

Characterization of prepreg and cured epoxy/fiberglass composite material for use in advanced composite piping systems

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Abstract

A company that uses epoxy/fiberglass prepreg material in advanced composite piping systems requested that the NASA/ Marshall Space Flight Center (MSFC) use several thermal analysis techniques to characterize the material. Dynamic and isothermal tests by use of the TA Instruments 2920 Differential Scanning Calorimeter (DSC) yielded cure kinetics on the prepreg. The dynamic data showed two exothermic cure reactions for the prepreg, but isothermal data showed that the first cure exotherm was a low temperature event and began to disappear near 105°C. For the second cure exotherm, activation energies (E_2) of 79.0 and 87.1 kJ/mol were obtained from the dynamic and isothermal data, respectively. Partial cure of the prepreg for several isothermal cure temperatures and times yielded a glass transition temperature (T_g) versus conversion plot with an approximate gelation point of the prepreg at 63% conversion. At a cure temperature of 135°C and a T_g of 103°C, most of the ultimate cure of the prepreg was achieved. The TA Instruments 983 Dynamic Mechanical Analyzer (DMA) yielded activation energies of cure of 140 (E_1) and 50.5 (E_2) kJ/mol for the first and second cure reactions, respectively, based on times to gelation at several cure temperatures. A DMA temperature sweep at several fixed frequencies yielded an average activation energy of 357 kJ/mol for the T_g of the epoxy/fiberglass composite in cured sheet form. The fiber filler is a fiberglass mat, and DMA data as well as thermomechanical analysis (TMA) data on the cured sheet material showed a slight dependence on mat direction for the measured properties. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

NASA/MSFC and the Department of Mechanical Engineering at Louisiana State University (LSU) teamed up in support of Specialty Plastics of Baton Rouge, LA to develop innovative joining/fitting technology for advanced composite piping systems. This high-risk technology will improve piping systems for the US oil and gas industry [1]. NASA/MSFC received

samples of the prepreg and cured sheet composite from Specialty Plastics, who primarily wanted to determine the cure kinetics of the prepreg by DSC through two-parameter autocatalytic cure modeling.

2. Experimental methods

The prepreg material used in the thermal analysis testing was the epoxy TCRTM prepreg made by Thio-kol Propulsion in Brigham City, UT, containing a proprietary curative and glass cloth filler with a 0/90°

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weave. This prepreg is unique in that it can be stored at ambient conditions from 6 months to 1 year, and still be processable if storage temperatures are less than 90°F. Although slightly different cure conditions for the prepreg were recommended by Thiokol, the following conditions were used in this cure study: 135°C/3 h, 145°C/2 h and 155°C/1 h [2].

Prepreg cure characterization was determined with a TA Instruments 2920 DSC and a DuPont Instruments 983 DMA.

2.1. DSC testing

The DSC testing was performed in both isothermal and dynamic heating modes. An argon gas sample purge was used for all DSC tests. The prepreg material is very sticky, and a hermetic stainless steel DSC pan with an O-ring seal was used for each sample. The stainless steel pan contains a much larger sample than an aluminium pan, and 60–70 mg samples were used which covered the entire prepreg thickness. In addition to the aforementioned cure conditions, isothermal ‘partial cures’ at these and lower cure temperatures were used below and above the gelation point of the prepreg. For isothermal testing, the sample chamber was preheated at the set point cure temperature, the sample pan was then introduced into the chamber, and each test was started when the actual temperature was within 4°C of the set point temperature. The average actual cure temperature during the cure time of each prepreg sample was within 2°C of the set point temperature. For dynamic testing, three linear heating rates of 2, 5 and 10°C/min were used over a temperature range of 30–300°C for also determining prepreg cure kinetics. The 10°C/min heating rate was used following each partial cure for determining the T_g and residual heat of reaction after curing to some time t ($H_{t,resid}$).

2.2. DMA testing

All DMA testing was performed in the fixed frequency mode at an oscillation amplitude of 0.2 mm, with no inert gas sample purge used. For isothermal DMA testing, each prepreg sample was approximately a 0.25 in. square cut through the entire prepreg sheet thickness, and adhered to the center of a strip of wire hardware cloth with a 0.25 in. square mesh size. Fig. 1

shows several of the DMA post-isothermal cure samples. Each prepreg sample was tested in the horizontal DMA mode at a frequency of 1 Hz. For DMA isothermal cure temperatures of 115–155°C, a programmed equilibration step from room temperature to the cure temperature averaged 5.4 min. The average actual cure temperature was within 0.2°C of the DMA set point temperature. Dynamic DMA heating tests were also performed on rectangular samples about 2 in.×0.375 in. cut from the cured sheet composite material (about 1.8 mm thick) in both parallel and perpendicular fiberglass mat directions. Each cured sample was tested in the vertical DMA testing mode at fixed frequencies from 0.25 to 2.0 Hz, and a temperature range of –50–200°C with a 2 or 3°C increment between frequency measurements. A cured sample length to thickness ratio of 5 was used to minimize a slight curvature in the cured sheet material.

