Pergamon

PII: S0014-3057(96)00243-1

Eur. Polym. J. Vol. 33, No. 6, pp. 837–840, 1997

Printed in Great Britain
0014-3057/97 $17.00 + 0.00

CURING KINETICS OF AN ACRYLIC RESIN/EPOXY RESIN SYSTEM USING DYNAMIC SCANNING CALORIMETRY

FUXIANG CHU,[1,2] TIMOTHY McKENNA[1] and SHIDU LU[2]
[1]C.N.R.S.-L.C.P.P./CPE, Bât. F308, 43 Bd du 11 Novembre 1918, B.P. 2077, 69616 Villeurbanne Cedex, France and [2]Research Institute of Chemical Processing and Utilization of Forest Products, Chinese Academy of Forestry, Nanjing 210037, P.R. China

(Received 26 April 1996; accepted 29 May 1996)

Abstract—An analysis of the cure kinetics of epoxy resin with an acrylic copolymer (acrylic acid–butyl acrylate–methylmethacrylate) using a dimethylbenzolamine (DMBA) catalyst is presented. The kinetic studies were carried out with a dynamic scanning calorimeter in both dynamic (Barret, Freeman–Carroll and Kissinger Methods) and isothermal modes of operation. The effects of heating rates and catalyst concentration on the activation energy and reaction order were investigated. The activation energy found in the dynamic experiments was on the order of 22 kcal/mol. In the same set of experiments, the frequency factor of the effective rate constant varied from 4.9×10^8 to $3.6 \times 10^9\ \mathrm{sec}^{-1}$, and the order of reaction increased from 1.2 to 1.4 as a function of the catalyst concentration. On the other hand, the isothermal experiments yielded slightly different results: a frequency factor on the order of $8.9 \times 10^8\ \mathrm{sec}^{-1}$, a reaction order of approximately 1.1, and an activation energy of $17.9\ \mathrm{kcal\ mol}^{-1}$. © 1997 Elsevier Science Ltd

INTRODUCTION

Acrylic resins are widely used in many industrial products, including coatings and adhesives, and are often cured with epoxies in order to improve their hardness, solvent resistance, and many other physical properties [1–3]. The curing reaction itself takes place between epoxy groups and the carboxyl side groups on the acrylic (co)monomers in the acrylic resin. Despite the relatively wide use of this technique, the kinetics of the curing reaction remain poorly understood, and data on polymerising systems remains scarce.

Dynamic scanning calorimetry (DSC) is a technique that has been widely used to evaluate the kinetics of low molecular weight (e.g. amine/epoxy resin, anhydride/epoxy resin) systems, but to the best of our knowledge, no work has been done using this method to evaluate the kinetics of curing reactions of acrylic resin/epoxy resin systems [4–7].

The goal of the present work is thus to use DSC to evaluate the kinetics of a model curing reaction, and to obtain estimates of the kinetic constants using different experimental and theoretical approaches.

EXPERIMENTAL

The experiments were carried out using a Perkin–Elmer DSC 2C dynamic scanning calorimeter (DSC) in both dynamic and isothermal modes. The epoxy resin employed in the current study was a bisphenol A resin (618) obtained from Shell Chemicals, and was used as received. The curing catalyst used here was reagent grade dimethylbenzolamine (DMBA), used as received from Merck.

The acrylic terpolymer of acrylic acid (AA), butyl acrylate (BA), and methyl methacrylate (MMA) was prepared in solution in an ethyl acetate solvent at reflux temperature for 15 hr using AIBN as the free radical initiator (0.2% of the mass of the monomers). The ethyl acetate was first added to the reactor, degassed with N_2 and then heated to reflux temperature. The monomer mixture and initiator were then added semi-batchwise for 5 hr. The polymerisation continued for an additional 10 hr. The composition of the terpolymer was 16.5/18.5/65 (mass) in AA/BA/MMA, respectively. At the end of the reaction, the monomer conversion was 91%. The copolymer thus obtained was precipitated in a mixture of methanol and water (1:1 by mass) and then dried at 120° for 10 hr. The fraction of carboxyl groups in the copolymer was determined by titrating with a KOH–ethanol solution.

