Thermochimica Acta, 112 (1987) 289–296
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ISOTHERMAL CALORIMETRIC MEASUREMENT OF POLYMER CURE KINETICS: THE MANGELSDORF METHOD OF ANALYSIS

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(Received 7 July 1986)

ABSTRACT

A useful calorimetric method for determining cure kinetics of polymers is demonstrated. The technique is an isothermal one in which $\dot{Q}$, the rate of thermal energy release (exothermic power), is monitored as a function of time. The time-dependence of heat released, $Q(t)$, can, in principle, be determined by integration of the power data; however, experimental considerations often make it difficult to evaluate $\dot{Q}$ for short times. Nevertheless, the use of a simple mathematical device advocated by Mangelsdorf makes it possible to obtain both cure rate constants and total heat release, even if initial values of $\dot{Q}$ are unknown. The only assumption of the method is that heat release be an exponential function of time. The method is illustrated by following the cure of a polyol/isocyanate system at several temperatures. The kinetics are shown to obey an Arrhenius relation, with an activation energy of 10.0 ± 0.1 kcal mol^{-1}.

INTRODUCTION

We have developed an experimental and analytical procedure for determining isothermal cure kinetics of polymers and have evaluated the procedure using a polyurethane-forming system. This paper describes the method and reports the test results.

The method is based on two fundamental aspects: (1) an isothermal calorimetric measurement of rate of heat evolved (exothermic power) during cure, and (2) a simple mathematical method of Mangelsdorf [1] for determining rate constants and other parameters for first-order reactions (exponential curves) for which some of the data for early times may be missing.

EXPERIMENTAL ASPECTS

The calorimeter used was a Perkin-Elmer DSC-2 differential scanning calorimeter with its associated TADS data station. This instrument can be operated in either a scanning or isothermal mode. Although scanning (or "dynamic") methods for determining cure kinetics have been experimentally demonstrated [2–6], it has long been known [7] that corrections are required for comparison with results of the more fundamental isothermal methods. In fact, some authorities argue that kinetic functions cannot be reliably obtained by dynamic methods [8]. Therefore, we elected to use the isothermal technique.

The experimental procedure was straightforward. A sample of polymer precursor for which the cure kinetics were to be measured was prepared and mounted in a DSC sample pan. This preparation sometimes involved some mixing. The mixing and mounting time amounted to several minutes during which, for chemically cured systems, some curing took place. Thus for epoxy systems and other chemically cured polymers, it was not possible to calorimetrically follow the initial portion of the cure process. (For radiation curing, this will not be the case; the cure will not be initiated until the sample is mounted in the calorimeter and irradiated, so that the entire cure process can be observed.)

The sample pan was placed in the calorimeter at room temperature and the temperature programmed rapidly to the desired temperature at which the heat release, $\dot{Q}$, was measured as a function of time until cure was essentially complete. From the time dependence of $\dot{Q}$ the cure reaction rate, k, was determined in the manner described in the following section. The activation energy associated with the cure process was then found from an Arrhenius plot of k.

THE MANGELSDORF METHOD

In 1959 Mangelsdorf [1] suggested a simple plotting method for analyzing experimental data for first-order processes (i.e., exponential time dependences):

$$y(t) = A\ \mathrm{e}^{-\alpha t} + B \tag{1}$$

where A, α and B may all be unknown. The technique involves plotting the retarded function $y(t+\Delta)$ versus $y(t)$. Such a plot is a straight line with slope $\exp(-\alpha\Delta)$. The choice of the parameter Δ is not critical, but its magnitude should fall in a range to give a Mangelsdorf plot with a slope not too close to 1.

Let us illustrate the method by applying it to an analysis of the exponential decay of heat release during a polymer cure which obeys first-order kinetics. For this case the time dependence of the rate of heat release is given by:

$$\dot{Q}(t) = \dot{Q}_0\ \mathrm{e}^{-kt} \tag{2}$$

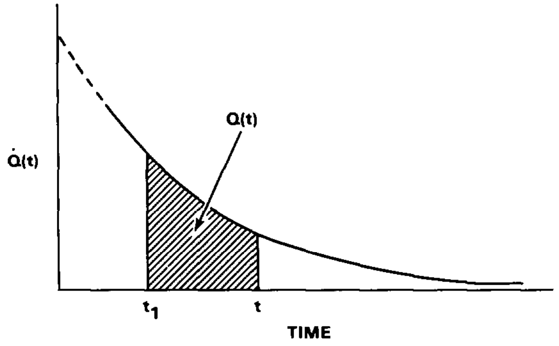

Fig. 1. Schematic diagram of heat release during cure.

