

Thermal Analysis Application Brief

A Comparison of Commercially Available DSC Kinetic Methods for Evaluating Bismaleimide Resins

Number TA-143

SUMMARY

DSC provides a convenient method for obtaining kinetics information on a wide variety of materials. This study compares the results obtained from three different commercially-available DSC kinetic approaches for bismaleimide resins, which are being used increasingly to replace epoxy resins in higher temperature ($\geq 200^{\circ}\text{C}$) applications.

INTRODUCTION

Differential Scanning Calorimetry (DSC) is used to measure heat flow into or out of a sample as it is exposed to a controlled thermal profile. DSC provides both qualitative and quantitative information about material transitions such as the glass transition, crystallization, curing, melting, and decomposition. For some of these transitions, DSC can provide not only the temperature at which the transition (reaction) occurs and how much total heat is involved, but DSC can also provide valuable information about the rate (kinetics) of reaction. Furthermore, with the advent of easy-to-use computer based data analysis programs, the ability to obtain such kinetic information has become practical.

TA Instruments currently offers three software packages (approaches) for DSC kinetic studies:

- Borchardt and Daniels
- ASTM E-698 Thermal Stability
- Isothermal Kinetics

Each of these kinetic packages provides rapid automatic calculation of reaction order (n and/or m), activation energy (E_a), pre-exponential factor (Z), and rate constant (k). Each also provides the ability to use the kinetics parameters obtained to generate predictive thermal curves which can be used to assess the transition in terms of percent conversion, time, and temperature. Since no single approach is satisfactory for all transitions, care must be taken to select the correct approach to obtain meaningful kinetic parameters. These three approaches are described in more detail in TA Instruments Publication (TA-073).

EXPERIMENTAL

Determination of kinetics by DSC is based on two assumptions - (1) the heat flow relative to the instrument baseline is proportional to reaction rate and (2) the temperature gradients through the sample as well as the temperature difference between the sample and reference are small. Those assumptions are generally reasonable provided small sample sizes ($\leq 10\text{mg}$) and slow heating rates (or isothermal experiments) are used.

In this case, the bismaleimide samples were weighed to within 0.1mg before encapsulation in crimped aluminum pans. Dry nitrogen gas at 50 ml/minute was used to purge the DSC cell during the experiments.

RESULTS

Figure 1 shows the curing exotherm for a modified bismaleimide heated at $20^{\circ}\text{C}/\text{minute}$. A sigmoidal baseline is used to calculate the enthalpy since the heat capacity change during cure causes a baseline shift. Using the Borchardt and Daniels kinetic approach, it is possible to obtain reaction order (1.43) and activation energy (119.4 kJ/mole) from a plot of $\ln k(T)$ versus $1/T$ as shown in Figure 2. Table 1 shows the influence of heating rate on the kinetic parameters obtained. The only parameter significantly affected is reaction order (n). A slower heating rate ($5^{\circ}\text{C}/\text{minute}$) is recommended in this case to obtain a good reaction order value.

The ASTM E-698 kinetics approach is based on the change in peak size and peak temperature as the heating rate changes (Figure 3). This method assumes that the extent of reaction is constant at the peak maximum temperature. However, the mathematics are 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 (a). The calculated kinetics constants are summarized in Table 2.



