

DSC Evaluation of Epoxy and Polyimide-Impregnated Laminates (Prepregs)

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Synopsis

Differential scanning calorimetry has been applied to the study of epoxy-glass and Kerimid 601 (polyimide-glass) prepregs used in making multilayer printed wiring boards. The data generated through thermal analysis are thermodynamic and kinetic. Thermodynamic properties of B-stage prepregs obtained are endothermal and exothermal peak temperatures, glass transition temperatures, and heats of residual cure. They were obtained from thermograms made at fixed scanning rates. Kinetic information obtained from isothermal cure scans gave rates of residual cure, cure times, and energies of activations. This information gives the process engineer useful information for controlling the processing of multilayer printed wiring boards.

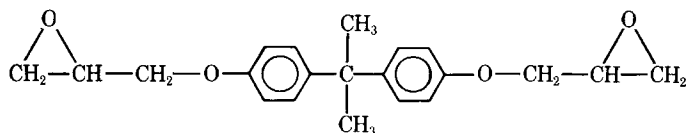
INTRODUCTION

With the minaturization of electronic components and telecommunication equipment the need for higher density circuitry becomes obvious. One solution is reduced conductor widths and spacings between conductors. Another is the integrated circuit device and still a third is the multilayer printed wiring board. The multilayer board with which we are concerned in this paper is constructed of alternate layers of copper-clad thin laminate (C-stage laminates) and partially cured B-stage laminate. It is a space-saving device in which the B-stage laminate serves as a bonding layer and dielectric between adjacent layers of copper conductors. For these B- and C-stage laminates, the dielectric material most commonly used is glass-reinforced epoxy resin. Another material, particularly for use at higher temperatures, is glass-reinforced Kerimid 601 polyimide resin.

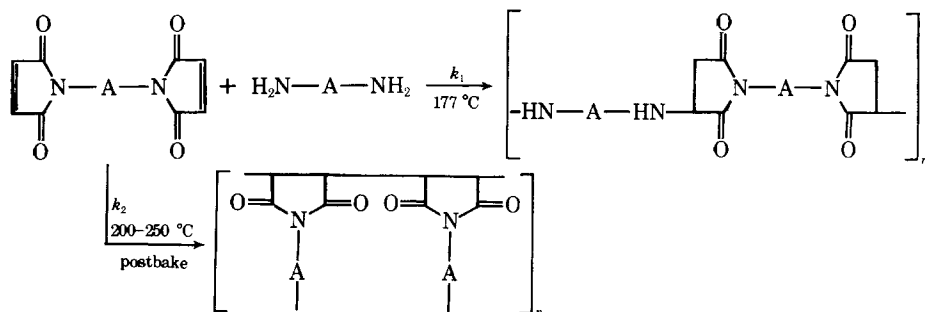
One of the difficulties in making multilayer boards is to prevent the entrapment of air and volatiles in the composite during the laminating process. This becomes more critical and difficult to overcome as the number of layers is increased and as the circuit geometry becomes more complex. Increased thickness results in a lower thermal conductance of the laminate which gives rise to a nonuniform cure rate of the various B-stage layers. The entrapped air and volatiles appear as random voids in the laminate matrix of the finished product. Voids occur then when resin from the B-stage does not purge the air and volatiles from between the layers of the assembly and from the etched holes in the copper. They can occur as a result of selecting improper process parameters or using B-stage materials of poor quality. They serve as a trap for ionic contaminants from subsequent processing operations, and the contaminants can lead to di-

electric breakdown due to the increased probability of shorts between adjacent layers. To minimize the appearance of laminating voids and to produce a higher-quality multilayer board, it is believed that a more thorough understanding of the thermochemical behavior of the B-stage composite is necessary. This paper, therefore, is primarily concerned with the calorimetric evaluation of the B-stage material.

