

# Physiorheological Characterization of a Carbon/ Epoxy Prepreg System

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## Synopsis

A model epoxy matrix resin was analyzed using differential scanning calorimetric and rheological techniques. The data was used to construct a time-temperature-phase transformation diagram to investigate the thermoset curing phenomena. Experimental techniques were developed to generate similar data on a carbon/epoxy prepreg material. The data were then compared to study the effects of the presence of the reinforcement on the processing characteristics of the epoxy matrix resin.

## INTRODUCTION

Curing schedules used in the production of carbon/epoxy hardware have traditionally been empirically derived. The proprietary nature of the composite prepreg materials and the lack of powerful analytical tools has led users to rely on vendor recommendations and limited shop experience in developing production cure schedules. The results have been far from satisfactory. The approach has led to expensive, inefficient use of time, materials, and facilities, poor process control, and erratic hardware performance.

The goal of this work is to demonstrate a methodology for obtaining quantitative, unambiguous information regarding the two key questions that must be answered in designing a process for the fabrication of thermosetting matrix composite materials: How can volatile removal be maximized and what is the most efficient cure schedule (in terms of time and energy) that results in a fully cured, free-standing part?

Gillham et al.<sup>1,2</sup> have developed the time-temperature-phase transformation (TTT) diagram (Fig. 1) to illustrate and further understand the complex curing phenomena of thermosets. We have combined differential scanning calorimetric (DSC) and rheological data to construct a TTT diagram for a model epoxy matrix system. Similar data was generated on a carbon/epoxy prepreg, based on the same matrix resin to determine how the processing characteristics of the matrix are influenced by the presence of the reinforcement.

From the TTT diagram, one can obtain considerable processing information: the time and temperature dependence of viscous flow, reaction kinetics, gelation, and vitrification. Thus, to optimize the cure of a particular resin system, time and temperature values for the devolatilization and optimum curing cycle can be initially chosen from the TTT diagram. The

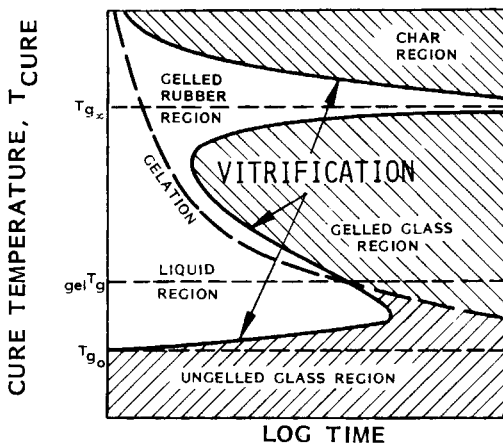


Fig. 1. Generalized time-temperature-transformation (TTT) cure diagram. A plot of the times to gelation and vitrification during isothermal cure vs. temperature delineates the regions of four distinct states of matter: liquid, gelled rubber, gelled glass, and ungelled glass (courtesy of Refs. 1 and 2).

approach leads to a more accurate, rapid and efficacious, and rational cure schedule development.

### EXPERIMENTAL

The resin system selected for the study is the 4,4'-diaminodiphenylsulfone (DDS)-amine-cured tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy. The system has the advantage of being closely related to commercially available materials; yet it is a relatively uncomplicated system without secondary epoxy resins, diluents or "tackifying" agents, or accelerators often found in commercial epoxy formulations.

The prepreg was prepared by coating the neat resin onto woven pyrolyzed polyacrylonitrile (PAN) carbon fiber reinforcement using a hot melt (solvent-free) process. The reinforcement was a five harness satin woven fabric with 6000 filaments per tow. The resin content for the prepreg material was 44%.

The dynamic shear viscosity profiles of the matrix resin were measured on a Rheometrics mechanical spectrometer, RMS Model 605, employing a parallel-plate geometry. The optimized instrumental parameters for the analyses are 35% strain and an angular frequency of 60 rads. The neat resin samples were conditioned at 2 torr for approximately 16 h at 22°C (74°F) to remove any volatiles, e.g., air, moisture, and residual solvents. A series of isothermal viscosity profiles was obtained by preheating the sample chamber to 10°C (18°F) above the desired isothermal temperature, inserting the sample and promptly starting the analysis.