2.3. TMA testing

Cured sheet composite samples were also tested with a TA Instruments 2940 TMA used in the expansion mode. The effect of fiberglass mat direction on the linear coefficient of thermal expansion (CTE) was determined for the parallel, perpendicular and cross-ply directions. Each TMA scan was performed from 25 to 160°C at a linear heating rate of 5°C/min with an argon gas sample purge. Each TMA sample was temperature scanned twice, and CTE data was reported on the second scan.

3. Results and discussion

3.1. DSC data

A dynamic DSC plot of heat flow versus temperature is shown for the ‘as received’ prepreg in Fig. 2 at a heating rate of 10°C/min revealing two exothermic peaks with a total heat of reaction (H_{RXN}) of 80 J/g. Although a single DSC exothermic peak (i.e. one overall cure reaction) is most often observed in thermoset curing, there are other examples of the two DSC peaks (i.e. two different cure reactions). Lee et al. [3] also showed two DSC peaks for the cure of Hercules 3501-6 epoxy resin.

A TA Instruments data analysis program for DSC isothermal kinetics was used to analyze the isothermal

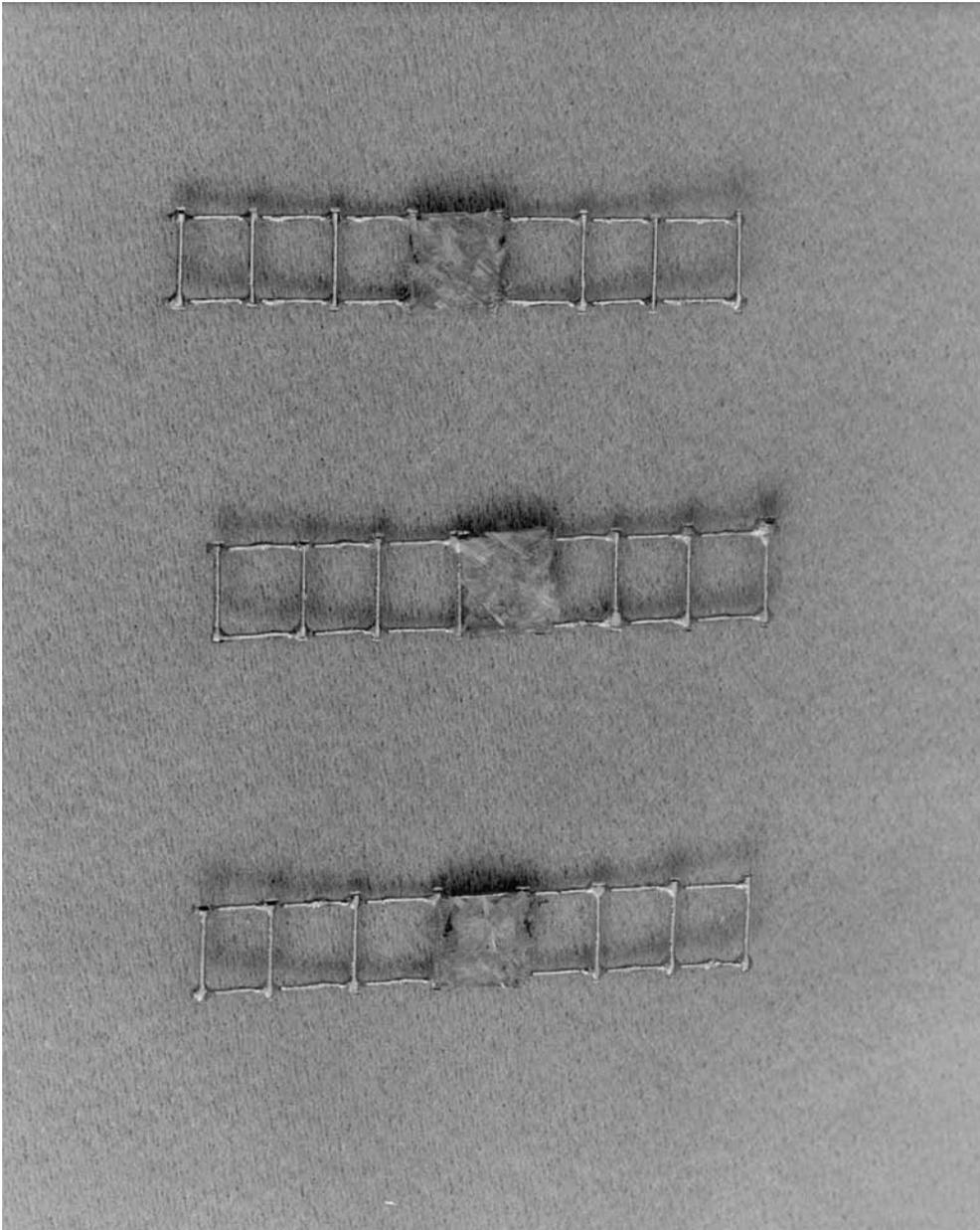


Fig. 1. Several DMA samples of epoxy/fiberglass prepreg adhered to wire hardware cloth following cure at isothermal conditions.

cure data on the prepreg at the three recommended cure conditions. This software utilizes a well-known two-parameter autocatalytic cure kinetics model:

$$\frac{dC}{dt} = kC^m(1 - C)^n \quad (1)$$

Lee et al. [3] believed that the two DSC exothermic cure peaks observed in their work could not be correlated by a single kinetics equation. They used a modified form of Eq. (1) with two rate constants (k_1 and k_2) for conversion $C \leq 0.3$, and an additional equation with a third rate constant (k_3) for $C \geq 0.3$.

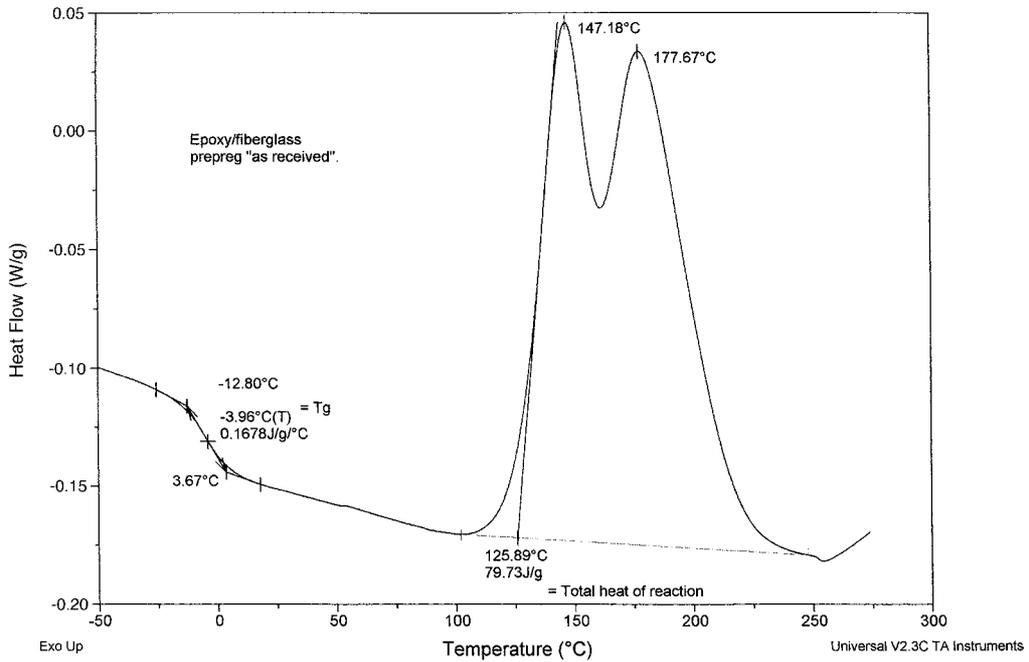


Fig. 2. DSC heating scan at 10°C/min on 'as received' epoxy/fiberglass prepreg.

