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A COMPARISON OF COMMERCIALLY AVAILABLE DSC KINETIC METHODS IN EVALUATING BISMALEIMIDE RESINS

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The ability of commercially available software, based upon literature methods, to derive kinetic data has been demonstrated. Care, however, must be taken in selecting the appropriate model for the reaction under investigation.

Keywords: bismaleimide resins, DSC, kinetic methods

Introduction

In the industrial, as opposed to the academic world the study of kinetics is usually a compromise between speed, accuracy and cost. In these circumstances there is not always the time, or necessity, to completely understand a reaction mechanism, such as the curing of a thermoset. Consequently, an increasing emphasis is being placed upon using commercially available software to provide kinetic data.

This paper reviews three commercially available kinetic programs and assesses their suitability in characterising the cure behaviour of bismaleimide resins. Bismaleimides are being used increasingly in place of epoxy resin based systems where higher temperatures (ca 200°C) are encountered.

The predicted isothermal cure behaviour derived from the kinetics methods is compared with the residual cure found by Differential Scanning Calorimetry (DSC) after holding a sample of the bismaleimide at a known temperature for a known time. The use of the multiple dynamic rate method (ASTM E–698) to rank the reactivity of a series of bismaleimides is also presented.

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Overview of DSC kinetic methods

Two basic assumptions in DSC kinetics are that the heat flow relative to the instrumental baseline is proportional to the reaction rate and that the temperature gradient through the sample and the sample-reference temperature difference is small. By using small sample sizes (10 mg) and slow heating rates (or isothermal experiments) these assumptions are reasonable.

An exothermic peak is recorded when heating a thermoset in a DSC due to the heat evolved from the cross-linking reaction. At any given time (or temperature) the rate of conversion ($d\alpha/dt$) is equal to the heat flow at that time or temperature divided by the total heat of reaction:

$$\frac{d\alpha}{dt}=\frac{dg/dt}{\Delta H_{\mathrm{Cure}}} \quad (1)$$

The fraction converted, α, is obtained by measuring the ratio of the partial area, ΔH_{T}, at temperature T to the total peak area:

$$\alpha=\frac{\Delta H_{\mathrm{T}}}{\Delta H_{\mathrm{Cure}}} \quad (2)$$

The detailed theory for the three kinetic methods evaluated here have been reviewed by Jang [1].

Experimental

All experiments were performed on a TA Instruments DSC 10 Differential Scanning Calorimeter and TA2000 Thermal Analyst Controller. Samples, weighed to within 0.1 mg, were encapsulated in standard aluminium pans. The DSC was purged with dry nitrogen at 50 cc/min. The software used to analyse the results by the various kinetics methods was also from TA Instruments.

Results and discussion

Single dynamic ramp

Figure 1 shows the exotherm detected by the DSC due to the cross-linking reaction of a modified bismaleimide heated at 20 deg·min^{-1}. A sigmoidal baseline has been used to calculate the enthalpy of cross-linking. This is often necessary at high (above 5 deg·min^{-1}) heating rates as the polymer does not have sufficient time to completely cure before it starts to decompose and degrade.

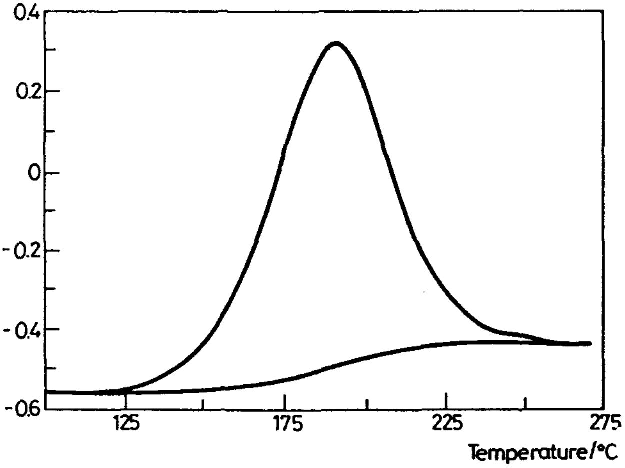

Fig. 1 The modified bismaleimide analysed by the Borchardt and Daniels kinetic method

The Arrhenius plot (Fig. 2) shows a straight line, indicating that the system appears to obey Eqs (3) and (4). At this heating rate the kinetic constants have been calculated as a reaction order of 1.43 together with an activation energy of 119.4 kJ/mole.