The data are presented in Figure 2 at a temperature of 180°C (356°F), 170°C (338°F), 160°C (320°F), 150°C (302°F), 140°C (284°F), and 130°C (266°F). As is expected, the initial viscosity of the resin (Fig. 2) decreases with increasing temperature, since the flow of a material with respect to tem-

perature obeys an Arrhenius or exponential function.<sup>3</sup> The time required to reach a particular viscosity, e.g., 10, 100, 500, and 1000 P at each isothermal temperature is determined from Figure 2. The gelation point is taken as the point where the shear modulus  $G'$  is equal to the loss modulus  $G''$  from the rheological data as described by Tung and Dynes.<sup>4</sup> The flow of the resin in the liquid state can be characterized by plotting the time to a particular viscosity versus the reciprocal of temperature (K). Figure 3 is a so-called "isoviscosity" plot displaying a linear time axis. Figure 4 has a log time axis. The latter is the form to be incorporated into the TTT diagram. It should be noted that  $1/T$  (K) is the true linear vertical axis with respect to temperature.

A DuPont Model 901 Differential Scanning Calorimeter controlled by a Model 1090 Microprocessor/Controller was used for the DSC experiments. A set of isothermal cures was conducted at 180°C, 170°C, 160°C, 150°C, 140°C, and 130°C with corresponding reaction periods of 165, 250, 265, 270 and 335 min, respectively. The time required for the instrument to reach thermal equilibrium after sample insertion is approximately 1 min. A plot of the thermograms is displayed in Figure 5. For isothermal studies, it is important that the calculations be based on an accurate value of the total heat of reaction. Upon completion of the isothermal experiments, the samples were cooled and a dynamic experiment was performed using a heating rate of 5°C/min to ensure that the reaction reaches 100% completion. Figure 6 shows the thermograms obtained in this manner. The total heat of reaction can be described as follows:

$$\Delta H_{\text{total}} = \Delta H_{\text{iso}} + \Delta H_{\text{dynamic}} \quad (1)$$

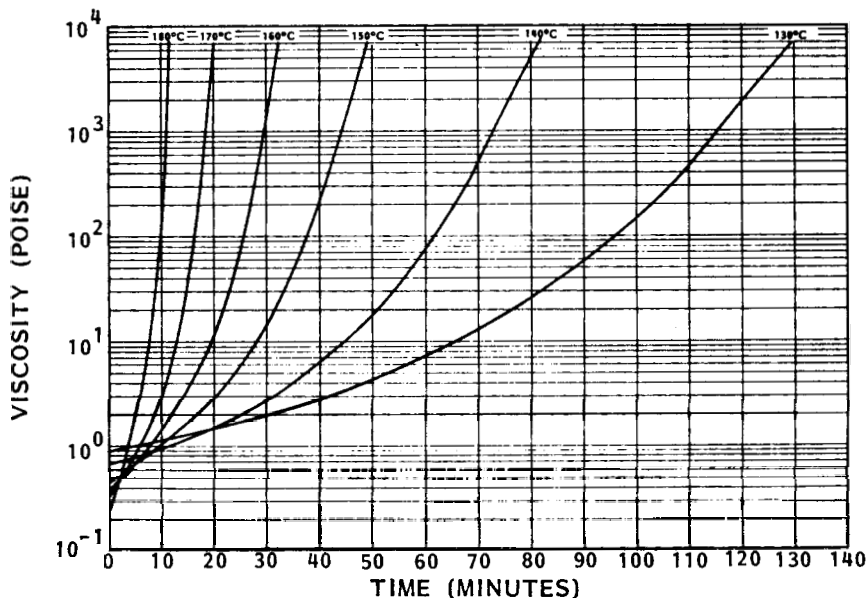


Fig. 2. TGDDM/DDS neat resin isothermal, viscosity profiles at 180°C, 170°C, 160°C, 150°C, 140°C, and 130°C.

