A REVIEW OF DSC KINETICS METHODS

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 more 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 (Ea), pre-exponential factor (Z), and rate constant (k). Each also provides the ability to use the kinetic 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. The purpose of this review is to briefly describe the theoretical basis for each kinetic approach and to indicate typical applications.

THEORY

Borchardt and Daniels

The Borchardt and Daniels (B/D) kinetics approach permits the calculation of activation energy (Ea), pre-exponential factor (Z), heat of reaction (ΔH), reaction order (n), and rate constant (k) from a single DSC scan.

This approach was originally described by Borchardt and Daniels [1] for solutions and was subsequently refined for solids by other researchers [2].

The Borchardt and Daniels approach assumes that the reaction follows nth order kinetics and obeys the general rate equation:

$$d\alpha/dt = k(T) \, [1-\alpha]^n \qquad\qquad\qquad (1)$$

where $d\alpha/dt$ = reaction rate (1/sec)
  α = fractional conversion
  $k(T)$ = specific rate constant at temperature T
  n = reaction order.

The Borchardt and Daniels approach also assumes Arrhenius behavior:

$$k(T) = Z\, e^{-Ea/RT} \qquad (2)$$

where Ea = Activation energy (J/mol)
       Z = pre-exponential factor or Arrhenius frequency factor (1/sec)
       R = gas constant = 8.314 J/mol K

Substituting equation (2) into equation (1), rearranging, and taking logarithms yields:

$$d\alpha/dt = Z\, e^{-Ea/RT} (1-\alpha)^n \qquad (3)$$

$$\ln [d\alpha/dt] = \ln (Z) - \frac{Ea}{RT} + n \ln [1 - \alpha] \qquad (4)$$

Equation (4) can be solved with a multiple linear regression of the general form: $z = a + bx + cy$ where the two basic parameters ($d\alpha/dt$ and α) are determined from the DSC exotherm as shown in Figure 1 for an epoxy prepreg.

The determination uses 20 segments of the curve, evenly spaced by temperature. The first segment starts at 10 percent of peak height and the last segment ends at 50 percent of peak area. A plot of $\ln[k(T)]$ versus 1/T (Arrhenius plot) from this data should be a straight line if the second assumption is valid (see Figure 2). The activation energy (Ea) and pre-exponential factor (Z) are obtained from the slope and intercept of this plot respectively.

Two predictive curves are obtained from the B/D kinetic modeling: isothermal plots (Figure 3) and isoconversion plots (Figure 4). Isothermal plots provide time conditions and degree of conversion information for specific isothermal temperatures. Isoconversion plots provide time and temperature conditions for a specific conversion level. Both predictive plots are useful in the development and control of reaction conditions in order to achieve the desired final product.

There are two additional experimental considerations necessary to achieve acceptable results with the B/D approach. First, no mass loss can occur during the reaction, since sample weight is used in the calculation of heat of reaction, and assumed constant in other calculations. To ensure that mass is constant, the sample is placed in a hermetically sealed pan, and weight is measured before and after the experiment. Second, it is necessary to avoid any thermal lag effects. This is accomplished by using heating rates which do not exceed 10°C/minute.

ASTM E698 Thermal Stability

The ASTM E698 kinetics approach is based on the variable program rate method of Ozawa (3) which requires three or more experiments at different heating rates, usually between 1 and 10°C/minute.

This approach assumes Arrhenius behavior and first order reaction kinetics, yielding the equation:

$$d\alpha/dt = Z\ e^{-Ea/RT}\ (1-\alpha) \qquad\qquad (5)$$

where: $d\alpha/dt$ = reaction rate (1/sec)
          α = fractional conversion
          Z = pre-exponential factor (1/sec)
          Ea = activation energy (J/mol)
          R = gas constant = 8.314 J/mol K

since $\beta = dT/dt$, where β = heating rate
equation 5 can be rearranged to yield:

$$\beta\ d\alpha/dT = Z\ e^{-Ea/RT}\ (1-\alpha) \qquad\qquad (6)$$

The method also assumes that the extent of the reaction at the peak exotherm, α_p, is constant and independent of heating rate (4,5).