The B-stage materials with which we are concerned are epoxy resins such as diglycidyl ether of bisphenol A,



or Kerimid 601, a bismaleimide, which is either homopolymerized or copolymerized (depending upon temperature) with an aromatic diamine. Kerimid 601 resin is manufactured by Rhodia Incorporated, a division of Rhône-Poulenc, France. Its chemistry is as follows:



In both systems, a varnish containing resin and appropriate curing agent and catalyst is impregnated in the glass cloth. It is then dried and thermally polymerized to an intermediate state (B stage) in which the resin neither flows nor is appreciably crosslinked and will remain stable under controlled storage conditions. The B-stage composite resulting is commonly called a prepreg. Final polymerization and crosslinking of the prepreg is accomplished with the application of additional heat.

The prepreg is characterized and purchased from suppliers according to its resin content, gel time, and resin flow for epoxy systems and resin content and resin flow for Kerimid systems. Other specified variables are the glass finish, style, and thickness as well as pressed thickness of the laminate. Resin content and resin flow give, respectively, the amount of resin in the prepreg and the percent weight loss of the prepreg due to resin flow from the laminate after it has been pressed at a prescribed temperature. There must be sufficient resin present to serve as a bonding agent between layers and sufficient resin flow to purge the air and volatiles from between these layers.

Gel time, applicable to epoxy but difficult to measure with polyimide systems, is the time required for the resin of the prepreg to solidify at a prescribed temperature. Gel time, a process control parameter, indicates to a process engineer the proper time to apply full pressure to the laminate in a laminating press.

Determination of the gel time is a highly subjective test that depends on the skill of the operator to establish the time it takes for a bead of the exuded resin to solidify and become rubbery (gel point) after a prepreg has been pressed. The test is crude and the results usually vary from operator to operator.

We, therefore, propose that the calorimetric or thermochemical evaluation of the B-stage composite be used as an additional test for raw materials. It is a well-known fact that prepregs are not uniform. The degree of cure, gel time, and resin flow may vary from lot to lot from a given supplier. Shipping procedures may also affect the properties of the composite. Storage conditions and time may have adverse effects on the stored material. The properties of the prepreg materials could change sufficiently to produce poorly bonded and void-ridden multilayer boards.

Thermal scans are performed using a differential scanning calorimeter (DSC). Thermodynamic quantities determined are heats of residual cure, exothermal peak temperatures, glass transition temperatures, and energies of activation. Kinetic parameters determined are the rates of residual cure at various temperatures. A basic assumption made is that, for a given material, the heats of reaction are directly proportional to the apparent extent of residual cure and that the fraction cured is, therefore, proportional to the area of the generated exotherm. In these prepreg evaluations, no attempt is made to analyze the resins to determine the catalyst, curing agent, or resin ratios. Also, no attempt has been made to analyze the results in terms of mechanisms of polymerization. Only thermal and kinetic interpretations are made.

Thermochemical analyses of this kind are a valuable aid to the process engineer in selecting prepreg laminates for use in fabricating multilayer boards. Thermal scans not only give heats of cure but also fingerprint patterns, the shape of which is indicative of lot to lot consistency of prepreg laminates from a given supplier.

EXPERIMENTAL

The basic du Pont DSC cell and cell base were used in conjunction with a 900 thermal analyzer for the epoxy work and a 990 thermal analyzer for the Kerimid 601 polyimide work. Both programmers are essentially the same, with the major difference being one of sensitivity. The 900 differential power output, dH/dt , varies from 0.2 to 20 millical/sec in., and the 990 varies from 0.05 to 50 millical/sec in. In order to calculate ΔH , a calibration coefficient had to be determined. This was accomplished by scanning a standard sample of known heat of fusion (indium) and determining the area bounded by the thermogram.

