ + +) 20 °C, (* * * *) 30 °C, (······) 40 °C, (-----) 50 °C, (·—·—·) 60 °C, (——) 70 °C. Cure time, $t = 240$ min.

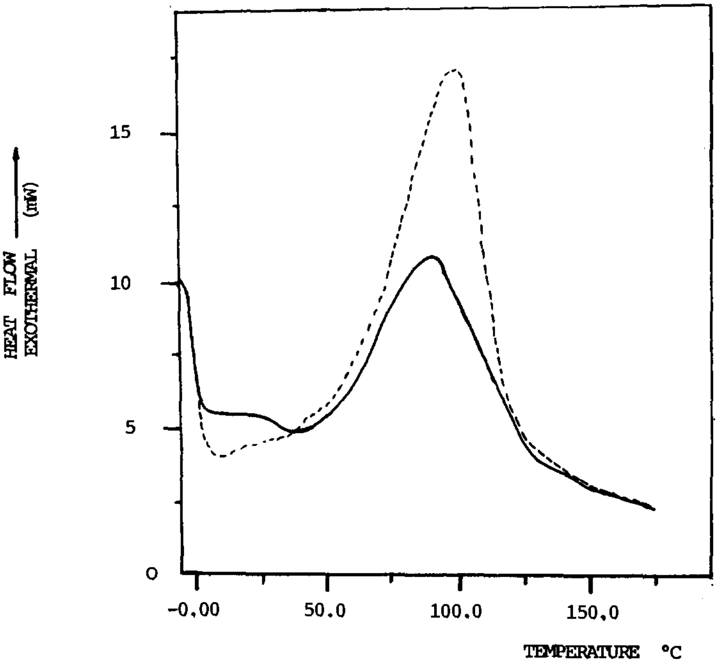

Fig. 4. Comparison between two DSC thermograms of the residual heats of reaction after the isothermal runs at $T = 20\,^\circ\mathrm{C}$, obtained at different curing times: (------) 240 min, (———) 800 min.

at a time different to zero provides evidence of the existence of an overall autocatalytic reaction mechanism. From the exothermic effect it can also be inferred that the conversion starts slowly, then accelerates and finally the rate of reaction decreases to an asymptotic value. Figures 1 and 2 show that in the experiments performed with a setting time of 240 min, or at lower temperatures, the reaction did not reach completion; this is due to the fact that the system becomes glassy and restricts species from reacting [8,9].

Further evidence of the incomplete reaction is shown in Figs. 3 and 4, which show the residual heat of reaction obtained with dynamic scans performed at a heating rate of $10\,^\circ\mathrm{C}\ \mathrm{min}^{-1}$ after each isothermal experiment. As can be observed, the residual heat increases when temperature or curing time diminishes.

The experimental values of isothermal heat, ΔH_{iso}, and residual heat, ΔH_{res}, are shown in Table 1 (columns 3 and 4). ΔH_{res} is also plotted as a function of curing temperature in Fig. 5. This plot shows the importance of the curing time in order to achieve elevated reaction extension at low temperatures. At elevated temperatures, the reaction rapidly reaches completion or the glassy state.

Column 5 of Table 1 shows the sum of isothermal and residual heats, ΔH_{tot}. These values, also represented in Fig. 5, seem to be constant; this has

TABLE 1

Summary of experimental and corrected values obtained from isothermal and residual heat curves

Curing temperature (K)	Time (min)	ΔH_{iso} (J g^{-1})	ΔH_{res} (J g^{-1})	ΔH_{tot} (J g^{-1})	$\Delta H^{\mathrm{c}}_{\mathrm{res}}$ (J g^{-1})	$\Delta H^{\mathrm{c}}_{\mathrm{tot}}$ (J g^{-1})	T_0 (K)	T_{m} (K)
283	240	54.1	270.4	324.5	415.0	469.1	298	384.5
283	480	91.9	209.1	301.0	346.7	438.6	298	380.3
288	240	124.1	214.7	338.8	356.8	480.9	298	383.0
293	240	132.7	177.7	310.4	317.3	450.0	293	376.5
293	800	206.2	91.5	297.7	193.6	399.8	308	369.1
298	240	171.3	113.9	285.2	232.6	403.9	298	369.0
303	240	191.2	88.6	279.8	179.0	370.2	313	367.1
303	800	233.4	59.7	293.1	137.9	371.3	325	371.8
308	240	233.2	63.7	296.9	150.6	383.8	320	372.0
313	240	257.1	50.2	307.3	121.8	378.9	328	370.8
323	240	263.0	30.4	293.4	94.4	357.4	338	376.3
323	480	280.3	23.1	303.4	68.2	348.5	348	375.0
333	240	278.2	13.7	292.9	53.0	331.2	353	376.5

