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Thermochimica Acta 289 (1996) 209–221

thermochimica acta

A new method for the determination of the Arrhenius constants for the cure process of unsaturated polyester resins based on a mechanistic model[1]

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Received 13 December 1995; accepted 15 March 1996

Abstract

Several models have been proposed to describe the kinetic behaviour of the cure of unsaturated polyester (UPs) resins as manifest by thermal data measurements. Ozawa proposed a method for the estimation of the overall Arrhenius constants for the cure process from an empirical rate expression which describes the relationship between the heating rate and the time taken to reach the maximum cure rate for data generated by various thermal analytical methods. This approach has been extended so as to be applicable to a realistic mechanistic kinetic model of the cure of UP resins in which diffusion-limited propagation and decreasing initiator efficiency with conversion are involved. The procedure was tested with a commercial UP resin system using dynamic DSC methods for the measurement of cure. The DSC measurements have indicated that the diffusion-limited period of cure only starts after the point of maximum reaction rate has been reached and, thus, the true propagation rate constant can be evaluated from DSC data up to that point without having to consider the effects of radical trapping processes or decreasing initiator efficiency in this particular case. The values of the activation energy and the frequency factor found were 23,590 J mol^{-1} and 6.78×10^5 dm^3 mol^{-1} min^{-1}, respectively. The technique is independent of experimental baseline accuracy and the total heat of cure. Moreover, unlike the time-consuming procedure of curve fitting over the whole conversion range which has been adopted previously to obtain multiple unknowns, this approach results in rapid, highly convergent parameter optimisation.

Keywords: Cure; Diffusion control; Kinetics; Model; Unsaturated polyester resin

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[1] This paper is a contribution to the special thematic issue "Reaction Calorimetry", edited by Ralph N. Landau.

PII: S0040-6031(96)03011-0

Nomenclature

α	fractional conversion
α_t	fractional conversion at time t
k	rate constant/min^{-1}
T	temperature/K
T_0	initial temperature/K
T_t	temperature at time t/K
T_p	temperature at the peak of the DSC curve/K
t	time/min
t_p	time at the peak of the DSC curve/min
t_z	inhibition time/min
R	molar gas constant/J K^{-1} mol^{-1}
β	heating rate/K min^{-1}
$[R]_a$	active radical concentration/mol dm^{-3}
$[R]$	radical concentration/mol dm^{-3}
$[I]$	initiator concentration/mol dm^{-3}
$[I]_0$	initial initiator concentration/mol dm^{-3}
$[M]$	monomer concentration/mol dm^{-3}
$[Z]$	inhibitor concentration/mol dm^{-3}
$[Z]_{eff}$	effective inhibitor concentration/mol dm^{-3}
k_p	propagation rate constant/dm^3 min^{-1} mol^{-1}
k_d	initiator decomposition rate constant/min^{-1}
k_z	inhibition rate constant/dm^3 min^{-1} mol^{-1}
E	activation energy/J mol^{-1}
E_p	activation energy of propagation reaction/J mol^{-1}
E_d	activation energy of initiator decomposition reaction/J mol^{-1}
E_z	activation energy of inhibition reaction/J mol^{-1}
A	frequency factor/min^{-1}
A_p	frequency factor of propagation reaction/dm^3 min^{-1} mol^{-1}
A_d	frequency factor of initiator decomposition reaction/min^{-1}
A_z	frequency factor of inhibition reaction/dm^3 min^{-1} mol^{-1}
α_D	fractional conversion at the onset of the diffusion-limited zone
α_p	fractional conversion at the peak of the DSC curve
f	initiator efficiency
ΔQ_{tot}	total heat of cure/J g^{-1}
ΔQ_t	heat generated at time t/J g^{-1}

