

Curing kinetics of diallyl phthalate in the presence of dicumyl peroxide as catalyst. A comparison of different data analysis techniques

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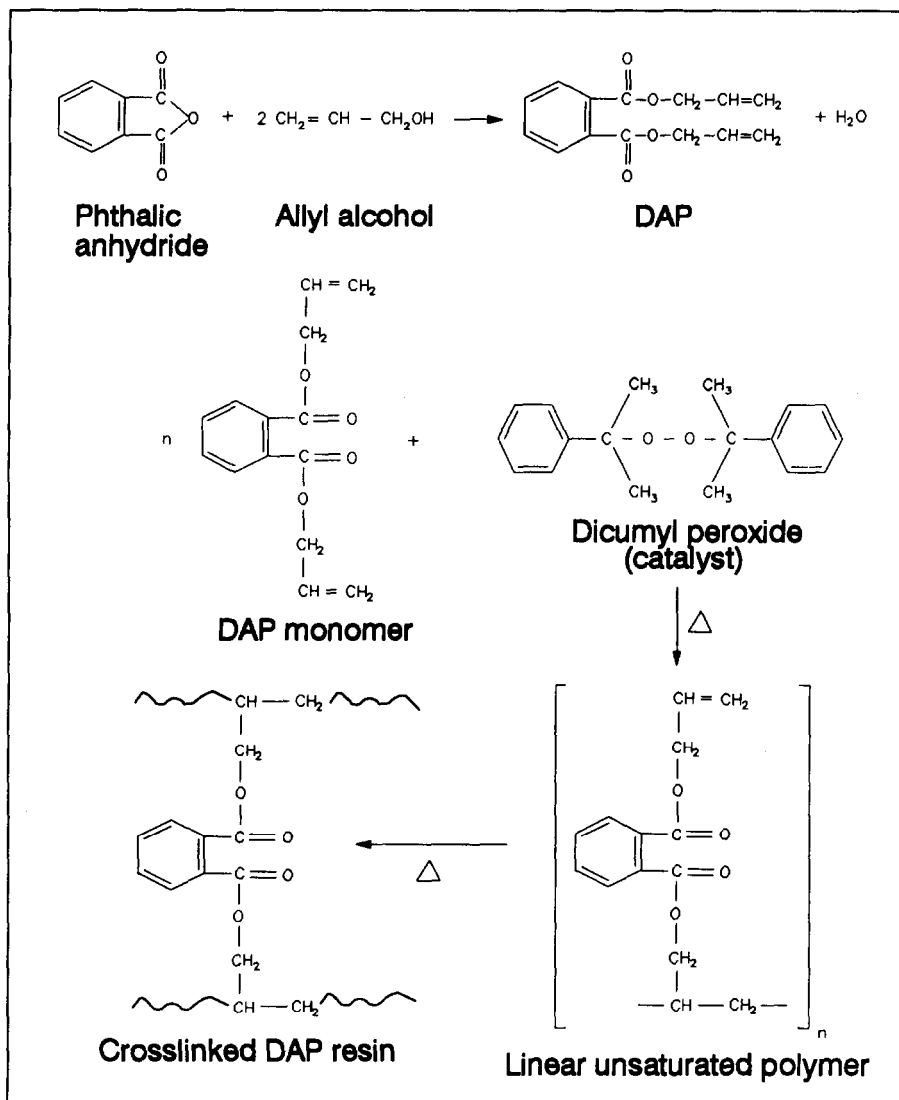
Abstract

The curing kinetics of diallyl phthalate in the presence of dicumyl peroxide as catalyst were studied by means of the single dynamic temperature scan DSC method. The curing process is accomplished by the liberation of heat and appears as an exotherm on the DSC thermogram. Different data analysis methods were employed to analyse the reaction exotherm and to obtain the kinetic parameters. The rate constants obtained by means of the cut-and-weigh method, as well as those calculated from the residual heats of reaction after different oven curing times, were in excellent agreement with the values obtained by using the Borchardt and Daniels DSC kinetics data analysis software (supplied by Du Pont). It was evident from the results of this study that all the data analysis methods were suitable for determining the kinetic parameters of thermoset curing reactions which follow first-order kinetics. However, this study has shown conclusively that the analysis speed and simplicity of the Borchardt and Daniels DSC kinetics program make this the preferred method for obtaining quantitative reaction kinetics information for the curing of thermoset resins.