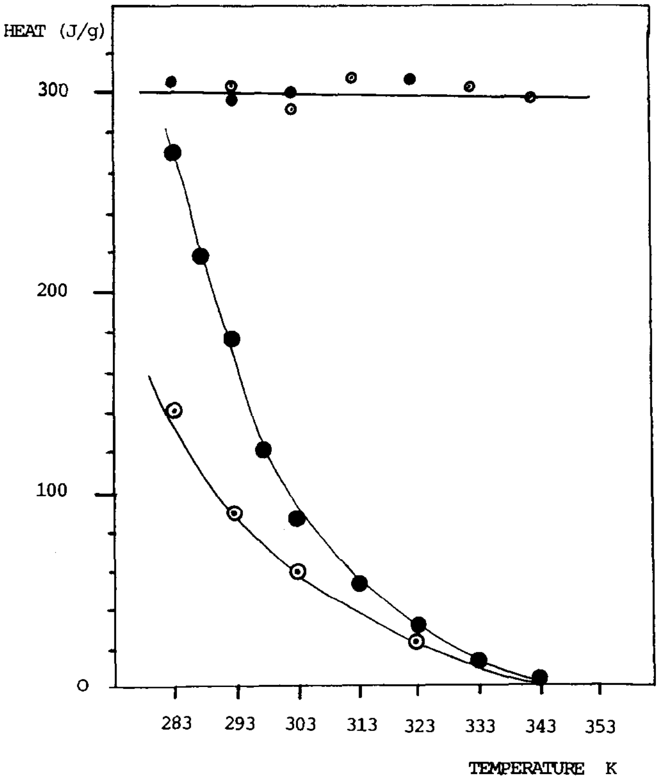

Fig. 5. Residual heat versus different curing temperatures obtained at different curing times: (⊙) 800 min, (●) 240 min. The sum of experimental isothermal and residual heats, ΔH_{tot}, is also represented.

also been reported by many other authors [7,10,11]. Some of them suggest that this sum represents the maximum possible heat of curing at an initial isothermal cure [10]. As pointed out by Sourour and Kamal [12], and according to eqn. (4), in order to compare isothermal and dynamic heats it is necessary to take into account the effect of the specific heat, C_p, on the actual heat obtained in the dynamical run. Column 6 of Table 1 shows the values of the residual heat corrected for c_p, ΔH^c_{res}. In order to do this correction, an overall c_p for the cured resin of 1.67 J g^{-1} K^{-1} was experimentally determined. Similar values are reported in the literature for this kind of resin [13,14]. The sum of the isothermal heats and the corrected residual heat, ΔH^c_{tot}, are shown in column 7 of Table 1. These values, from our point of view, represent the total isothermal curing heat, and should be approximately equal. The differences that can be observed show the experimental errors due to unrecorded heat; this must be attributed to the lack of instrument sensitivity or the short setting time that permits loss of the initial stages of curing [5]. The sum of isothermal heat and residual heat without correction mask these errors, as the important effect of c_p at lower temperatures (high values of ΔH_{res}) is balanced by the important loss of isothermal heat at elevated ones.

Dynamic experiments

The DSC thermograms for the samples at various heating rates are given in Fig. 6. The peak temperature, T_m, and the overall heat of reaction, ΔH_{din}, are reported in columns 2 and 3 of Table 2. Column 4 shows the values of the dynamic heat reaction corrected with the effect of specific heat according to eqn. (2), ΔH^c_R. A constant specific heat of 1.67 J g^{-1} K^{-1} has been used for the cured resin in the temperature intervals varying between the initial temperature of peak evaluation and the temperature of the exothermic peak.

Figure 7 shows the experimental and corrected exothermic reaction heats as functions of heating rate. As can be observed, the values obtained in the range 5–20 °C min^{-1} are constant, and important deviations exist outside this range. For heating rates below 5 °C min^{-1}, the lack of sensitivity of the instrument may be the cause of errors. Above 20 °C min^{-1}, the exothermic curing effects compete, in the present case, with the endothermic effect due to evaporation of styrene. It can be supposed that the most probable dynamic reaction heat has a value of 341.6 J g^{-1}, or 502.2 J g^{-1} if it is corrected for the effect of specific heat.

