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**CHARACTERIZATION OF THE CURE OF  
RESINS BY DIFFERENTIAL  
SCANNING CALORIMETRY**

(Technical Report)

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# Characterization of the cure of resins by differential scanning calorimetry (Technical Report)

## ABSTRACT

The cure of resins has long been characterised by using DSC to measure a "heat of reaction" ( $\Delta H$ ). Unfortunately, although useful as a quality control parameter,  $\Delta H$  is rarely equal to the thermodynamic heat of reaction. As a result, derived data such as the extent and rate of reaction are in error and subsequent predictions of the kinetic behaviour may be seriously flawed.

This collaborative programme was devised to investigate the magnitude of the problem using a well-behaved system to obtain conventional data. These were combined with heat capacities of reactants and products to show how errors arise with a variety of baselines. Emphasis is placed on the need for correct physical foundations before the cure kinetics of a particular system can be considered.

## 1. INTRODUCTION

The cure of resins has long been characterised by measurement of the heat of reaction ( $\Delta H$ ) and differential scanning calorimetry (DSC) is now widely used for this purpose because of its experimental convenience and speed of operation. Applications cover the whole area from quality control to the development of improved resin systems and DSC has the additional benefit that the increase in the glass transition temperature ( $T_g$ ) can also be monitored (there is an approximately stepwise increase in the specific heat capacity -  $c_p$  - over the  $T_g$  region and this is reflected by the DSC signal which is related to  $c_p$ ).

Although simple in principle, a number of problems must be overcome before a meaningful  $\Delta H$  can be derived using DSC. "Cure" is usually a summation of several, often competing, reactions each of which may have a different activation energy. As the sample experiences the linear time-temperature ( $T$ ) programme of a conventional DSC experiment the signal represents some "average" reaction that may show fine structure when some particularly energetic process is activated; termination of cure is frequently masked by another type of competing reaction - thermal degradation. A simplification is to observe the development of  $\Delta H$  isothermally but this approach also has problems in both the initial and final stages of reaction:

A finite time is needed to raise the sample to temperature:

How is this done? Is all enthalpy recorded?

Can the final asymptotic approach to equilibrium be distinguished from instrumental drift?

Procedures have been described to overcome the several problems described above [1,2] but these are often semi-empirical and results may be a function of a particular make, or even model, of calorimeter. The combination of this "instrumental" effect with a heat of reaction that is often thermodynamically ill-defined leads to uncertainties in those quantities (extent,  $\alpha$ , and rate,  $d\alpha/dt$ , of reaction) that are derived from the evolution of  $\Delta H$  with time or temperature. The net result is that " $\Delta H$ ", and the dependent kinetic parameters, are poorly defined (even if reproducible) quantities that lack transferability even when instruments are correctly calibrated. The object of the present collaborative work was to estimate the magnitude of the problem and to suggest methods by which results of thermodynamic significance can be obtained. Any subsequent treatment, which will depend on the specific resin system investigated, will then be based on data that have a sound measurement foundation.

## 2. PARTICIPANTS

Participants in the programme, and the relevant instrumentation, are shown in Table I. Initial plans covered a wider range of instruments but personnel and laboratory changes reduced these to the major representative of the two types of DSC - power compensation (Perkin Elmer) and heat flux (Du Pont, now TA Instruments).

Table 1 Participants and Instrumentation

DSC2*	Hohne/Mattheij/Richardson
DSC7*	Bajaj/van Hastenberg/Hohne/Ichihara/Nakagawa/Shanks
DSC10 <sup>+</sup>	Lever
DSC912 <sup>+</sup>	Rieger
* Perkin Elmer + Du Pont (now TA Instruments)	
(Laboratories in subsequent Tables refer to receipt of data, not alphabetical order)	

### 3. EXPERIMENTAL

#### 3.1. Materials

The most convenient system to investigate would have been a B-staged resin - one that has been partially reacted to give a  $T_g > \text{ambient}$ . Unfortunately, even in this state there are slow chemical and physical changes that become significant on the time scale (months) that must be allowed for collaborative work - especially when the uncontrollable conditions of transport and storage through many climatic regions are considered.

To ensure reproducibility of material from one laboratory to another it was essential to compound the resin immediately prior to use. After some trials, the system finally chosen was Ciba-Geigy MY750/HY917/DY070 (a low viscosity epoxy resin/methyltetrahydrophthalic anhydride hardener/heterocyclic amine accelerator). This has several desirable features:

1. All components were liquid, ensuring easy dispersion of the 100/90/2 parts by mass mixture.
2. Individual components had adequate shelf lives (at least two years).
3. Cure was "complete" on the time scale of a normal DSC run (heating rates,  $q$ , from 1-40 K min<sup>-1</sup>) with completion being judged by the return of the curve to the normal linear  $c_p$ - $T$  behaviour at high temperatures.
4. There was only a small difference between the heat capacities of the reactants and products so that  $\Delta H$  was only a weak function of temperature.

Viscosities of the components were such that the appropriate concentrations of reactants were most conveniently obtained by adding premixed HY917/DY070 to the more viscous MY750. Mixing was most efficient if reactants were compounded to give batches of tens of grams from which many DSC samples were prepared. A full set of experiments could extend over several days so that samples had to be stored below -30 °C - the approximate glass temperature of the initial resin (Fig. 3). No detectable reduction in  $\Delta H$  with storage times of up to fourteen days was found under these conditions; it was enough to maintain material at 0 °C if it was prepared and run on the same day, it was found that the decrease in  $\Delta H$  after 24 hours at 0 °C was 2% - almost within the experimental error. The samples in laboratory 9 were kept at ambient temperature and measurements extended over three days; results (Table III), obtained in the order -318 (1), -291/-306 (2), and -282 J g<sup>-1</sup> (3) (day of measurement in brackets), clearly demonstrated ongoing cure at room temperature. Allowance for an earlier sample preparation time brings  $\Delta H$  into line with the majority of other data in Table III.