A plot of the natural logarithm of the program rate versus the peak temperature (Figure 5), provides the information necessary to calculate the activation energy (Ea), pre-exponential factor (Z), rate constant (k), and half-life ($t_{1/2}$). Refinements of the approximated activation energy (Ea) are attained by reiterations using a fourth degree polynomial.

As with the B/D approach, the calculated kinetic parameters (Ea, Z, and k) can be use to generate isothermal and isoconversion predictive plots (Figures 3 and 4), as well as half-life plots.

Isothermal

The two dynamic kinetic approaches described previously are rapid and simple, however, they are not quantitatively applicable to autocatalyzed systems. Autocatalyzed systems are characterized by the formation of some intermediate species which markedly accelerates the reaction. Epoxy systems used in industry, for example are autocatalyzed systems (6, 7, 8).

The isothermal kinetics approach can be applied theoretically to both nth order and autocatalyzed exothermic systems. It should be noted, however, that this approach is generally not used to model either endothermic reactions or crystallization kinetics.

An nth order reaction will follow equation (1), whereas an autocatalyzed reaction will follow the empirical relationship:

$$d\alpha/dt = k\,\alpha^m\,(1-\alpha$$

65°C. The sudden drop observed in activation energy after aging for 12 hours at 65°C is believed to be due to a significant change in the cure mechanism. This phenomenon is reflected also in the glass transition of the aged thermoset. Figure 11 is a plot of glass transition temperature (Tg) versus aging time at 65°C. A large increase in Tg occurs after aging for 14 hours. Hence, the glass transition temperature can be used as a quality control parameter for autocatalyzed thermosets.

For autocatalyzed thermosets, the ASTM E-698 method generally gives an accurate assessment of the activation energy. However, the pre-exponential factor (Z) may not be valid since the calculation of Z assumes nth order behavior. To determine whether the ASTM E-698 approach successfully describes the thermoset kinetics, the 60-minute half-life test should be used. In this procedure, the residual heat of cure of a sample which has been isothermally cured for 60 minutes at at a temperature where half-life is about 120 minutes is compared to the heat of cure (ΔH_O) of a freshly prepared sample. The ratio of the two exotherms (ΔH residual/ΔH_O) should be 0.5 $\pm$ 0.05. If it is not, then the ASTM E-698 method does not successfully model the cure kinetics of the thermoset; probably due to an incorrect assessment of Z. A more accurate estimation of the pre-exponential factor can be subsequently made using an autocatalyzed cure-rate expression.

Dynamic Versus Isothermal Techniques

As described previously, the Borchardt and Daniels approach requires only a single temperature programmed experiment. In theory, a dynamic DSC trace should contain all the kinetic information normally embodied in a series of isothermal experiments (9). This makes the B/D approach highly attractive. This technique is fairly rapid and works reasonably well for simple, first order reactions. On the other hand, previous work (4, 10, 11, 12) indicates the B/D method is not applicable in any of the following cases:

- Overlapping reaction peaks
- Decomposition occurs during reaction
- Autocatalyzed reactions