INTRODUCTION

Diallyl phthalate (DAP) is prepared by the reaction of phthalic anhydride with allyl alcohol [1]. The most valuable property of DAP is its ability to be transformed from the liquid state to a tough thermoset solid. The conversion is accomplished by the addition of a chemically active compound. In most applications, DAP is polymerized in two stages. In the first stage, the monomer is carefully heated at about 100°C in the presence of a free-radical initiator. This yields an essentially linear polymer composed of monomer units that are linked through one allyl group per

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Scheme 1.

unit. On further heating of the polymer, a highly crosslinked structure is obtained. The polymerization and crosslinking reactions are summarized in Scheme 1. The curing process is accomplished by the liberation of heat and appears as an exotherm on the differential scanning calorimetry (DSC) thermogram. It is this exotherm that must be analysed to determine the kinetics of the curing reaction.

Reaction kinetics in general has been studied extensively and numerous techniques have been used. These include monitoring the change in refractive index, determining the amount of unreacted groups by NMR,

infrared, Fourier transform infrared and UV spectroscopy, and classical volumetric titration methods. Various methods have been reported for determining reaction kinetics by DSC. Isothermal reaction kinetics requires numerous thermograms over a range of reaction temperatures. The multiple dynamic temperature scan methods followed by Ozawa [2] and Kissinger [3] utilize a number of thermograms generated by the use of different heating rates.

Methods for obtaining reaction kinetics information from a single dynamic differential scanning calorimetry/differential thermal analysis (DSC/DTA) temperature scan greatly decrease the time necessary for analysis and have been reported by several authors [4–17]. Various reaction kinetics methodologies for DSC, including the multiple dynamic temperature scan approach [2, 3], the single dynamic temperature scan approach of Prime [5, 6] and the single dynamic temperature scan approach of Borchardt and Daniels [4], have been reviewed comprehensively by Provder et al. [18]. Useful quantitative reaction kinetics information regarding the curing of coating systems such as powder coatings, gel coat systems, and an alkyd amino-based casket varnish coating, have been obtained by using the single dynamic temperature scan DSC method [18].

Willard [8] has studied the polymerization and curing of DAP monomer catalysed with dicumyl peroxide and has proposed a method for determining the kinetic parameters, i.e. the reaction rate constant, activation energy and Arrhenius frequency factor, by DSC. A linearly-rising temperature program was used and the curing times for specific degrees of cure at a constant temperature were calculated. The degrees of cure were then compared with those obtained by means of infrared spectroscopy, where the ratio of the absorbance at 1598 cm^{-1} (due to double bonds in the aromatic ring) to the absorbance at 1645 cm^{-1} (due to unsaturation in the olefinic monomer) has been used to calculate the concentration of unreacted monomer.

In the present study, the curing kinetics of DAP in the presence of dicumyl peroxide as catalyst were studied by means of the single dynamic temperature scan DSC method. Three different data analysis techniques were employed. In the first approach, the basic methodology of Borchardt and Daniels was used. Du Pont supplies the Borchardt and Daniels DSC kinetics data analysis software (hereafter referred to as BDK), which simplifies the task of analysing the reaction exotherm and determining the kinetic parameters. In the second approach, the thermograms were analysed manually by means of the cut-and-weigh method (hereafter referred to as CWM), using the data analysis method of Willard [8].

The third approach, discussed by Cizmeioglu et al. [19], was to determine the extent of cure from the residual heats of reaction after different curing times. This paper discusses and compares the kinetic

parameters obtained by means of these three different data analysis techniques.

DATA ANALYSIS METHODS

Method according to Du Pont's BDK software

In the single dynamic temperature scan approach of Prime [5, 6], it has been shown that the fraction reacted $F(t, T)$ is a function of time and temperature and therefore the total derivative $dF(t, T)$ must be expressed as a function of time and temperature

$$dF(t, T) = \left[\frac{\partial F(t, T)}{\partial t} \right]_T dt + \left[\frac{\partial F}{\partial T} \right]_t dT \quad (1)$$

The rate expression $dF(t, T)/dt$ is then given by

$$\frac{dF(t, T)}{dt} = \left[\frac{\partial F(t, T)}{\partial t} \right]_T + \left[\frac{\partial F(t, T)}{\partial T} \right]_t \phi \quad (2)$$

where t is the time (s), T is the absolute temperature (K), and $\phi = dT/dt$ (K s^{-1}).