If it is assumed that the isothermic reaction heat does not vary appreciably with temperature in the range studied, then the value of 502.2 J g^{-1}, the corrected dynamic exothermic heat, should be the same as those reported in column 7 of Table 1, the sum of isothermal and residual corrected reaction

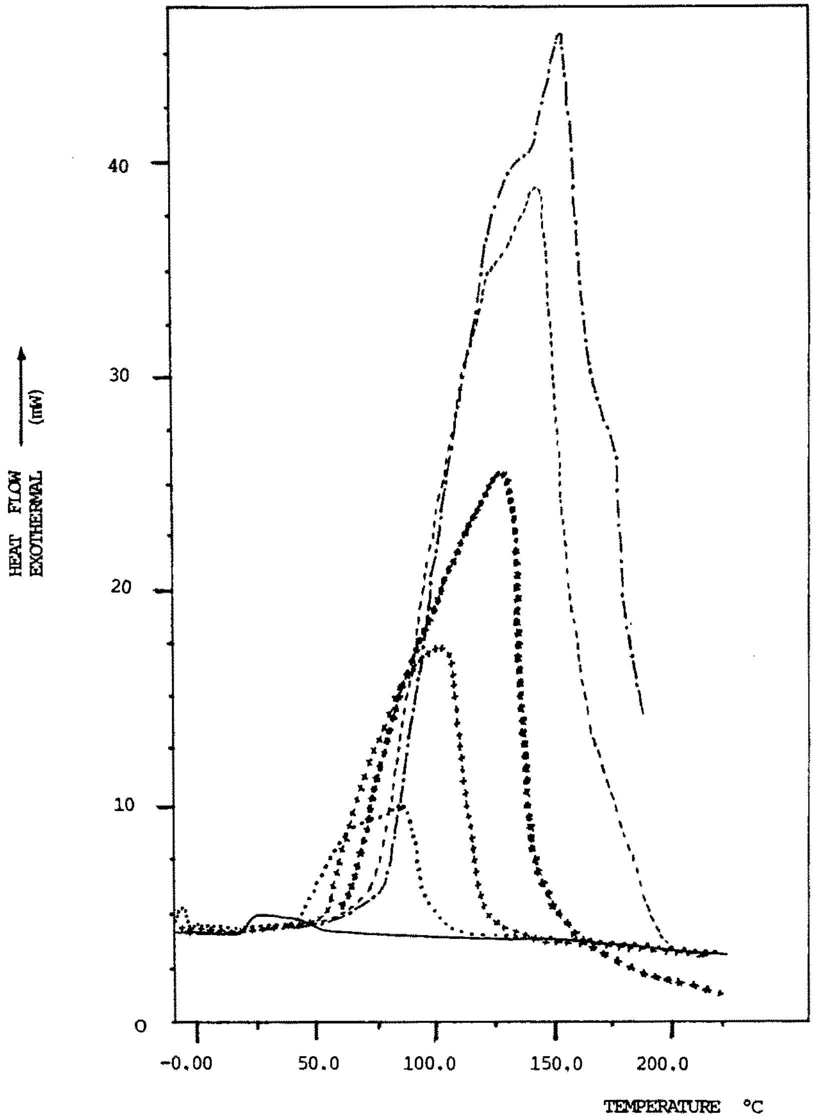

Fig. 6. Dynamic DSC thermograms obtained at different heating rates (°C min^{-1}): (———) 0.2, (······) 2, (+ + + +) 5, (* * * *) 10, (- - - - -) 20, (·—·—·) 30.

heats. It must be supposed that the differences obtained are due to experimental error.

Figure 8 shows the variation of the different experimental and corrected heats as functions of curing temperature. From a practical point of view, one can conclude that the difference between dynamic and residual corrected exothermic heats, $\Delta H'_{\text{iso}}$ represents a more accurate approximation to isothermal heat that those values obtained with isothermal experiments.