1. Introduction

The mechanistic kinetic modelling of the cure of unsaturated polyester (UP) resins is of considerable importance for the optimisation of the many manufacturing processes involving UPs, provided that realistic predictive models can be produced. Not surprisingly, considerable attention has been given to modelling and simulation studies in recent years [1–10]. A number of attempts have been made to model UP cure chemistry using the generally accepted mechanistic steps invoked to describe free radical polymerisation processes. Because of the rapid build-up of a crosslinked network in the cure of unsaturated resins, any model which might be adopted has to account for phenomena such as diffusion-controlled propagation rates and decreasing initiator efficiency with conversion. There have been a number of reports where it has been assumed that the propagation rate constant decreases in an empirical way with conversion [1–7]. Batch and Macosko [8] used a semi-empirical approach to model separately radical trapping processes and falling initiator efficiency with conversion. Other workers have attempted to model cure behaviour by employing the free volume concept and the quasi-steady stage assumption (QSSA) [9, 10]. However, whatever the predictive merits of these methods, they all involve time-consuming parameter optimisation procedures to estimate the kinetic parameters.

A rapid method of obtaining the activation energy and the frequency factor of the overall rate constant of an empirical rate expression, from the relationship between the heating rate and the time to maximum reaction rate, has been described by Ozawa [11]. The approach can be applied to measurements made by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). In this study, the method has been modified so as to be applicable to a mechanistic kinetic model of the cure of UP resins. The theoretical approach was tested by monitoring the cure behaviour of a commercial UP resin using benzoyl peroxide (BPO) as an initiator. An examination of dynamic DSC cure data shows that diffusion-control of the cure is only significant after the point of maximum reaction rate has been reached in this particular case and, thus, the propagation rate constant for the chemically controlled reaction can be evaluated without having to deal with radical trapping or initiator efficiency problems in the model.

2. Theory

2.1. Degree of conversion from reaction exotherm

The basic assumption when monitoring cure kinetics using DSC is that the degree of cure is proportional to the reaction exotherm. Provided that the cure reaction is the only thermal event and that the specific heat capacity of the resin remains constant, the degree of cure α at time t can be obtained from the DSC curve from the equation

$$\alpha_t = \frac{1}{\Delta Q_{\text{tot}}} \int_0^t \frac{\mathrm{d}(\Delta Q_t)}{\mathrm{d}t} \mathrm{d}t \qquad (1)$$

2.2. The Ozawa method for obtaining kinetic parameters

The cure rate of a thermoset resin can, in the most general way, be described by the equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \qquad (2)$$

in which α is the degree of conversion and k is a rate constant which obeys the Arrhenius relationship. For a constant heating rate, β, i.e. $\beta = \mathrm{d}T/\mathrm{d}t$, integration from $\alpha = 0$ to the degree of conversion at time t gives the equation

$$\int_0^{\alpha_t} \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_{T_0}^{T_t} \frac{A}{\beta} \exp(-E/RT)\mathrm{d}T \tag{3}$$

where T_0 it the initial temperature, T_t the temperature at time t, A the frequency factor, E the activation energy and R the molar gas constant. Since the reaction rate is extremely slow at $T < T_0$, it follows that the approximation shown in Eq. (4) can be made

$$\int_{T_0}^{T_t} \frac{A}{\beta} \exp(-E/RT)\mathrm{d}T \approx \int_0^{T_t} \frac{A}{\beta} \exp(-E/RT)\mathrm{d}T \tag{4}$$

Integration of the right-hand side of Eq. (4) gives

$$\left(\frac{AE}{\beta R}\right) F(E/RT) \tag{5}$$

in which the function $F(E/RT)$ can be approximated [12] by use of the relation

$$\log F(E/RT) \approx -2.315 - 0.4567(E/RT) \tag{6}$$

Eq. (6) is valid when $E/RT > 20$. Now, for a given value of α_t, the left-hand side of Eq. (3) is constant. Thus, for a given value of α_t the following is true for any two different heating rates β_1 and β_2 with the corresponding temperatures T_{t1} and T_{t2}

$$\left(\frac{AE}{R\beta_1}\right) F(E/RT_{t1}) = \left(\frac{AE}{R\beta_2}\right) F(E/RT_{t2}) = \ldots \tag{7}$$

