

Cure Analysis of Printed Wiring Boards Containing Reactive Adhesive Layers

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This paper presents a method for analyzing the cure of multilayer circuit boards containing chemically reactive adhesive interlayers. The cure kinetics of the adhesive are first quantified by differential scanning calorimetry, using the method of Freeman and Carroll to obtain the numerical kinetic parameters. These parameters are then used in a finite-element model of the circuit board which solves the heat and species transfer equations simultaneously. It is then possible to predict the temperature and extent of reaction at any time and position within the laminate, enabling the curing program to be optimized.

INTRODUCTION

The growing complexity of electronic circuits and the miniaturization of electronic components has led to very high density circuitry. Modern circuits often employ multilayer printed wiring boards, so that electrical connections may be made on more than one level. Fabrication of these wiring boards is complex enough to make trial-and-error approaches inefficient, and analytical models which can help optimize board processing should be considered. As an example of such an analysis, we have studied boards consisting of alternating layers of copper-clad fiberglass/epoxy laminate and reactive adhesive layers. The adhesive is a partially-cured ("B-staged"), glass-reinforced polyimide resin known as Kerimid 601. Once fully cured during the fabrication process, the adhesive layer serves as both a dielectric and a bonding layer between the conducting copper layers.

After the various layers of a wiring board have been stacked in the desired sequence, they are subjected to a specific cycle of applied heat and pressure. Heat activates the cure reaction in the resin, and the pressure is intended to inhibit gaseous void formation and board warpage. Heat is usually transferred through the board by conduction from heated press platens, so

that the temperature and thus the reaction rate of the adhesive is nonuniform through the board thickness.

MATERIAL

Epoxy resins are a traditional choice for the adhesive layers of multilayer printed wiring boards. But as electronic components have been designed for increasingly demanding applications, resins which can maintain their structural integrity at elevated temperatures and humidities have become attractive. According to Darmory (1), aromatic polyimide resins appear to possess the qualities needed: good mechanical properties, high heat resistance, cryogenic temperature stability, excellent dimensional stability, chemical inertness, and non-flammability. However, processing procedures for these polyimides are not so well optimized as for the more traditional epoxies, and this paper hopes to assist in this regard.

The early aromatic polyimides were condensation type polymers, and creation of the imide group was accompanied by the release of H₂O as an off-gas. As a result, voids were created between layers of the laminate by elimination of H₂O during processing of the wiring boards. This caused a degradation of the mechanical properties in the finished product.

Kerimid 601 (Rhone-Poulenc Company, France) is based on short, linear, polymerizable

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monomers containing the imide group, and was developed to overcome the problems associated with off-gas generation. At elevated temperatures, the preimidized segments polymerize at the end groups without producing any volatiles (2). It can be crosslinked by mixing 2.5 moles of the 4,4'-bis (maleimide diphenyl methane) with 1 mole of 4,4'-diamino diphenyl methane. The reaction may proceed by homopolymerization at the maleimide double bonds, or by addition of the diamine at the maleimide double bonds as shown in Fig. 1 (3). During cure, both reactions occur simultaneously.

DIFFERENTIAL SCANNING CALORIMETRY

Experimental

Differential scanning calorimetry (DSC) can be used to measure the rate of heat absorption or evolution by a specimen as the temperature is raised at a constant rate. In these scanning experiments the data are recorded on a thermogram as a trace of the heat flow (or rate of heat evolution), dH/dt , given as a function of the temperature T . Positive deviation from the base line in the thermogram indicates an increase in the specific heat of the specimen, or that an exothermic reaction is occurring in the specimen. The Kerimid 601 curing reaction is exothermic, and the reaction can be observed easily using DSC.

The Kerimid 601 material used in this research was supplied in the form of B-staged prepreg, with an unspecified quantity of glass fibers in the reactive polyimide resin. All of the specimens were taken from the same sheet of prepreg to avoid the possibility of inconsistency between lots. The prepreg was stored in a sealed bag at 0°F until the specimens were prepared to prevent exposure of the material to heat and moisture, and specimens were not prepared until the time of each individual run.

