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# SHELF-LIFE DETERMINATION OF EPOXY PREPREGS AND FILM ADHESIVES


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## INTRODUCTION

Epoxy prepregs and film adhesives are composed of partially cured ("B" staged) epoxy resins and, in the case of the prepregs, a fiber matrix. Purchased epoxy prepreg lots typically are accepted or rejected on the basis of resin content, gel time, and resin flow. The shelf-life storage conditions of both materials generally are based on vendor recommendation. At The Bendix Corporation, Kansas City Division, there has been concern recently with shelf-life aging of a Kevlar*/epoxy prepreg. At present, lot acceptance of this prepreg is partially based on flow test data which was considered of questionable merit for shelf-life extension determinations.

Film adhesive lots are generally accepted or rejected on the basis of lap shear strength data. When film adhesive is bought as a small preformed shape, whose size and configuration prevent lap-shear testing, it must be lot accepted by vendor certification only.

Differential scanning calorimetry (DSC) is a method for performing thermochemical analysis. DSC can readily be applied to epoxy prepregs for acceptance testing and observing the kinetics of the curing reaction.[1] In this study, the practical aspects of such methods were further investigated, and additional ways for determining the effects of "B" stage conditioning on the processing parameters of epoxy prepregs and predicting the shelf-life of these materials, as well as film adhesives, were developed.

## EXPERIMENTAL

Differential scanning calorimetry was performed using a thermalanalyzer. Samples of Kevlar/epoxy prepreg and film adhesives (approximately 20 mg) were analyzed in both the isothermal and dynamic modes of operation.

*Du Pont trademark

Isothermal runs were performed at 353, 373, and 393 kelvins; dynamic scans were run at a program rate of 2, 5, and 10 kelvins per minute from 25 to 573 kelvins.

Percent resin flow was measured by placing 4 plies of Kevlar/epoxy prepreg, each 10.16 by 10.16 cm, between a release film of Kapton in a heated press at 135°C at 69 kPa for 10 minutes. The resin that flowed outside the Kevlar cloth was broken off and weighed. The resin flow was measured as the percent of resin removed from the initial weight of the 4 plies of prepreg.

Percent resin solids was measured on samples of prepreg (approximately 2.5 g) by extracting with acetone for four hours in a Soxhlet extractor. The weight of the sample before and after extraction was then used to calculate resin solids.

Lap shear tests were performed on film adhesive specimens with a bond area of 3.2 cm. Shear test specimens were prepared and tested in accordance with ASTM-D 1002.

## DISCUSSION AND RESULTS

Three methods were evaluated for determining the kinetic data describing the cure of the epoxy systems. The first method required isothermal DSC runs at three different temperatures. The natural log of the heat of reaction remaining (lnHr) versus time (t) was plotted (Figure 1). The resulting curves were straight lines indicating a first order reaction. The Arrhenius plot (Figure 2) was obtained by plotting the slope of the three curves in Figure 2 versus 1/T. The slope of the Arrhenius curve (Figure 2) is equal to Ea/R resulting in an activation energy of 24.8 kcal/mol.

The second method required dynamic DSC runs (Figure 3) at different heating rates (β). Using the Freeman-Carroll method of analysis and the equation[2,3]

$$\frac{\ln(\beta/T)^2}{1/T} = \frac{-Ea}{R} \qquad (1)$$

resulted in an activation energy of 23.12 kcal/mol.

The third method required only one dynamic DSC run and the equation,[4]

$$\frac{Ea}{n} = \frac{RT^2}{Hr\beta}\left(\frac{dH}{dt}\right)_{max.} \qquad (2)$$

This equation, where the heat of reaction remaining (Hr) and the temperature (T) are measured at the point of maximum exotherm (dH/dt) max, results in the ratio Ea/n equal to 23.8 kcal/mol. This method of analysis was used for the remainder of the study, and a reaction order of n = 1 was assumed. The frequency factor, A, was calculated from the equation

$$\ln A = \ln\frac{dH}{dt} \cdot \frac{1}{H_t} \quad -\ln\left(\frac{Hr}{Ht}\right) + \frac{Ea}{RT} \qquad (3)$$

where the total heat of reaction (Ht) is measured as the total area under the DSC curve. The kinetic data obtained from triplicate DSC scans of three lots of the Kevlar/epoxy prepreg and some physical data are in Table 1.