TABLE 2

Summary of experimental and corrected values obtained from dynamical heat curves

Heating rate (°C min^{-1})	ΔH_R (J g^{-1})	T_0 (K)	T_m (K)	ΔH_R^c (J g^{-1})
0.2	265.9	288	306.1	296.21
2	320.6	298	357.1	419.47
5	341.9	298	377.1	474.13
8	341.2	298	386.5	484.16
10	341.7	298	396.3	506.1
15	325.2	298	404.2	502.74
20	324.7	298	411.1	513.84
25	306.3	298	415.8	503.25
30	273.5	298	420.8	469.48
35	225.7	298	422.5	433.87

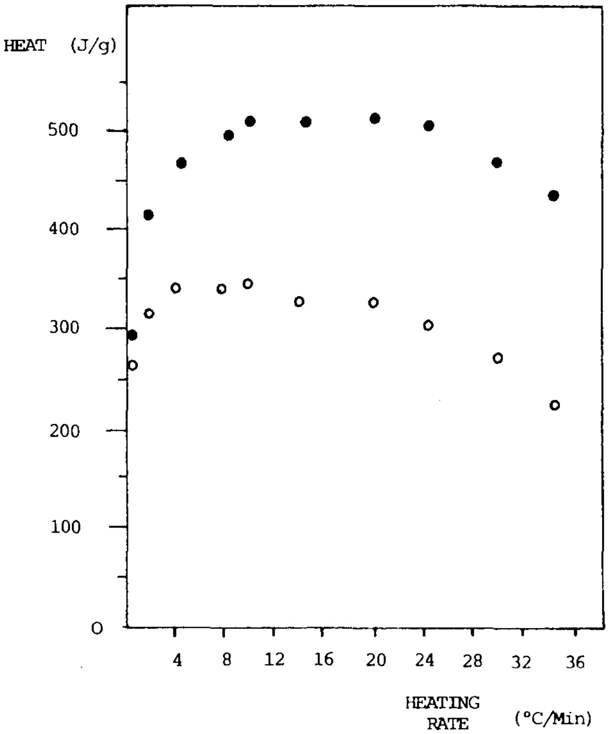

Fig. 7. Comparison between experimental dynamic heat values, ΔH_R (○), and corrected values, ΔH_R^c (●), at different heating rates.

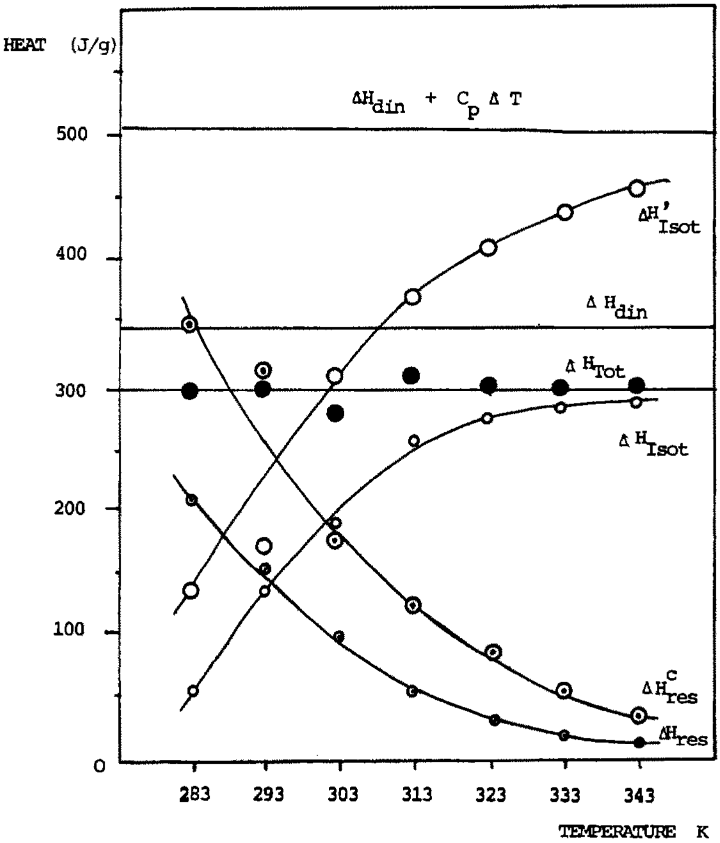

Fig. 8. Comparison between the different experimental and corrected heats as functions of curing temperature.

Degree of conversion

The values of the degree of conversion, α, will depend upon the choice of the total heat generated (ΔH_R) and the evolution of heat as a function of time $\Delta H_R(t)$.