B&D KINETICS - MODIFIED BISMALIMIDE

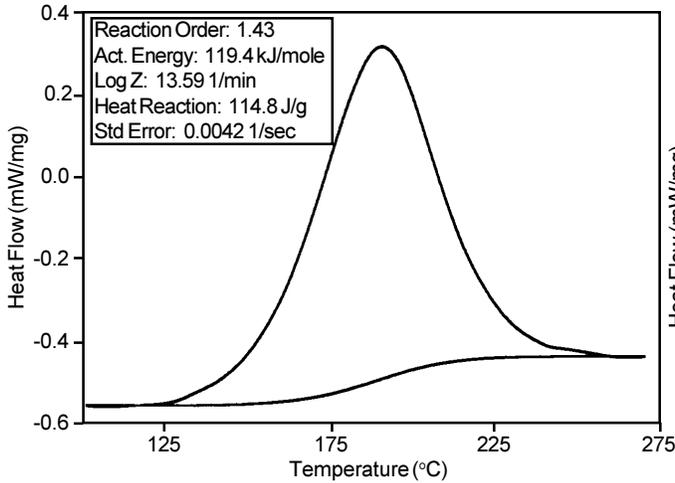


Figure 1

ASTM E698 KINETICS - MODIFIED BISMALIMIDE

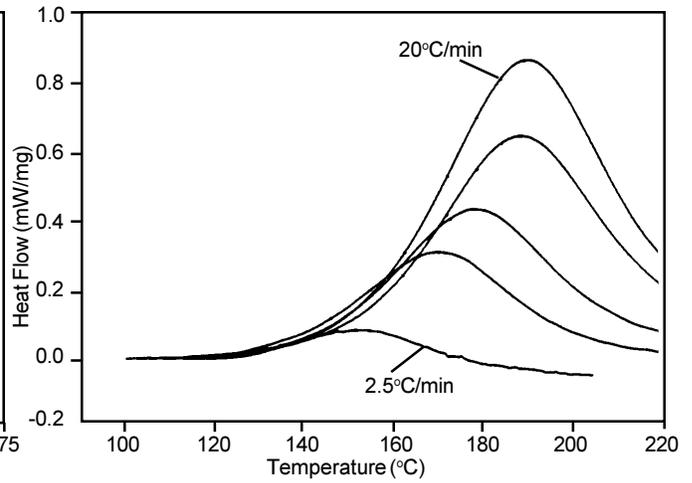


Figure 3

ARRHENIUS PLOT (B&D METHOD)

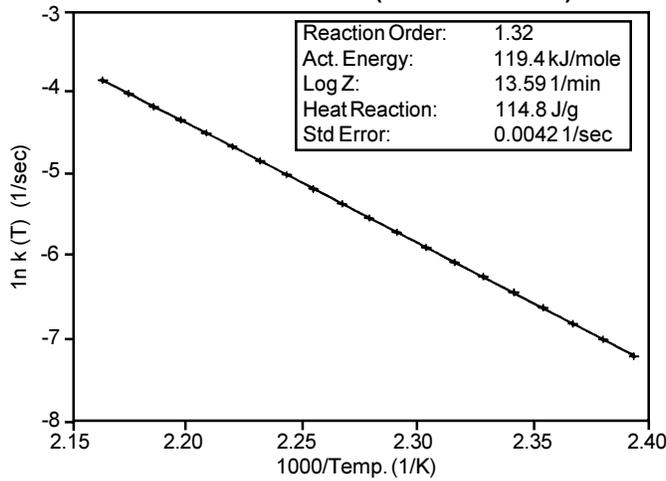


Figure 2

% Conversio	Activation Energy (kJ/mol)	Log Z (1/min)	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

Table 2

Heating Rate (°C/min)	Reacti order (n)	Activat Energy (kJ/mo)	Log Z (1/mi)	Heat of Reacti (J/g)	Std Error
20	1.43	119.4	13.5	114.0	0.004
15	1.45	113.6	12.7	119.5	0.014
10	1.50	122.3	13.9	120.0	0.005
7.5	1.59	118.6	13.6	117.1	0.010
5.0	1.74	121.4	13.9	121.9	0.014
Averag	1.54	119.1	13.6	118.5	0.009

Table 1

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 nth order kinetics and is not autocatalytic. Subsequent calculations yield the kinetic values shown in Table 3. Table 3 also shows the B&D and ASTM results for comparison.

Once the kinetic parameters are determined, they can be quickly verified by partially reacting a sample of the material and then comparing its residual reactivity to that projected by the calculated kinetics. In the bismaleimides, for example, if a sample of uncured material is held isothermally at a temperature and time which partially completes

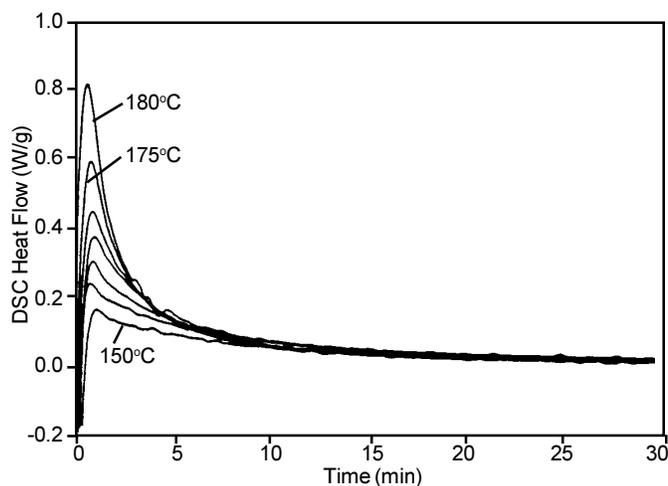


Figure 4

SUMMARY OF DERIVED KINETIC CONSTANTS

Method	Activatio Energy (KJ/mol)	Log Z (1/min)	Reaction Order (n)
Borchar 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)
Isother Nth Order	118.0 +/- 3.4	13.30 +/- 0.41	1.75 +/- 0.069

Table 3

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.