The heat energy released in a time interval t_1 to t (see Fig. 1) is given by

$$Q(t) = \dot{Q}_0 \int_{t_1}^{t} e^{-kt}\, dt = \frac{\dot{Q}_0}{k}\left[e^{-kt_1} - e^{-kt}\right]$$

$$= Q_0\left[e^{-kt_1} - e^{-kt}\right] \tag{3}$$

where Q_0 is the total heat release from $t = 0$ to ∞.

The retarded function is

$$Q(t+\Delta) = Q\left[e^{-kt_1} - e^{-k\Delta}\, e^{-kt}\right]$$

$$= Q_0\, e^{-kt_1}\left[1 - e^{-k\Delta}\right] + e^{-k\Delta} Q_0\left[e^{-kt_1} - e^{-kt}\right]$$

$$= Q_0\, e^{-kt_1}\left[1 - e^{-k\Delta}\right] + e^{-k\Delta} Q(t) \tag{4}$$

Thus a plot of $Q(t+\Delta)$ versus $Q(t)$ is a straight line with slope S given by

$$S = \exp(-k\Delta) \tag{5}$$

and intercept Y given by (see Fig. 2)

$$Y = Q_0\, e^{-kt_1}\left[1 - e^{-k\Delta}\right] \tag{6}$$

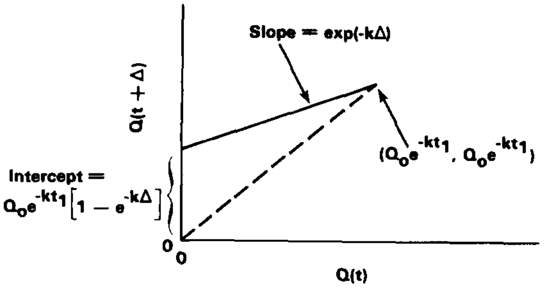

Fig. 2. Schematic Mangelsdorf plot.

By judicious choices of t_1 and Δ, we obtain both Q_0 and k, even in the absence of data for $t_1 = 0$. From Fig. 2 we see that the intersection of $Q(t+\Delta)$ with a line through the origin having slope $= 1$ occurs at the point (I, I) where

$$I = Q_0 \exp(-kt_1) \tag{7}$$

The value of I thus gives a second determination of Q_0.

It is worth pointing out that the linearity of the Mangelsdorf plot is a test of the exponential nature of the data. Since the derivation of the linear relation between the retarded function $Q(t+\Delta)$ and $Q(t)$ in eqn. (4) is based on the assumption of an exponential time dependence (eqn. 1), a departure from linearity indicates that the kinetics are not first order.

CURE KINETICS OF A POLYURETHANE

We tested the Mangelsdorf method by analyzing the cure kinetics of a polyurethane. The polyurethane precursors consisted of a polyol blend [(TP440 + TP410) containing ca. 0.05% of dibutyl tin dilaureate catalyst] and an isocyanate (Desmodur W). Each calorimetry sample was a mixture of 10 parts by volume of polyol with 7.5 parts Desmodur.

A number of samples weighing ca. 10 to ca. 14 mg were prepared and hermetically sealed in aluminum sample pans. Those samples which were not immediately calorimetrically analyzed were stored in a freezer at about $-15\,^\circ$C until run. Cooling of the stored samples was intended to inhibit the cure reaction. However, some curing did occur, as indicated by a reduction in Q_0 values for samples stored for many hours before running (Table 1).

As mentioned above, the heat evolution during cure was measured using a Perkin-Elmer DSC-2 calorimeter operated in the isothermal mode. After a sample was mounted in the calorimeter sample enclosure, its temperature was programmed rapidly (80 or 160 K min^{-1}) to the cure temperature. Due to thermal imbalances, data immediately after the rapid scan to the cure temperature were invalid and were rejected. This loss of initial data rendered the Mangelsdorf method particularly useful. The delay time t_1, after which reliable $Q(t)$ values could be determined, was usually one or two minutes after the initial interval of imprecise data. The values of $Q(t)$ were calculated * at equally spaced time increments Δ from t_1 to times beyond which no further change in $Q(t)$ was observed.

Figure 3 shows a typical plot of $\dot{Q}$ versus time for the isothermal cure of polyol and Desmodur at 375 K; by convention, experimental exotherms point downward. Q-values were determined by integration with respect to

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* The Q-values were determined by an integration routine in the calorimeter's isothermal software.