The copolymer and epoxy resin were then dissolved in acetone and mixed. The ratio of carboxyl groups to epoxy groups was 1:1 (mol). The DMBA was then added to the homogeneous solution in the different quantities shown in Table 1. Here, the first letter refers to the different concentrations of catalyst, and the accompanying numbers to the heating rates of 2.5, 5, 10 and 20 K min^{-1} in dynamic mode, or temperatures of 400, 410, 420, 430, 440 K in isothermal mode.

The different mixtures were placed on Teflon plates and dried under vacuum for 8 hr at ambient temperature. The DSC runs were performed immediately after drying.

RESULTS AND DISCUSSION

For lack of a more mechanistic description, the rate of the curing reaction under study is often described using an expression of the following form [8]:

$$r_c = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\cdot f(\alpha) = \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\frac{1}{H_0}$$

$$= k(1-\alpha)^n = A\mathrm{e}^{-E_a/RT}(1-\alpha)^n \quad (1)$$

Table 1. Experimental conditions

Experiment	Equivalent groups (mol) Carboxyl:epoxy:catalyst	Heating rate (K min^{-1})	Sample mass (mg)	Total heat (cal g^{-1})
Dynamic				
A20	1:1:0.015	20	11.04	32.58
A10	1:1:0.015	10	13.74	32.28
B20	1:1:0.0315	20	9.74	31.66
B10	1:1:0.0315	10	11.95	32.40
B5	1:1:0.0315	5	12.20	32.83
B2.5	1:1:0.0315	2.5	14.78	33.73
C10	1:1:0.045	10	12.51	30.87

Isothermal

Experiment	Equivalent groups (mol) Carboxyl:epoxy:catalyst	Temperature (K)	Sample mass (mg)	Total heat (cal g^{-1})
B440	1:1:0.0315	440	12.15	25.87
B430	1:1:0.0315	430	12.76	28.94
B420	1:1:0.0315	420	13.13	29.17
B410	1:1:0.0315	410	13.65	28.53
B400	1:1:0.0315	400	12.66	27.63

where α is the conversion, k an effective reaction rate constant (assumed to obey the Arrhenius law: $k = A\exp(-E_a/RT)$), E_a is the activation energy (kcal mol^{-1}) of the curing reaction, A is the Arrhenius frequency factor, R the universal gas constant, T the absolute temperature (K), H the amount heat released by the reaction up to time t, H_0 is the total amount of heat released (total heat in Table 1), over the course of the entire reaction, and n is the reaction order.

If equation (1) is rewritten in the well known form of the Barret equation [8]:

$$\ln\left(\frac{\mathrm{d}H}{\mathrm{d}t}\frac{1}{H_0}\right) - n\ln\left(1 - \frac{H}{H_0}\right) = -\frac{E_a}{RT} + \ln A = \ln k \tag{2}$$

then a single dynamic DSC experiment can be used in order to determine any two of n, $\ln A$ or E_a if the third quantity is known *a priori*. Figure 1 shows a plot of this equation for experiment B10 (n assumed to be equal to 1.3). A linear relationship was found for the conversion interval 1–90% (even higher in some experiments).

By evaluating the total heat released (H_0) and instantaneous rate of heat release ($\mathrm{d}H/\mathrm{d}t$) for a given interval of time (Δt), the Freeman–Carroll relationship can be used to estimate the both activation energy and n without requiring that any parameters be known beforehand [9]:

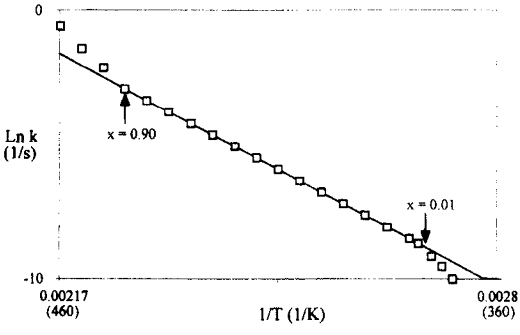

Fig. 1. Graph of equation (2) (ln k vs $1/T$) for experiment B10 with n assumed to be of the order of 1.3. x = conversion (mol.).

$$\frac{\Delta\ln(\mathrm{d}H/\mathrm{d}t)}{\Delta\ln(H_0 - H)} = -\frac{E_a\Delta(1/T)}{R\Delta\ln(H_0 - H)} + n \tag{3}$$