Furthermore, the isothermal method offers the advantages of easier data interpretation and broader applicability. This technique has been successfully applied in both nth order (17, 18) and autocatalytic (6, 7) reactions. For the investigation of a new reaction where the order and the reaction mechanism are not known, the isothermal method should be used.
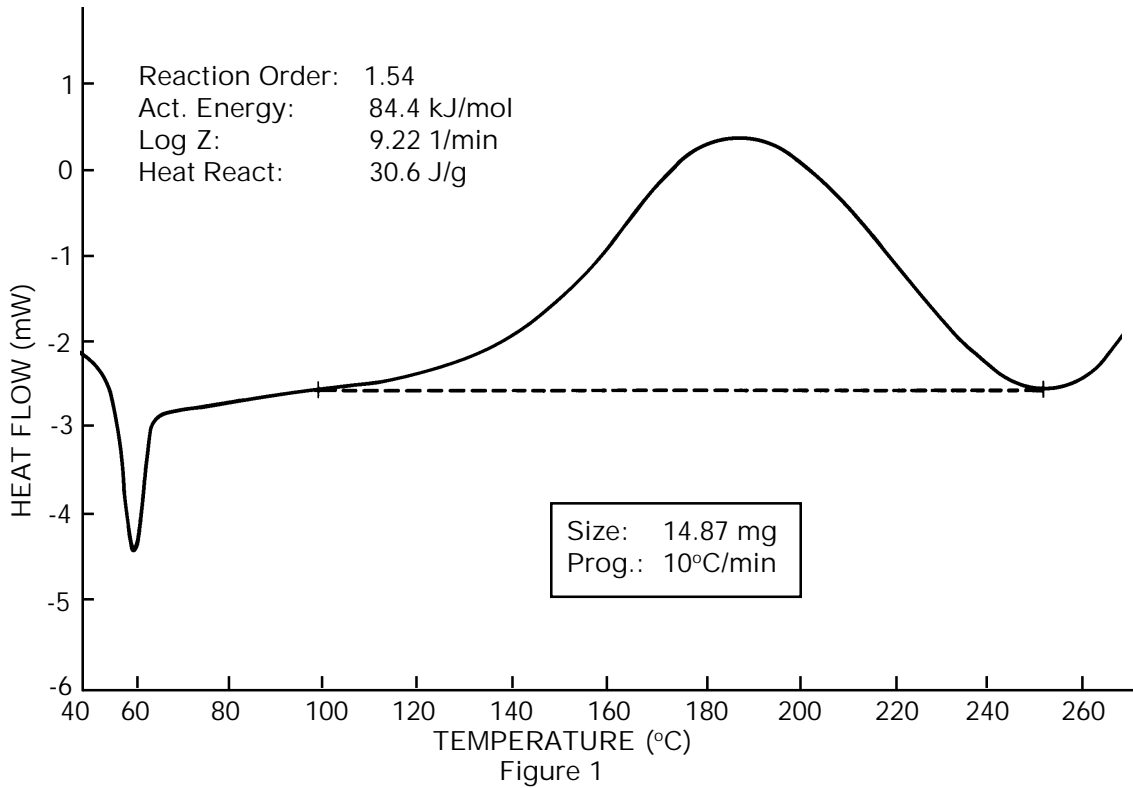
Although the isothermal experiments may be more time consuming, they often generate more reliable kinetic parameters. This is because the isothermal method introduces fewer experimental variables into a single measurement so that the scope for ambiguity in the interpretation of data is reduced (19).