#### 3.2. Calorimetry

Although the cure chemistry indicated that no volatile components were formed during polymerisation, the accelerator (DY070) had an appreciable vapour pressure and it was necessary to contain the resin in sealed pans.

Any DSC requires calibration with respect to temperature and enthalpy and/or specific heat. Participants in this programme generally used the manufacturers' recommended calibration procedures. Two metals were normally used for temperature calibration: one was indium for which the extrapolated onset was taken to be 429.8 K. Enthalpy calibration used the heat of fusion of indium (28.59 J g<sup>-1</sup>),  $\alpha$ -alumina (synthetic sapphire) was the heat capacity calibrant.

DSC investigations of the cure of resins yield, in order of increasing experimental and computational complexity, the temperature at which the reaction rate peaks ( $T_p$ ) and the glass temperature of the cross-linked product ( $T_g$ ), the overall heat of reaction ( $\Delta H$ ), the extent of reaction ( $\alpha$ ) and the reaction rate ( $d\alpha/dt$ ). All participants reported  $T_p$ ,  $T_g$  and  $\Delta H$  as functions of the heating rate ( $q$ ). Some additional results were also available for the heat capacities of the reactants (individually and compounded) and products so that the effect of temperature on  $\Delta H$  could be determined.

Additional measurements were carried out in this laboratory when all results had been received and ambiguities and inconsistencies became apparent - the major points of difference concerned  $T_g$  and  $c_p$ .

## 4. RESULTS

### 4.1. Peak reaction temperatures

Fig. 1 and Table II show how  $T_p$  varied with  $q$ . Values were generally averages from two or three experiments; reproducibility when  $q = 10 \text{ K min}^{-1}$  was tested by laboratories 1 and 7 (8 and 13 runs respectively) and the maximum deviations from the averages are indicated in the footnotes to Table II. Most data could be accommodated within an average  $\pm 1.5 \text{ K}$  although in two cases there are wider, unexplained variations. Prereaction has little effect on  $T_p$ ; results from laboratory 9 (3.1) are similar to others in Table II.

### 4.2. Glass temperatures

The glass temperatures of the cured resin showed gross differences (Fig. 2), values ranging from 365-415 K with some laboratories reporting an inverse relationship between  $T_g$  and  $q$  and others the reverse ( $T_g$  was taken as the temperature at which the increment in  $c_p$  had reached half its overall value, measurements being made with  $q = 10 \text{ K min}^{-1}$  on material that had previously been cooled through  $T_g$  at the same rate). Since  $T_g$  can normally be determined to  $\pm 1 \text{ K}$ , further work was undertaken and this confirmed a suggestion (laboratory 7) that the discrepancies were caused by thermal degradation at relatively modest temperatures - even though there was no evidence for this on the DSC curves (deviations from linear  $c_p$ - $T$  behaviour or drift in isothermal regions might be anticipated). Experiments were generally terminated when the linear "postcure" region was sufficiently well defined (ca. 10-20 K), this

Table II Effect of heating rate,  $q$ , on peak temperature,  $T_p$

$T_p$ , K									
$q$ (K min <sup>-1</sup> )	Laboratory								
	1	2	3	4	5	6	7	8	9
1	-	-	-	-	-	-	378.5	-	-
2	-	-	-	-	384.4	-	388.2	-	-
2.5	391.5	392.7	392.6	390.2	-	-	-	389.7	390.3
5	402.0	406.0	403.5	401.5	395.3	423.6	403.0	401.2	400.3
7.5	-	-	-	-	402.3	-	-	-	-
10	413.8*	416.2	414.7	413.1	407.8	437.8	415.5 <sup>+</sup>	413.4	413.5
15	-	-	-	-	416.5	445.9	-	422.1	-
20	425.2	428.4	426.1	425.5	422.7	452.7	428.3	428.6	427.4
40	436.8	443.7	-	-	-	-	-	-	-
	* + 0.7, -0.8					<sup>+</sup> + 0.2, -0.6			
$E$ , kJ mole <sup>-1</sup>	77.7 (79.4)	75.4 (73.6)	79.4	73.7	72.7	69.2	73.5	67.7	70.3

Bracketed values of  $E$  are obtained if  $q = 40 \text{ K min}^{-1}$  data are included.

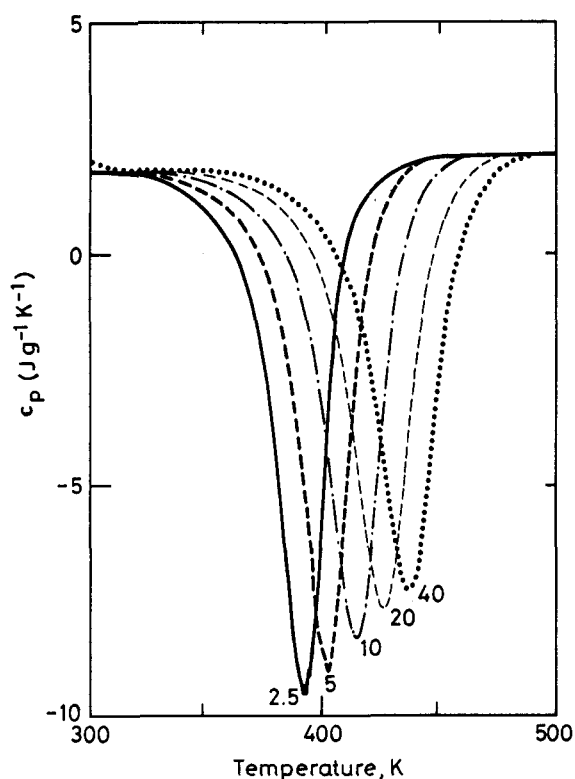


Fig 1 Cure of 100/90/2 (mass ratio) MY750/HY917/DY070 as a function of the heating rate ( $\text{K min}^{-1}$ ) shown.

