

Differential Scanning Calorimetry Studies of the Cure of Carbon Fiber-Epoxy Composite Prepregs*

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Synopsis

Diaminodiphenyl sulfone (DDS) cured tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) epoxies, whose cure reactions are accelerated by BF_3 :amine catalysts, are the most common composite matrices utilized in aerospace high performance, fibrous composites. To process reproducible composites requires an understanding of the cure reactions and how these reactions are modified by the BF_3 :amine catalysts. In this article we report systematic differential scanning calorimetry (DSC) studies of (i) the constituents of BF_3 : $\text{NH}_2\text{C}_2\text{H}_5$ -catalyzed TGDDM-DDS epoxies and their mixtures, (ii) the effect of BF_3 : $\text{NH}_2\text{C}_2\text{H}_5$ concentration on the cure reactions, (iii) the nature of the catalyzed cure reactions, and (iv) the environmental sensitivity of the catalyst. DSC studies are also reported on the cure reaction characteristics and environmental sensitivity of commercial C fiber-TGDDM-DDS epoxy prepregs.

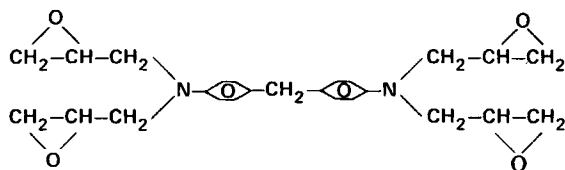
INTRODUCTION

Diaminodiphenyl sulfone (DDS)-cured tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) epoxies are the most common composite matrices utilized in aerospace high performance, fibrous composites. The structures of the TGDDM epoxide monomer, which is a liquid at 23°C and the DDS monomer, which is a crystalline powder with a mp of 162°C are illustrated in Figure 1. The commercially available C fiber-epoxy prepreg systems such as Narmco 5208,[†] Fiberite 934, and Hercules 3501 all primarily consist of the TGDDM-DDS epoxy; the latter two systems also contain boron trifluoride catalysts.¹⁻³

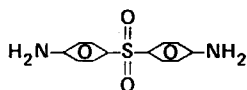
To manufacture reproducible C fiber-TGDDM-DDS epoxy composites with well-defined lifetimes in service environment requires a knowledge of the parameters that affect composite processing conditions and the resultant structure of the epoxy within the composite. The cure reactions directly control the composite processing and final epoxy network structure. Hence, it is important to understand the cure reactions and the variables that affect such reactions. In previous studies we have reported: (i) the relations between the physical structure, the modes of deformation and failure, and mechanical properties of TGDDM-DDS epoxies⁴; (ii) how specific combinations of moisture, heat, and stress affect their physical and mechanical

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[†] Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.



Tetraglycidyl 4, 4' diaminodiphenyl methane epoxy TGDDM
(liquid at 23°C)



4, 4' diaminodiphenyl sulfone DDS
(crystalline solid, mp 162°C)

Fig. 1. Chemical structures of TGDDM epoxide and DDS amine monomers.

integrity⁵; (iii) the effects of inhomogeneous physical mixing of the TGDDM-DDS components and their degree of chemical purity on the resultant epoxy chemical and physical structure⁶⁻⁸; (iv) systematic Fourier transform infrared spectroscopy (FTIR) studies of the cure reactions of TGDDM-DDS epoxies as a function of cure conditions, DDS concentration, and the presence or absence of a BF_3 :amine catalyst^{6,7,9,10}; and (v) nuclear magnetic resonance studies of the chemical characterization, environmental sensitivity, and catalytic mechanisms of cure of the BF_3 :amine catalysts.¹¹

The cure reactions, the viscosity-time-temperature profile, the processing conditions, the resultant epoxy chemical and physical structure, and the mechanical response of a C fiber-TGDDM-DDS-cured epoxy composite are modified by the presence of a BF_3 :amine complex catalyst within the prepreg. These factors will also be modified by the distribution of the catalyst within the prepreg, its chemical composition, and any modification of its structure and activity as a result of exposure to and/or interaction with heat, moisture, and the epoxide and amine components within the prepreg.