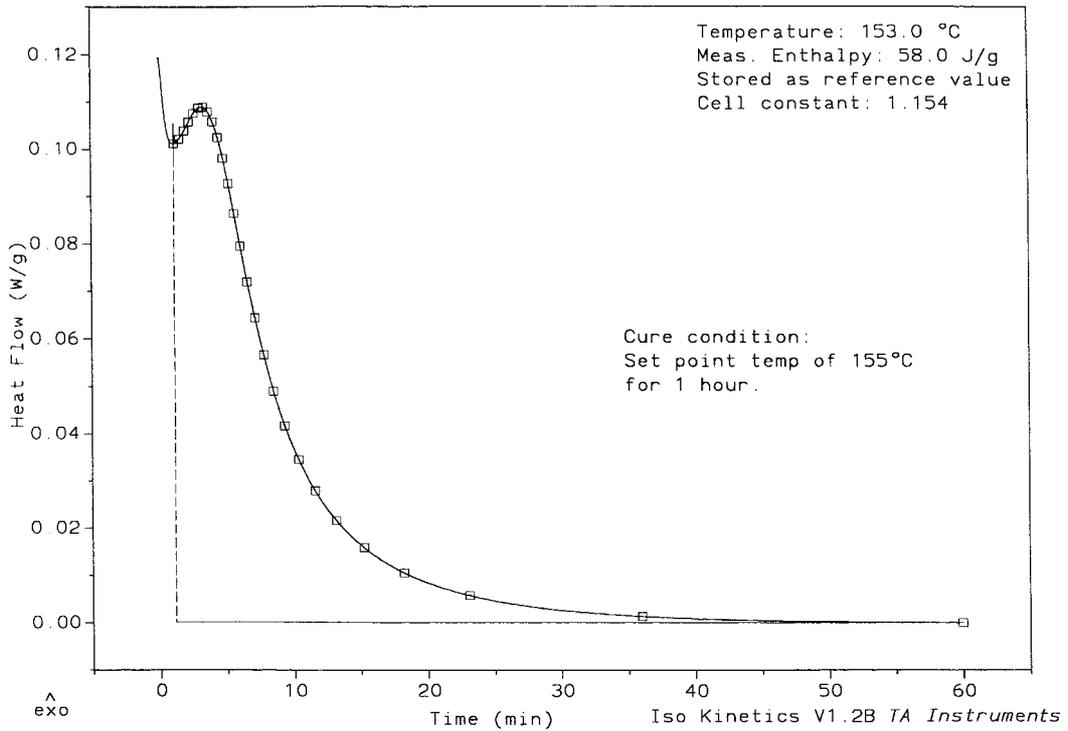


Fig. 3. DSC isothermal cure of epoxy/fiberglass prepreg for 1 h at a set point temperature of 155°C.

Table 1

DSC isothermal cure temperature (°C)	Autocatalytic kinetic parameters		
	n	m	k (min ⁻¹)
133.2	1.16	0.170	0.0667
143.0	1.17	0.140	0.120
153.1	1.14	0.114	0.190

Table 2

Type of DSC experiment	Arrhenius kinetic constants			
	Activation energy, E (kJ/mol)		Pre-exponential factor, Z (min ⁻¹)	
	E_1	E_2	log Z_1	log Z_2
Dynamic	137.1	79.0	17.1	8.78
Isothermal	–	87.1	–	10.0

Fig. 3 shows a DSC plot of heat flow versus time for the prepreg at a cure condition of 155°C/1 h for the second exothermic event in Fig. 2, based on a conversion (C) range of 0.04–0.99. For the three recommended cure conditions at 135, 145 and 155°C, a plot of $\log(dC/dt)$ versus $\log((1-C)C^{(m/n)})$ at each temperature yielded m , n and k from Eq. (1). For the three cure temperatures collectively, a plot of $(1/k) \times (dC/dt)$ versus C yielded values of the activation energy of cure (E_2) and the pre-exponential factor ($\log Z_2$). These values of E_2 and $\log Z_2$ (87.1 kJ/mol and 10.0 min⁻¹) were comparable to those determined

from DSC dynamic heating data (79.0 and 8.78). The Arrhenius kinetic constants were determined from the dynamic heating data by the ASTM E 698 method through iterative calculations. The kinetics data is summarized in Tables 1 and 2.

The above kinetics data for the three cure conditions at 135, 145 and 155°C was also used in finite difference modelling (FDM) with numerical computational techniques for solving the one-dimensional heat conduction equation with chemical kinetics. Such a thermal characterization is necessary for optimizing the