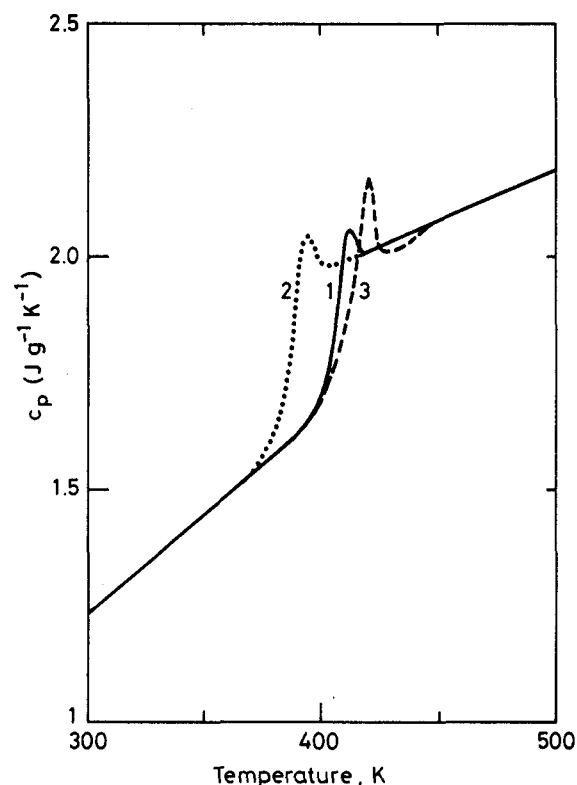


Fig 2 The glass transition region after heating to 460 (1), 520 (2) and 410 K (3). Example (3) was initially kept at  $T_{\text{max}}$  for 40 mins, it shows an enthalpy relaxation peak.

implies a relatively low temperature for low  $q$  (Fig. 1) and therefore less thermal degradation. In some laboratories, however, all samples were taken to a common, high, final temperature and lower  $T_g$  values were necessarily associated with low  $q$  because of additional degradation during the time required to reach the final temperature. With a better understanding of the behaviour of the cross-linked product it was possible to determine the limiting value of  $T_g$ , prior to any thermal degradation. Runs were terminated at various temperatures in the range 410–440 K (ie. when still curing, Fig. 1) and cure completed isothermally. Cure at 420–430 K gave  $T_g \sim 415$  K, a value that decreased after any exposure to higher temperatures. Strong support for  $T_g \sim 415$  K came after curing at 410 K; the subsequent determination of  $T_g$  showed an enthalpy relaxation peak (Fig. 2) that is typical of glasses that have been annealed close to, but below,  $T_g$ . Although the cure rate is much reduced at  $T_g$  this is a region rather than a unique temperature and the curve of Fig. 2 shows that in this case the reaction was almost complete - there was little residual cure. Decreases in  $T_g$  were small ( $\sim 2$  K) after 30 m at 435 K but very obvious ( $T_g \sim 400$  K) after only two or three minutes at 470 K.

#### 4.3. Heat of reaction

The heat of reaction is given in Table III where  $\Delta H$  is defined by a linear baseline that joins the start and end of the reaction. The definition of "start" and "end", and the resultant uncertainties, are discussed in more detail below. At this stage it is sufficient to note that  $\Delta H$  is independent of  $q$  (the low  $q$  values from laboratory 4 show wide variations) and the various laboratories generally agree to  $\pm 2$ -3%, implying that for this particular system the baseline is well-defined and reproducible. The effects of prereaction on the data from laboratory 9 (Table III) have already been discussed (3.1). The low, but very consistent, data from laboratory 8 were almost certainly due to loss of accelerator from the unsealed pans that were used. Subsidiary TGA work showed that DY 070 vapourised early in the reaction and the data therefore refer to accelerator-free systems.

Table III Effect of heating rate,  $q$ , on heat of reaction,  $\Delta H$ 

$-\Delta H, \text{J g}^{-1}$									
$q \text{ (K min}^{-1}\text{)}$	Laboratory								
	1	2	3	4	5	6	7	8*	9 <sup>+</sup>
1	-	-	-	-	-	-	352	-	-
2	-	-	-	-	364	-	348	-	-
2.5	338	332	349	443	-	-	-	295	318
5	337	330	352	393	344	313	348	293	282
7.5	-	-	-	-	337	-	-	-	-
10	344	337	349	363	361	315	342	295	306
15	-	-	-	-	343	326	-	294	-
20	339	335	358	355	341	339	338	299	291
40	338	346	-	-	-	-	-	-	-

\* See 4.3, + See 3.1.