TABLE 1

Polyurethane cure kinetics results

Sample mass (mg)	Storage time [a] (min)	Scan rate to T_{cure} (K min^{-1})	T_{cure} (K)	t_1 (min)	Δt (min)	Δ (min)	k (min^{-1})	Q_0^{uncorr} (cal g^{-1})	Q_0^{corr} (cal g^{-1})	T_g [b] (K)
11.65 [c]	0	80	330	2.35	0.125	2	0.1109	40.58	41.14	308.1
10.91 [c]	70	80	330	2	0.125	1	0.09569	34.64	35.06	306.5
10.90 [c]	28	80	360	2	0.25	0.5	0.3707	40.07	43.96	306.5
10.77 [c]	1204	80	360	2	0.25	0.4	0.3338	33.84	36.79	304.3
10.79 [c]	1620	80	360	2	0.25	0.4	0.3771	31.89	35.04	305.0
12.87	21780	80	360	2	0.25	0.4	0.2913	16.61	18.52	306.0
13.85	21810	160	360	2	0.125	0.4	0.3518	18.78	19.62	304.0
10.87 [c]	124	80	375	0.9	0.3125	0.3	0.6807	32.28	39.69	306.4
10.23 [c]	0	80	390	0.8	0.375	0.2	1.1786	25.06	38.99	311.5
12.83 [c]	4440	80	390	0.9	0.375	0.3	1.1229	21.03	32.04	302.3

[a] At −15°C.

[b] Taken to be the temperature at the midpoint of specific heat change associated with glass transition.

[c] Data for these samples used in Arrhenius plot (i.e., for samples not stored for an excessively long time).

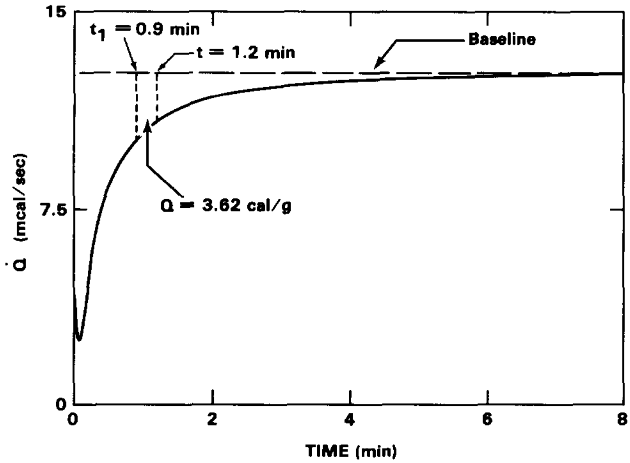

Fig. 3. $\dot{Q}$ versus t for cure of polyol plus Desmodur at $T = 375$ K; $t_1 = 0.9$ min and $\Delta = 0.3$ min.

the indicated baseline. Under certain circumstances it was appropriate to make an additive correction to t_1 in order to take into account the curing which occurs during the warm-up scan from 300 K to the cure temperature. We took the correction increment Δt to be (roughly)

$$\Delta t = (T_{\mathrm{cure}} - 300)/(3 \times \text{scan rate}) \tag{8}$$

a quantity which is appreciable only for slow scan rates and high cure temperatures. Δt will not affect the value of the cure rate constant derived from the slope of the Mangelsdorf plot, but it will increase the Q_0 value found from the intercept. The corrected value is given by

$$Q_0^{\mathrm{corr}} = Q_0^{\mathrm{uncorr}} \exp(k \Delta t) \tag{9}$$

It should be kept in mind that the correction is a rather crude attempt to take account of the curing which takes place during warmup. At any rate the correction is negligible if $\Delta t \ll k^{-1}$.

In Fig. 4 a Mangelsdorf plot is shown for the data of Fig. 3, using $t_1 = 0.9$ min and $\Delta = 0.3$ min. It should be noted that as $t \to \infty$, the data points become more closely spaced. A straight line fits the data very well, indicating first-order kinetics. From the slope S, we find $k = 0.6807$ min^{-1}; from the intersection I and intercept Y, we obtain uncorrected Q_0 values of 32.29 cal g^{-1} and 32.27 cal g^{-1}, respectively. The warm-up correction time Δt was estimated to be 0.3125 min so that the corrected value of Q_0 is 39.69 cal g^{-1}.