In C fiber-TGDDM-DDS prepreps that do not contain a BF_3 :amine catalyst one exotherm peak associated with the cure reactions is observed by differential scanning calorimetry (DSC).¹²⁻¹⁴ However, prepreps that contain BF_3 :amine catalyst exhibit two or three additional DSC peaks at lower temperatures, which are associated with the catalyzed cure reactions.^{12,15} To understand the parameters that control and modify the processing conditions of C fiber-TGDDM-DDS prepreps, it is necessary to determine the nature of the catalyzed cure reactions and how such reactions are modified by prepreg manufacturing and processing conditions and environmental exposure.

In this paper we report systematic differential scanning calorimetry (DSC) studies of (i) the constituents of boron trifluoride monoethylamine (BF_3 : $\text{NH}_2\text{C}_2\text{H}_5$) catalyzed TGDDM-DDS epoxies and their mixtures; (ii) the nature of the catalyzed cure reactions; (iii) the environmental sensitivity of the BF_3 : $\text{NH}_2\text{C}_2\text{H}_5$ catalyst. DSC studies are also reported on the cure reaction characteristics and environmental sensitivity of commercial prepreps that contain BF_3 :amine catalysts.

EXPERIMENTAL

Materials

The C fiber-TGDDM-DDS commercial prepregs that were investigated were Fiberite 934 and Hercules 3501. The reported composition of these prepregs are summarized in Table I.¹

The individual components of these commercial prepregs and mixtures of these components were also investigated by DSC. These components were obtained from the following sources: TGDDM (MY720, Ciba-Geigy); DDS (Eporal, Ciba-Ceigy); DGOP (Gly-Cel-A-100, Celanese); $\text{BF}_3\cdot\text{NH}_2\text{C}_2\text{H}_5$ (Harshaw); and boron trifluoride piperidine, $\text{BF}_3\cdot\text{NHC}_5\text{H}_{10}$ (Harshaw). (Our nuclear magnetic resonance studies identified the BF_3 :amine catalysts in Fiberite 934 and Hercules 3501 as $\text{BF}_3\cdot\text{NH}_2\text{C}_2\text{H}_5$ and $\text{BF}_3\cdot\text{NHC}_5\text{H}_{10}$, respectively.¹¹)

Epoxy mixtures were prepared by (i) stirring the $\text{BF}_3\cdot\text{NH}_2\text{C}_2\text{H}_5$ into the DGOP at 90°C for 2–3 min and then cooling to 23°C and (ii) dissolving and stirring the DDS in the TGDDM at 130°C for 90 min followed by the addition of the $\text{BF}_3\cdot\text{NH}_2\text{C}_2\text{H}_5$ /DGOP mixture (23°C) to the TGDDM/DDS mixture (130°C) which is then allowed to cool to 23°C while stirring.

Experimental

DSC studies were carried out on a DuPont 990 Thermal Analyzer with a DuPont 910 DSC attachment at a heating rate of 10°C/min in an N_2 atmosphere.

RESULTS AND DISCUSSION

Prepreg Mixtures and Their Components

In Figures 2(a) and (b) DSC plots are compared for a standard TGDDM (64 wt %)/DDS (25 wt %)/DGOP (11 wt %) epoxy prepreg mixture containing 0 and 0.4 wt % of the $\text{BF}_3\cdot\text{NH}_2\text{C}_2\text{H}_5$ catalyst, respectively. In the absence of the $\text{BF}_3\cdot\text{NH}_2\text{C}_2\text{H}_5$ catalyst [Fig. 2(a)] a large exotherm occurs at 240°C ($\Delta H = 470$ J/g) with a smaller exotherm at 125°C ($\Delta H = 30$ J/g), whereas upon addition of the catalyst [Fig. 2(b)] four peaks designated α , β , γ , and δ are present at 240°C ($\Delta H = 210$ J/g), 200°C ($\Delta H = 190$ J/g), 160°C ($\Delta H = 70$ J/g), and 125°C ($\Delta H = 25$ J/g), respectively.