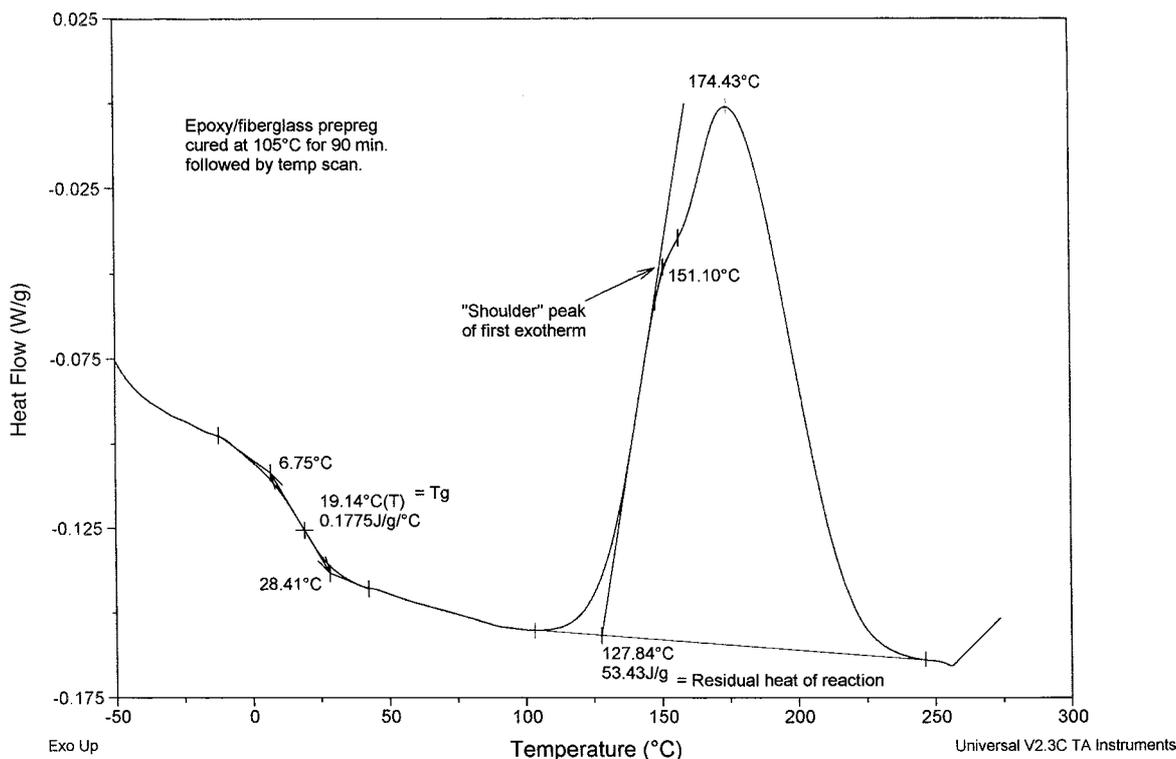


Fig. 4. DSC heating scan at 10°C/min on epoxy/fiberglass prepreg following isothermal cure at 105°C for 90 min.