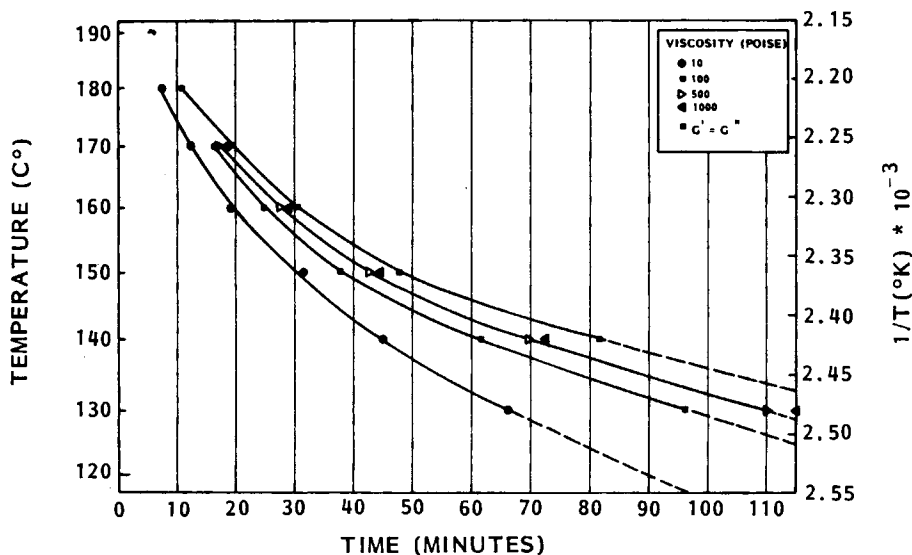


Fig. 3. TGDDM/DDS neat resin isoviscosity plot (P): (●) 10; (■) 100; (▷) 500; (◁) 1000; (■)  $G' = G''$ .

where  $\Delta H_{\text{iso}}$  and  $\Delta H_{\text{dynamic}}$  are the areas under the isothermal and dynamic thermograms. The data corresponding to the area calculations are presented in Table I. The total area for the 180°C isothermal plus dynamic cure is somewhat lower than the others. Possibly this is due to the limited sensitivity of the method on the first couple of minutes where the heat generation is relatively high. The 180°C data were not utilized in the treatment which follows. The heat of reaction,  $\Delta H$ , is  $531 \pm 7$  J/g for the 170–140°C cures, with a standard deviation of 1.3%, quite acceptable for DSC experiments.

Once the total heat of reaction and the partial heat of reaction with

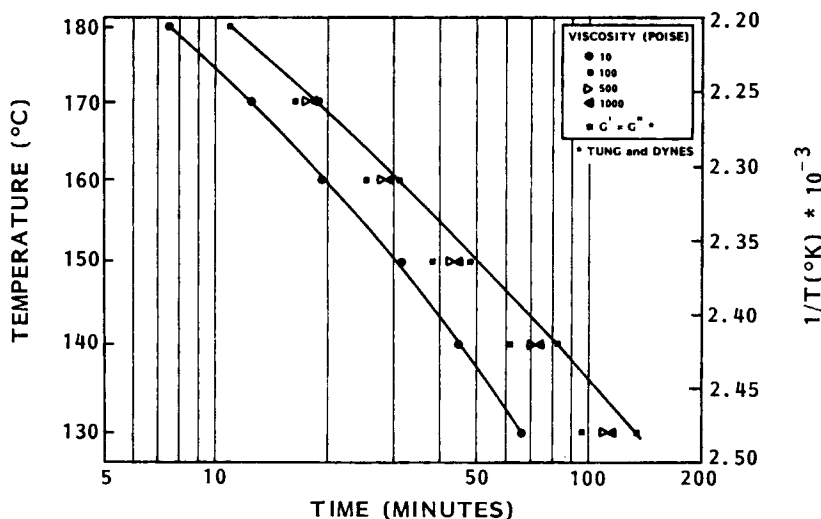


Fig. 4. TGDDM/DDS neat resin isoviscosity plot (log time axis) (P): (●) 10; (■) 100; (△) 500; (▼) 1000; (■)  $G' = G''$  (Tung and Dynes).