$H_T$ values for epoxy resin prepregs have been suggested as useful for measuring shelf life aging and predicting processing characteristics.[1] There appears to be a correlation between the $H_T$ values of Table 1 and the resin flow data.

Further evidence for this correlation was found by "B" staging (partially curing) the epoxy prepreg at 80°C for various time intervals and measuring both the $H_T$ and resin flow of the "B" staged material (Figure 4). The percent resin flow is directly proportional to the $H_T$ of the prepreg. The current Bendix specification for a resin flow of 25 to 35 percent would correspond to an $H_T$ of 50.5 to 60 cal/g.

Although the $H_T$ would appear to be useful as an alternate to the resin flow method for lot acceptance, it alone is not sufficient for predicting the processibility of the prepreg. During the processing of the prepreg to yield a part having specific density and dimensional requirements, the prepreg is "B" staged for a specified time and temperature prior to molding. The amount of "B" staging controls the amount of flash which is removed after molding. Too much "B" staging results in less flash, a lower density, and a larger part. Too little "B" staging results in excessive flash, a higher density, and a smaller part.

An equation was derived to predict the effect of "B" staging on the heat of reaction remaining ($H_r$)

$$H_r = H_T e^{-t(Ae^{(-Ea/RT)})} \qquad (4)$$

where

$H_T$ = the initial total heat of reaction,

T = the "B" stage temperature in kelvins, and

t = the "B" stage time in seconds.

If a specific remaining heat of reaction ($H_r$) is desired, the following equation can be used to determine the "B" stage time required.

$$t = \frac{e^{Ea/RT}}{A} \ln \frac{H_T}{H_r} \qquad (5)$$

The three lots of the Kevlar/epoxy prepreg were subjected to the same amount of "B" staging (one hour at 80°C), and then the $H_r$ was determined by duplicate DSC scans. The results of this testing, along with the predicted $H_r$ values derived by using Equation 4, are shown in Table 2. The predicted $H_r$ values (Table 2) match the measured $H_r$ fairly closely and demonstrate the usefulness of the DSC data.

It can also be seen from Table 2 that using the same "B" stage conditions for three different lots of prepreg resulted in material having a large difference in resin flow properties. These differences would lead to finished parts having different densities and dimensions and could account for production problems experienced with different lots of prepreg. Using Equation 5, it is possible to determine the "B" stage time and temperature required to yield the desired $H_r$ and percent resin flow and to allow better control of the final part density and size.

Equation 5 also can be used for evaluating the shelf-life at various storage temperatures for this or similar epoxy prepregs. If, for example, a heat of reaction of 49 cal/g is chosen as the minimum value required to meet acceptance tests, then, using Equation 5, the shelf-life of lots A and B would be as shown in Table 3. The information in Table 3 demonstrates the need for maintaining a subambient storage temperature and avoiding temperature excursions prior to the epoxy prepreg's being used. Shelf-life of Lot C was not calculated, because its heat of reaction initially was below the arbitrary minimum value.

Another epoxy material investigated was a film adhesive. DSC analysis showed kinetic properties very similar to the Kevlar/epoxy prepreg. This finding was not surprising because both materials were composed of similar epoxy resins and both used dicyandiamide as a cure agent. The film adhesive used nylon net (roughly 4 percent by weight) as the carrier, instead of Kevlar as in the Kevlar/epoxy prepreg. The results of DSC analysis and lap shear testing are shown in Table 4.

To determine the effect of aging on the adhesive properties of this material, Lot 3 was "B" staged for 4, 8, and 16 hours at 60°C. After "B" staging, the aged material was analyzed by DSC and lap shear tested. Again, the predicted heat of reaction remaining after "B" staging matched the actual measured values fairly closely (Table 5). Also, a correlation was found between the remaining heat of reaction and lap shear data. This correlation is further shown in Figure 5.