B-stage epoxy-glass prepregs were obtained from five different suppliers, and B-stage Kerimid 601 polyimide prepregs were obtained from three suppliers. Samples were cut from each of these composites and then weighed to give 15–25 mg of sample. The samples were subsequently placed in shallow aluminum pans 0.6 cm in diameter and capped with a cover. Experiments of two types were performed on the prepregs examined. These were dynamic scans from room temperature to 275°C for epoxies and from room temperature to 350°C for Kerimid 601, and isothermal scans from 130° to 183°C for epoxies and 175° to 235°C for Kerimid 601.

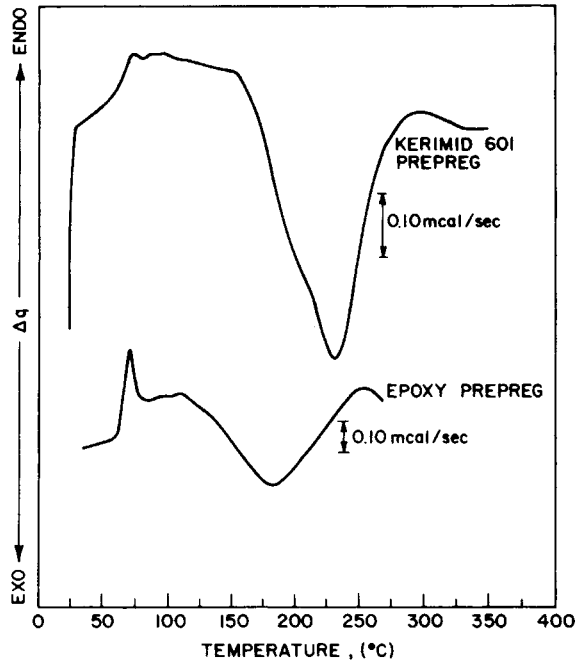


Fig. 1. Dynamic thermograms of a B-stage epoxy-glass prepreg and of a B-stage Kerimid 601-glass prepreg cured at 10°C/min.

RESULTS AND DISCUSSION

Dynamic scans were made at 10°C/min for all prepregs examined. This rate was selected because it approximates equilibrium conditions better than faster scans. The epoxy and Kerimid scans exhibit similar features, Figure 1. An inflection onset occurs near 50°C for epoxies, 60°C for Kerimid. This is taken as the glass transition temperature T_g of the prepregs. The Kerimid T_g averages about 7–8°C higher than epoxies. Following the glass transition temperature, an endothermic peak appears. For epoxies, this peak is found on average at about 61°C, for Kerimid 601, at 73–75°C. The heat liberated as a result of cure begins at a much higher temperature for Kerimid. It starts at 150°C, peaks at 230°C, and terminates at 300°C. Epoxies range from 100° to 225°C, with a peak at 183°C. This information suggests that Kerimid prepregs require higher temperatures than epoxies to promote cure and to achieve the same rate of cure. In multilayer board manufacture, this would mean longer cure cycles and/or higher temperatures.

Fava¹ and Creedon² have shown, in thermochemical studies of epoxy resins, that the glass temperature will increase and the exothermic heat will decrease as the degree of cure of the resin is advanced. For example, in Figure 2, scan 1 of an epoxy prepreg from supplier E shows a T_g at 55°C with a visible exotherm when initially scanned from room temperature to 275°C at 10°C/min. When the cured resin is rescanned, the T_g has been advanced to 116°C with no visible exotherm.

This information is invaluable for epoxies as well as Kerimid polyimides in determining the state of cure of the prepreg resin system. If, for example, the