#### 4.4. Specific heat capacity

Only a few of the participating laboratories reported  $c_p$  data. Those available are shown in Figs. 3 and 4. Although there is reasonable overall agreement there are unexplained variations in  $dc_p/dT$ , for example, so that extrapolations are uncertain. There are also inconsistencies in the sense that results for the fully cured product should agree between the initial and subsequent runs: this is rarely the case. Differences might be accounted for by thermal degradation at high temperatures but, whatever the cause, a knowledge of both  $c_{pr}$  and  $c_{pp}$  ( $r$  = reactant,  $p$  = product) is essential for a full discussion of the results. Comprehensive  $c_p$  measurements were therefore made in this laboratory and data obtained not only for  $c_{pr}$  and  $c_{pp}$  but also for the individual components of the initial mixture. The last covered a temperature range that was extended downwards to locate the glass temperature of the freshly mixed resin (Fig. 3). This both defined a safe storage temperature (the reaction rate is essentially zero below  $T_g$ ) and also showed the plasticising effect of HY917/DY070 on MY750 (Fig. 3). Direct results on  $c_{pr}$  covered only this low temperature region because it was important to ensure that the final isothermal baselines were not perturbed by the onset of the exothermic reaction. As it was, there was enough (260-300 K) overlap between results for  $c_{pr}$  and the individual components to be confident that  $c_p$  contributions are additive and  $c_{pr} = \sum w_i c_{pi}$  where the  $w_i$  are the mass fractions of MY750, HY917, and DY070; direct measurements for  $c_{pr}$ , for example, gave 1.668 (260 K) and 1.757 J g<sup>-1</sup> K<sup>-1</sup> (300 K), by additivity these were 1.675 and 1.757 respectively.

## 5. DISCUSSION

### 5.1. Heats of reaction: $\Delta H$ and $\Delta H(T)$

DSC work on the cure of resins has two very different applications: quality control and kinetic studies. Both require, at least formally, an extent of reaction  $\alpha = \Delta h_T/\Delta H$ ,  $\Delta h_T$  is the partial heat of reaction up to a temperature  $T$  in a scanning experiment,  $\Delta H$  is the total heat of reaction) but quality control emphasises behaviour at the extremes of  $\alpha$  - has the resin partially reacted ( $\alpha \geq 0$ ) or is the sample incompletely cured ( $\alpha \leq 1$ )? B-staged, or partially cured resins, are brought into the former category by redefining  $\Delta H$  to be the heat of reaction from B-stage to total cure. If there is to be agreement between laboratories (eg. resin suppliers and users) it is important to demonstrate that  $\Delta H$  characterises the material rather than the method of measurement. It is clear from Table III this desirable condition is satisfied for the resin system used here and there is transferability of data between heat flux and power compensation calorimeters. Unfortunately, many qualifications are necessary before this conclusion can be extended to all curing systems. These will be discussed after considering the thermodynamic aspects of the cure process. These clearly show the problems - and the solutions.

The overall heat of reaction has been "defined" by a baseline linking two temperatures - one ( $T_1$ ) when the reaction starts and one ( $T_2$ ) when it is complete. Even if the two can be located with any certainty, the

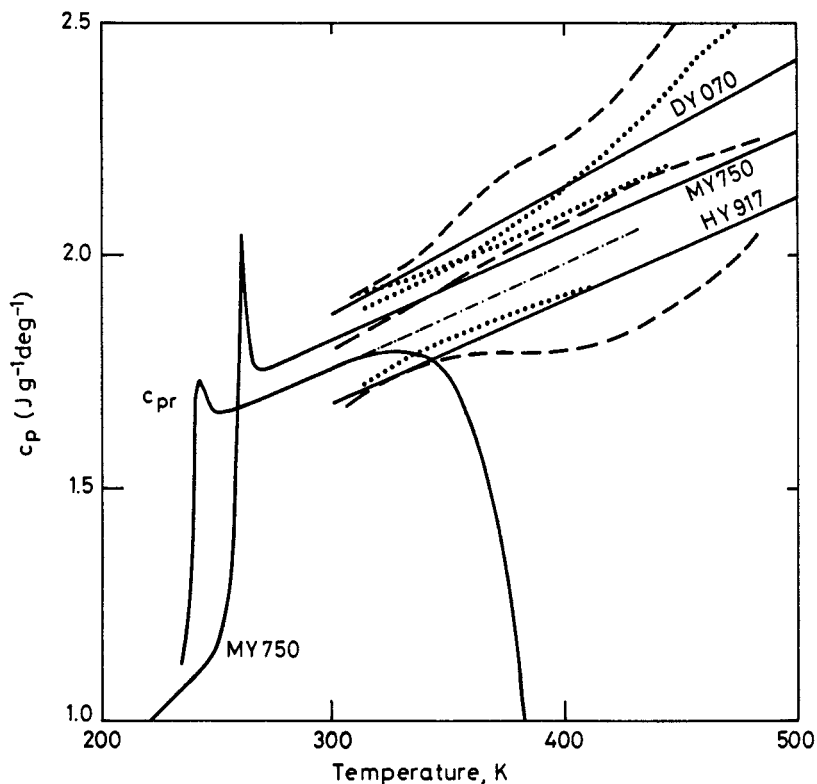


Fig 3 Heat capacities of the individual reactants and their mixture  $c_{pr}$ :  
 -- direct measurements (showing the onset of cure > 300 K),  
 - - - calculated (see text).  
 Symbols - - - and . . . . . refer to two different laboratories.

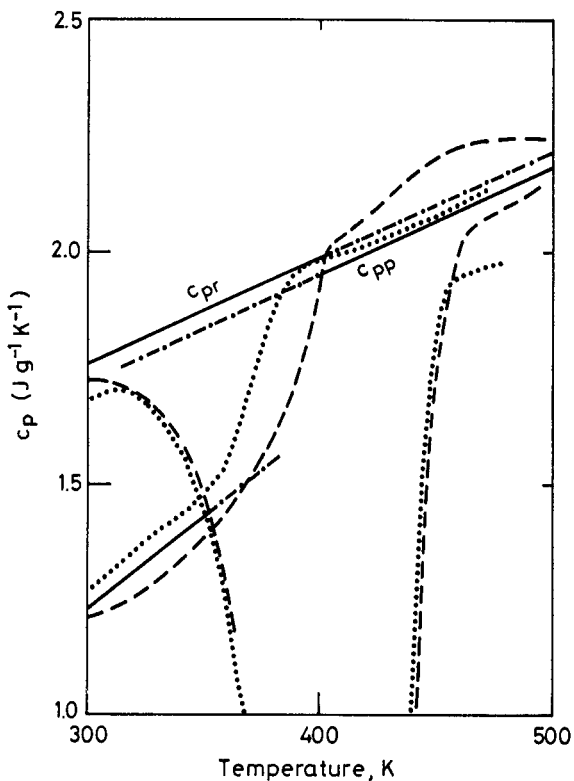


Fig 4 Heat capacities of the reactant mixture and the products;  $c_{pr}$  and  $c_{pp}$  show the data of Table IV. Symbols - - - and . . . . . refer to two different laboratories.