Some authors [15] obtain conversions by subtracting from unity the ratio of the partial heat of reaction at time t to overall dynamical heat of reaction

$$\alpha = 1 - (\Delta H_{res}/\Delta H_R) \tag{8}$$

To obtain the degree of conversion, we suggest the use of the corrected isothermal curve, $\Delta H'_{iso}$ (see Fig. 8) with the overall dynamic corrected heat

$$\alpha = \Delta H'_{iso}/\Delta H^c_R = 1 - (\Delta H_{res} + C_p\ \Delta T_{res})/(\Delta H_R + C_p\ \Delta T) \tag{9}$$

Figures 9 and 10 show the ultimate degree of conversion as a function of curing temperature using eqns. (8) and (9). As can be seen, at elevated

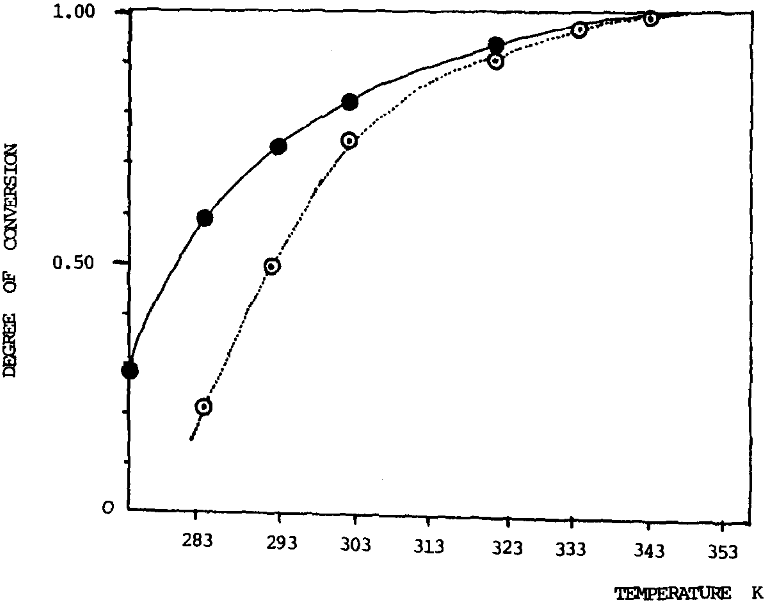

Fig. 9. Ultimate extent of curing versus curing temperature using eqn. (8): (●) cure time of 240 min and (⊙) cure time of 800 min.

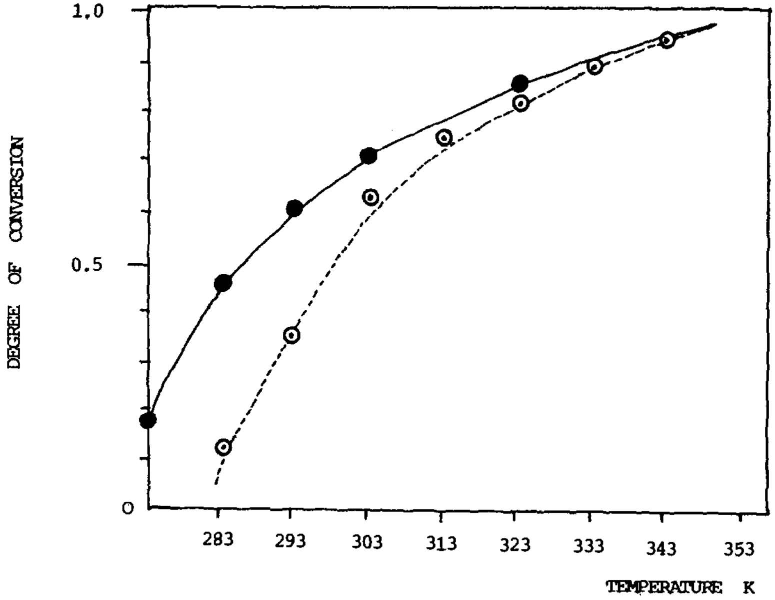

Fig. 10. Ultimate extent of curing versus curing temperature using eqn. (9): (●) cure time of 240 min and (⊙) cure time of 800 min.

curing temperatures the results are very similar, but at low temperatures eqn. (9) predicts lower conversions than eqn. (8).

The adiabatic temperature reaction

From eqn. (5), the adiabatic temperature of this system can be obtained by solving the following equation

$$\Delta H_{\mathrm{iso}} + m\int_{T_1}^{T_2} c_{\mathrm{p}} \,\mathrm{d}T = 0$$

Assuming c_{p} is a constant and equal to 1.67 J g^{-1} K^{-1}, $T_1 = 298$ K and ΔH_{iso} is the isothermal curing heat equal to 502.2 J g^{-1}, an adiabatic temperature of 326 °C is obtained.

Figure 11 represents in a logarithmic plot the peak temperature as a function of the inverse of heating rate. It is interesting to note that at elevated heating rate the peak temperature tends asymptotically to a value of 146 °C, the boiling point of styrene; this shows, as previously mentioned, that at these heating rates the actual reaction heat is masked by the endothermic heat associated with styrene evaporation.