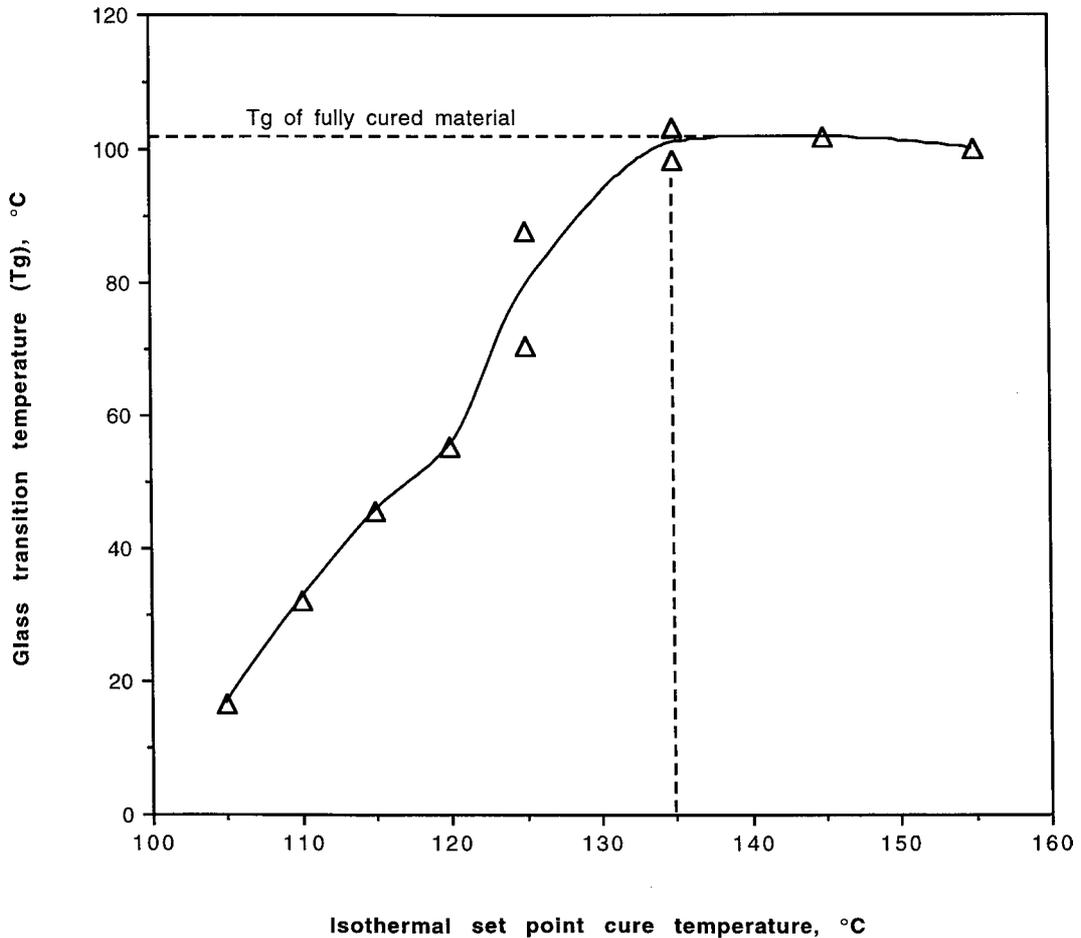


Fig. 5. Glass transition temperature (T_g) vs. isothermal set point cure temperature by DSC for epoxy/fiberglass prepreg.

curing process of the prepreg to produce a superior heat-activated composite-to-composite pipe joint, in addition to assessing the effects of induced thermal stress in the joint [4].

Fig. 4 shows a DSC temperature scan following a cure of the prepreg at 105°C for 90 min, yielding T_g and $H_{t,resid}$. Fig. 4 also shows that for a 105°C cure, the first exotherm in Fig. 2 has almost disappeared and is indicated only by a 'shoulder' peak near 151°C. Fig. 4 corresponds to a conversion of 33% (Eq. (2)), which follows the cure kinetics model of Lee et al. [3] near the point where the third rate constant begins to take effect at $C \geq 0.3$. For a number of DSC isothermal partial cures, a plot of T_g versus cure temperature in Fig. 5 shows that most of the ultimate cure of the prepreg was achieved at a cure temperature of 135°C

and a T_g of 103°C. The percent conversion was calculated from the following equation [5]:

$$\% \text{ cure (conversion)} = \left(1 - \frac{H_{t,resid}}{H_{RXN}} \right) \times 100 \quad (2)$$

Therefore, a plot of T_g versus percent conversion was generated in Fig. 6 for a good curve fit with a third-degree polynomial. Tangent lines drawn to the curve at low and high conversion intersect at 63% conversion, indicating the approximate gel point of the prepreg [6]. Other calculated DSC parameters, such as the heat capacity change (C_p) at T_g and the T_g width ($T_{g,w}$) also showed a dependence on the increases in T_g and crosslink density after the gel point. Even a small DSC exotherm (0.5 J/g) following the onset of material decomposition (235°C) showed such a dependence.