Use of Eq. (6) gives

$$\log \beta_1 + 0.4567 \frac{E}{RT_{t1}} = \log \beta_2 + 0.4567 \frac{E}{RT_{t2}} = \ldots \tag{8}$$

If $\log \beta_i$ is plotted against $1/T_i$ for constant values of α, a set of parallel straight lines will be obtained with gradients equal to $(0.4567E)/R$. Thus, E can be determined. Using the value of E, it is then possible to obtain A from the equation

$$\log\left(\frac{AE}{R\beta_i}\right) = \log\left(\int_0^{\alpha_t} \frac{\mathrm{d}\alpha}{f(\alpha)}\right) + 2.315 + 0.4567\left(\frac{E}{RT_{ti}}\right) \tag{9}$$

It has been shown by a number of groups that the degree of conversion at the peak temperature, α_p, on a DSC curve is constant. Hence the method described by Ozawa and used by others appears to provide an effective way of obtaining the overall activation energy and frequency factor of the process from the peak temperatures and the heating rates of a series of dynamic scans. However, the weakness in the approach is that it does not embrace a *mechanistic* kinetic model of the chemistry.

2.3. Kinetic model

Establishing a realistic kinetic model of UP cure is not a simple task. The cure involves the crosslinking of a linear unsaturated polyester with styrene, using a free radical initiator to trigger the process. The formulations are such that a rapid build-up of a 3-D network structure should occur, with the natural consequence that a number of the fundamental reaction steps in the process shown below will become diffusion controlled. The onset of diffusion control leads to radical trapping (unimolecular termination) and to a decrease in initiator efficiency. In most models for the cure of UP resins, these two phenomena have been lumped together and accounted for empirically by a propagation rate constant that decreases with conversion [1–7]. Batch and Macosko [8] proposed a model where the decreasing initiator efficiency and the effect of radical trapping on the radical concentration were treated separately in a semi-empirical fashion, the active radical concentration being computed from the active radical fraction, i.e. the fraction of non-trapped radicals.

It has been assumed by a number of researchers [1–7], and it was shown by Batch and Macosko [8], that the rate constant for bimecular termination is negligible due to the high diffusion resistance in a crosslinking system. The values of the activation energy and the frequency factor of the propagation rate constant obtained in the present study are applicable both to models that use a rate constant that decreases empirically with conversion and to models that use the approach introduced by Batch and Macosko [8].

The following assumptions have been made in deriving the model used in this work:

(i) All the polymerisable double bonds are considered to be identical and a lumped concentration [M] is used as a measure of total unsaturation.

(ii) All free radicals in the system are considered to be identical and a lumped concentration [R] is used as a measure of the concentration of these species.

(iii) Termination by bimolecular processes is negligible.

(iv) The rate constants for initiation, inhibition and propagation obey the Arrhenius relationship.

(v) There are no concentration gradients, e.g. due to the formation of microgels, or temperature inhomogeneities.

(vi) Diffusion control of reaction rate can be accounted for by the use of a propagation rate constant that decreases in an empirical way with conversion or by use of the active radical concept coupled with decreasing initiator efficiency.