The shelf-life of the film adhesive can be evaluated by the method previously described for the Kevlar/epoxy prepreg. If a heat of reaction of 49 cal/g is again chosen as the minimum value required to meet acceptance tests, then, by using Equation 5, the shelf-life of the three lots would be as shown in Table 3.

It is evident that the film adhesive, like the Kevlar/epoxy, must be stored at a subambient temperature. Any exposure to room temperature during transportation or delays during processing greatly shorten the shelf-life of these materials.

## CONCLUSIONS

The kinetic data describing the cure of two epoxy systems, a Kevlar/epoxy prepreg and epoxy film adhesive, were determined by the use of DSC.

Correlations were found between the heat of reaction and resin flow for the prepreg and between the heat of reaction and lap shear strength for the film adhesive. These correlations show that DSC analysis could be a suitable method for incoming inspection of both epoxy systems.

An equation, which allows the determination of the shelf-life at any storage temperature for the two epoxy resin systems, was derived.

## ACKNOWLEDGEMENTS

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[2]J. H. Flynn and L. A. Wall, *Journal of Research of the National Bureau of Standards*, 70A, 487 (1966).

[3]E. S. Freeman and B. Carroll, *Journal of Physical Chemistry*, 62, 384 (1958).

[4]P. Peyser and W. D. Bascom, *Journal of Applied Polymer Science*, 21, 2359 (1977).

Table 1. Physical Properties of a Kevlar/Epoxy Prepreg

| Physical Property | Lot Number | | |
|---|---|---|---|
| | A | B | C |
| Temperature, $T_{(dH/dt)_{max}}$ (K) | 401 | 399 | 397 |
| Heat of Reaction, $H_T$ (cal/g) | 51.1 ±0.6 | 53.7 ±0.4 | 48.1 ±1.0 |
| Arrhenius Activation Energy, Ea (kcal/mol) | 23.8 ±0.6 | 22.9 ±0.6 | 24.6 ±0.6 |
| Arrhenius Equation Frequency Factor, ln A ($s^{-1}$) | 24.1 ±0.8 | 23.1 ±0.8 | 25.5 ±0.9 |
| Resin Flow (Percent) | 26.1 | 28 | 23 |
| Resin Solids (Percent) | 44.3 | 47.2 | 49.4 |

Table 2. "B" Stage Effects on a Kevlar/Epoxy Prepreg

| Physical Property | Lot Number A | Lot Number B | Lot Number C |
|---|---|---|---|
| Initial $H_T$ (cal/g) | 51.1 ±0.6 | 53.7 ±0.4 | 48.1 ±1.0 |
| $H_r$ After "B" Staging (cal/g) | 45.1 ±2.6 | 35.1 ±2.1 | 31.9 ±1.2 |
| Predicted $H_r$ (cal/g) | 42.1 | 35.8 | 32.0 |
| Initial Resin Flow (Percent) | 26.1 | 28 | 23 |
| Resin Flow* After "B" Staging (Percent) | 18.8 | 7.8 | 4.5 |

*Predicted flow, obtained from Figure 4.

Table 3. Shelf-Life Determination

| Epoxy System | Lot Designation | Shelf-Life (Days) at Storage Temperature 0°C | 25°C |
|---|---|---|---|
| Kevlar/ Epoxy | A | 188 | 4.7 |
| Prepreg | B | 212 | 6.2 |
| Film | 1 | 560 | 10.7 |
| Adhesive | 2 | 466 | 7.6 |
| | 3 | 206 | 4.2 |

Table 4. Physical Properties of a Film Adhesive

| Physical Property | Lot Designation | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $T\ (dH/dt)_{max}$ (K) | 392 | 391 | 395 |
| $H_T$ (cal/g) | 53.2 | 51.2 | 50.7 |
| Ea (kcal/mol) | 25.6 | 26.6 | 25.1 |
| ln A ($s^{-1}$) | 2.0 | 28.4 | 26.2 |
| Lap Shear* (MPa) | 27.7 | 21.3 | 20.5 |

*Average values for five specimens.