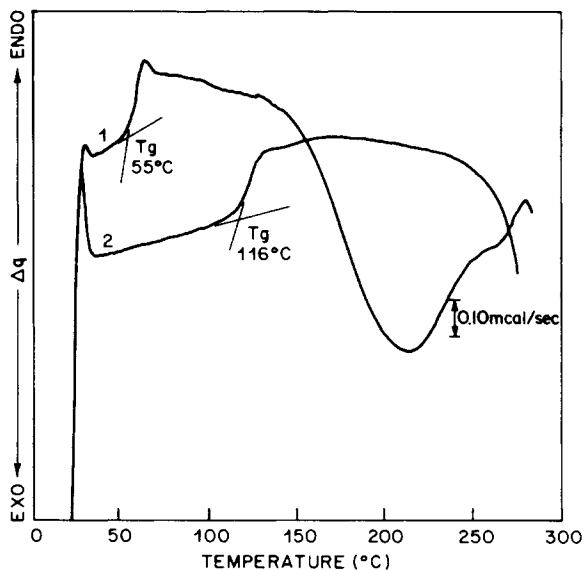


Fig. 2. Dynamic thermograms of a B-stage epoxy-glass prepreg cured at 10°C/min. Scan 1: Initial scan from room temperature to 275°C; T_g is 55°C. Scan 2: Rescan of cured resin; T_g advances to 116°C with no visible exotherm.

system exhibits a high T_g and endothermal peak temperature, its residual cure has been advanced to a state that may preclude its use in fabricating multilayer boards. This may occur with poor lots of delivered prepregs that, having advanced in cure during processing or storage, are no longer usable. DSC scans, therefore, can be made on delivered and stored prepregs and compared to previous scans.

A rapid method of determining the quantity of residual cure of prepregs is to calculate its heat of cure. Heat of cure, ΔH , expressed in calories per gram, is determined by measuring the area bounded by the exotherm. Results obtained for Kerimid 601 and epoxy prepregs are tabulated in Table I. For the epoxy prepreg samples scanned, the calculated ΔH varied from 13.3 to 29.7 cal/g. Prepreg A-1, stored 20 months prior to analysis, gave a ΔH value of 14.0 cal/g as compared to a similar product stored two months prior to analysis which gave a ΔH value of 27.6 cal/g. Prepreg A-1 did not process well in making multilayer boards. Prepregs E-17 and 18 also exhibits low ΔH values: 14.0 and 13.3 cal/g, respectively. The T_g values and endothermal peak temperatures are higher compared with other prepregs examined. On the other hand, E-16 from the same company shows a high ΔH value of 29.6 cal/g and a T_g of 50°C, which is comparable with that of other materials. Kerimid prepregs (F, G, and H) were analyzed at most two months after the data of manufacture. All gave comparable ΔH results varying from 21.6 to 23.2 cal/g.

It is reasonable to believe that a low ΔH and high T_g is indicative of a too advanced state of reaction either during B-staging or as a result of additional polymerization in storage. Such an advanced state of reaction decreases the pliability needed for good lamination. It is also conceivable that a low ΔH may be the result of improper ratios of curing agent/catalyst/resin which will affect processability. However, the thermogram has a characteristic shape and area

that can be used to characterize a given material and to ensure lot-to-lot consistency. For each resin system formulated by a given supplier, one might expect that there is a limiting ΔH value below which the processability becomes poor, and experience appears to support this view.

Kinetic parameters of epoxy and Kerimid prepregs were obtained by making isothermal cure studies, which gives the extent of polymerization as a function of time at a given temperature. Cure rates and energies of activation were then calculated. Isothermal scans were made at 130°, 150°, 171°, and 183°C for epoxy prepregs and at 175°, 200°, 225°, and 235°C for Kerimid prepregs. These temperatures were selected since they fell within the temperature range of dynamically determined thermograms. Cure temperatures below 130°C for epoxies and 175°C for Kerimid would exhibit inordinately slow rates. Cure temperatures above 183°C for epoxies and 235°C for Kerimid would be too rapid to exercise laminating control.