Using these assumptions, the kinetic mechanism can be expressed as follows

Initiation: $\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}$

Inhibition: $\mathrm{R}_n + \mathrm{Z} \xrightarrow{k_Z} \mathrm{Q}$

Propagation: $\mathrm{M} + \mathrm{R}_n \xrightarrow{k_p} \mathrm{R}_{n+1}$

where I is initiator, R is free radical, Z is inhibitor, M is monomer, Q is a stable species and *n* is the degree of polymerisation. The governing rate expressions can thus be written

$$\mathrm{d}\alpha/\mathrm{d}t = k_\mathrm{p}[\mathrm{R}](1-\alpha) \tag{10}$$

$$\mathrm{d}[\mathrm{I}]/\mathrm{d}t = -k_\mathrm{d}[\mathrm{I}] \tag{11}$$

$$\mathrm{d}[\mathrm{Z}]/\mathrm{d}t = -k_\mathrm{z}[\mathrm{Z}][\mathrm{R}] \tag{12}$$

$$\mathrm{d}[\mathrm{R}]/\mathrm{d}t = 2fk_\mathrm{p}[\mathrm{I}] - k_\mathrm{d}[\mathrm{Z}][\mathrm{R}] \tag{13}$$

where f is the initiator efficiency and α the fractional conversion. The rate constants are given by

$$k_\mathrm{d} = A_\mathrm{d}\mathrm{e}^{-E_\mathrm{d}/RT} \tag{14}$$

$$k_\mathrm{z} = A_\mathrm{z}\mathrm{e}^{-E_\mathrm{z}/RT} \tag{15}$$

$$k_\mathrm{p} = A_\mathrm{p}\mathrm{e}^{-E_\mathrm{p}/RT} \tag{16}$$

2.4. *Radical trapping and initiator efficiency*

The fraction of the total number of radicals that are trapped in the 3-D network increases with the degree of conversion. The same is true for the initiator efficiency; as the cure proceeds, the initiator efficiency decreases from an initial value to a value close to zero. The onsets of these two phenomena can be estimated by plotting the active radical concentration $[\mathrm{R}]_\mathrm{a}$ versus time as obtained from the equation

$$[\mathrm{R}]_\mathrm{a} = \frac{1}{k_\mathrm{p}(1-\alpha)}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{17}$$

The rate of conversion and the extent of conversion are obtained from DSC curves. The $[\mathrm{R}]_\mathrm{a}$ profile can be obtained straight from isothermal DSC data since k_p is a constant at constant temperature. Employing this technique, it has been estimated that the onsets of decreasing initiator efficiency and radical trapping occur at conversions of approximately 20% under isothermal conditions for a particular vinyl ester resin system [8]. The present study uses dynamic DSC data; hence it is necessary to know the temperature dependence, i.e. the activation energy, of the propagation rate constant to calculate the concentration of active radicals. Since we are only interested in the shape of the curve, it is not necessary to know the value of the frequency factor (nor the value of the propagation rate constant in the isothermal case). Fig. 1 shows $[\mathrm{R}]_\mathrm{a}$ for a 5 K min^{-1} dynamic DSC scan using the activation energy obtained by the method of the present study ($E_\mathrm{p} = 23{,}590\ \mathrm{J\ mol^{-1}}$).

It has been argued that the initiator efficiency starts to decrease at the point on the curve where the gradient starts to decrease [8], and this marks the beginning of the diffusion-limited zone (where $\alpha > \alpha_\mathrm{D}$). The reduction in active radical concentration is due to radical trapping since a decrease in the initiator efficiency on itself cannot cause the gradient to become negative. Thus, it appears as if radical

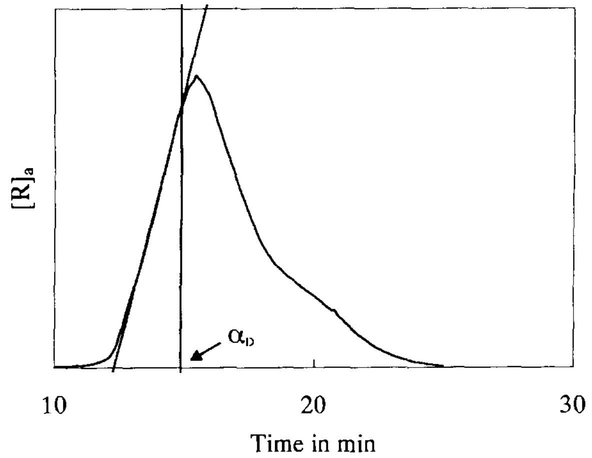

Fig. 1. Active radical concentration profile during a 5 K min^{-1} DSC scan.

trapping on an appreciable scale only begins some time after the initiator efficiency starts to decrease.