Linear regression of equation (3) yields values for E_a and n. The results of this type of analysis of the DSC results are shown in Table 2 [note that the conversion interval considered refers to that portion of the results where a linear relationship was observed between the left hand side of equation (3)—see Fig. 1—and $\Delta(1/T)/(R\Delta\ln(H_0 - H))$], where it can be seen that the order of reaction depends on both heating rates and catalyst concentration, with the reaction rate order increasing as the heating rate decrease, and decreasing as the catalyst concentration increases. Any effect of heating rate on E_a is difficult to discern clearly with this technique, and, as seen from the value of the correlation coefficient (r^2), the overall fit of the data for each experiment is satisfactory.

We can use the values of n shown in Table 2 to evaluate E_a and $\ln A$ (equivalently, $\ln k$) using expression (2). These results are shown in Table 3.

From these results, it appears that both the activation energy and the Arrhenius constant are essentially independent of the heating rate (as with the Freeman–Carroll analysis) and the catalyst concentration. The average activation energies observed using the Freemann–Carroll method and equation (2) are in good agreement.

In a slightly different vein, Kissinger [10] developed the following relationship to calculate E_a and $\ln A$ from the maxima of the curves of a DSC experiment:

$$\frac{\phi}{T_p^2} = \left[\frac{AR}{E_a}n(1 - \alpha_p)^{n-1}\right]e^{-E_a/RT_p}, \tag{4}$$

where ϕ is the rate of temperature increase, and the subscript "p" refers to the value of the given parameter at the peak, or maximum of the DSC curve of the corresponding experiment. Using this method and assuming that the term $n(1 - \alpha_p)^{n-1}$ is independent of the heating rate, Kissinger proposed that a series of experiments using different heating rates (the log of ϕ^2/T_p^2 is plotted vs $1/T$) could be used to estimate an activation energy. Peak temperature and

Table 2. Results of Freeman–Carroll analysis

	E_a	Conversion	Correlation	Correlation
Experiment	n	(kcal mol^{-1})	interval	coefficient
A20	1.39	20.69	0.026–0.986	0.996
A10	1.41	22.48	0.043–0.995	0.998
B20	1.25	22.9	0.025–0.999	0.998
B10	1.29	22.63	0.029–0.987	0.999
B5	1.31	23.77	0.048–0.999	0.995
B2.5	1.33	22.76	0.20–0.993	0.995
C10	1.17	24.38	0.011–0.986	0.992
Average E_a (kcal/mol)		22.80		

Table 3. E_a and ln A estimated using equation (2) and Table 2

E_a	ln A	Conversion	Correlation	Correlation
Experiment	(kcal/mol)	(s^{-1})	interval	coefficient
A20	21.56	20.5	0.007–0.983	0.9989
A10	21.54	20.5	0.008–0.987	0.9995
B20	22.15	21.8	0.007–0.926	0.9993
B10	22.02	21.8	0.006–0.895	0.9992
B5	22.15	22.1	0.003–0.931	0.9995
B2.5	21.1	21.0	0.020–0.912	0.9995
C10	21.92	22.0	0.010–0.855	0.9978
Averages	21.78	21.4		

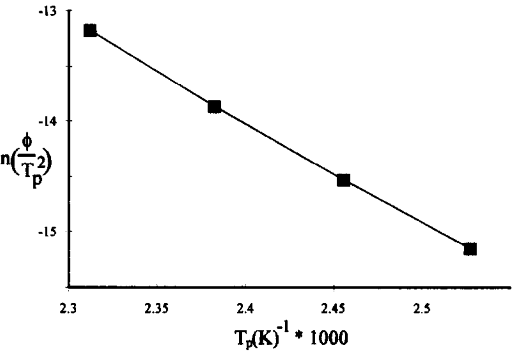

Fig. 2. Plot of the Kissinger relationship (equation (4)) for catalyst concentration B. Linear regression yields an estimate of $E_a = 18.9$ kcal mol^{-1}, and ln $A = 20.6$ sec^{-1}.

conversion data are given in Table 4, and a plot of the logarithmic form of equation (4) is shown in Fig. 2 for the B-series of experiments.