Table 5. Aging Effects on Physical Properties of a Film Adhesive

| Aging Time at 60°C | $H_T$ (cal/g) | | Lap Shear (MPa) | $T_s$ (°C) |
|---|---|---|---|---|
| | Actual | Predicted | | |
| Initial | 50.7 | | 20.5 | 18 |
| 4 hr | 46.0 | 45.2 | 17.5 | 35 |
| 8 hr | 39.6 | 40.2 | 12.9 | 45 |
| 16 hr | 31.1 | 31.9 | 10.9 | 54 |

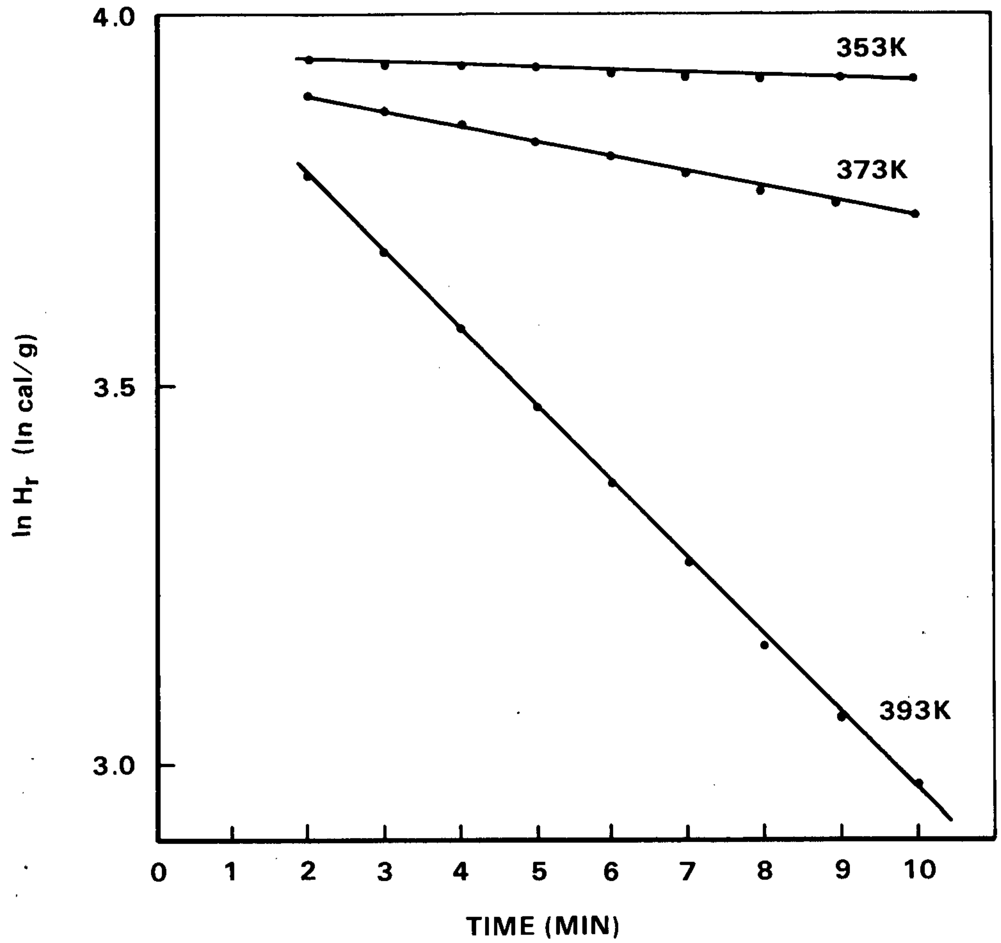


Figure 1. Isothermal Reaction Rates for a Kevlar/Epoxy Prepreg

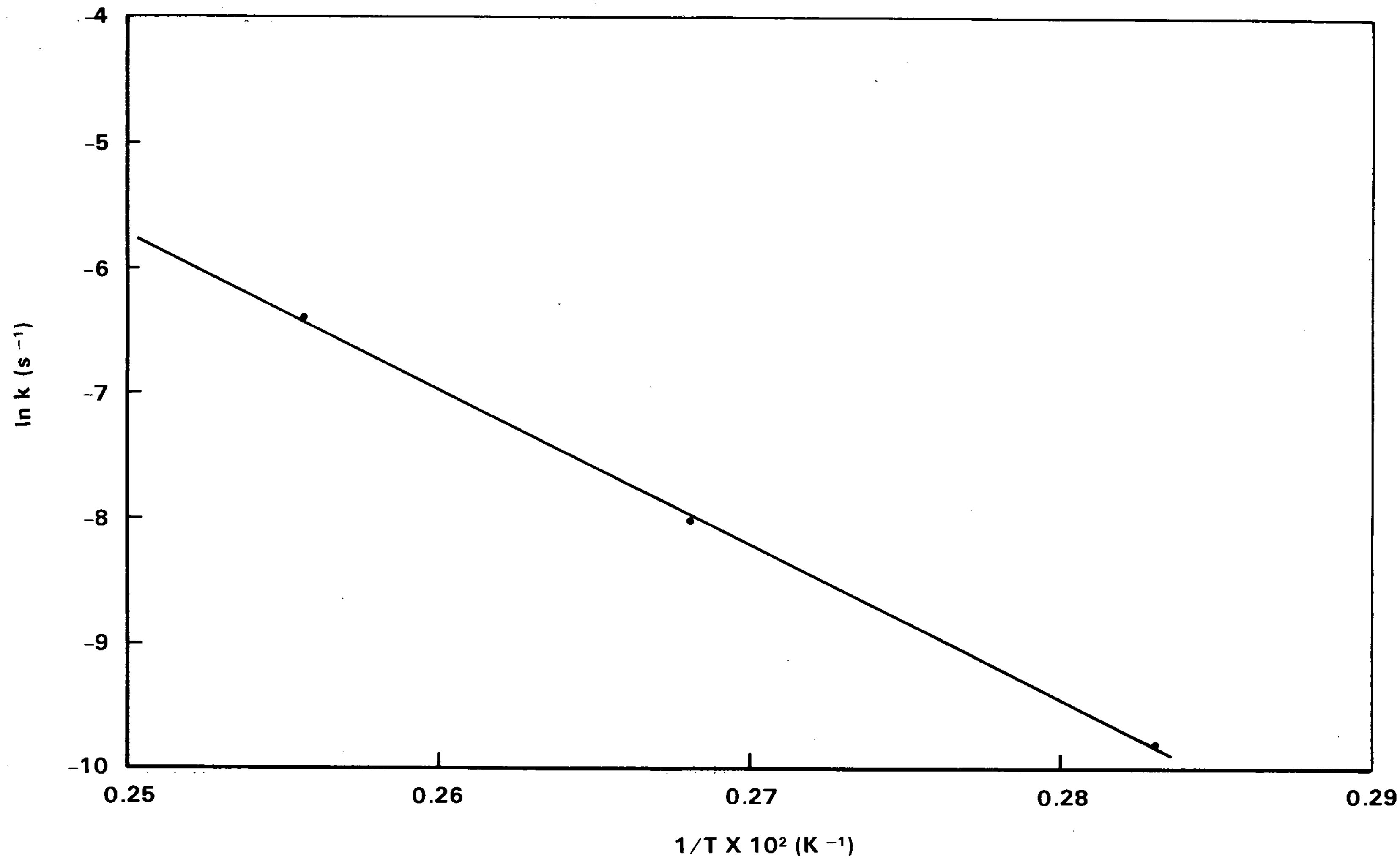


Figure 2. Arrhenius Plot of Isothermal DSC