resultant  $\Delta H$  has no thermodynamic validity. Any heat of reaction should be a function of temperature defined by  $\Delta H(T) = H_p(T) - H_r(T)$  where subscripts refer, as previously, to products and reactants, respectively (equivalent physical states, rubber or liquid, are assumed). The total enthalpy change between  $T_1$  and  $T_2$ ,  $H_p(T_2) - H_r(T_1) (\equiv Q)$ , is transformed to a thermodynamically meaningful  $\Delta H(T)$  by baselines that are defined by the properties of the reactants and products:

$$\Delta H(T) = H_p(T) - H_r(T) = [H_p(T_2) - H_r(T_1)] - [H_p(T_2) - H_p(T)] - [H_r(T) - H_r(T_1)] \quad (1)$$

$$= Q - \int_T^{T_2} c_{pp} dT - \int_{T_1}^T c_{pr} dT \quad (2)$$

$$= Q - \int_{T_1}^{T_2} c_{pp} dT + \int_{T_1}^T \Delta c_p dT \quad (3)$$

The quantity  $Q$  is equivalent to the area bounded by  $T_1$ ,  $T_2$ ,  $c_p = 0$ , and any cure curve of Fig. 1. The second and third terms on the right-hand sides of equations (1) and (2) show that the baseline (equation (2)) is generally discontinuous and corresponds to extrapolations of data for the original resin and cured product. It is only linear when  $\Delta c_p (= c_{pp} - c_{pr}) = 0$  and under these circumstances  $\Delta H \neq f(T)$ . The normal behaviour is shown in equation (3), here the first two terms give  $\Delta H(T_1)$  and the subsequent effect of temperature is shown by the term in  $\Delta c_p$ . If this is zero, and the two components of the baseline are colinear, no care is needed in locating  $T_1$  and  $T_2$  except for the obvious requirement that both should be outside the cure region. However, even for the present near-ideal system (for which  $c_{pp}$  is only about 2% less than  $c_{pr}$ , Table IV),  $\Delta H(T)$  increases from -341 to -345 J g<sup>-1</sup> as  $T$  increases from 380 to 480 K (4 to 100% cure) and for most resins  $\Delta c_p$  is much greater than for the present example. The "observed"  $\Delta H$  is -341.4 J g<sup>-1</sup> - the value of  $\Delta H(T)$  for  $T \approx 390$  K and some way, because of asymmetry in the cure curve, from the majority of "peak" temperatures (Table II).

## 5.2. Enthalpy changes and complex reactions: Scanning/isothermal combinations

Enthalpy changes corresponding to those of equations (1)-(3) are shown in Fig. 5 [3]. The full line represents  $Q$  for  $T_2 = 490$  K,  $T_1 = T$ , and  $q = 10$  K min<sup>-1</sup> (the location of the step in the  $H$ - $T$  curve varies with  $q$ , the temperature of maximum slope being  $T_p$ , Table II). The extrapolated baselines are shown as broken lines which together define both  $\Delta H(T)$  and  $\Delta h(T)$ , the thermodynamic partial heat of reaction up to a temperature  $T$ . (It should be noted that both  $\Delta H(T)$  and  $\Delta h(T)$  are negative quantities). The treatment leading to Fig. 5 is direct and, with modern microcomputers, as simple as those that generate sigmoidal baselines (and assume  $\Delta H \neq f(T)$ ). Enthalpy diagrams also demonstrate how to overcome the problem of overlapping regions of cure and degradation. The vertical line XY represents residual cure when a scanning experiment is stopped prior to completion of cure. If the sample is left to cure under isothermal conditions, the isothermal area (shaded, Fig. 6) is equivalent to this residual enthalpy. Fig. 6 shows a real example of the problems met with in the cure of a B-staged resin that is used in the manufacture of printed circuit boards. Cure is complex and it is tempting to draw a baseline such as AB to obtain  $\Delta H$  - but the location of B is much influenced by the choice of the upper isothermal temperature,  $T_{\max}$  (= 520 K in Fig. 6). A conventional baseline (DE, Fig. 6) cannot be drawn because the completion of cure via a scanning experiment (ca. BD, Fig. 6) is impossible. By contrast, the thermodynamic heat of reaction  $\Delta H(T)$  presents no problems at low temperatures. The quantity  $Q$  (equations (2), (3)) is equivalent to the summation of the shaded area + CBLAEGJ, the former area is always negative, the latter, positive in Fig. 6, may become negative for a very exothermic reaction. The corresponding "baseline" is well-defined by the rerun for the fully cured product. This is linear over a wide range of temperature and the extrapolation to  $T_1$  may be made with some confidence to obtain  $\Delta H(T_1)$  (equation (3) with  $T_2 = T_{\max} = 520$  K). It is difficult to extend the calculation to higher temperatures for the resin of Fig. 6 because of the limited range around  $T_1$  from which to obtain  $dc_{pr}/dT$ . Some extension to lower temperature is possible by erasing the large relaxation peak (which, however, contains valuable information about the prior history of the sample). The peak is eliminated by heating to  $T$ , where  $T_g < T < T_{\text{cure}}$ , cooling to below  $T_g$  and immediately running the experiment. A very reasonable approximation is to assume that  $\Delta c_p \neq f(T)$  and use  $c_{pr}$  from the  $T_1$  region.