The technique employed in making DSC isothermal studies is to heat the DSC cell to the preselected temperature and to place the sample in the heated cell quickly rather than to heat the cell, with the sample, from room temperature to the required temperature. This minimizes thermal lag and produces a true thermogram at the temperature of interest. Typical isotherms obtained for

TABLE I
Prepreg Thermochemical Properties

Supplier	Sample	Storage time prior to analysis, months	Resin content, %	ΔH , cal/g	T_g , °C	Exothermal peak temp., °C
Epoxy						
A	1	20	57.0	14.0	62	182
	2	3	57.3	19.5	54	175
	3	2	54.3	27.6	52	163
B	4	15	52.4	17.3	50	173
C	5	3	63.5	29.7	37	182
D	6	4	57.2	22.4	55	190
	7	4	53.6	22.6	52	185
	8	4	61.3	26.4	49	183
	9	4	57.0	24.9	52	185
B	10	12	64.0	23.1	57	178
	11	12	63.0	27.9	53	175
	12	10	76.1	21.7	58	170
	13	10	76.1	23.4	56	170
C	14	3	66.2	25.0	44	188
	15	3	64.3	25.7	42	188
E	16	5	57.6	29.2	50	175
	17	4	78.9	14.0	67	205
	18	4	53.0	13.3	67	200
	19	4	65.0	17.3	55	205
Kerimid 601						
F	20	2	60.8	23.2	60	233
G	21	1	56.2	22.6	61	230
H	22	0	54.1	21.6	—	183

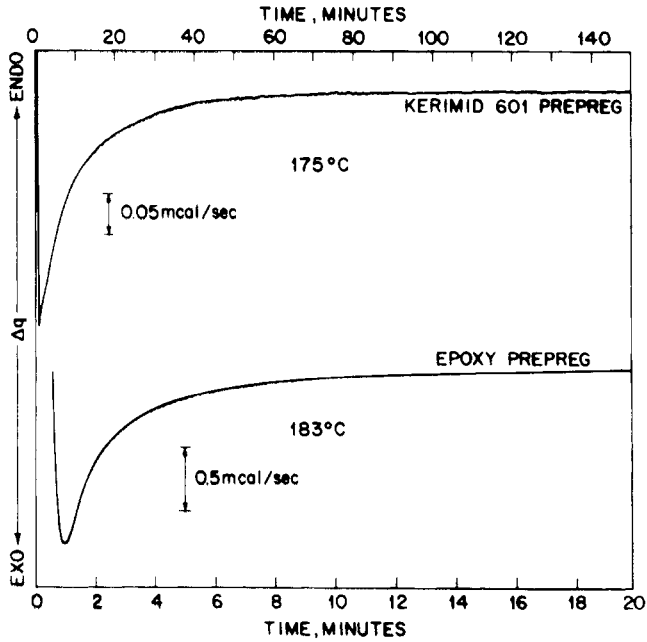


Fig. 3. Isothermal thermograms of a B-stage epoxy-glass prepreg cured at 183°C and of a B-stage Kerimid 601-glass prepreg cured at 175°C.

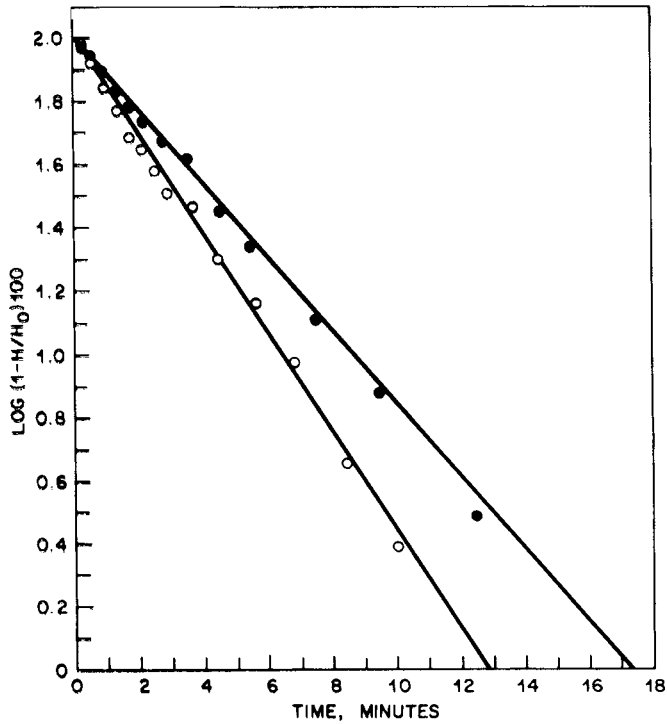


Fig. 4. Log plots of per cent of resin fraction uncured vs. time, at (●) 171°C and (○) 183°C, of a B-stage epoxy-glass prepreg.