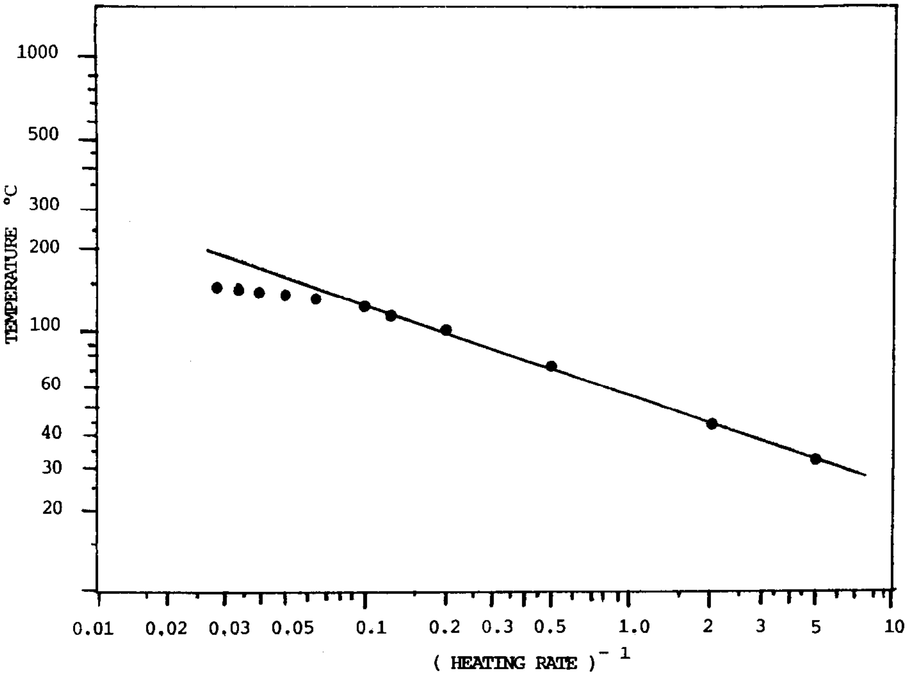

Fig. 11. Peak temperature of dynamic DSC curves versus inverse of heating rate.

CONCLUSIONS

(1) Polyester resin cured at room temperature with a catalytic-promoter system presents an example of an autocatalytic reaction system. It is difficult to deduce for such a system the extent of reaction from calorimetric isothermal experiments. This is due to the lack of instrument sensitivity at lower temperatures and, at higher ones, some heat is lost before the instrument can detect it.

(2) For the system studied, from experiments carried out at different temperatures and setting times, a residual curing heat was detected. This shows not only time and temperature dependence, but also that the reaction may not reach completion because the material becomes glassy and restricts further reaction. Residual curing heat can be of practical use to determine rapidly the ultimate extent of curing for a cured system.

(3) In order to compare dynamic and isothermal heats, the effect of c_p must be taken into account. The degree of conversion, defined from the residual experimental heat and the dynamic exothermic heat, is similar but not equal to the degree of conversion obtained from the preceding heats corrected for the effect of specific heat of the cured resin.

(4) From dynamic experimental results, a value of 326 °C has been obtained as the adiabatic reaction temperature of the unsaturated polyester studied, using the energy analysis of the reaction process.

LIST OF SYMBOLS

C_p	specific heat associated with m (J K^{-1})
c_p	specific heat associated with unit mass (J g^{-1} K^{-1})
ΔH_R	overall exothermic heat
$\Delta H_R(t)$	exothermic heat associated to time t
ΔH_{res}	residual heat of reaction
α	degree of cure
$d\alpha/dt$	reaction rate
ΔH_{iso}	exothermic heat in an isothermal process
ΔH_{tot}	$\Delta H_{iso} + \Delta H_{res}$
ΔH^c_{res}	residual heat corrected for C_p
H^c_{tot}	$\Delta H^c_{res} + \Delta H_{iso}$
T_m	peak temperature
T_0	onset temperature of peak reaction
ΔH_{din}	overall heat of reaction from dynamic experiment
ΔH^c_R	corrected overall heat reaction from dynamic experiment by C_p
$\Delta H'_{iso}$	$\Delta H^c_R - \Delta H^c_{res}$
ΔT_{res}	$T_m - T_0$ of residual peak
ΔT	$T_m - T_0$ of dynamic curve

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