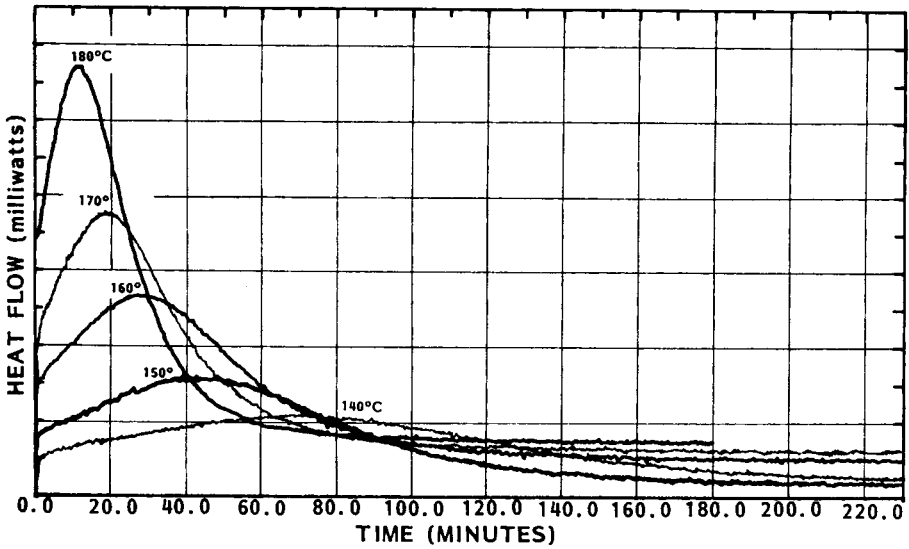


Fig. 5. TGDDM/DDS neat resin isothermal DSC profiles at 180°C, 170°C, 160°C, 150°C and 140°C.

respect to time for the isothermal cure are computed, the fraction reacted ( $\alpha$ ) is obtained, where

$$\alpha = \Delta H_{\text{isoi}} / \Delta H_{\text{total}} \quad (2)$$

These values can be used to construct an "isoreaction" plot (Fig. 7), where various values of  $\alpha$  are plotted as a function of  $1/T$  (K) vs. log time. These data together with the rheological data in a similar format are used to construct the TTT diagram.

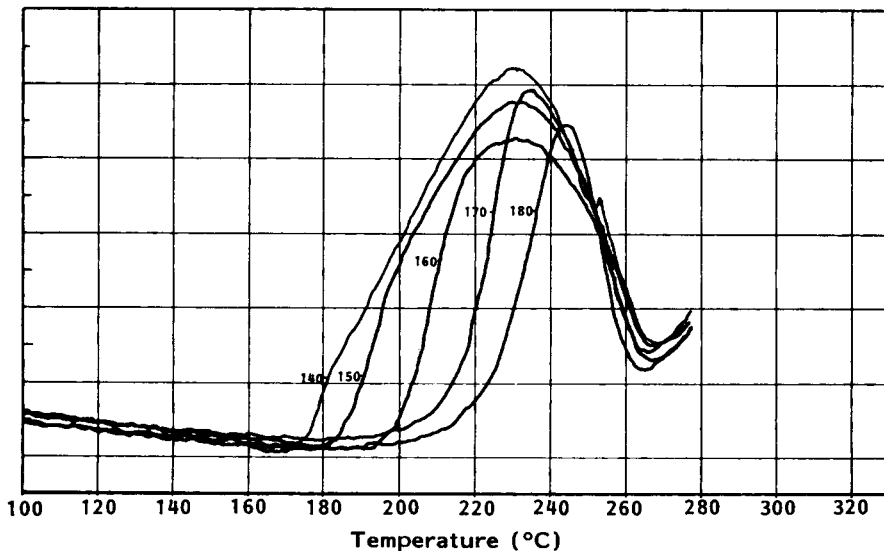


Fig. 6. Dynamic DSC profiles subsequent to isothermal DSC cures at 180°C, 170°C, 160°C, 150°C, and 140°C.