The method proposed in the present study only utilises dynamic DSC data from zero conversion to the point on the curve of maximum reaction rate. Thus if $\alpha_D \geq \alpha_p$, the method allows the determination of E_p and A_p without having to consider the effects of radical trapping and decreasing initiator efficiency on the overall kinetics of the process. The onset of the diffusion-limited zone was estimated graphically as outlined above for all the dynamic DSC scans using the value of $E_p = 23{,}590\ \mathrm{J\ mol^{-1}}$ as obtained in this study. The value of α_D decreases with increasing E_p. If $\alpha_D \geq \alpha_p$ with the E_p obtained from the method proposed, then it is safe to say that the criterion $\alpha_D \geq \alpha_p$ is met. The reason for this is that if $\alpha_D < \alpha_p$, the method will given a k_p that is too low, implying that E_p is too high. Reducing E_p to come closer to the true value will increase α_D. If $\alpha_D < \alpha_p$, the vales of E_p and A_p not only define the propagation rate constant for a reaction which is chemically controlled, but also the rate constant where the reaction rate is lowered due to diffusion control. Moreover, if $\alpha_D < \alpha_p$, the radical concentration will be overestimated since the initiator efficiency will actually decrease when $\alpha > \alpha_D$. This will cause a decrease in the estimated value for k_p. These two effects combined will result in too low a value for k_p if the condition $\alpha_D \geq \alpha_p$ is not fulfilled. Rates of conversion from dynamic DSC curves for different heating rates are displayed in Fig. 2. The results summarised in Table 1 show that the onset of the diffusion-limited zone is indeed after the peak on the dynamic DSC curve. The initiator efficiency can thus be assumed to be constant and there is no need to modify the expression for the propagation rate constant or the radical concentration when $\alpha < \alpha_p$.

2.5. *Effective inhibitor concentration*

Commercial UP resins contain a small amount of inhibitor to prevent premature reaction. The inhibitor concentration is often unknown and oxygen, another unknown

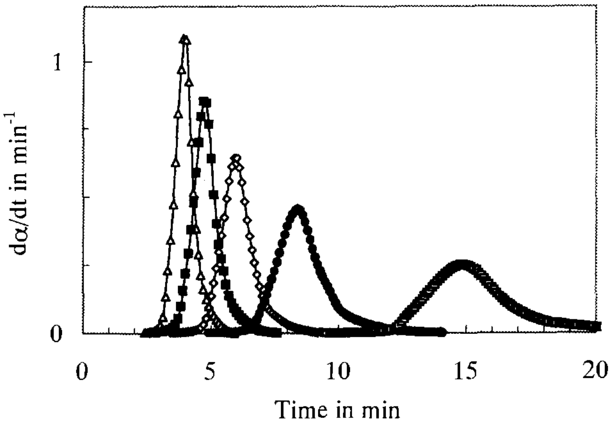

Fig. 2. Rate of conversion from dynamic DSC scans at different heating rates: $T_0 = 293$ K; Δ, 25; ■, 20; ◇, 15; ●, 10; □, 5 K min⁻¹.

Table 1
Conversion at the onset of the diffusion-limited zone and at the peak of the DSC curve for different heating rates.