Data, Kevlar/Epoxy Prepreg, Lot A

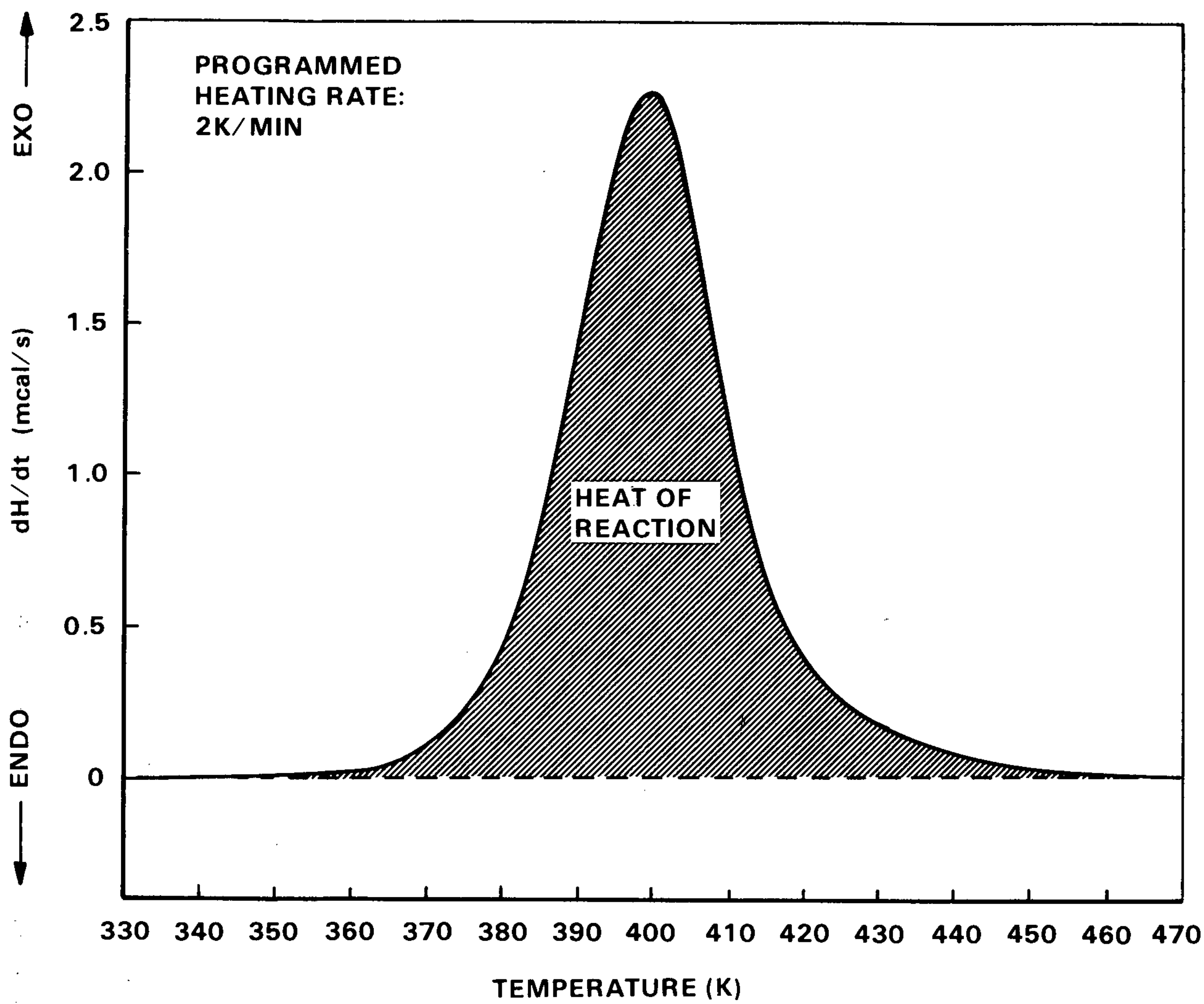


Figure 3. Typical Dynamic DSC Curve

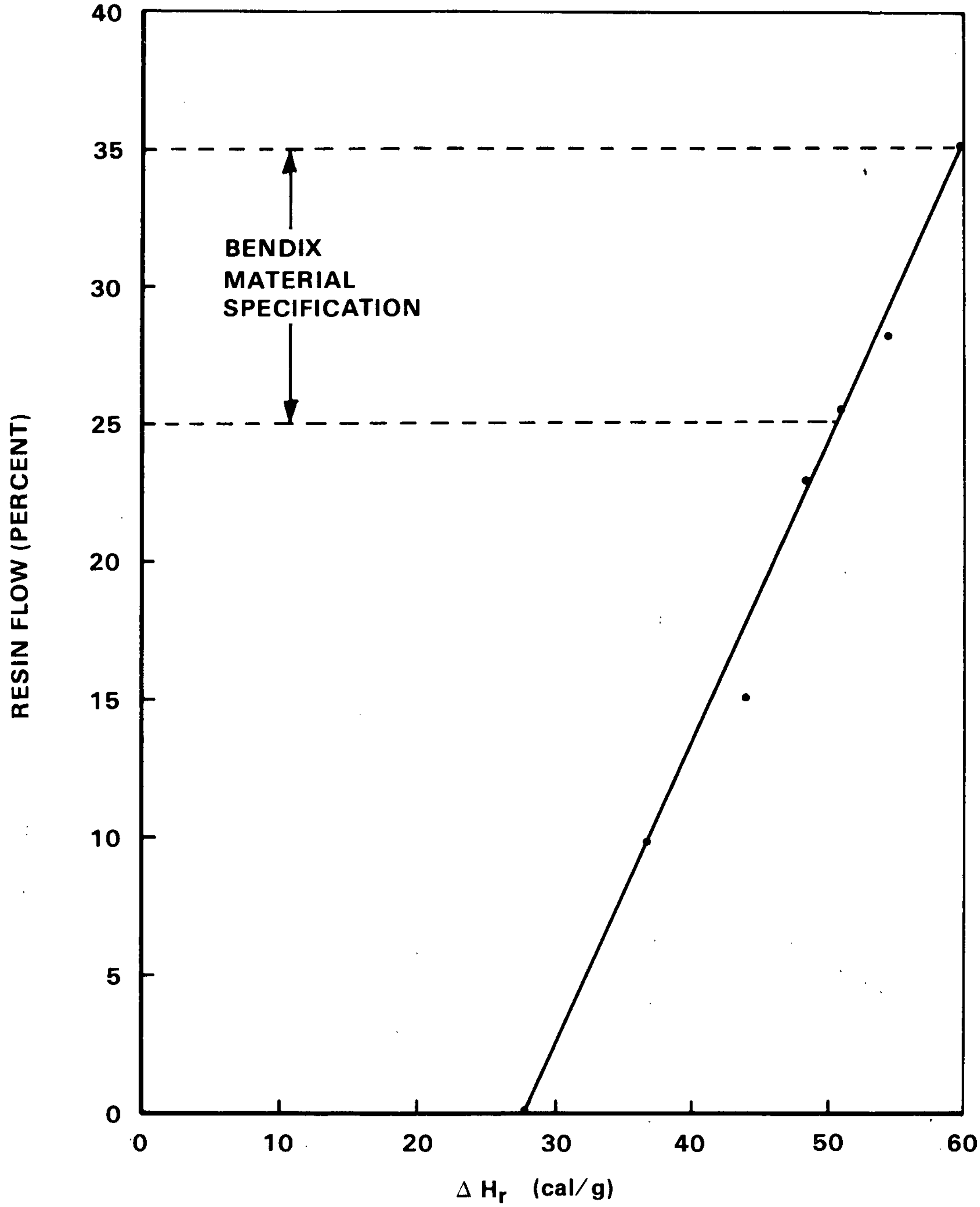