Table IV Specific Heat Data for Components and Resins

Material	MY750	HY917	DY070	Uncured Resin ( $c_{pr}$ )*	Cured Product ( $c_{pp}$ )	
					Glass	Rubber
$c_p = a + bT$ ( $J g^{-1} K^{-1}$ )						
$a$	1.148	1.021	1.054	1.088	-0.003	1.017
$b$ ( $\times 10^3$ )	2.24	2.21	2.73	2.23	4.08	2.32
*Calculated assuming mass fraction additivity (see text) for 100/90/2 mixture						

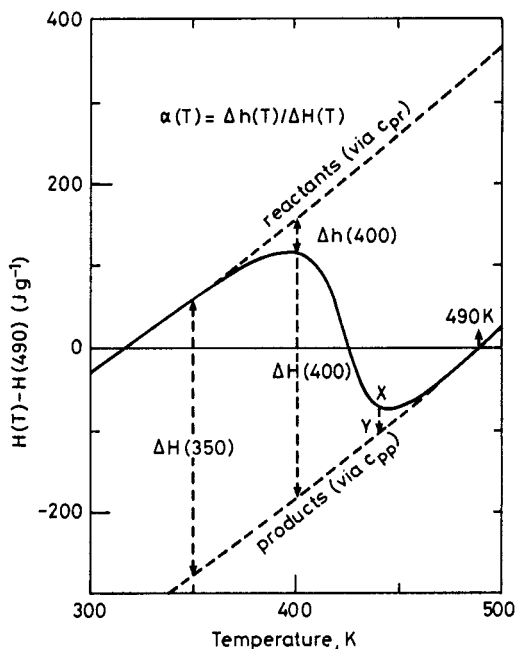
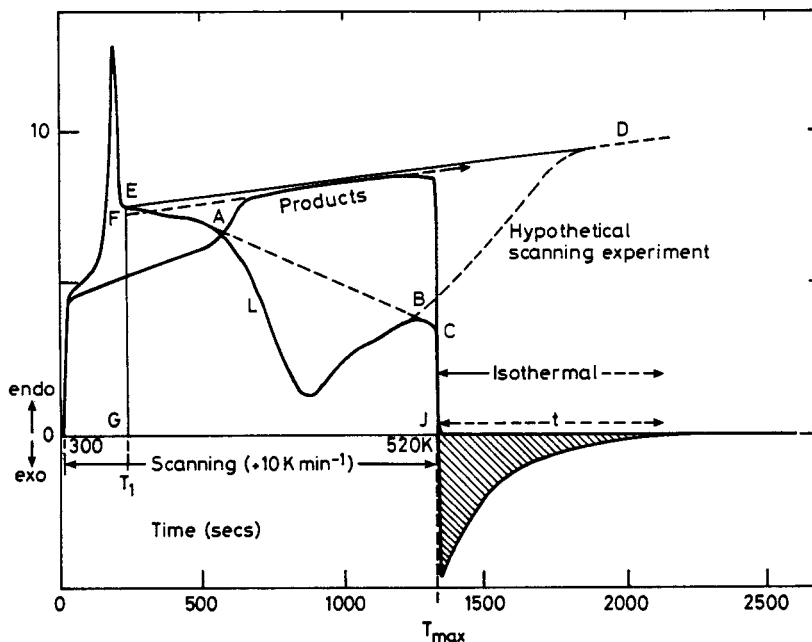


Fig 5 Enthalpy - temperature curves ( $H(490 K) \equiv 0$ ) for cure at  $10 K min^{-1}$ . In general  $c_{pr} > c_{pp}$  and  $|\Delta H(T)|$  increases with temperature. The line XY shows the effect of terminating the scan at 440 K and allowing cure to finish isothermally.

Fig 6 A combination of scanning and isothermal runs, above  $T_{max}$  thermal degradation becomes important. Without the isothermal region it is impossible to draw a meaningful baseline.



For quality control purposes a simple procedure is required and the thermodynamic approach outlined here has the surprising advantages of both simplicity and rigour. It does, however, require time, both for the isothermal period,  $t$ , at  $T_{\max}$  and for the rerun. Against this must be set the great advantage of elimination of the very subjective baseline AB. The only choice to be made is the value of  $T_1$ .

Whatever procedure is used, the selection of  $T_{\max}$  must be a matter of trial and error:  $T_g$  is observed as a function of  $T_{\max}$  and the isothermal cure time  $t$ , any decrease in  $T_g$  implies that degradation has set in. The slight deviation from linearity in the rerun curve as  $T_{\max}$  is approached (Fig. 6) suggests (and  $T_g$  results confirm) that 520 K is too high for the optimum degree of cure for this material.

### 5.3. Kinetic information

Many procedures have been described for the derivation of kinetic information from DSC data. Those of Borchardt and Daniels [4] and of ASTM E698 [5] are particularly widely used and most instrument manufacturers provide suitable programmes. The resultant parameters are generally used to calculate isothermal conversion  $v$  time curves from which appropriate conditions are selected for the cure of a given resin.

All treatments assume that the rate constant has an Arrhenius temperature dependence so that the rate,  $d\alpha/dt$ , is given by

$$d\alpha/dt = f(\alpha)A \exp(-E/RT) \quad (4)$$

where  $A$  is the pre-exponential factor,  $E$  the activation energy and  $R$  the gas constant. The function  $f(\alpha)$  is generally unknown but it is often assumed (eg. Borchardt and Daniels) to have the form  $(1 - \alpha)^n$ . Data treatments either manipulate (4) or some integral form - although Flynn [6] has drawn attention to the advantages of (4) when it is allied with modern computing facilities. Notwithstanding this, the great simplicity of application of E698, which uses an integral form of (4) due to Ozawa [7] and requires only  $T_p$  (Table II) as a function of  $q$ , makes this a natural starting point for any discussion of the kinetics of cure.