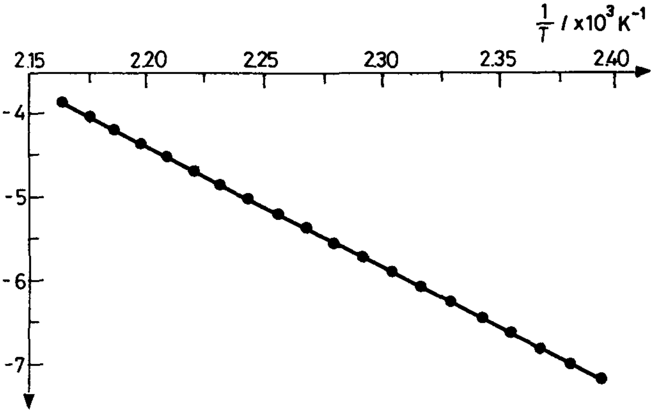

Fig. 2 Arrhenius plot obtained from the Borchardt and Daniels method for the modified bismaleimide

As the ASTM–E698 method requires a number of scans at different heating rates, it is often useful to analyse these scans by the single dynamic ramp method as well. Table 1 shows the kinetic results of separate samples analysed at a number of heating rates.

Table 1 Summary of kinetic constants obtained by the Borchardt and Daniels method

Heating rate / deg·min^{-1}	Reaction order n	Activation energy E / kJ·mol^{-1}	Log Z/ min^{-1}	Heat of reaction / J·g^{-1}	Std error
20	1.43	119.4	13.59	114.0	0.0042
15	1.45	113.6	12.77	119.5	0.0144
10	1.50	122.3	13.99	120.0	0.0053
7.5	1.59	118.6	13.65	117.1	0.0106
5.0	1.74	121.4	13.97	121.9	0.0147
Average	1.54	119.1	13.60	118.5	0.0098

As the heating rate decreases, thermal gradients within the sample will be smaller. This has little effect upon the calculated values of Z and E, but the reaction order is seen to increase with decreasing heating rate.

Multiple dynamic scans

The DSC scans used to create Table 1 were then analysed by the ASTM–E698 method. From Fig. 3 it can be seen that as the heating rate increases so does the peak size and peak moves to higher temperatures.

The ASTM E–698 method assumes that the extent of reaction is constant at the peak maximum temperature. However, the mathematics is similar if the assumption is made that the degree of reaction is equivalent at equivalent peak partial areas, e. g. at 10% peak area 10% of the reaction has occurred, regardless of heating rate. This permits kinetic values to be obtained as a function of the degree of conversion, α. The calculated kinetics constants are summarised in Table 2.

Table 2 Summary of kinetic constants obtained by the ASTM–E698 method

% Conversion	Activation energy/ kJ·mol^{-1}	Log Z/ min^{-1}	60 min 1/2 life
Peak Maximum	84.9	9.492	114.8
10	87.7	9.537	126.0
20	82.5	8.974	121.6
30	80.0	8.726	118.8
40	78.5	8.585	116.7

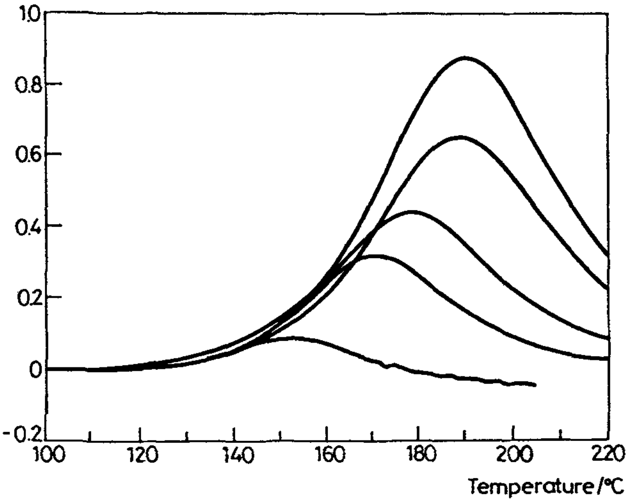

Fig. 3 Overlay of several DSC runs at heating rates between 2.5 deg·min^{-1} and 20 deg·min^{-1} for the modified bismaleimide

Multiple isothermal scans

Figure 4 shows the isothermal DSC scans for the modified bismaleimide as a function of isothermal temperature. As the temperature increases the peak height and peak area increase as the degree of conversion increases. As the peak maximum occurs close to $t = 0$ and there appears to be no induction time to the reaction it is assumed that the reaction follows *n*th order kinetics and is not autocatalytic.