SUMMARY

Modeling the kinetics of material reactions provides the scientist and engineer with valuable information for: process development and prediction of optimum reaction temperatures, process control by optimization of reaction advancement or conversion, and estimation of material lifetimes. Several DSC approaches are available for obtaining this kinetic information. The chart shown in Figure 12 provides broad guidelines for deciding which DSC method is most appropriate.
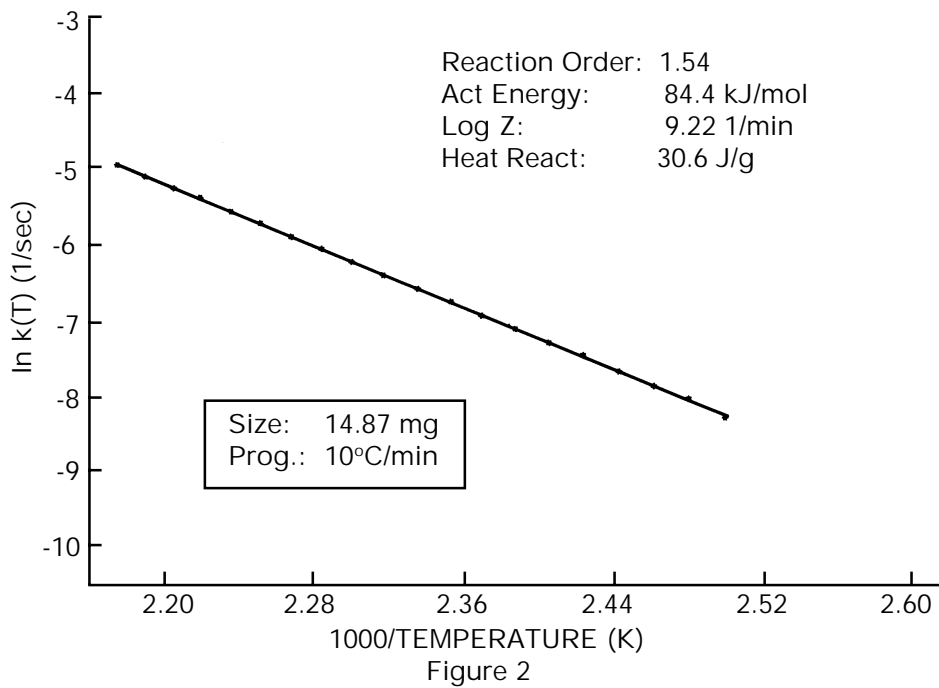
EPOXY PREPREG CURE KINETICS
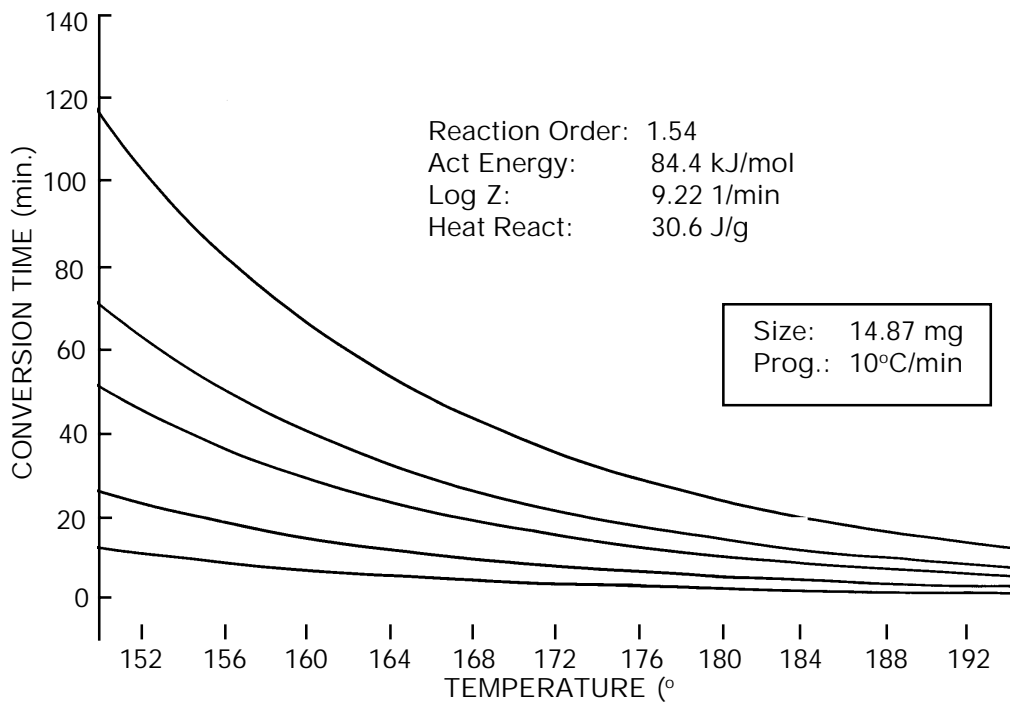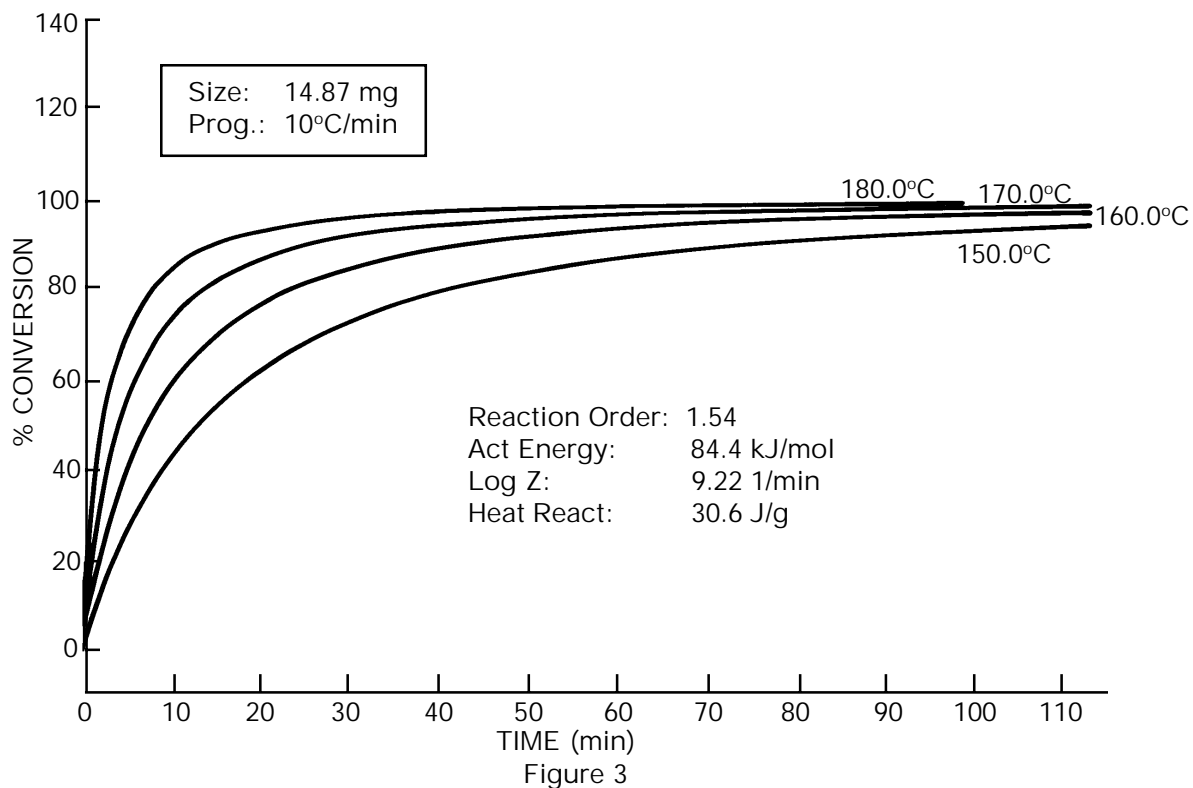## RAW DATA WITH CALCULATION