Kissinger [17], Hill [16] and Simmons and Wendlandt [20] have shown that the term $[\partial F(t, T)/\partial T]_t$ in eqn. (2) is always zero. The rate expression therefore becomes

$$\frac{dF(t, T)}{dt} = \left[\frac{\partial F(t, T)}{\partial t} \right]_T dt \quad (3)$$

The rate expression for the single dynamic temperature scan approach is therefore described by the isothermal kinetics equations. The working equations consist of the general n th-order rate expression and the Arrhenius equation, and are analogous to the equations proposed by Borchardt and Daniels [4] for studying reaction kinetics by DTA. The general rate expression is given by

$$\frac{dF(t, T)}{dt} = k(T)[1 - F(t, T)]^n \quad (4)$$

where $F(t, T)$ is the fractional conversion, $k(T)$ is the reaction rate constant (s^{-1}), n is the reaction order, and T is the temperature (K). The fractional conversion $F(t, T)$ is defined as the ratio of the partial heat of reaction at a given temperature $H(t, T)$ to the total heat of reaction ΔH_0

$$F(t, T) = H(t, T)/\Delta H_0 \quad (5)$$

The rate constant $k(T)$ can be expressed in terms of the observable

variables obtained from the DSC scan and, subsequently, can be related to the activation energy E and the frequency factor Z of the Arrhenius equation. Substituting eqn. (5) into eqn. (4) and solving for the rate constant $k(T)$ in logarithmic form yields the expression

$$\ln k(T) = \ln \left\{ \left[\frac{dH(t, T)}{dt} \right] / \frac{[\Delta H_0 - H(t, T)]^n}{\Delta H_0^{n-1}} \right\} \quad (6)$$

where ΔH_0 is the total heat of reaction (mW), $H(t, T)$ is the amount of heat evolved up to time t and temperature T (mW), $dH(t, T)/dt$ is the time- and temperature-dependent heat flow (mW s⁻¹), and n is the reaction order.

All of the quantities on the right side of eqn. (6) are observable parameters except for the reaction order n . By substituting the Arrhenius expression shown in eqn. (7) into eqn. (6), eqn. (8) is obtained

$$\ln k(T) = \ln Z - E/RT \quad (7)$$

where E is the activation energy (J mol⁻¹), Z is the Arrhenius frequency factor (s⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (K)

$$\ln Z - E/RT = \ln \left\{ \left[\frac{dH(t, T)}{dt} \right] / \frac{[\Delta H_0 - H(t, T)]^n}{\Delta H_0^{n-1}} \right\} \quad (8)$$

The isothermal fractional conversion as a function of time (t) and temperature (T) is obtained by integrating the rate expression to yield

$$F(t, T) = 1 - [(n - 1)k(T)t + 1]^{1/(1-n)} \quad (9)$$

For the case where $n = 1$

$$F(t, T) = 1 - e^{-k(T)t} \quad (10)$$

Equation (8) can be rewritten to give

$$\ln \left\{ \frac{1}{\Delta H_0} \left[\frac{dH(t, T)}{dt} \right] \right\} = \ln Z - E/RT + n \left\{ \ln \left[\frac{\Delta H_0 - H(t, T)}{\Delta H_0} \right] \right\} \quad (11)$$

which is of the form

$$P = a + bx + cy \quad (12)$$

Data are fitted to this expression by a multiple regression technique [21]. The BDK method therefore permits the calculation of the parameters E and Z in the Arrhenius expression (eqn. (7)), as well as the heat of reaction (ΔH_0) and the reaction order (n), from a single DSC scan of a reaction exotherm. Details of the automated data acquisition of the DSC were reported by Niemann et al. [22] and Kah et al. [23, 24]. The rate constant $k(T)$ can be calculated from eqn. (7).

Data analysis method of Willard [8]

Figure 1 shows a typical reaction exotherm obtained by the single dynamic temperature scan DSC method. Basically, the method of Willard [8] involves the determination of the area under the curve. This area is equivalent to the total heat evolved during the reaction. The total area is symbolized by A . Similarly, the area up to a certain temperature or time, which is equivalent to the partial heat of reaction, is determined. This area is symbolized by a .