In Table 1 the results for ten samples cured at four temperatures are summarized. Five samples stored at approximately $-15\,^{\circ}$C for a wide range of times were cured at 360 K. It is evident from the lower Q_0 values for longer storage times that the cure reaction proceeds at an appreciable rate even at a temperature as low as $-15\,^{\circ}$C. Glass transition temperatures T_g were also measured for most of the samples; it appears that samples which

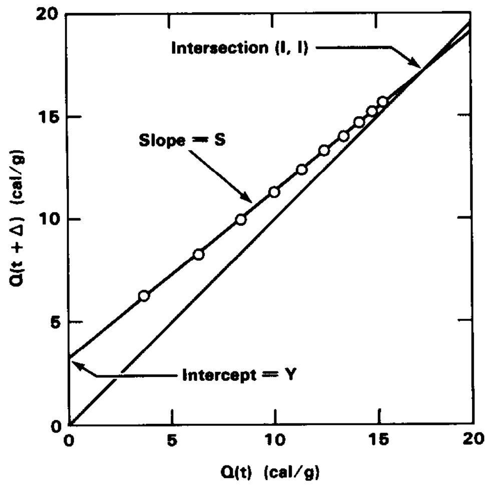

Fig. 4. Mangelsdorf plot for cure of polyol plus Desmodur at 375 K; $t_1 = 0.9$ min and $\Delta = 0.3$ min. From the slope S, a rate constant $k = 0.6807$ min^{-1} was found. From I, $Q_0 = 32.29$ cal g^{-1}; from Y, $Q_0 = 32.27$ cal g^{-1}.

were cured immediately after mixing have a slightly higher T_g than those which were stored for a long time at −15°C before curing.

The corrected values of Q_0 (the total heat evolved during cure) for samples cured soon after mixing appear to lie in the range 39 to 44 cal g^{-1},

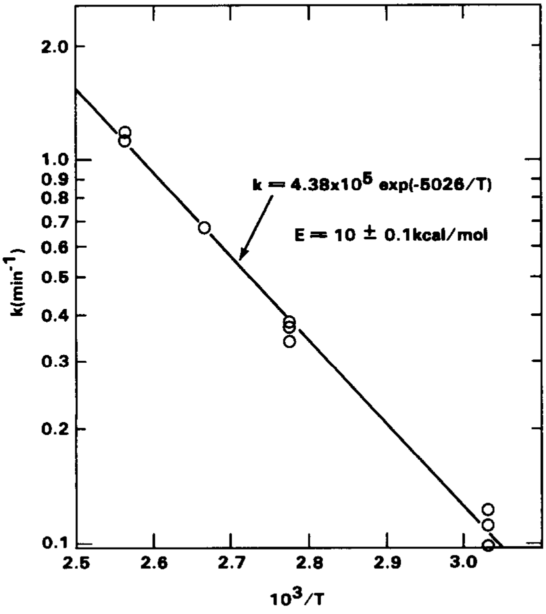

Fig. 5. Arrhenius plot of the indicated k-values from Table 1.

independent of the cure temperature. Furthermore, an Arrhenius plot of the reaction rates k (Fig. 5) exhibits an excellent straight-line dependence and gives an activation energy of 10.0 ± 0.1 kcal mol^{-1}.

CONCLUDING REMARKS

The Mangelsdorf plot has been shown to be a valuable method for analyzing first-order cure kinetics. The method is particularly useful for evaluating reaction-rate constants which, by use of an Arrhenius plot, yield the activation energy E_{act} for the cure process. For the specific case of a particular polyurethane cure, we obtained $E_{act} = 10.0 \pm 0.1$ kcal mol^{-1}.

ACKNOWLEDGMENTS

The author thanks G.P. Montgomery, N.A. Vaz, W.R. Rodgers and W.R. Short for valuable discussions, and Drs. Rodgers and Short for supplying the polyurethane precursor materials.

REFERENCES

1 P.C. Mangelsdorf, J. Appl. Phys., 30 (1959) 443. See also E.A. Guggenheim, Philos. Mag., 2 (1926) 538.
2 R.A. Fava, Polymer, 9 (1968) 137.
3 L.W. Crane, P.J. Dynes and D.H. Kaelbe, J.Polymer Sci., Polymer Lett. Edn., 11 (1973) 533.
4 A.A. Duswalt, Thermochim. Acta, 8 (1974) 57.
5 S.J. Swarin and A.M. Wims, Anal. Calorim., 4 (1977) 155.
6 K. Kreitzschmar and K.W. Hoffmann, Thermochim. Acta, 83 (1985) 139.
7 R.B. Prime, Anal. Calorim., 2 (1970) 201.
8 T.B. Tang, Thermochim. Acta, 58 (1982) 373.