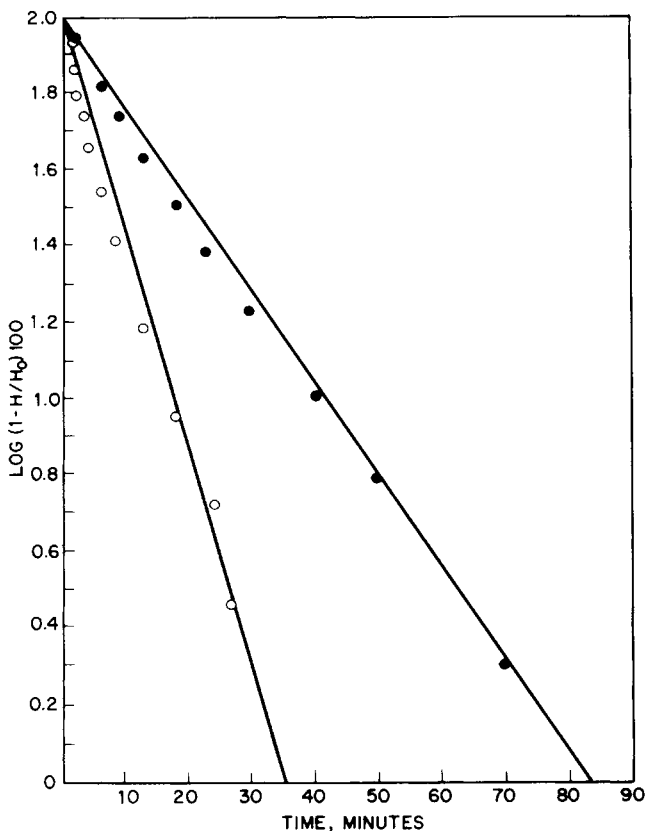


Fig. 5. Log plots of per cent of resin fraction uncured vs. time, at (●) 175°C and (○) 200°C, of a B-stage Kerimid 601-glass prepreg.

epoxy and Kerimid prepreps are shown in Figure 3. In this work, the area bounded by the exotherm represents 100% of residual cure, and the heat of reaction, H , is directly proportional to the area. We can express the fraction cured at time t as the ratio H/H_0 , where H is the heat of cure measured up to time t and H_0 is the total heat of cure. Then, if curing is a reaction of order n , we have

$$\frac{d(H/H_0)}{dt} = k \left(1 - \frac{H}{H_0}\right)^n$$

where k = reaction rate constant and n = order of reaction.

The extent of cure, at given time intervals for each thermogram, was then determined at the temperature indicated. Plotting this information as a function of time, isothermal cure-time profiles were obtained for each thermogram. The term $\log (1 - H/H_0) \times 100$ was then plotted against t for each isotherm. Typical plots for epoxy and Kerimid prepreps are shown in Figures 4 and 5. Straight lines were obtained for each prepreg, indicating that the overall rate of residual cure was first order.³ The specific cure rate constants determined are recorded in Table II.