It is assumed that the reaction does not occur before departure from the baseline and that it is completed by return to the baseline. It is also assumed that the amount of unreacted material ($A - a$) is given to the right of an ordinate at any particular time or temperature. Therefore, in Fig. 1 the dotted baseline has a dotted ordinate erected and the area to the right of this ordinate is considered to be unreacted material at that time or temperature [8].

For first-order kinetics, the rate equation is

$$-dC/dt = kC \quad (13)$$

If the reaction follows the Arrhenius relationship

$$k = Z e^{-E/RT} \quad (14)$$

and if the temperature increases at a rate given by

$$T = T_0 + qt \quad (15)$$

eqns. (13)–(15) can be combined to obtain

$$dC/dt = -ZC e^{[E/R(T_0+qt)]} \quad (16)$$

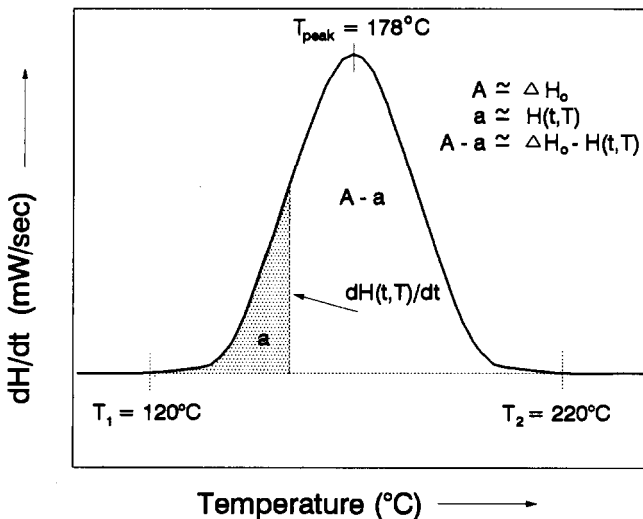


Fig. 1. Schematic diagram of a typical exothermic peak observed by DSC for the curing of DAP.

For first-order reactions, the reaction rate constant is given by

$$k = \frac{dH/dt}{A - a} \quad (17)$$

By measuring the heights of the ordinates at given temperatures and the areas under the curves to the right of these ordinates, the reaction rate constants k for a series of temperatures can be calculated from a single DSC scan. The areas under the curves can be determined by means of either a numerical method or a planimeter. If the reaction follows first-order kinetics, a plot of $\ln k$ versus the reciprocal of the absolute temperature will be linear. The activation energy E can be calculated from the slope of the $\ln k$ versus $1/T$ plot. For any given temperature, the concentration at any time at that temperature can be calculated by using the expression

$$\log C = \frac{kt}{-2.303} \quad (18)$$

Extent of cure from residual heats of reaction

The measurement of the residual heat of reaction after different curing times represents another independent technique by which the degree of cure can be determined. The extent of cure can be calculated from

$$x = \frac{H_T - H_R}{H_T} \quad (19)$$

where x is the fraction that has reacted, H_T is the total heat of reaction and H_R is the residual heat of reaction [19].

EXPERIMENTAL

Materials

Diallyl phthalate (99%) was purchased from Aldrich Chemical Company and dicumyl peroxide was obtained from Hercules Inc., Wilmington, USA.

DSC experiments and BDK analyses

Samples of DAP which contained 3 parts per hundred of dicumyl peroxide were analysed by DSC, using a Du Pont 9900 computer/thermal analyser and its Model 910 DSC module. Indium metal was used as calibration standard. Samples were heated in open aluminium pans at a linear heating rate of $10^\circ\text{C min}^{-1}$. The sample mass was restricted to approximately

15 mg. The resulting reaction exotherms were analysed by means of the BDK software, which permitted the calculation of the reaction order, the heat of reaction, the activation energy and the Arrhenius frequency factor, as well as the calculation of the rate constants at various temperatures.

Cut-and-weigh method (CWM)

A baseline was drawn to the DSC curve and the curve was cut out and weighed. The mass of the curve is equivalent to the total heat of reaction ΔH_0 . The value of $dH(t, T)/dt$ was obtained by erecting ordinates at different temperatures and measuring the heights of these ordinates. The partial heat of reaction $H(t, T)$ at a particular temperature was obtained by cutting away the area to the left of the ordinate and by weighing the remaining area. The latter is equivalent to the amount of unreacted monomer.