TABLE I  
Numerical Integration Data for the Thermal Profiles Presented in Figures 5 and 6

$T$ (°C)	Weight (g)	$H$ (iso) (mW · min)	$H$ (dynamic) (mW · min)	$H$ (total) (mW · min)	$H$ (J/g)
180.	0.01713	128.64	16.13	144.77	507.
170.	0.01755	129.74	23.26	153.00	523.
160.	0.01769	128.18	30.64	158.82	539.
150.	0.01763	118.63	39.60	158.23	537.
140.	0.01783	109.84	45.88	155.72	524.

## RESULTS AND DISCUSSION

As previously described, rheological profiles are utilized to characterize the flow behavior of thermosets in the liquid state with respect to time and temperature. DSC experimentation provides a means to characterizing the curing behavior (fraction reacted,  $\alpha$ ) with respect to time and temperature. By combining the results on a common graph, a TTT diagram (Fig. 8) is obtained. The diagram is quite useful to the manufacturing engineer for processing the material since all of the critical thermal events are shown.

Viscosity can be related to the fraction of resin reacted (advancement) by the superposition of the isoviscosity data onto the isoreaction data. For the diagram, the time to a particular level of viscosity can be estimated. This is quite useful for B-staging, debulking and degassing procedures. Thus the TTT diagram provides a solution to the problem of volatiles removal.

The time of the gelation point is taken as the point where the shear modulus is equivalent to the loss modulus.<sup>4</sup> For the resin system, gelation occurs between a value for  $\alpha$  of 0.33–0.36. A slight temperature dependence is noted. This is in agreement with Hagnauer et al.,<sup>5</sup> who states that the

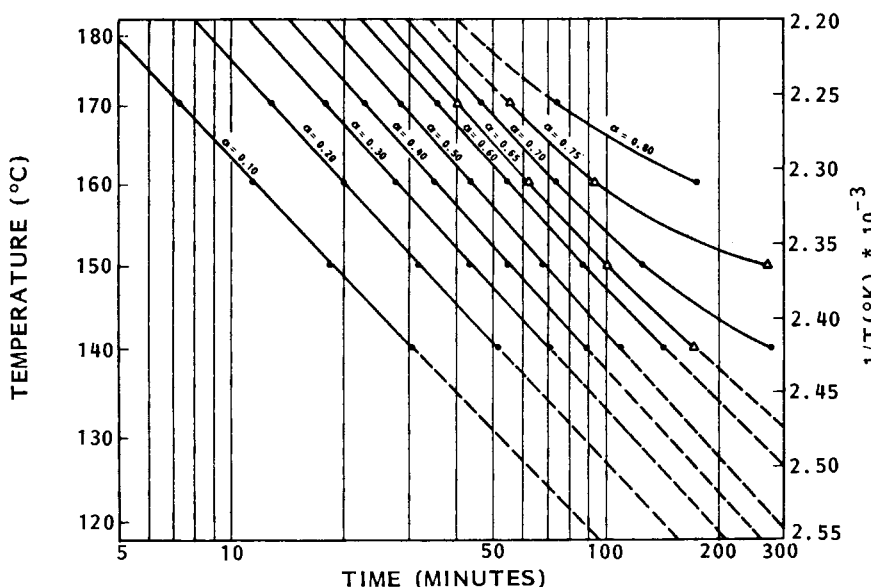


Fig. 7. TGDDM/DDS neat resin isoreaction plot (log time axis).