Pappalardo (4) reported that the polymerization reaction of Kerimid 601 initiates at 150°C, peaks at 230°C, and terminates at 300°C. Using this as a guideline, the DSC was set to heat the

Kerimid 601 specimens from room temperature to 350°C to ensure that the entire reaction exotherm would be recorded. A typical thermogram is shown in Fig. 2.

Kinetic Analysis

Thermograms of the sort shown in Fig. 2 are valuable in providing an intuitive guide to the range of temperatures and energies expected in curing reactions. In addition, the thermograms can provide an experimental means of determining the numerical parameters in hypothesized kinetic models, and this model fitting procedure can yield analytical means of studying and optimizing the fabrication of complex items containing the reactive polymer. Several procedures have been proposed during the past several decades to perform model fitting using thermal analysis data (5-9), and recently Dhar (10) has provided a useful review which includes a numerical program for comparing the results of several methods.

In the analysis to be outlined below, we assume an n -th order thermally activated curing process, and we employ the method of Freeman and Carroll (11, 12) to fit the model to the thermogram. Some comments as to the reliability of this approach should be given at the outset. The method of Freeman and Carroll is one of the most convenient available, in that only a single scanning DSC experiment is needed to obtain all of the kinetic parameters. However, one might expect that this convenience could be accompanied by a loss of accuracy, and a number of workers feel this to be true (13).

Further, we must keep in mind that our assumption of thermally activated n -th order kinetics might be incorrect as well. We have already noted that the Kerimid cure is thought to consist of simultaneous addition and crosslinking reactions, and the combination of these reactions might not be describable with our model. Finally, Sichina (14) notes that curing reactions which exhibit autocatalyzing effects

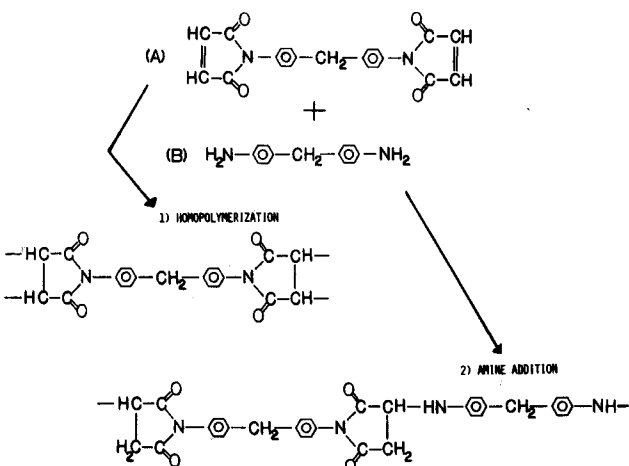


Fig. 1. Cure chemistry of Kerimid 601 polyimide resin.

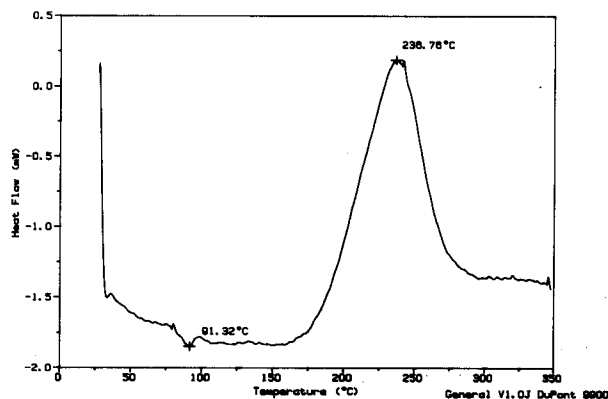


Fig. 2. DSC thermogram of Kerimid 601 prepreg material tested at 10°C/min in nitrogen atmosphere. (14.1 mg specimen mass, including glass fibers.)

may not obey the simple kinetic scheme used here.

While the above concerns should be kept in mind, the results to be shown below appear reasonable, and are considered useful for an initial examination of the wiring board curing process and to illustrate the general approach. A more exhaustive study would be required to assess fully the validity of the underlying assumptions.