COMPARISON OF ACTUAL & PREDICTED CURE LEVELS

Sample Treatm	% Cure level found	% Cure level predicted By Kinetics		
	Dynami DSC after Isother Hold	Single Dynam Scan (B&D)	Multiple Dynamic Scan (ASTM E-698)	Multiple Isother Scans (Nth order)
30 mins at 160 deg. C	78	90	99	80
30 mins at 140 deg. C	40	52	83	42
30 mins at 120 deg. C	9	10	37	8

Table 4

cure and then the material is dynamically heated, comparison of the remaining heat of cure to the ΔH for uncured material yields a % conversion (cure) which agrees with that kinetically projected. Table 4 compares the actual and kinetically predicted cure levels for a modified bismaleimide using the different kinetics approaches after several time/temperature treatments. These results indicate that the B&D and isothermal kinetic approaches are the most accurate for bismaleimide.

Despite the lower accuracy obtained with the ASTM approach, there are situations where this approach has value, particularly in production situations where rapidly screening different formulations is desirable. Commercial bismaleimide formulations, as an example, are often blends of bismaleimide monomers with a variety of co-monomers and other additives designed to improve processing and mechanical properties. A common component in these type formulations, 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 (Figure 5), and any of the DSC kinetic methods can be used to analyze this material. However, as other co-monomers and additives are added, the cure process becomes more complicated and multiple cure exotherms are observed (Figure 6). This behavior 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 analyzed by the isothermal method with isothermal temperatures being selected so that the individual reaction processes could be separated. This, however, would involve more time than is desirable.

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 analyzed 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 behavior, materials from other potential suppliers can be evaluated easily in the laboratory.

**4,4' - BISMALLEIMIDODIPHENYLMETHANE
MELT & CROSS LINKING AT 5, 10 & 20 °C/minute**

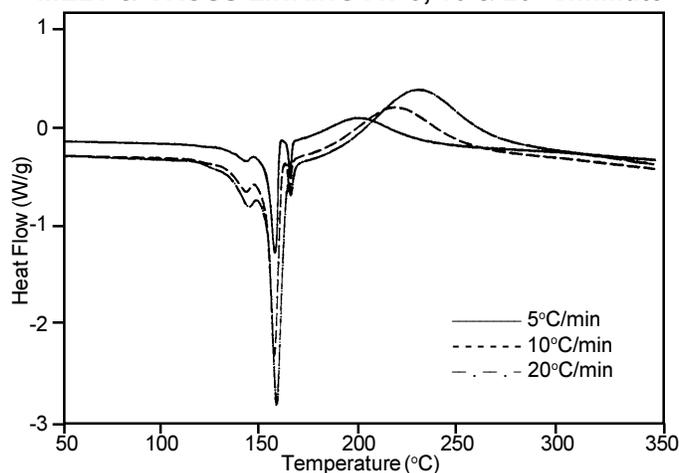


Figure 5

**COMPARISON OF KINETICS FOR
BISMALLEIMIDE SYSTEMS**

Sample	Activation Energy (kJ/mol)	log Z (1/mi)	ΔH_{Cure} (J/g)
"Basic" bismaleimid	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

Table 5

**COMPARISON OF DSC RESULTS FOR
MODIFIED 4,4' - BISMALLEIMIDODIPHENYLMETHANES**

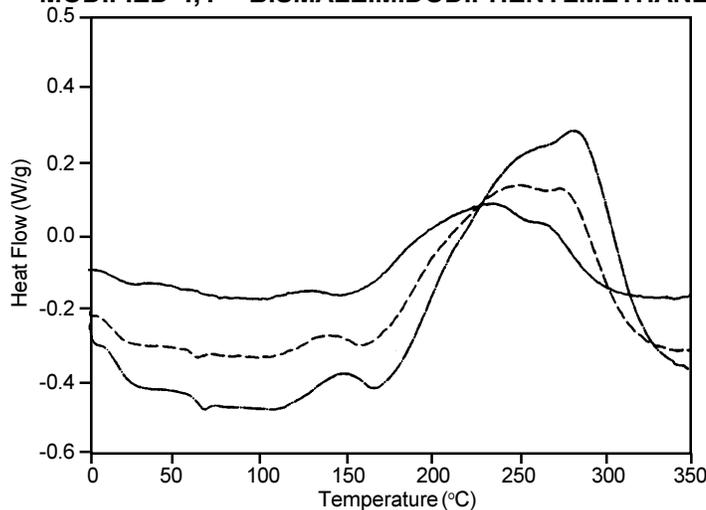


Figure 6

ACKNOWLEDGEMENT

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