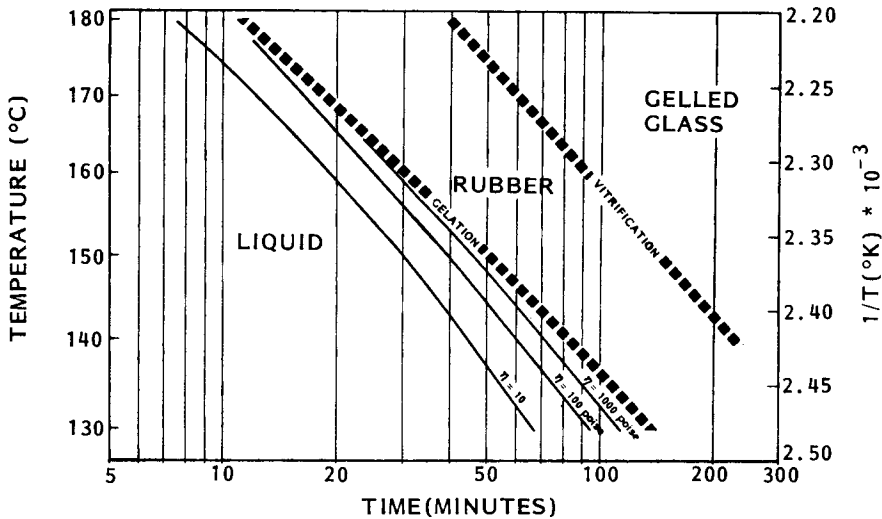


Fig. 8. TGDDM/DDS neat resin TTT diagram.

gelation occurs at a value for  $\alpha$  of 0.35–0.42, depending on the reactant stoichiometry, as determined by gel permeation chromatography.

During the early stages of the polymerization, the reaction mechanism obeys the laws of chemical kinetics. Since the reaction mechanism changes to diffusion control (slower reaction rate) as the material vitrifies, the onset of vitrification can be taken as the region where the  $\alpha$  lines become non-linear for a particular cure temperature. An arbitrary line estimating the onset of vitrification is indicated in Figure 8. From this, one can approximate a time to vitrification at any particular temperature. For example, at 177°C (350°F) the time to vitrification is approximately 40 min. Once the material has vitrified, further reaction at that temperature is relatively slow, and often a postcure at a higher temperature is performed.

Once the characterization of the matrix resin was complete, a nagging question remained unanswered. How does data generated on neat resins translate to a heavily reinforced carbon/epoxy prepreg?

Hardware is fabricated from prepreg, not neat resin. If the resin sample is extracted from the prepreg material for characterization purposes, significant chemical and physical changes can occur. The effects of solvents (plasticisers, increased mobility leading to advancement), heat (staging), and mechanical manipulations (change in the molecular weight distribution) on the resin can greatly affect its processing characteristics. Conversely, preparing prepreg from neat resin and fiber can result in similar changes in the resin. Therefore, testing the neat resin before the prepreg is prepared raises the same questions.

Additional considerations may be even more significant. The carbon fiber reinforcement has a large surface area which contains numerous chemically active sites. It is possible that the presence of the reinforcement significantly affects the resin chemically and/or physically during fabrication, and so altering the curing process. If the kinetics or the rheology of the resin in the presence of the fiber reinforcement is significantly different from that

of the neat resin, neat resin studies are of limited value. We, therefore, decided to carry out parallel rheological and kinetic studies on the model prepreg material as previously described for the neat resin.

We attempted to run a rheological characterization study on the mechanical spectrometer using the technique described by Maximovich and Galeos.<sup>6</sup> Some initial problems were encountered due to the nature of the prepreg. In order to follow the entire curing process through gelation, a 10,000 g · cm torque transducer was required. The low viscosity data required a 2000 g · cm torque transducer, so dual runs were performed to obtain a complete cure for any set of experimental conditions. A more serious problem was the fact that the resin remains at a relatively low viscosity for an appreciable length of time during cure. This resulted in resin flow out the sides of the parallel-plate fixture, distortion of the woven, reinforcing fibers (fiber wash), and major anomalies in the data. It became apparent that new test geometry was required.