Heating rate/K min^{-1}	α_D	α_p
5	0.40	0.40
10	0.44	0.42
15	0.41	0.41
20	0.48	0.46
25	0.49	0.47

quantity, is also known to act as an inhibitor. If the quasi-steady state assumption is made for the inhibition zone and if the initial inhibitor concentration is small compared to the initial initiator concentration, the following relationship between the effective inhibitor concentration $[\mathrm{Z}]_{\mathrm{eff}}$ and the inhibition time t_z can be derived [8]

$$[\mathrm{Z}]_{\mathrm{eff}} = 2f[\mathrm{I}]_0 k_d t_z \tag{18}$$

The value of $[\mathrm{Z}]_{\mathrm{eff}}$ was calculated using experimental values of the inhibition time from a series of isothermal DSC measurements.

2.6. Modification of the Ozawa method to include a mechanistic kinetic model

From the model equations for the cure of UP resin, the following relationships can be derived

$$\text{Rate of conversion:}\quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_p[\mathrm{R}](1-\alpha) \tag{19}$$

Heading rate: $$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{20}$$

$$\Rightarrow \frac{\mathrm{d}\alpha}{(1-\alpha)} = \frac{A_\mathrm{p}}{\beta}[\mathrm{R}]\exp(-E_\mathrm{p}/RT)\mathrm{d}T \tag{21}$$

Integration: $$\int_0^{\alpha_\mathrm{p}} \frac{\mathrm{d}\alpha}{(1-\alpha)} = \frac{A_\mathrm{p}}{\beta}\int_0^{T_\mathrm{p}}[\mathrm{R}]\exp(-E_\mathrm{p}/RT)\mathrm{d}T \tag{22}$$

$$\Rightarrow \ln\left(\frac{1}{1-\alpha_\mathrm{p}}\right) = \frac{A_\mathrm{p}}{\beta}\int_0^{T_\mathrm{p}}[\mathrm{R}]\exp(-E_\mathrm{p}/RT)\mathrm{d}T \tag{23}$$

Since α_p is a constant, it follows that the left-hand side of Eq. (23) is constant and does not depend on the heating rate. Thus, for a set of data points (β_i, $T_{\mathrm{p}i}$) Eq. (24) can be written

$$\frac{A_\mathrm{p}}{\beta_1}\int_0^{T_{\mathrm{p}1}}[\mathrm{R}]_1\exp(-E_\mathrm{p}/RT)\mathrm{d}T = \frac{A_\mathrm{p}}{\beta_2}\int_0^{T_{\mathrm{p}2}}[\mathrm{R}]_2\exp(-E_\mathrm{p}/RT)\mathrm{d}T = \ldots \tag{24}$$

Change of the operator to time and simplification gives

$$\int_0^{t_{\mathrm{p}1}}[\mathrm{R}]_1\exp(-E_\mathrm{p}/R(T_0+\beta_1 t))\mathrm{d}t = \int_0^{t_{\mathrm{p}2}}[\mathrm{R}]_2\exp(-E_\mathrm{p}/R(T_0+\beta_2 t))\mathrm{d}t = \ldots \tag{25}$$

where $T = T_0 + \beta t$.

2.7. *Estimation of* E_p *and* A_p

2.7.1. *Optimisation to determine* E_p

For a series of data points (β_i, $t_{\mathrm{p}i}$) from dynamic DSC curves, the value of the activation energy E_p can be determined by minimising the function G shown in Eq. (26), which is derived from Eq. (25)

$$G(E_\mathrm{p}) = \sum_{j=1}^{m} \left| \frac{\int_0^{t_{\mathrm{p}i}}[\mathrm{R}]_i\exp(-E_\mathrm{p}/R(T_0+\beta_i t))\mathrm{d}t}{\int_0^{t_{\mathrm{p}k}}[\mathrm{R}]_k\exp(-E_\mathrm{p}/R(T_0+\beta_k t))\mathrm{d}t} - 1 \right|_j \tag{26}$$

where m is the number of combinations of data points.