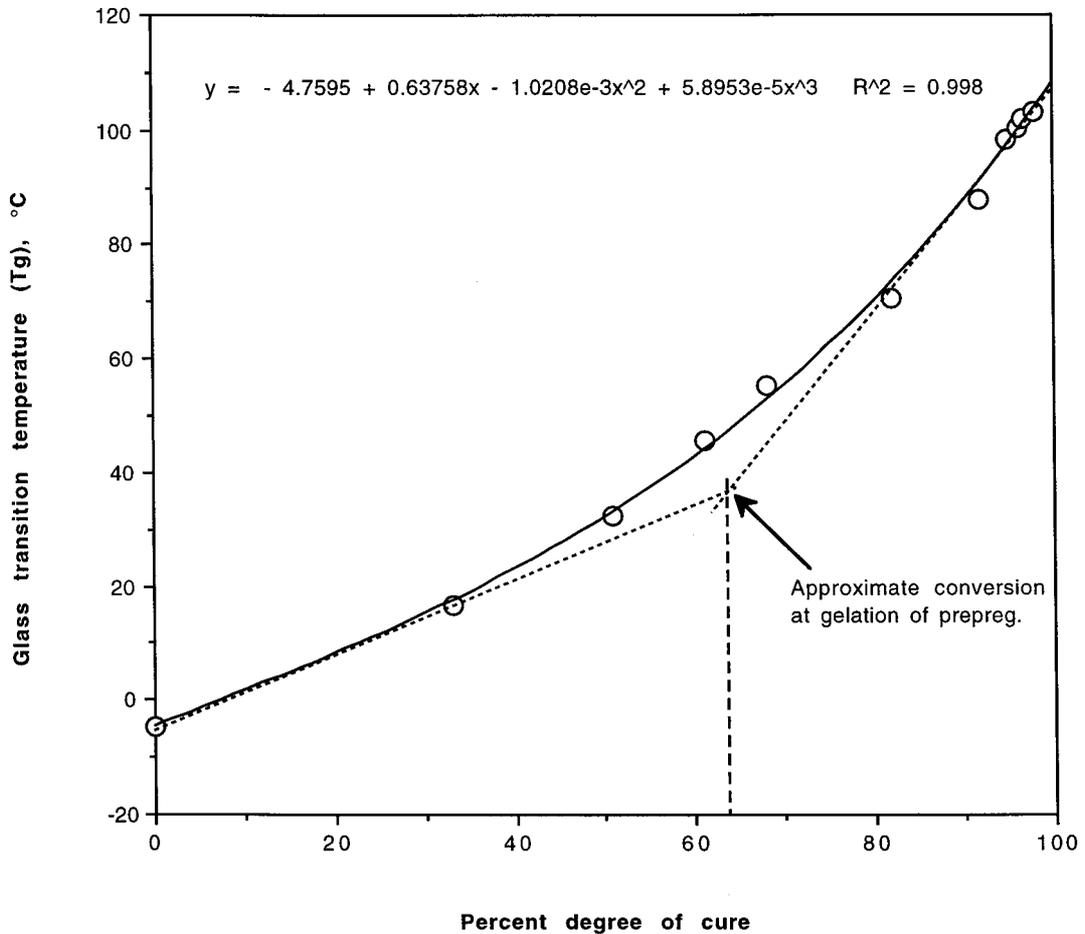


Fig. 6. Glass transition temperature (T_g) vs. percent conversion by DSC for epoxy/fiberglass prepreg.

3.2. DMA data

DMA data on the prepreg material was obtained as a plot of flexural storage modulus (E') versus time for isothermal cure temperatures from 115 to 155°C. It was shown that the increase in modulus of the prepreg (relative to the modulus of the wire hardware cloth sample support) during cure was at a maximum at a cure temperature of 125°C. Fig. 7 shows a DMA plot of E' and $\tan \delta$ versus time for a cure condition of 130°C/210 min. The peak maximum of $\tan \delta$ in Fig. 7 can be referred to as the gel point of the prepreg material. For seven isothermal cure temperatures from 115 to 155°C, a plot of DMA \ln (gel time) versus reciprocal absolute cure temperature yielded two

straight line segments producing the activation energies of cure of 140 and 50.5 kJ/mol for E_1 and E_2 , respectively. This value of E_2 is lower than the values of 79.1 and 87.1 determined from DSC dynamic and isothermal tests, but the variation may be largely due to differences in the DMA and DSC techniques.

DMA data on the cured sheet composite material was obtained as a plot of E' versus temperature at four fixed frequencies of 0.25, 0.5, 1.0 and 2.0 Hz for the T_g region as shown in Fig. 8. There is a secondary transition below room temperature in Fig. 8, but it was shown to be fairly independent of the chosen range of frequencies. The $\tan \delta$ peak maximum yielded the T_g at each frequency, and the activation energy (E_a) was determined from a plot of \ln (frequency)