The problems were solved by the use of a 25 mm cone plate with a cone angle of 0.04 rad and a 26 mm shallow cup fixture shown in Figure 9. Percent strain and frequency sweeps were performed on prepreg samples to determine the optimum experimental parameters. Linear regions were observed for both sweeps with the optimum parameters being 35% strain and an angular frequency of 60 rad/s.

The same series of isothermal data as generated on the neat resin was obtained for the prepreg. Again, samples were preconditioned to remove volatile species. Figure 10 shows a series of isothermal apparent viscosity profiles from 130°C (266°F) through 180°C (356°F) at 10°C (18°F) intervals. Although the set of curves resemble those generated for the neat resin, some interesting differences are observed. The apparent initial viscosity of the prepreg increases with increasing test temperature, except for the 130°C cure. The typical Arrhenius dependence with respect to temperature for viscous flow is not observed using this geometry.

The data treatment used for the neat resin samples were followed, and isoviscosity curves were drawn for the prepreg (Figs. 11 and 12). Over-laying these curves on those generated for the neat resin (Figs. 4 and 5) shows

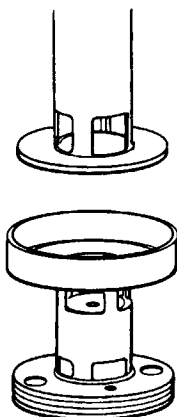


Fig. 9. Plate and cup fixture.



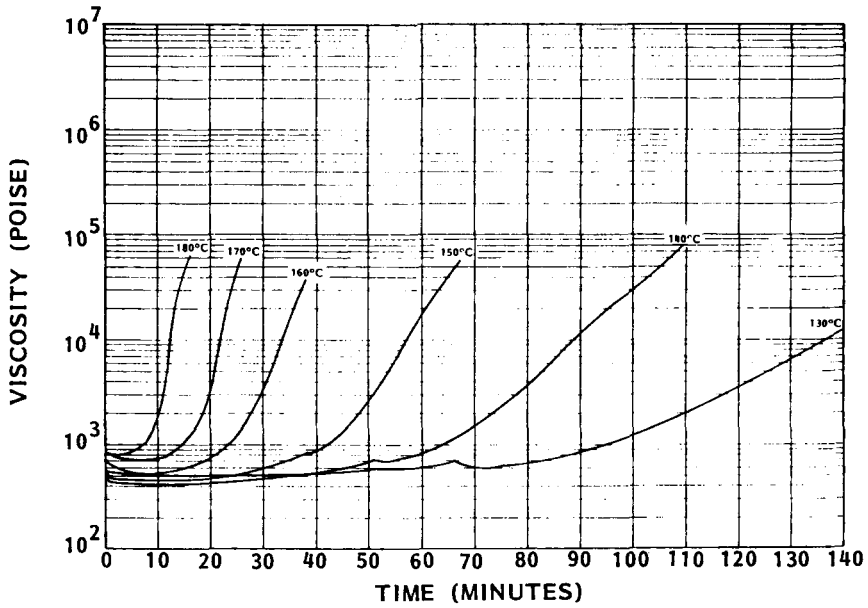


Fig. 10. TGDDM/DDS-based prepreg isothermal "apparent" viscosity profiles.

great similarities and subtle differences. It is apparent that smooth, reproducible isoviscosity curves can be generated on the prepreg which are quite comparable to those obtained on the neat resin. Of course, there are questions concerning the relative nature of the apparent viscosity values due to the reinforcement, ply orientation, etc., for comparison purposes. By plotting the data in this manner (buildup as a function of time and tem-