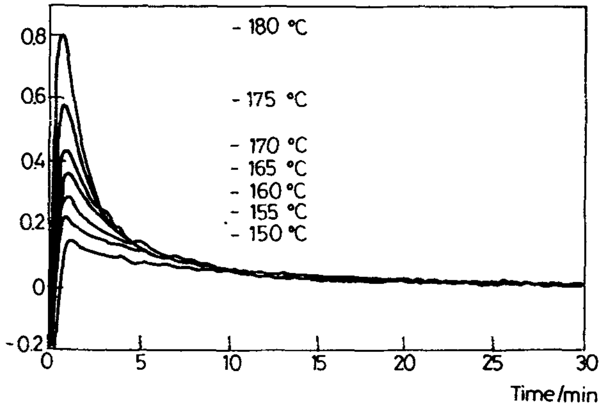

Fig. 4 The modified bismaleimide curing at a range of isothermal temperatures between 180°C and 150°C

The maximum peak area for the isothermal scan was found to be 128 J/g at 180°C and this value was used as the 100% ΔH_{Cure} figure for calculating the % reacted at the lower isothermal temperatures. A summary of all derived kinetic constants is given in Table 3.

Table 3 Summary of derived kinetic constants

Method	Activation energy/ kJ·mol^{-1}	Log Z/ min^{-1}	Reaction order n
Borchardt and Daniels (Note 1)	119.1 + / – 3.2	13.60 + / – 0.39	1.54 + / – 0.20
ASTM–E698	84.9	9.49	1 (Note 2)
Isothermal *n*th order	118.0 + / – 3.4	13.30 + / – 0.41	1.75 + / – 0.069

Note 1: Average of values obtained at 5 different heating rates. At low heating rates values tend to those obtained by isothermal method

Note 2: Reaction order of 1 is assumed in the method

Validation

The validity of the predicted isothermal conversion behaviour was checked by reheating the samples that had been used for the isothermal experiments to determine the residual cure. At the lower isothermal temperatures used in these isothermal experiments the bismaleimide would not have been fully cured. The residual cure found is compared to the predicted behaviour from the three kinetic methods in Table 4.

For the modified bismaleimide studied here the best prediction of behaviour is found from the multiple isothermal method. However, the Single Dynamic Scan also gives good agreement from a single run, especially at low conversion levels. It is interesting to note that for this system the multiple heating rate method does not give good kinetic results or predicted cure behaviour. It is possible that this is due to the assumption of 1st order reaction rate as both the other methods indicate a reaction order of between 1.75 and 1.45.

Comparison of commercial bismaleimides

In industry it is often necessary to compare samples of commercially available bismaleimides with respect to their cure behaviour. Rather than sacrificing time and money testing a material on the shop floor the DSC can be used to compare and rank samples in a few hours.

Often a commercial resin system will be manufactured from blends of bismaleimide monomers with a variety of co-monomers and other additives designed to improve processing and mechanical properties. A common building

Table 4 Comparison of actual and predicted cure levels from the three kinetic models

Conditions	% Cure level found	% Cure level predicted		
	Dynamic DSC after isothermal hold	Single dynamic scan	Multiple dynamic scan	Multiple isothermal scans (n^{th} order)
30 min at 160°C	78	90	99	80
30 min at 140°C	40	52	83	42
30 min at 120°C	9	10	37	8

block is 4,4'–bismaleimidodiphenylmethane. This material displays a glass transition temperature of around 140°C followed immediately by two sharp melting peaks and a single cure exotherm, Fig. 5. Any of the DSC kinetic methods can be used to analyse this material. However, as other co-monomers and additives are added the cure process becomes more complicated and multiple cure exotherms