2.7.2. *Optimisation to determine* A_p

The value of the frequency factor A_p can be determined by minimising the function P, which is derived from Eq. (23), with respect to A_p using the value of E_p obtained from Eq. (26)

$$P(A_\mathrm{p}) = \sum_{i=1}^{n} \left| \ln\left(\frac{1}{1-\alpha_\mathrm{p}}\right) - A_\mathrm{p}\int_0^{t_{\mathrm{p}i}}[\mathrm{R}]_1\exp(-E_\mathrm{p}/R(T_0+\beta_i t))\mathrm{d}t \right|_i \tag{27}$$

where n is the number of data points.

3. Experimental

3.1. Materials

A general purpose UP resin (Resinous Chemicals Ltd, Ref. No. 1696/18) which comprised maleic anhydride, phthalic anhydride and propylene glycol together with 35% styrene by weight was used as supplied.

Benzoyl peroxide (BPO) (Aldrich Chemical Co. Ltd.) was used as initiator. The peroxide contained 30% water and was purified by extraction with acetone and reprecipitated by adding two volumes of distilled water. The precipitate was dried under vacuum at room temperature for at least 24 h prior to use.

3.2. Differential scanning calorimetry

A differential scanning calorimeter (Perkin-Elmer Model DSC 7) was used for all kinetic studies, which were carried out under an atmosphere of dry nitrogen. Dynamic DSC measurements were carried out from 298 to 473 K with heating rates of 5, 10, 15, 20 and 25 K min^{-1}. Isothermal measurements were made at 348, 353, 358, 363 and 368 K. Typically, the initiator was added to the resin and approximately 10 mg of the reaction mixture was subsequently placed in a previously weighed aluminium sample pan which was re-weighed to obtain the quantity of material used in the DSC measurements. The initiator content was accurately known and approximately 1% wt/wt for the isothermal measurements and 2% wt/wt for the dynamic measurements.

3.3. Simulation and parameter optimisation

A commercially available software package (VisSim Professional Version 1.5d, Visual Solutions Incorporated) was used for simulation and optimisation purposes. Numerical integration was carried out using either the Euler or Backward Euler integration algorithms and parameter optimisation using the Powell routine.

4. Results and discussion

4.1. Total heat of cure

The total heat of cure of the resin was calculated as -374 J g^{-1} based on the theoretical heat of copolymerisation between styrene and fumarate unsaturation in the prepolymer chain of 69,000 J mol^{-1} as estimated by Lucas et al. [13]. Heats of polymerisation are available for many polymerisation systems which makes it possible to use more widely the approach taken in this work [14, 15].

4.2. Isothermal DSC experiments and calculation of $[Z]_{eff}$

The rates of conversion from representative isothermal DSC curves at 348, 358 and 368 K are shown in Fig. 3. The value of $[Z]_{eff}$ was calculated from Eq. (18) for each

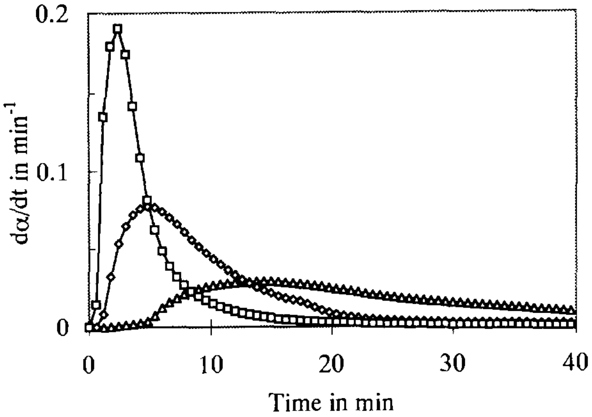

Fig. 3. Rate of conversion from isothermal DSC curves: □, 368; ◇, 358; Δ, 348 K.

temperature employed using values of t_z estimated from the isothermal DSC data. The average value, $[Z]_{eff}$ (1.43×10^{-4} mol dm^{-3}), was subsequently used to compute the radical concentrations as functions of time for the implementation of the method of the present study.