It is interesting to note when comparing two epoxy prepregs from the same supplier (A-1, A-2) that the one which was found to process well, A-2, had a higher cure rate constant, 0.31 min^{-1} , than the one which processed poorly, A-1, 0.26 min^{-1} . The better processing material also had a relatively higher heat of cure. The cure rate constants for epoxies at 171°C , the normal laminating temperature, vary from 0.26 to 0.38 min^{-1} . The rate constants for Kerimid are 0.06 min^{-1} at 175°C and 0.29 to 0.38 min^{-1} at 235°C . This indicates that in order to achieve the same rate of cure as epoxies in the laminating press (Table II), Kerimid prepreg laminates have to be laminated at 235°C . The laminating temperature for Kerimid as recommended by manufacturers is 177°C . The average cure rate constant, at this temperature, is 0.06 min^{-1} , or 15% of the rate of epoxies.

From the isotherms obtained, prepreg cure times were determined at various temperatures. They can also be determined from the log of the residual cure-versus-time plots by extrapolation to log 1 (99% cure) or calculated from the first-order rate expression

$$\log \frac{1}{1 - \frac{H}{H_0}} = \frac{kt}{2.303}$$

TABLE II
Specific Cure Rate Constants at Various Temperatures
and Activation Energies of Epoxy Prepregs

	k, min^{-1}				
	A-1 ^a	A-2	A-3	B-4	C-5
Temperature, $^\circ\text{C}$					
130	0.04	0.06	0.09	0.06	0.03
140 ^b	0.06	0.09	0.14 ^b	0.09 ^b	0.05 ^b
150	0.10	0.13	0.23	0.11	0.09
171 ^c	0.26	0.31	0.38	0.28	0.30
183	0.35	0.43	0.52	0.43	0.41
Energy of activation, kcal/mole	15.0	13.1	11.9	12.9	17.8

Specific Cure Rate Constants at Various Temperatures
and Activation Energies of Kerimid 601 Polyimide Prepregs

	k, min^{-1}		
	F-20	G-21	H-22
Temperature, $^\circ\text{C}$			
175	0.06	0.06	0.06
200	0.12	0.13	0.14
225	0.19	0.20	0.19
235	0.29	0.38	0.35
Energy of activation, kcal/mole	13.3	14.3	13.8

^a Supplier and sample number (see Table I).

^b Calculated values.

^c Normal laminating temperature.

at 99% cure. The observed, extrapolated, and calculated values agree for epoxy and Kerimid. The results are given in Table III. At 171°C, the normal laminating temperature for epoxies, the cure time varies from 12.1 to 17.7 min. At 175°C, the cure time for Kerimid prepregs is 76.8 min; and at 235°C, the variation was 12.1 to 15.9 min. The cure time for Kerimid at 235°C is, therefore, equivalent to epoxies at 171°C. This indicates that if the recommended press temperature of 177°C for Kerimid prepregs is used, the dwell time in the laminating press should not be less than 77 min in order to reach the same degree of reaction, from a calorimetric viewpoint, as the epoxies in the lamination process.

Typical Arrhenius plots of $\log k$ versus $1/T$ are shown in Figure 6 for an epoxy and Kerimid prepreg, respectively. Activation energies were then calculated (Table II). Epoxies average from 11.0 to 17.8 kcal/mole; Kerimid, from 13.3 to 14.3 kcal/mole. Knowledge of this energy can serve as a guide to the process engineer as to the quality of the prepreg. Results indicate that prepregs of lower activation energy, from a given supplier, process better than prepregs of high energy. Knowledge of the activation energy can also be used to calculate cure rate constants and cure times at other temperatures.

CONCLUSIONS

Differential scanning calorimetry can be used in obtaining critical thermochemical parameters necessary to ensure the consistency of epoxy and Kerimid prepreg properties. These parameters are thermodynamic and kinetic and should aid the process engineer in fabricating multilayer boards. The thermodynamic parameters of the B-stage materials obtained are glass transition

TABLE III
Total Residual Cure Time at Various Temperatures of Epoxy Prepregs

Temperature, °C	Time, min				
	A-1 ^a	A-2	A-3	B-4	C-5
130	115.2	76.8	51.2	76.8	153.5
140 ^b	76.8	51.2	32.9	51.2	92.1
150	46.1	35.4	20.0	41.9	51.2
171	17.7	14.9	12.1	16.5	15.4
183	13.2	10.7	8.9	10.7	11.2

Total Residual Cure Time, at Various Temperatures,
of Kerimid 601 Polyimide Prepregs

Temperature, °C	Time, min		
	F-20	G-21	H-22
175	76.8	76.8	76.8
200	38.4	35.4	32.9
225	24.2	23.0	24.2
235	15.9	12.1	13.2

^a Supplier and sample number.