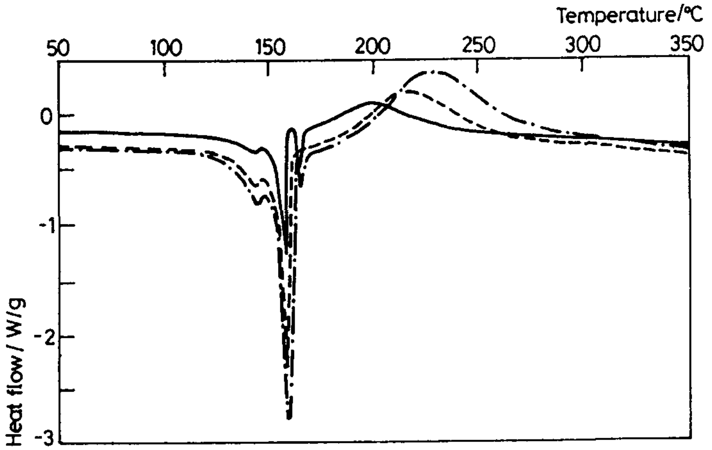

Fig. 5 DSC scans showing the melt and cross-linking of 4,4'–bismaleimidodiphenylmethane at 5 deg·min^{-1}, 10 deg·min^{-1} and 20 deg·min^{-1}

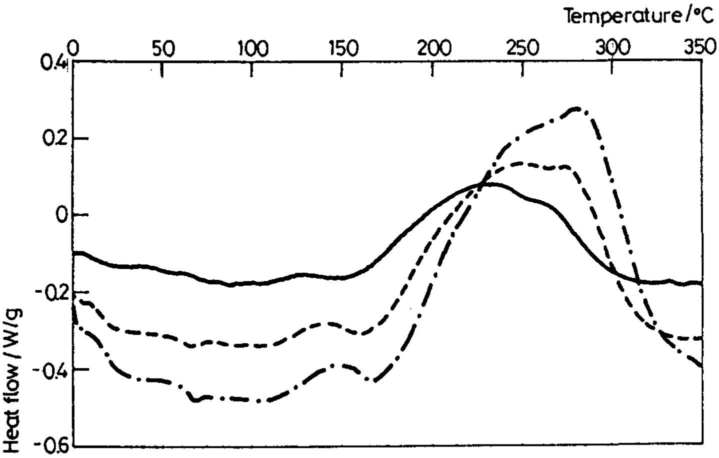

Fig. 6 Typical DSC results for 4,4'–bismaleimidodiphenylmethane modified by the addition of other co-polymers

are observed, Fig. 6. This has been explained by chain extension as well as cross-linking processes.

In order to compare these types of materials a decision has to be made about the most appropriate kinetic model. The Borchardt and Daniels method is not suitable for overlapping reactions or where choosing baseline limits is difficult. The material could be analysed by the isothermal method with isothermal temperatures being selected so that the individual reaction processes could be separated. This would involve more time than is available in the industrial world.

Table 5 Comparison of kinetic constants for several bismaleimide resin systems

Sample	Activation energy E / kJ·mol^{-1}	log Z/ min^{-1}	ΔH_{Cure}/ J·g^{-1}
'Basic' bismaleimide	68.4	6.69	150.4 + / − 20.4
Resin System 1	78.1	7.28	271.5 + / −10.8
Resin System 2	79.7	7.40	262.9 + / − 9.4
Resin System 3	85.3	7.76	156.2 + / − 47.3

A compromise is reached where the speed and simplicity of detecting peak maximum temperatures for the curing process using the ASTM–E698 method takes higher priority than the assumption of 1st order reaction kinetics. The results from a number of systems analysed by the ASTM–E698 method is given in Table 5.

The 'basic' bismaleimide can be seen to have the lowest activation energy and pre-exponential factor, therefore it will cure faster than the commercially modified bismaleimides. The commercially available materials have slower cure profiles, and are designed to achieve optimum processing characteristics in terms of viscosity, time to gelation and cure time. By comparing the kinetic constants of a material which has a known processing behaviour, materials from other potential suppliers can be evaluated easily in the laboratory.

References

1 W. Jang, A review of DSC Kinetic Methods. TA Instruments, Delaware.

Zusammenfassung — Es wird die Fähigkeit von handelsüblicher, auf in der Literatur beschriebenen Methoden beruhender Software zur Ermittlung kinetischer Daten demonstriert. Für die untersuchte Reaktion muß jedoch eine sorgfältige Auswahl des entsprechenden Modelles erfolgen.