#### 5.3.1. ASTM E-698

This method has been fully discussed by Prime [1]. The activation energy  $E$  is derived from the gradient of  $\ln q v l/T_p$  together with Doyle's tabulation [8] for the exponential integral - two approximations were adequate. The Standard gives relevant practical details. The main problems concern self-heating effects for large sample masses and/or high heating rates. Experimental results, the change of  $T_p$  with  $q$ , are given in Table II together with the derived values of  $E$ . Most  $T_p$  values were checked to show that they were independent of sample mass. It is unusual to include  $q$  as high as  $40 \text{ K min}^{-1}$  and the two sets of Table II were added to demonstrate the effect of high  $q$ . There is a change of only 2% in  $E$  if the  $q = 40$  data are omitted from the calculations ( $79.4 \rightarrow 77.7$  and  $73.6 \rightarrow 75.5 \text{ kJ mole}^{-1}$ , respectively, for sets 1 and 2 of Table II); perhaps of greater significance is the different sign for the two cases - self-heating should always bias the results in one direction. However, it will be seen later that there is other evidence that for laboratory 1 (NPL data) the high  $q$  results are atypical. For consistency, therefore, all  $E$  values in Table II have been derived from  $q \leq 20 \text{ K min}^{-1}$ . Almost identical activation energies are found if data are treated using the alternative approach plotting  $\ln(q/T_p^2)$  against  $1/T_p$  [9].

The average of all  $E$  (Table II) is  $73 \text{ kJ mole}^{-1}$  ( $\pm 8\%$ ). Because  $E$  is derived from a gradient, errors in the temperature calibration will have an element of self-compensation about them. For this reason the rather different  $T_p$  reported by laboratory 6 are only mildly reflected in the corresponding  $E$ . The practical effect of the range of  $E$  values is not large. For an  $n$ -th order reaction the pre-exponential factor can be calculated as  $A = (qE/RT_p^2) \exp(E/RT_p)$  [9] from which the rate constant  $k$  can be calculated at any temperature. Assuming, for simplicity, that  $n = 1$ , the reaction half life can be calculated as  $t_{1/2} = 0.693/k$  (other values of  $n$  change the numerical factor) and Table V shows  $t_{1/2}$  at 100 and 150 °C for the several  $E$  values of Table II. The only significant differences are for laboratories 5 and 6. These are those with the greatest differences from the mean  $T_p$  values - the effect is due to the  $1/T_p^2$  term in the expression for  $A$ . Laboratory 2 checked the  $t_{1/2}$  calculation experimentally and found  $\alpha = 0.6$  after 30 min at 90 °C (calculated 0.5 assuming  $n = 1$ ); the agreement is acceptable for practical applications, especially when the uncertainty in  $n$  is considered. The general consistency of the data of Table II shows the applicability of E698 and this is especially true for complex reactions for which the separate behaviour of individual peaks can be followed. A negative feature is that the method cannot be used to characterise the initial state of a B-staged resin, for example, because the location of  $T_p$  is little changed by the degree of cure. Detailed information on the state of a resin and the cure kinetics can only be obtained by using all information that a cure curve contains.

### 5.3.2. Rate and extent of cure

The basis of most procedures for the derivation of kinetic data from DSC curves is the logarithmic form of (4)

$$\ln(d\alpha/dt) = \ln[Af(\alpha)] - E/RT \quad (5)$$

Many forms of  $f(\alpha)$  have been suggested. One of the most widely used assumes  $n$ -th order kinetics  $f(\alpha) = (1-\alpha)^n$ . Substitution in (5) leaves, for a given point on a cure curve, three unknowns,  $A$ ,  $n$ , and  $E$ . The total curve gives many such points and the three constants are obtained using a multiple regression analysis; more complex forms of  $f(\alpha)$  can obviously be used. A good test of the validity of the whole procedure is to fit the data over various ranges of  $\alpha$ . When this is done there are often great changes in the derived parameters ( $n$  may even change sign). Under these circumstances the fitting constants have only mathematical, rather than chemical or physical, significance. Of course, there is no reason why the reaction mechanism should *not* change with  $\alpha$  but this can be better demonstrated by the use of isoconversion data.

The procedure has been described by Flynn [6]. Reaction rates,  $(d\alpha/dt)$ , for the several heating rates are plotted against  $1/T_i$  for  $\alpha_i = 0.1, 0.2, \dots$  etc. For a given  $\alpha_i$ ,  $f(\alpha_i)$  is constant and the result is a set of  $E$  and  $\ln[Af(\alpha)]$  values as functions of  $\alpha_i$ . Results are shown in Fig. 7. If the reaction mechanism is constant  $E$  should be independent of  $\alpha$  and this is very nearly the case for the present results - especially if the data obtained at  $q = 40 \text{ K min}^{-1}$  are omitted (compare the full and broken lines of Fig. 7). The two sets of curves give similar results at their extremes and this strongly suggests that the results at  $40 \text{ K min}^{-1}$  are perturbed by self heating in the region of high reaction rates. (There are only minor additional changes in  $E - < 1\%$  - if  $q = 20 \text{ K min}^{-1}$  data are also omitted).