Reaction Order: 1.54
Act. Energy: 84.4 kJ/mol
Log Z: 9.22 1/min
Heat React: 30.6 J/g

Size: 14.87 mg
Prog.: 10°C/min

HEAT FLOW (mW)

TEMPERATURE (°C)

Figure 1

EPOXY PREPREG CURE KINETICS
ARRHENIUS PLOT

Reaction Order: 1.54
Act Energy: 84.4 kJ/mol
Log Z: 9.22 1/min
Heat React: 30.6 J/g

Size: 14.87 mg
Prog.: 10°C/min

ln k(T) (1/sec)

1000/TEMPERATURE (K)

Figure 2

Figure 3

EPOXY-N0VALAC-AMINE COMPOSITE ANALYSIS OF HIGH TEMPERATURE

1.8
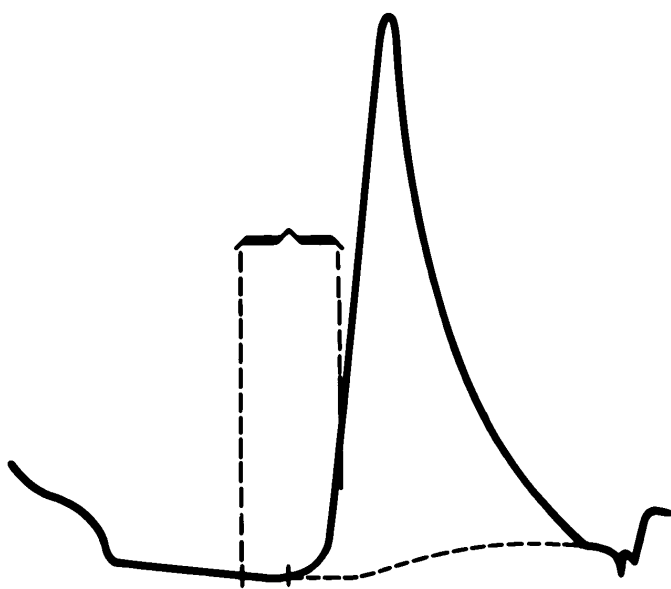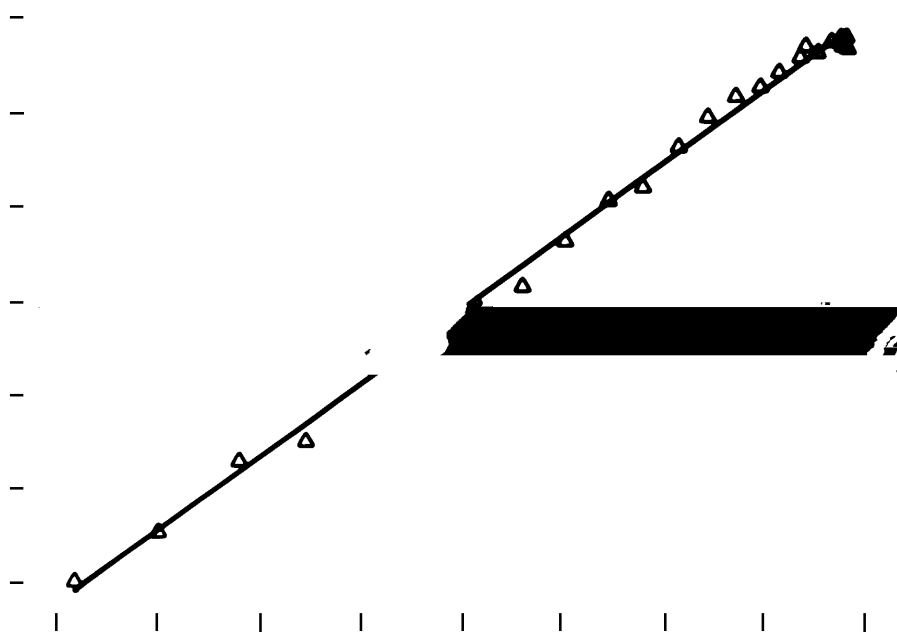
ISOTHERMAL CURE OF MATERIAL
FOLLOWING nTH ORDER KINETICS