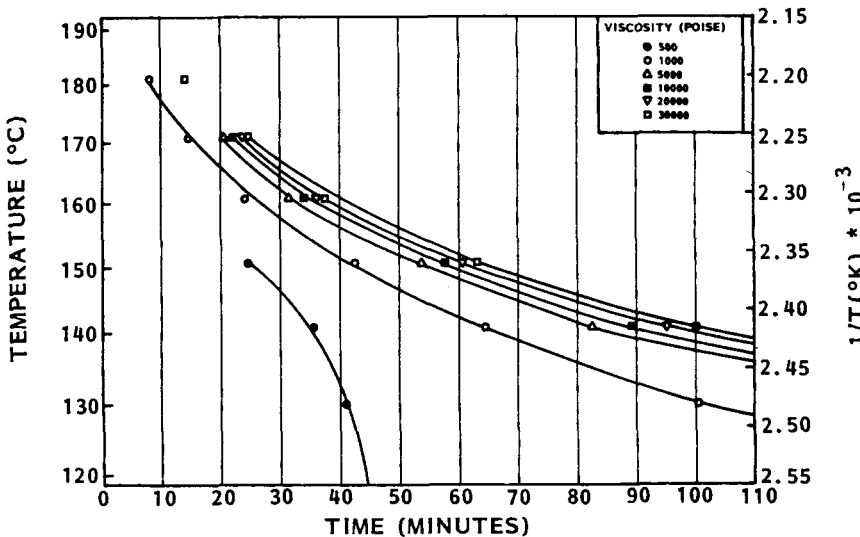


Fig. 11. TGDDM/DDS-based prepreg "apparent" isoviscosity plot (P): (●) 500; (○) 1000; (△) 5000; (■) 10,000; (▽) 20,000; (□) 30,000.

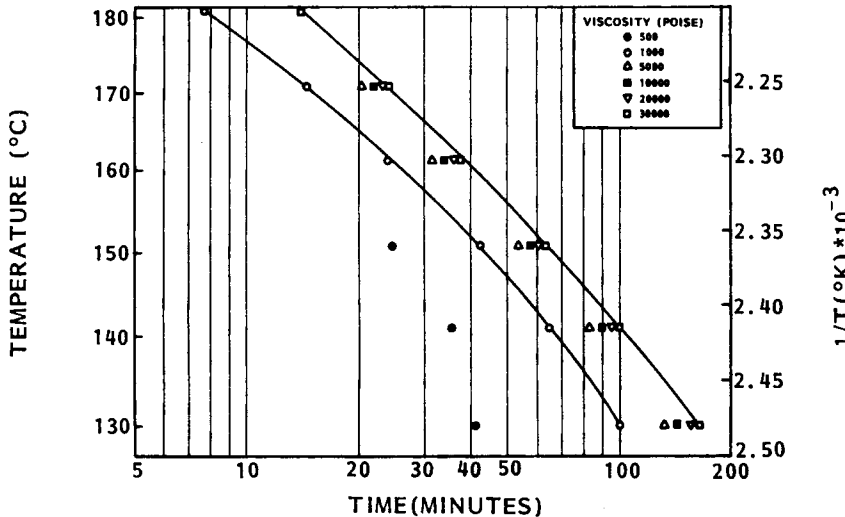


Fig. 12. TGDDM/DDS-based prepreg "apparent" isoviscosity plot (log time axis) (P): (●) 500; (○) 1000; (△) 5000; (■) 10,000 (▽) 20,000 (□) 30,000.

perature) the effects due to the reinforcement are minimized, and the processing information for the prepreg is applicable.

DSC studies were also performed on the prepreg. It was apparent that there had been some B-staging or prereaction during the processing of the material. The kinetic treatment comparable to that obtained on the unreacted neat resin is not available at this time. Work is currently being performed to incorporate B-staging information obtained from high-performance liquid chromatography (HPLC) with the DSC analyses for an accurate kinetic evaluation.

### CONCLUSIONS

The most significant observations resulting from this investigation can be summarized as follows:

1. DSC and rheological data can be used to construct a TTT diagram for curing process of the neat resin.
2. "Apparent" rheological data generated on the fiber-reinforced prepreg material closely resembles data generated on the neat resin. Differences may be due to prepreg B-staging effects, which are currently under investigation.
3. Either neat resin or prepreg "apparent" rheological characterization can be utilized to characterize the flow and cure behavior of production prepreg materials through gelation.
4. The TTT diagram provides an estimation of the time and temperature requirements for optimizing the devolatilization process and determining the most efficient cure schedule of the prepreg material.

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