^b Calculated values.

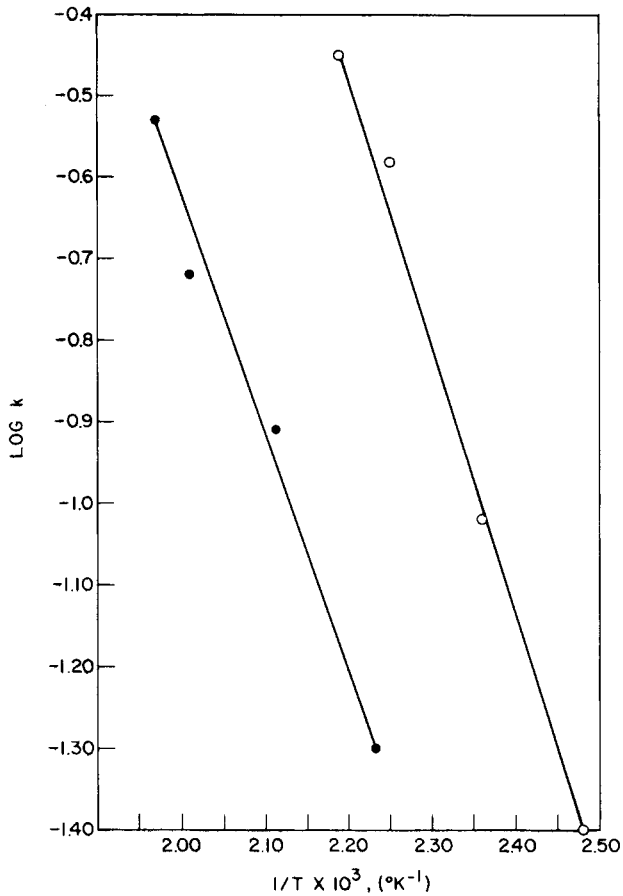


Fig. 6. Arrhenius log plots of cure rate constants vs. $(1/T) \times 10^3$ ($^{\circ}\text{K}^{-1}$) of a B-stage epoxy-glass prepreg and of a B-stage Kerimid 601-glass prepreg: (●) Kerimid 601 prepreg; (○) epoxy prepreg.

temperatures, heats of residual cure, and activation energies, and the kinetic parameters obtained are rates of residual cure and cure times. Judicious use of this information should result in minimal occurrence of laminating voids and production of higher-quality multilayer boards.

The following generalizations can be made with epoxy and Kerimid prepregs:

1. They should exhibit low endothermal and glass transition temperatures with sufficient cure present, however, to prevent low viscosity at laminating temperatures and hence multilayer board resin starvation.

2. They should exhibit high heats of residual cure. This indicates that no premature crosslinking has taken place and that there is sufficient potential cure present to fabricate a multilayer board.

Kinetic parameters obtained from isothermal DSC scans of epoxy and Kerimid prepregs give the process engineer process control information. They show that the cure rate constants obtained at 235°C for Kerimid are equivalent to the cure rate constants obtained for epoxies at 171°C . This indicates that in order to

achieve the same rate of cure as with epoxies, Kerimid prepreg laminates have to be laminated at 235°C. Since the recommended cure temperature for Kerimid prepreps is 177°C, the average rate constant for curing at this temperature is 15% of that observed with epoxies. Calculated cure times are correspondingly longer, and dwell times in the laminating press should be longer than those used for epoxy lamination.

References

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