4.3. *Determination of* E_p

The value of E_p was determined by minimising Eq. (26) with respect to E_p. The function that is to be minimised, i.e. that known as the "cost function" in the jargon of the software package used, was designed so as to avoid the minimum being at $E_p = \infty$. Parameter optimisation resulted in a minimum for E_p at 23,590 J mol^{-1}. The values used for the constants appearing in the equations for optimisation are listed in Table 2.

4.4. *Determination of* A_p

In order to minimise the function P (Eq. (27)) with respect to A_p, it is necessary to input a value for the constant α_p. As can be seen in Table 1, the experimental estimation

Table 2
Parameters for optimisation procedures.

Parameter	
Initiator efficiency, f	0.6
E_d [16]	119,600 J mol^{-1}
A_d [16]	9.3242×10^{14} min^{-1}
E_z [4]	70,463.6 J mol^{-1}
A_z [4]	1.062×10^{16} dm^3 mol^{-1} min^{-1}
α_p	0.43
$[Z]_{eff}$	1.43×10^{-4} mol dm^{-3}

Table 3
Results of parameter optimisation procedures using Eq. (27) for different values of α_p

α_p	A_p/dm^3 mol^{-1} min^{-1}
0.43 (average value)	6.78×10^5
0.40	6.09×10^5
0.50	8.27×10^5
0.60	1.09×10^6

of α_p varies between 0.40 and 0.47 although A_p is relatively insensitive to its value, certainly in the context of other published data [1–7]. The accuracy of these values of α_p depends on the accuracy of the DSC method and the value used for the total heat of reaction. Parameter optimisations were carried out using a range of values for α_p, one of which was the average of the values from Table 1. The results are displayed in Table 3.

The values obtained for E_p and A_p result in a lower value for k_p than some reported in the literature [1–7]. It is suggested that this stems from the fact that previously reported values are based on empirical models and that k_p decreases with conversion from the very beginning of reaction. Batch and Macosko [8] provided evidence that diffusion control starts at a later stage and their k_p values are in good agreement with those of the present study.

It is noteworthy that the parameter optimisation was rapid taking approximately 5 min in any given case when using a relatively slow PC. This is in sharp contrast with the methods which require curve fitting over the whole conversion range to obtain multiple unknowns which can be a tedious task. Furthermore, the proposed method requires only two parameters to be determined but not simultaneously, thus avoiding the problem of multiple solutions and local minima. The errors in the estimated parameters are similar in magnitude to those of the Ozawa method, stemming largely from the assumption that the degree of conversion is constant and independent of the heating rate at the point of maximum reaction rate. A full model for the cure process of UP resins utilising the values obtained in the present study and incorporating the free volume concept will be presented elsewhere [17].

5. Conclusions

A new, rapid method has been proposed for the estimation of the activation energy and the frequency factor of the propagation rate constant of a mechanistic kinetic model for the cure of a UP resin from the position of the peak of dynamic DSC cure data. The method has a number of advantages associated with it:

- It uses a realistic model of the cure chemistry and, therefore, has significant advantages over the more commonly reported empirical methods, which are restricted to the specific resin formulation and experimental conditions which have been studied.

- The method does not require an understanding of the effects of radical trapping or the decrease in initiator efficiency on the kinetics at higher conversions.
- The procedure is much less time consuming than methods which require the DSC results to be curve-fitted over the whole conversion range in order to find multiple unknowns.
- Because the optimisation procedure has to estimate only one parameter, the problem of local minima is avoided.
- The method is independent of the quality of the DSC baseline, the initial concentration of polymerisable double bonds in the resin and the total heat of cure.
- The technique can be applied to other mechanistic kinetic models of free radical crosslinking reactions by making suitable adjustments to the model.

Acknowledgement

The authors wish to thank Resinous Chemicals Ltd. for financial support and the EPSRC for their support of the IRC in Polymer Science and Technology.

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