The estimate of 18.9 kcal/mol obtained from the regression of these data is appreciably lower than the values previously estimated for the activation energy. This is usually the case with the Kissinger technique, as has been illustrated by other authors, for example Ref. [11]. Furthermore, if one supposes that the value of the term $n(1-\alpha_p)^{n-1} \approx 1$ (e.g. for B20, $n(1-\alpha_p)^{n-1} \approx 1.019$), then the simplified form of the Kissinger expression can be used to find the frequency factor. Here it is estimated that ln$A$ is 20.6 sec^{-1}—a value that agrees more or less with that obtained using equation (2) (see Table 3).

In a similar fashion, if we rearrange equation (1) in terms of $(1-\alpha)^n$ and substitute the result into equation (4), we can use the resulting expression to estimate E_a/n:

$$\frac{E_a}{n} = \frac{RT_p^2}{(1-\alpha_p)\phi}\left(\frac{d\alpha}{dt}\right)_p = \frac{RT_p^2}{(H_0-H)\phi}\left(\frac{dH}{dt}\right)_p. \qquad (5)$$

This approach yields an estimate of the ratio in question using only one experiment, as opposed to a series of several experiments as is needed in the Kissinger approach. However, as with equation (2), it is necessary to know n in order to determine E_a (or vice versa). The results of this type of analysis are shown in Table 5.

Here we see the values of E_a/n estimated using equation (5), values of E_a computed using the calculated ratio and the values of n from Table 2, and estimates of n using the same ratio and values of E_a from Table 3.

The results shown in Table 5 are similar to those in Tables 2 and 3, with, as expected, the order of reaction decreasing as catalyst concentration increases, and increasing as the heating rate decreases. Again, as with the results in Tables 2 and 3, the average activation energy estimated from these experiments is higher than that obtained with the Kissinger technique. However, the average value of this last parameter is not significantly different from the estimates obtained using the other two tech-

Table 4. Peak values for Kissinger expression

Experiment	T_p (K)	α_p	$(dH/dt)_p$ (cal sec^{-1})
A20	445.15	0.5606	19.26×10^{-5}
A10	432.29	0.5530	10.06×10^{-5}
B20	432.79	0.5577	20.88×10^{-5}
B10	419.49	0.5552	11.29×10^{-5}
B5	407.40	0.5501	5.98×10^{-5}
B2.5	395.61	0.5414	3.19×10^{-5}
C10	414.22	0.5683	11.4×10^{-5}

Table 5. E_a/n using equation (5), and estimates of E_a and n

Experiment	E_a/n	E_a	n (Table 3)
A20	15.90	22.10	1.37
A10	15.54	21.91	1.40
B20	16.89	21.11	1.29
B10	16.44	21.21	1.32
B5	16.02	20.99	1.36
B2.5	15.40	20.48	1.41
C10	17.5	20.48	1.24
Average E_a (kcal mol^{-1})		21.18	

Table 6. Results of isothermal runs and data for regression of equation (6)

Experiment	n	Conversion $(1\text{-}n)\ln H_0 + \ln k$	Correlation interval	Correlation coefficient	$\ln k$ ($k[=]\mathrm{s}^{-1}$)
A440	1.14	−4.10	0.193–0.860	0.9998	−3.64
A430	1.12	−4.51	0.152–0.865	0.9999	−4.10
A420	1.11	−5.04	0.196–0.894	0.9991	−4.67
A410	1.10	−5.44	0.214–0.922	0.9997	−5.12
A400	1.04	−5.80	0.223–0.860	0.9997	−5.67

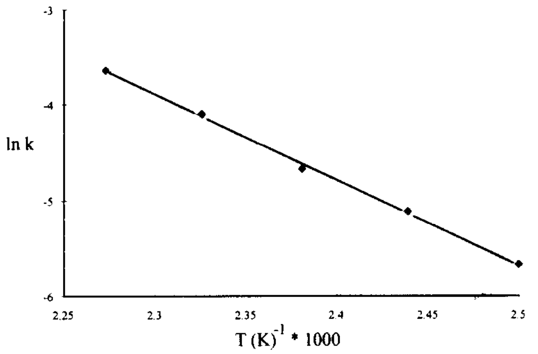

Fig. 3. Arrhenius plot of isothermal runs. $E_a = 17.92$ kcal mol^{-1}, $\ln A = 22.9$ s^{-1}.

niques. On the other hand, a temperature effect is visible: it appears that decreasing the heating rate also leads to a decrease in the estimated activation energy.