In Fig. 1, the vertical dotted line represents the ordinate $dH(t, T)/dt$. By applying conversion factors, the masses (in mg) were converted to mW for $[\Delta H_0 - H(t, T)]$ and the heights of the ordinates (in mm) were converted to mW s^{-1} for $dH(t, T)/dt$. The rate constants k at various temperatures were obtained by using eqn. (17).

Extent of cure from residual heats of reaction

The extent of cure was determined by DSC as described earlier. The residual heat of reaction H_R (eqn. (19)) was determined on partially cured samples in open aluminium pans. The samples were partially cured for different periods of time in an air-circulating oven at a temperature of 160°C before they were analysed by DSC. The total heat of reaction H_T was obtained by using an uncured sample. Reaction exotherms were analysed by means of the BDK software to obtain the values of n , ΔH , E , and Z .

RESULTS AND DISCUSSION

A DSC thermogram of DAP catalysed with 3 parts per hundred of dicumyl peroxide is shown in Fig. 2. The reaction exotherm appeared in the temperature range of 120 – 220°C , with a peak maximum at 178°C . Analysis of this exotherm by means of the BDK program gave a reaction order n of 0.71, a total heat of reaction ΔH_0 of 558 J g^{-1} , an activation energy E of $146.6 \text{ kJ mol}^{-1}$ and an Arrhenius frequency factor $\log Z$ of 16.91 min^{-1} . The temperature-dependent rate constants $k(T)$, determined by BDK analysis of the reaction exotherm, are shown in Table 1.

Kinetic data obtained by the CWM and data analysis according to the method of Willard [8] are given in Table 2. In Fig. 3, the rate constants

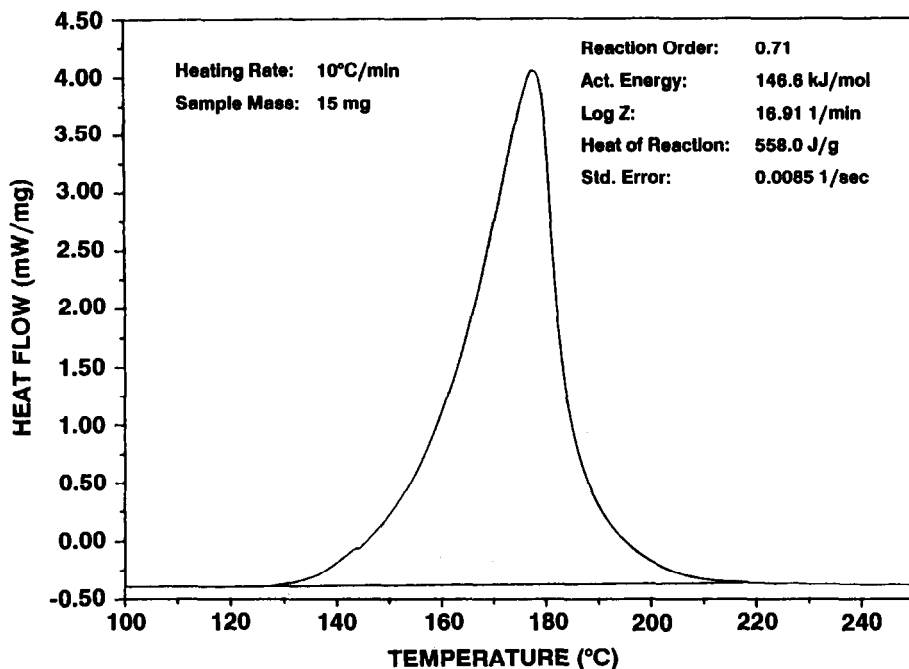


Fig. 2. DSC thermogram of DAP catalysed with 3 parts per hundred of dicumyl peroxide.

$k(T)$ determined by the CWM are compared with those calculated by means of the BDK program. This figure shows that, in the temperature range of 140–168°C, the results obtained by means of the CWM were in excellent agreement with those obtained by using the BDK software. Above 160°C, the values obtained by the CWM were slightly higher than those obtained by BDK analysis.