Our assumed kinetic expression can be written as:

$$(d\alpha/dt) = Z \exp(E/RT) (1 - \alpha)^n \quad (1)$$

where α is the extent of reaction, Z is a frequency factor, E is the activation energy, R is the gas constant, T is the absolute temperature, and n is the reaction order. The extent of reaction α and the rate of reaction $d\alpha/dt$ can be measured directly from the DSC thermogram, assuming each reaction event to liberate the same quantity of heat:

$$d\alpha/dt = (1/H_0) (dH/dt) \quad (2)$$

$$\alpha = \int (d\alpha/dt) dt \quad (3)$$

Here dH/dt , the rate of heat evolution, is just the ordinate of the DSC thermogram, and H_0 is the area between the DSC base line and the ordinate over the range of temperatures comprising the reaction. H_0 is the total heat evolution of the cure reaction; in our case this quantity is not that of the resin alone, since the specimen also contains an unmeasured quantity of glass fibers.

The Freeman-Carroll approach linearizes Eq 1 by taking logarithms:

$$\log(d\alpha/dt) = \log Z + (E/2.303RT) + n \log(1 - \alpha) \quad (4)$$

This equation is then evaluated at various temperatures spaced at equal increments of $(1/T)$, and the corresponding experimental values of α and $d\alpha/dt$ are used in a difference equation obtained from Eq 4:

$$\Delta \log(d\alpha/dt) = \Delta \log Z + (E/2.303R)\Delta(1/T) + n \Delta \log(1 - \alpha) \quad (5)$$

This equation predicts that a plot of the differences of the logs of the rates of reaction at various temperatures, spaced at equal increments of reciprocal temperature, vs. the corresponding differences of logs of the extent of reaction at those temperatures, should be a straight line whose slope is the reaction order n and whose intercept can be used to compute the activation energy E . (Of course $\Delta \log Z = 0$, since Z is a constant.) Once E and n are known, Z can be found by evaluating Eq 1 at any selected temperature. This procedure can be performed

easily using spreadsheet software on personal microcomputers. Figure 3 shows a typical Freeman-Carroll plot for our Kerimid material.

Three such plots were made in this study, each from separate DSC experiments. (Each experiment, however, used specimens from the same batch of Kerimid prepreg.) The analysis appears reproducible, as seen in the following listing of numerical parameters obtained from these three plots:

Test	1	2	3
Reaction order	1.35	1.40	1.31
Activation energy, kcal/mole	27.8	27.7	26.9
Log (Z, 1/sec)	11.2	10.6	10.2
Correlation coefficient	0.97	0.94	0.95

APPLICATION TO CIRCUIT BOARD PROCESSING

Finite Element Formulation

During the processing of wiring boards, the kinetics of the chemical curing reaction are complicated by the nonuniform nature of the process. An overall model of board lamination must combine the curing kinetic model with the equation for conductive transient heat transfer, so as to obtain the spatial and temporal variation of temperature and extent of reaction during the process. Numerical approaches are suggested due to the complexity of the laminate, and we used finite element methods for this purpose.

As part of our continuing research in polymer processing, we have developed a finite element code which is able to solve simultaneously the conservation equations for transport of momentum, thermal energy, and reactive species for a variety of two-dimensional geometries and a number of problem types (15-17). As developed in standard texts in transport theory (e.g. Ref. 18) these equations can be written as:

$$\begin{aligned} \rho \left[\frac{\partial u}{\partial t} + u \nabla u \right] &= -\nabla p + \nabla(\eta \nabla u) \\ \rho c \left[\frac{\partial T}{\partial t} + u \nabla T \right] &= \mathcal{Q} + \nabla(k \nabla u) \\ \left[\frac{\partial C}{\partial t} + u \nabla C \right] &= R + \nabla(D \nabla u) \end{aligned} \quad (6)$$

Here u , T , and C are fluid velocity (a vector), temperature, and concentration of reactive species; these are the principal variables in our formulation. Other parameters are density (ρ), pressure (p), viscosity (η), specific heat (c), thermal conductivity (k), and species diffusivity (D). The ∇ operator is defined as $\nabla = (\partial/\partial x, \partial/\partial y)$.