Figure 4. Resin Flow Versus Heat of Reaction for a Kevlar/Epoxy Prepreg

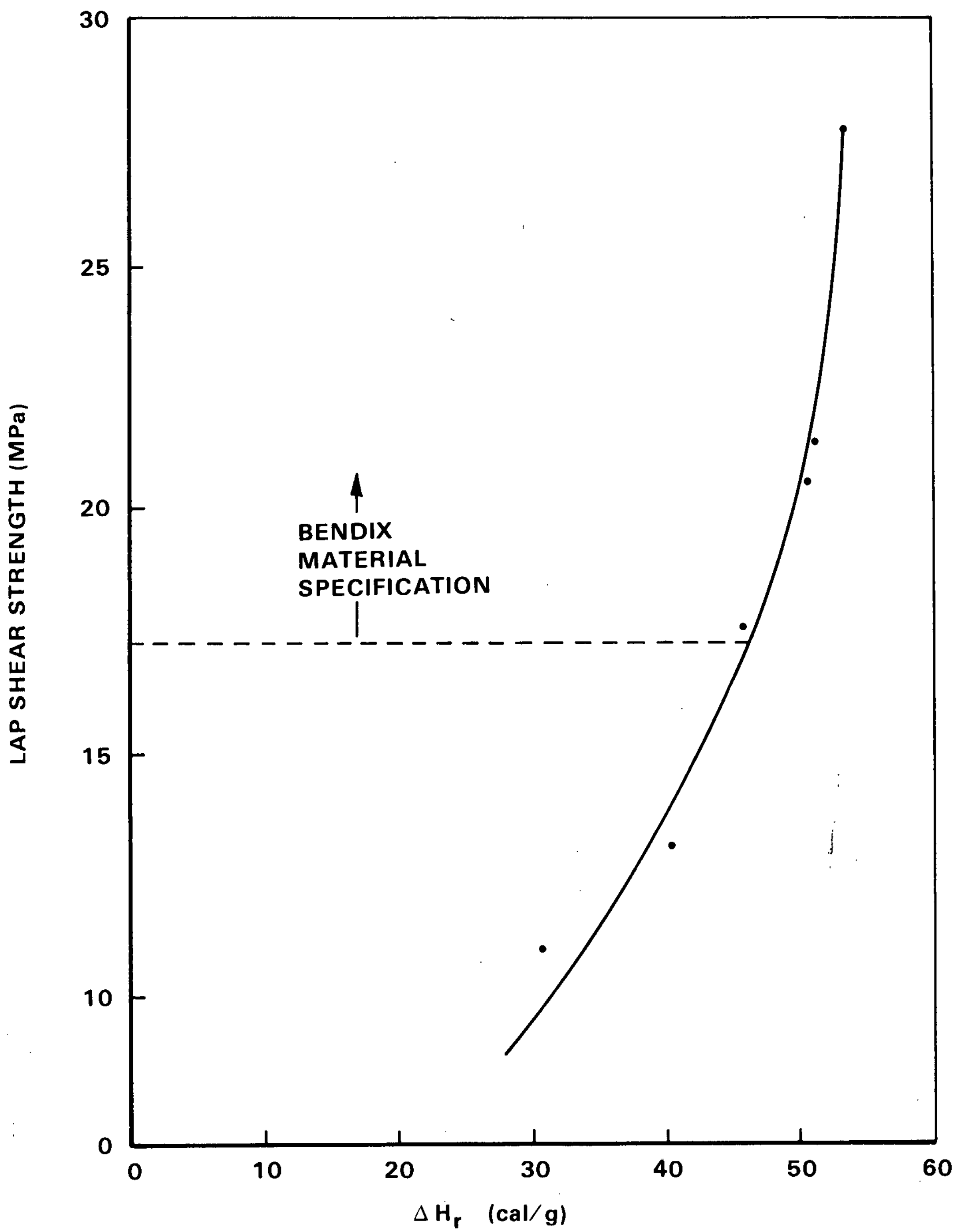


Figure 5. Lap Shear Strength Versus Heat of Reaction for a Film Adhesive