Samples of DAP cured in an air-circulating oven for different periods of time have also been analysed by means of the single dynamic temperature scan DSC method. The curing exotherms were analysed by means of the BDK program to obtain the residual heats of reaction. The values of E , $\log Z$, ΔH and n , obtained after various oven curing times, are shown in Table 3. The extent of cure of these samples was calculated from the residual heats of reaction by using eqn. (19). The rate constants k at 160°C, determined by measuring the residual heats of reaction H_R after different curing times, are given in Table 4. The rate constants were calculated by using the first-order rate equation

$$k = \frac{2.303}{t} \log \frac{100}{100 - x} \quad (20)$$

where x is the extent of cure after time t .

The average rate constant at 160°C was 0.00291 s^{-1} . This value compares very well with the values obtained by means of the CWM and the BDK

TABLE 1

Rate constants $k(T)$ at various temperatures obtained by BDK analysis of reaction exotherm

Temp. (°C)	Temp. (K)	1000/Temp. (K ⁻¹)	$k(T)$ (s ⁻¹)	ln $k(T)$ (s ⁻¹)	Half life (min)
140	413.15	2.4204	0.00040	-7.83	26.36
142	415.15	2.4088	0.00049	-7.63	21.47
144	417.15	2.3972	0.00060	-7.42	17.52
146	419.15	2.3858	0.00073	-7.22	14.32
148	421.15	2.3745	0.00089	-7.02	11.73
150	423.15	2.3632	0.00109	-6.82	9.62
152	425.15	2.3521	0.00132	-6.63	7.91
154	427.15	2.3411	0.00161	-6.43	6.52
156	429.15	2.3302	0.00195	-6.24	5.38
158	431.15	2.3194	0.00235	-6.05	4.44
160	433.15	2.3087	0.00284	-5.86	3.68
162	435.15	2.2981	0.00343	-5.68	3.05
164	437.15	2.2875	0.00412	-5.49	2.54
166	439.15	2.2771	0.00496	-5.31	2.11
168	441.15	2.2668	0.00594	-5.13	1.76
170	443.15	2.2566	0.00712	-4.95	1.47
172	445.15	2.2464	0.00851	-4.77	1.23
174	447.15	2.2364	0.01016	-4.59	1.08
176	449.15	2.2264	0.01211	-4.41	0.86
178	451.15	2.2166	0.01440	-4.24	0.73
180	453.15	2.2068	0.01711	-4.07	0.61
182	455.15	2.1971	0.02030	-3.90	0.52
184	457.15	2.1875	0.02405	-3.73	0.44
186	459.15	2.1779	0.02844	-3.56	0.37
188	461.15	2.1685	0.03359	-3.39	0.31
190	463.15	2.1591	0.03962	-3.23	0.26

program. In Table 5, the rate constants at 140 and 160°C, obtained using the three different data analysis techniques, are compared with the values obtained by Willard [8]. It is clear that the rate constants obtained by means of the different data analysis techniques employed in this study are in very good agreement with the values reported in the literature.

The BDK program can generate an Arrhenius plot within seconds after the curing exotherm has been analysed. It also supplies the values of the activation energy and the Arrhenius frequency factor after each analysis. As mentioned earlier, the value of the activation energy obtained by BDK analysis of the exotherm was 146.6 kJ mol⁻¹. This value compares well with the activation energy obtained by Willard [8], namely 35.99 kcal mol⁻¹ (which is equivalent to 150.8 kJ mol⁻¹).

The kinetic data obtained by the CWM, as summarized in Table 2, were used to draw an Arrhenius plot, i.e. a plot of ln $k(T)$ versus 1000/temp.

TABLE 2

Rate constants $k(T)$ at various temperatures obtained by CWM and data analysis according to Willard [8]