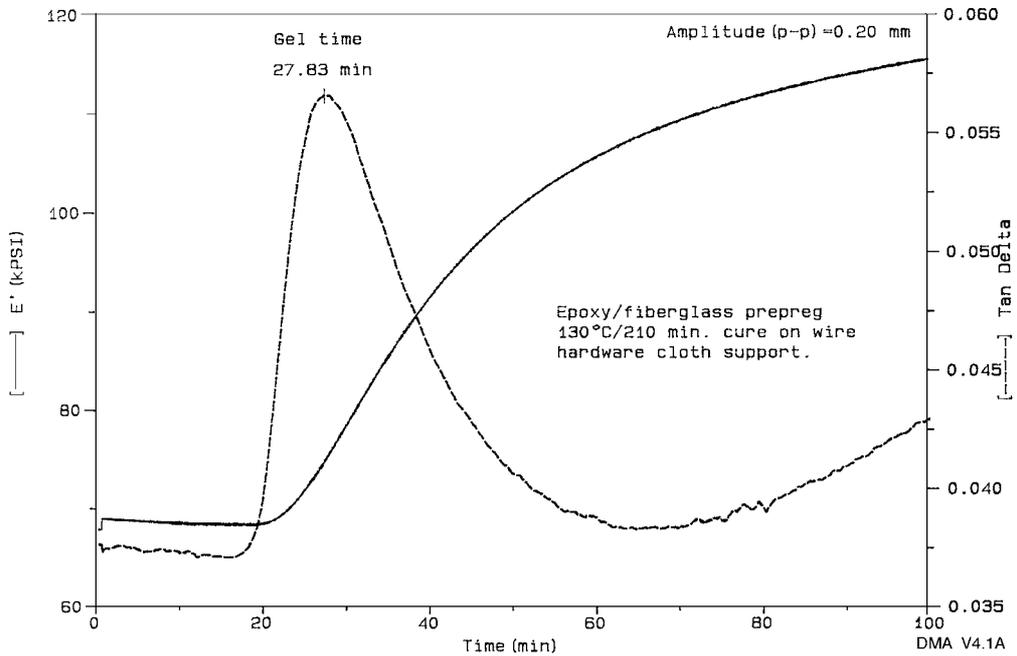


Fig. 7. DMA isothermal cure of epoxy/fiberglass prepreg for 210 min at a set point temperature of 130°C and a frequency of 1 Hz.

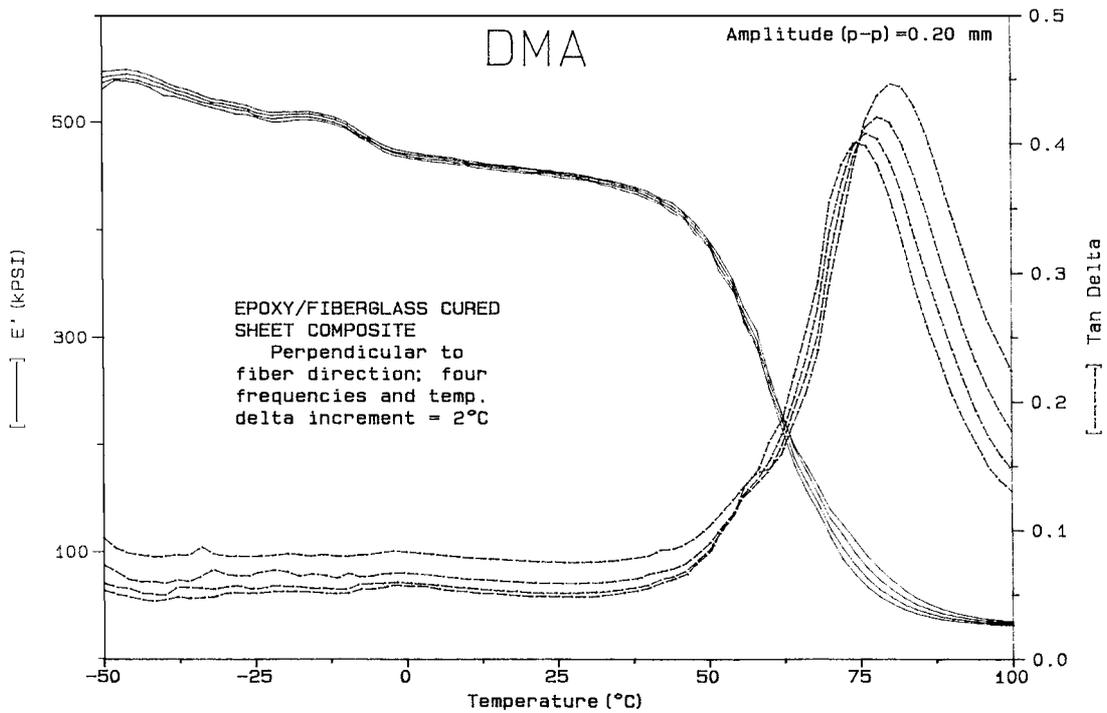


Fig. 8. DMA plot of flexural storage modulus E' vs. temperature at four fixed frequencies (0.25–2.0 Hz) on cured sheet epoxy/fiberglass material in the perpendicular to fiber mat direction.

versus reciprocal absolute peak temperature. Several DMA samples were tested in both the parallel and perpendicular fiberglass mat direction. The E_a was similar for both mat directions, averaging 357 kJ/mol overall. The average E' at 24°C was 4069 MPa (590 kpsi) for the parallel direction and 3421 MPa (496 kpsi) for the perpendicular direction, but there was some scatter in the data. The average values of E' in the rubbery plateau region past the T_g (at 150°C) were 414 and 200 MPa (60 and 29 kpsi) for the parallel and perpendicular mat directions, respectively, which imply a lower molecular weight between crosslinks (M_c) in the parallel mat direction if the interaction between the epoxy matrix and fiberglass mat is considered.

3.3. TMA data

TMA data on the cured sheet composite was obtained as a plot of dimension change versus tem-

perature, and there was little difference in the linear CTE between samples for parallel and perpendicular fiberglass mat directions.

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