Size: 6.743 mg
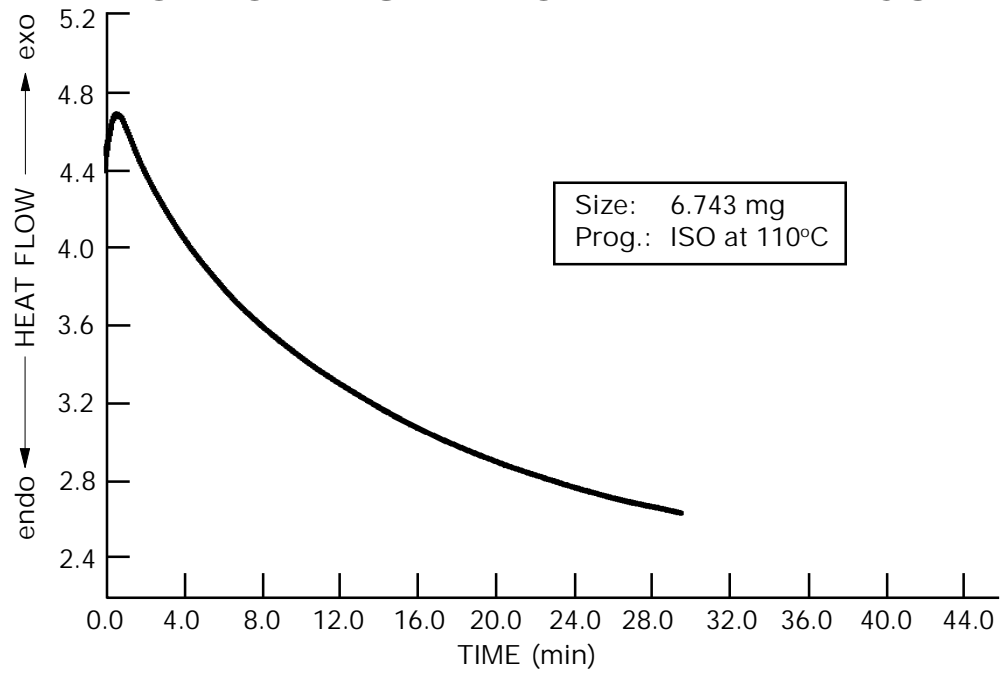Prog.: ISO at 110°C

Figure 9

EFFECTS OF AGING AT 65°C ON AN
AUTOCATALYZED THERMOSET
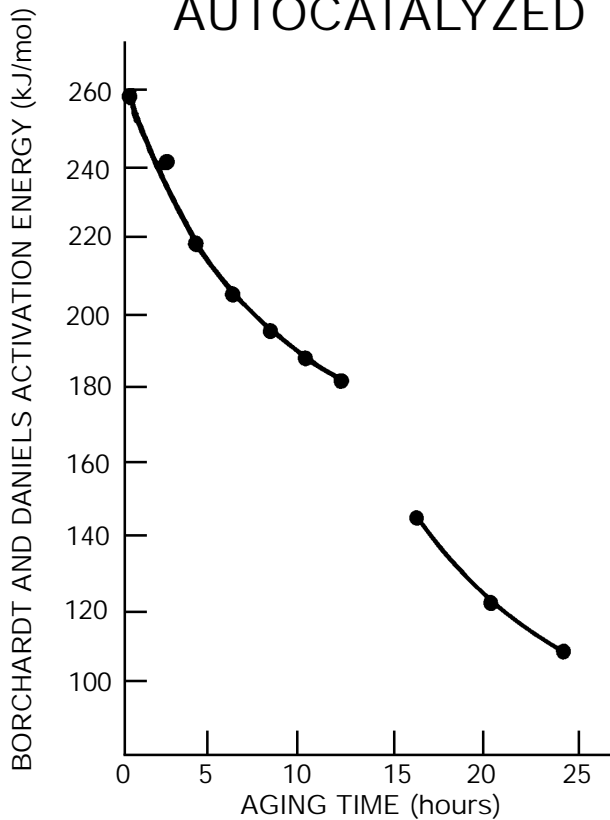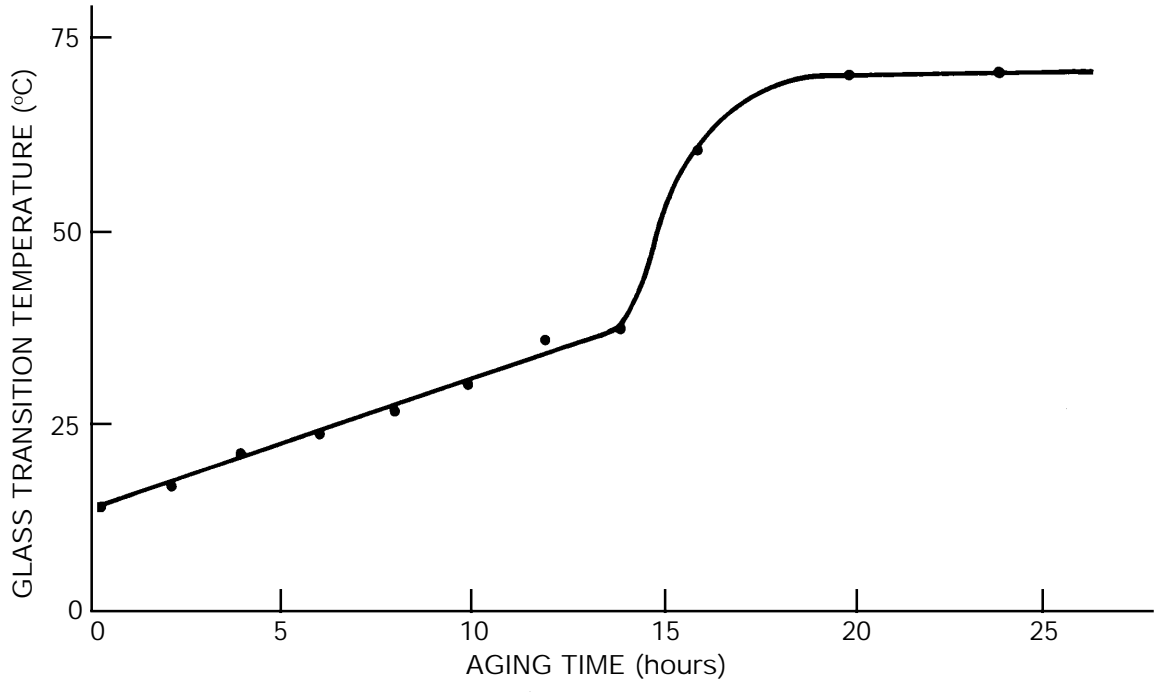

Figure 10

Figure 11

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