Temp. (°C)	Mass (mg)	$A - a$ (mW)	dH/dt (mm)	dH/dt (mW s ⁻¹)	$k(T)^a$ (s ⁻¹)	$\ln k(T)$ (s ⁻¹)	1000/temp. (K ⁻¹)
120-220	320.4	8906.9	-	-	-	-	-
140	317.7	8831.8	6.0	3.18	0.00036	-7.93	2.4204
142	316.1	8787.3	7.5	3.98	0.00045	-7.71	2.4088
144	314.3	8737.3	9.0	4.77	0.00055	-7.51	2.3972
146	311.8	8667.8	11.0	5.83	0.00067	-7.31	2.3858
148	308.9	8587.2	14.5	7.69	0.00090	-7.01	2.3745
150	305.4	8489.9	17.0	9.01	0.00106	-6.85	2.3632
152	301.0	8367.6	21.0	11.13	0.00133	-6.62	2.3521
154	296.1	8231.4	25.0	13.25	0.00161	-6.43	2.3411
156	289.6	8050.7	30.0	15.90	0.00198	-6.23	2.3302
158	282.2	7844.9	35.5	18.82	0.00240	-6.03	2.3194
160	273.4	7600.3	42.0	22.26	0.00293	-5.83	2.3087
162	262.5	7297.3	49.0	25.97	0.00356	-5.64	2.2981
164	250.5	6963.7	57.0	30.21	0.00434	-5.44	2.2875
166	236.7	6580.1	66.0	34.98	0.00532	-5.24	2.2771
168	220.3	6124.2	76.0	40.28	0.00658	-5.02	2.2668
170	201.8	5609.9	86.5	45.85	0.00817	-4.81	2.2566
172	180.7	5023.3	96.5	51.15	0.01018	-4.59	2.2464
174	156.8	4358.9	110.0	58.30	0.01338	-4.31	2.2364
176	130.1	3616.7	120.0	63.60	0.01759	-4.04	2.2264
178	101.2	2813.3	125.0	66.25	0.02355	-3.75	2.2166
180	70.8	1968.2	108.0	57.24	0.02908	-3.54	2.2068
182	51.0	1417.8	67.0	35.51	0.02505	-3.69	2.1971
184	38.4	1067.5	46.5	24.65	0.02309	-3.77	2.1875
186	29.1	809.0	33.0	17.49	0.02162	-3.83	2.1779
190	17.7	475.4	19.0	10.07	0.02118	-3.85	2.1591

^a $k(T) = (dH/dt)/(A - a)$.

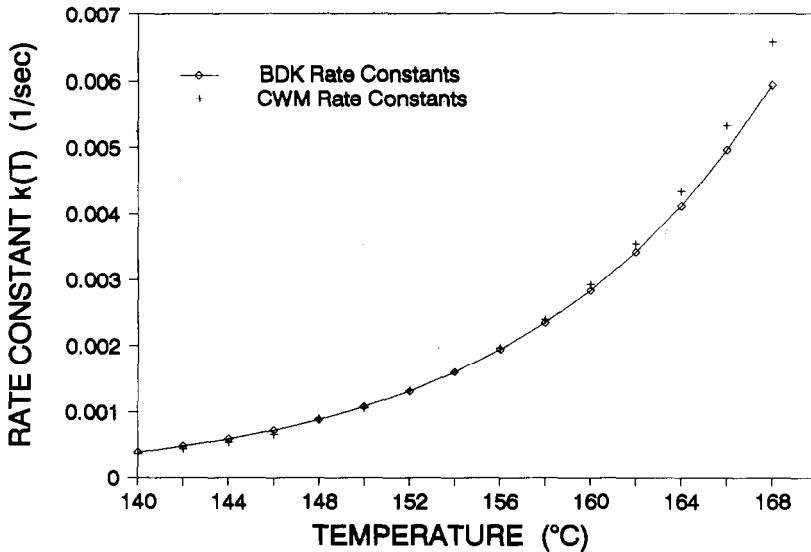


Fig. 3. Comparison of the temperature-dependent rate constants obtained by the CWM and BDK analysis.

TABLE 3

Arrhenius parameters and residual heats of reaction obtained by BDK analysis of curing exotherms for partially cured DAP samples

Oven curing time (min)	Reaction order n	Activation energy E (kJ mol ⁻¹)	log Z (min ⁻¹)	Heat of reaction ΔH (J g ⁻¹)	Std. error (s ⁻¹)
0	0.71	146.6	16.91	558.0	0.0085
2	0.71	143.1	16.46	437.1	0.0039
4	0.65	138.9	15.96	349.1	0.0048
5	1.03	146.3	16.92	198.6	0.0085
7	1.13	148.9	17.25	172.4	0.0077
9	1.37	142.5	16.56	93.2	0.0121
10	1.75	150.8	17.64	72.8	0.0094
15	3.29	222.3	25.82	34.2	0.0367
17	2.63	195.0	22.36	20.1	0.0830
20	2.94	240.5	27.62	16.0	0.0606
25	1.35	169.8	19.12	8.0	0.1746

This plot is shown in Fig. 4, together with an Arrhenius plot generated by the BDK program. The activation energy can be obtained from the slope of the Arrhenius plot. The value of E , calculated from the CWM data, was 156.3 kJ mol⁻¹.