In conventional closed-form analysis, one generally seeks to simplify the governing equations by dropping those terms which are zero or whose numerical magnitudes are small relative to the others, and then proceeding with a math-

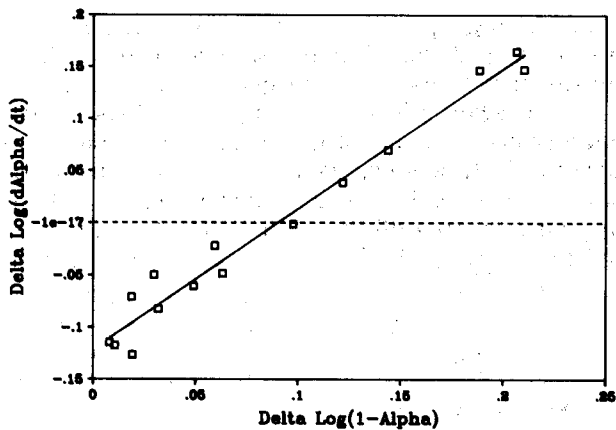


Fig. 3. Freeman-Carroll plot corresponding to thermogram of Fig. 2.

emathical solution. In contrast, our code is written to contain all of the terms, and the particularization to specific problems is done entirely by the selection of appropriate numerical parameters in the input dataset. In this present problem, the momentum equation is not needed and all terms containing the flow velocity are dropped; this is accomplished by setting appropriate flags in the dataset.

Q and R are generation terms for heat and chemical species respectively, while the pressure gradient ∇p plays an analogous role for momentum generation. The heat generation arises from viscous dissipation and from reaction heating:

$$Q = \tau:\gamma + R(\Delta H) \quad (7)$$

where τ and γ are the deviatoric components of stress and strain rate, R is the rate of chemical reaction, and ΔH is the heat of reaction. R in turn is given by a kinetic chemical equation; in our model we have implemented the n -th order Arrhenius expression given previously as Eq 1.

Numerical Results

We wish to examine the curing of a specific multilayer board consisting of symmetric outer layers of copper-clad laminate and one central copper-clad layer, bonded by the Kerimid adhesive prepreg material. The finite element simulation follows the same approach taken earlier for analyzing cure in composites pultrusion processing (19). Noting that the thermal and reactive species gradients are much larger in the board through-thickness direction than in the plane of the board, we place a single strip of elements running from the board centerline to the outer edge (see Fig. 4). The time-temperature program of the selected press cure cycle is imposed on the topmost nodes as a boundary condition, and the code is operated in a time-stepping fashion to compute the internal temperatures and degrees of reaction as the cure proceeds.

Figure 5 shows the temperature profiles

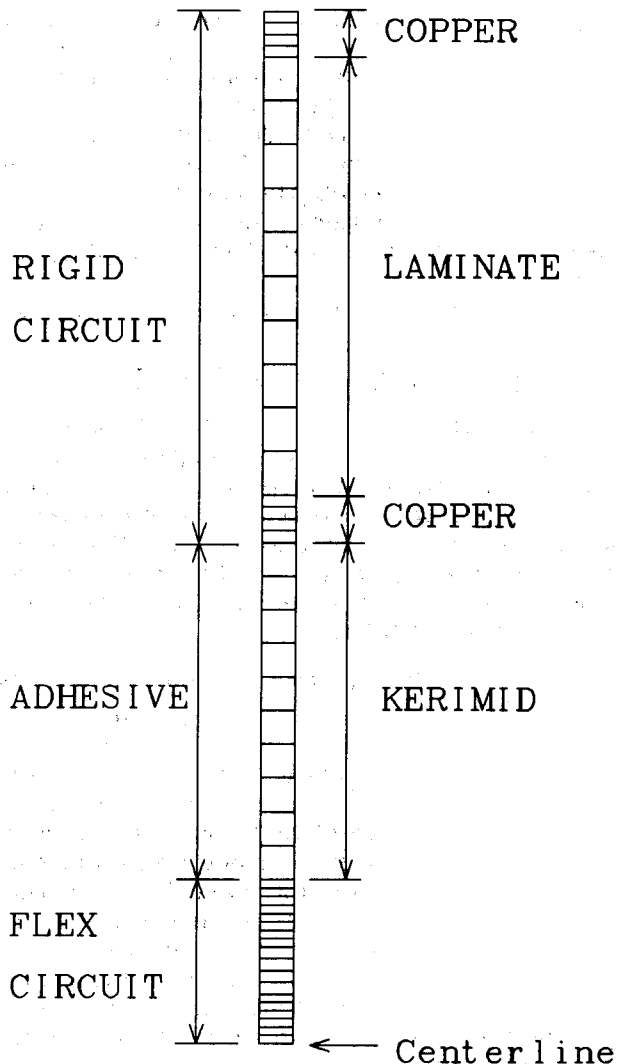


Fig. 4. Finite element grid for one-dimensional simulation of wiring board cure.