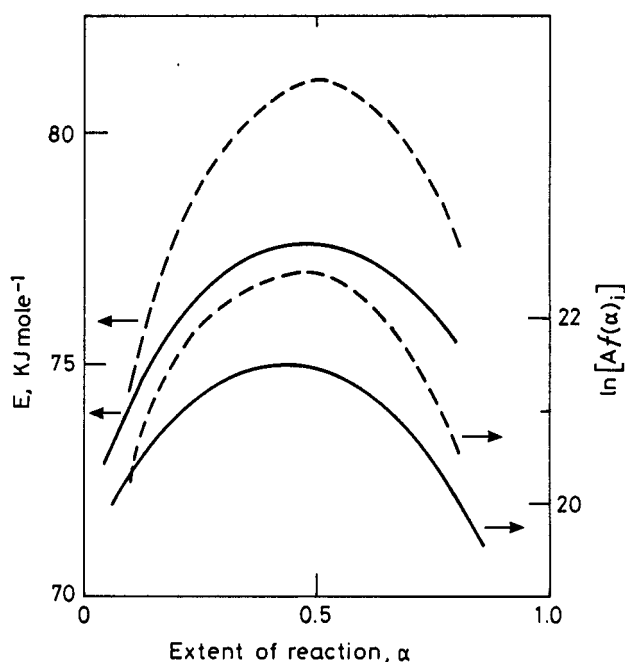


Fig 7 Activation energy  $E$  and  $\ln[Af(\alpha)]$  as functions of  $\alpha$ ; - - - all  $q$  included; — excluding  $q = 40 \text{ K min}^{-1}$ , (there is little additional effect when  $q = 20$  is omitted).

Table V Reaction Half-Life (Min)

Laboratory	Temperature	
	100 °C	150 °C
1	14.8	0.77
2	16.3	0.92
3	16.2	0.79
4	13.2	0.80
5	9.6	0.60
6	42.8	3.08
7	15.1	0.75
8	12.1	0.75
9	12.4	0.85

Table VI Extent of Reaction at  $T_p$

$q(\text{K min}^{-1})$	$\bar{\alpha}_p$
2.5	.585 (.582/.593/.579/.586)
5	.577 (.571/.570/.578/.587)
10	.579 (.577/.578/.581/.586) (.588/.573/.581/.568)
20	.566 (.566/.579/.574/.554)
40	.562 (.524/.594/.561/.569)

One of the assumptions leading to E698 is that the extent of reaction,  $\alpha_p$ , at  $T_p$  is constant and NPL data for the various  $q$  are given in Table VI. Although a small decrease in  $\bar{\alpha}_p$  (the mean value) with increasing  $q$  is indicated, individual results overlap and for all practical purposes  $\alpha_p \neq f(q)$ . (The wide scatter in the  $40 \text{ K min}^{-1}$  results is a data collection problem - the sampling rate was too slow to define the peak region adequately). It is encouraging to note that the value of  $E$  at  $\alpha = \alpha_p = 0.58$  (Fig. 7) is  $77.4 \text{ kJ mole}^{-1}$  - in excellent agreement with the E698 value of  $77.7 \text{ kJ mole}^{-1}$ .

In principle it is now possible to derive  $\ln A$  from the dependence of  $\ln[Af(\alpha)]$  on  $\alpha$  because many forms of  $f(\alpha)$  tend to unity as  $\alpha$  tends to zero. Unfortunately, numerical values are such that any kind of extrapolation leads to considerable uncertainty in  $\ln A$ . All that can be achieved is to note that the E698 procedure, with  $E = 77.7 \text{ kJ mole}^{-1}$  and the several approximations necessary, gives  $\ln A = 22.0$  - a value that could reasonably be obtained by extrapolation of the  $\ln Af(\alpha)$  curve in the vicinity of  $\alpha = \alpha_p = 0.58$ .

## 6. CONCLUDING REMARKS

The present collaborative work has shown that peak temperatures can be determined to  $\pm 1.5 \text{ K}$  using either heat flux or power compensation DSC: the few problems that arise when using DSC in a thermometric mode are generally due to errors of calibration rather than material-related difficulties. It was very surprising, therefore, to find (4.2) the wide range (some 50 K) reported for  $T_g$  of the cured polymer since this is normally a well-defined material property (for a given thermal history). The discussion in 4.2 showed how the uncertainty was caused by the thermal instability of the cross-linked product - an instability for which there is a conspicuous lack of DSC evidence in the shape of exo- or endothermic events in the rubbery region.

Although much useful information can be derived (5.3.1) from  $T_p$  it is not possible to obtain any impression of the initial extent of cure which is often the object of quality control work (for the resin of Fig. 6, for example). Here  $\Delta H$  is required and problems may arise even for correctly calibrated instruments. Difficulties are caused by uncertainties in the definition of the appropriate baseline. These are not severe for the near-ideal system used here (4.3 and Table III) although unreported work from this laboratory shows that it is possible to introduce errors of several percent by incorrect adjustment of the instrumental baseline. This should, of course, be removed in the setting-up of any instrument but in quality control work this may not receive the attention it deserves. More important problems arise when there is no obvious "dynamic" baseline, as in Fig. 6. Here, when steady state conditions are still perturbed by reaction, seemingly equivalent positions may refer to different states because of the different time constants of the various instruments. Even an arbitrary (and quite acceptable) quality control " $\Delta H$ " will therefore require time-consuming work to establish equivalence between values for different instruments. The procedures of 5.2, although longer than conventional operations, give absolute values and, more important, allow transferability of data between different instruments. They should be an option in the various programmes that all manufacturers now supply for "cure" work.

The cure of any resin is chemically complex and reaction mechanisms have only briefly been touched upon. The derivation of basic physical parameters has been emphasised and an introduction given of their use in tests for consistency. Mechanisms may be introduced at this stage but for them to have any value it is essential that verification is based on sound data. The aim of this work is to indicate how such data may be obtained.

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