The linearity of the Arrhenius plot and the close agreement between

TABLE 4

Rate constants k at 160°C, determined by measuring the residual heats of reaction after different oven curing times

Oven curing time (min)	Heat of reaction ΔH^a (J g ⁻¹)	Extent of cure x^b (%)	Rate constant k^c (s ⁻¹)
0	558.0	—	—
2	437.1	21.7	0.00204
4	349.1	37.4	0.00195
5	198.6	64.4	0.00344
7	172.4	69.1	0.00280
9	93.2	83.3	0.00331
10	72.8	87.0	0.00340
15	34.2	93.9	0.00311
17	20.1	96.4	0.00326
20	16.0	97.1	0.00295
25	8.0	98.6	0.00285

^a Determined by means of the BDK program. ^b Calculated by using eqn. (19). ^c Calculated by using eqn. (20).

TABLE 5

Comparison of rate constants obtained by different data analysis methods

Data analysis method	Rate constant $k(T)$ (s^{-1})	
	140°C	160°C
Willard ^a	0.00039	0.00291
Willard ^b	0.00042	0.00291
Residual heats of reaction ^c	–	0.00291
CWM ^d	0.00036	0.00293
BDK ^e	0.00040	0.00284

^a Ref. 8; calculated rate constant. ^b Ref. 8; observed rate constant. ^c Equations (19) and (20). ^d Cut-and-weigh method, followed by data analysis method of Willard (eqn. (17)).

^e Borchardt and Daniels DSC kinetics program (Du Pont).

the rate constants after different curing times at 160°C, as shown in Table 4, indicate that the curing reaction of DAP follows first-order kinetics.

CONCLUSIONS

This study has, once again, demonstrated the reliability and efficiency of the single dynamic temperature scan DSC method of Borchardt and Daniels. It is evident from the results that all the data analysis methods employed in this study are suitable for determining the kinetic parameters of thermoset curing reactions which follow first-order kinetics. The kinetic

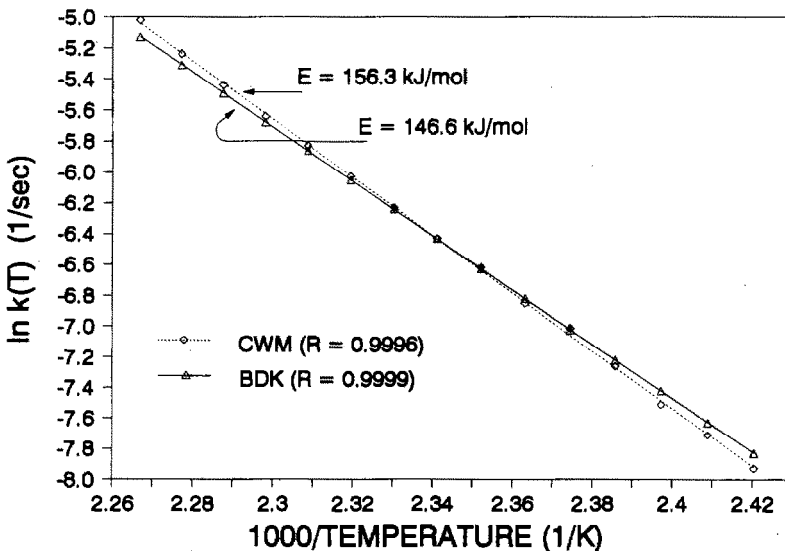


Fig. 4. Comparison of Arrhenius plots obtained by the CWM and BDK analysis.

parameters obtained by means of the cut-and-weigh method, as well as those calculated from the residual heats of reaction after different oven curing times, were in excellent agreement with the values obtained by using the Borchardt and Daniels DSC kinetics data analysis software. The rate constants obtained by using the three different data analysis methods discussed in this paper also compared very favourably with the values previously reported in the literature. However, there can be no doubt that the analysis speed and simplicity of the Borchardt and Daniels DSC kinetics program make this the preferred method for obtaining quantitative reaction kinetics information for the curing of thermoset resins.

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