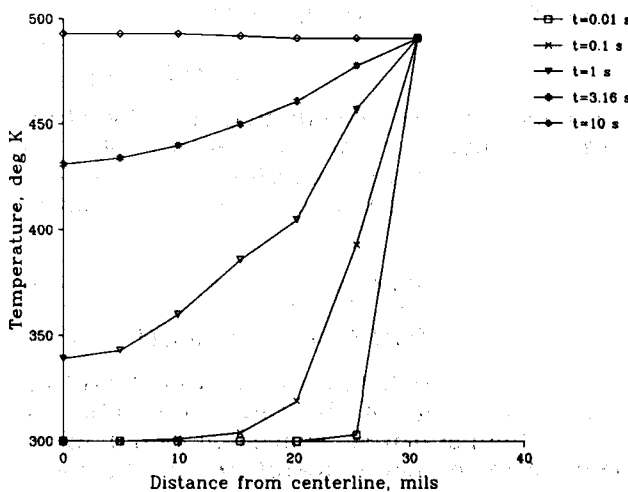


Fig. 5. Predicted temperature profiles at various times for cure program in which outer surfaces of wiring board are brought suddenly to 425°F (491 K).

which are predicted within the board at various times when the board is placed in a heated mold and the outer surfaces brought suddenly to the curing temperature of 425°F (491°K). The tem-

peratures equilibrate in times on the order of 10s, and in this time the reaction proceeds to completion as well. Processing time is obviously minimized by such a cure cycle, but the thermal strains produced by the nonuniform temperatures at early times may be problematic in terms of board warpage and interlayer delamination.

Figure 6 shows the results of heating more gradually at 10°F/min until 425°F is reached, and then holding at that temperature. In this case the heating rate is slow enough compared to the thermal equilibration time that the board is at essentially uniform temperature and degree of reaction during the process, and the reaction proceeds to completion during the heat-up phase of the cure cycle. The high-temperature hold following the heat-up is unnecessary with regard to chemical reaction in the adhesive.

CONCLUSIONS

In spite of the somewhat preliminary nature of these results, especially in regard to the assumption of the kinetic model, we hope we have demonstrated a systematic and comprehensive approach to process analysis of complicated structures containing reactive polymers. With the kinetic parameters of the adhesive prepreg

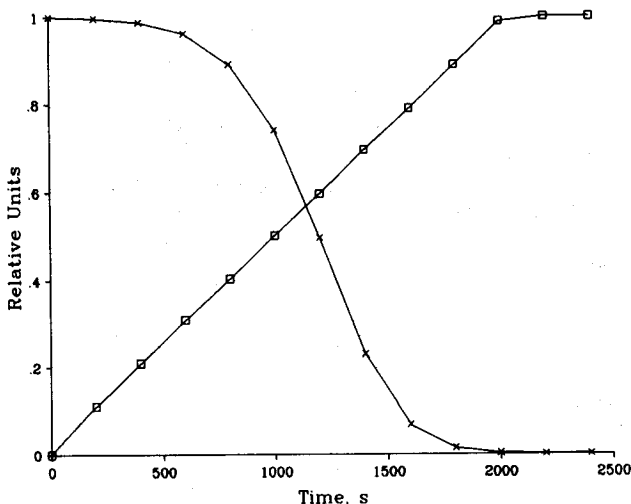


Fig. 6. Normalized temperature (ascending line) and fraction of resin unreacted (descending curve) for cure program consisting of heating at 10°F/min to 425°F followed by hold at 425°F.

material known, the finite element model can be used to simulate a number of trial cure cycles. The code output gives clear indication of such process variables as thermal strain and chemical conversion time, which should be useful in process development and optimization.

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