In the case of the isothermal experiments, it should be noted that the total heat released (i.e. H_0) is very difficult to measure with precision due to the extremely rapid rate of reaction that occurs during the first instants of the experiments. However, after the first few moments, during which accurate estimates of H (and thus H_0) are difficult to obtain, it is possible to precisely measure the difference $H_0 - H$. With this in mind, the isothermal form of equation (2) can be written:

$$\ln\left(\frac{dH}{dt}\right) = n\ln(H_0 - H) + (1-n)\ln H_0 + \ln k, \quad (6)$$

where the slope of the regression line $\ln(dH/dt)$ vs $\ln(H_0 - H)$ is independent of the absolute value of H_0. By plotting this line, one can estimate a value of n with precision and $\ln k$ from a given experiment. By performing this operation at different temperatures, one can use the data for $\ln k$ to draw an Arrhenius plot and simultaneously estimate E_a and A, but to do so it is necessary to use the estimate of H_0 obtained from this technique (which, as stated above, is difficult to estimate accurately because of the initial exotherm). Estimates of k obtained in this fashion should thus be viewed with caution, but the value of n obtained from the regression of equation (6) can be assumed to be accurate. The data from the isothermal runs are shown in Table 6, and the resulting Arrhenius plot is shown in Fig. 3. The results of the isothermal run are distinctly different from those of the dynamic experiments. It can be seen from Table 6 that the order of the isothermal reaction is significantly lower than that observed in the other runs, between 1.04 and 1.14, and that it increases with increasing temperature. The activation energy is also estimated to be much lower, of the order of 17.92 kcal mol^{-1}. This last result has been observed for many similar curing reactions, where it was found that the kinetic parameters obtained from the isothermal experiments were lower than those obtained from the dynamic runs [12–14]. This value is relatively close to the value of 18.9 kcal/mol obtained with the Kissinger method—a result that is not particularly surprising given the similarity of the two methods in the approach they take in estimating E_a.

CONCLUSIONS

The amine catalysed cure reaction of an acrylic resin/epoxy resin system was studied using both dynamic and isothermal DSC experiments to obtain kinetic data. The dynamic DSC experiments performed in this work revealed that the frequency factor and activation energy of the curing reaction between an epoxy resin and an acrylic copolymer appear to be independent of the catalyst concentration and heating rate. However, decreasing the catalyst concentration increased the order of reaction—a result which is to be expected. A decrease in the heating rate also had the same effect. The isothermal experiments yielded slightly different results, with all kinetic parameters being lower in these tests.

REFERENCES

1. Japanese Patent No. 63,56,520, 1988.
2. European Patent No. 286,904, 1988.
3. German Patent No. 2,621,656, 1977.
4. Duffy, J. V., Hui, E. and Hartmann, B., *J. Appl. Polym. Sci.*, 1987, **33**, 2959.
5. Patel, M. B., Patel, R. G. and Patel, V. S., *Thermoc. Acta*, 1988, **129**, 277.
6. Padma, A., Rao, R. M. V. G. K., Subramaniam, C. and Nagendrappa, G., *J. Appl. Polym. Sci.*, 1995, **57**, 401.
7. Jagadeesh, K. S. and Siddaramaiah, *J. Appl. Polym. Sci.*, 1991, **43**, 1459.
8. Barret, K. E. J., *J. Appl. Polym. Sci.*, 1967, **11**, 1617.
9. Freemann, E. S. and Carroll, B., *J. Phys. Chem.*, 1958, **62**, 394.
10. Kissinger, H. E., *Anal. Chem.*, 1957, **29**, 1702.
11. Reed, R. L., Weber, L. and Gottfried, B. S., *Ind. Eng. Chem. Fund.*, 1965, **4**, 38.
12. MacCallum, J. P. and Tanner, J., *Nature*, 1970, **225**, 1127.
13. Prime, R. B., *Anal. Calorimetry*, 1970, **2**, 201.
14. Prime, R. B. and Sacher, E., *Polymer*, 1972, **13**, 455.