In an effort to characterize the chemical reactions associated with each peak, DSC runs were performed on each of the constituents of the epoxy

TABLE I
Chemical Constituents in Prepreg Epoxies

Constituent	% by weight	
	Fiberite 934	Hercules 3501
TGDDM	64	75
DDS	25	24
Diglycidyl orthophthalate epoxy (DGOP)	11	0
BF_3 :amine catalyst	0.4	1

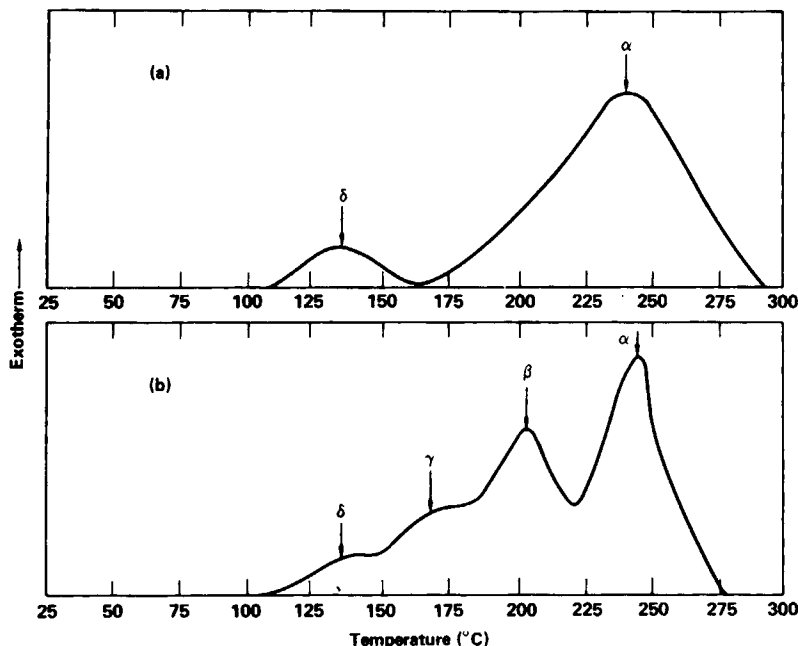


Fig. 2. DSC plots for TGDDM (64 wt %)/DDS (25 wt %)/DGOP (11 wt %) epoxy prepreg mixture with (a) 0.0 wt % and (b) 0.4 wt % $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalyst.

prepreg and systematic 2, 3, and 4 constituent mixtures. (The constituent mixtures were formulated at the same relative compositions that were present in a standard epoxy prepreg mixture.) These DSC studies were conducted in conjunction with nuclear magnetic resonance (NMR) studies of the reactions that occur between the epoxy prepreg constituents and the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalyst.¹¹ The ΔH values and temperatures associated with maximum peak intensity for each DSC peak for each component and epoxy prepreg mixture were determined and are plotted in Figure 3. The DSC peaks are represented by lines in the ΔH -temperature plots in Figure 3, with the magnitude of each line representing the ΔH value associated with each peak, and its position on the temperature scale representing the temperature of maximum peak intensity. All line magnitudes represent exotherm peaks with the exception of the DDS and $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ endotherm mp's, which are designated by negative symbols -2 and -4 , respectively. The five ΔH -temperature plots in Figure 3 represent, from the top to the bottom of the figure, one-, two-, three-, and four-component prepreg mixtures and Fiberite 934, respectively. From this systematic study illustrated in Figure 3 we conclude the α peak at 240°C is associated with the non-catalyzed cure reactions and the β , γ , and δ peaks with $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalyst-epoxy prepreg constituent reactions. The δ peak is absent in DSC scans of TGDDM alone but sometimes appears when either $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ or DDS are added to the TGDDM (Fig. 3). Hence, we associate the δ peak with TGDDM impurity reactions that are catalyzed by either $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ or DDS. [Fourier transform infrared spectroscopy (FTIR) studies indicate that there are three principal cure reactions, namely, primary amine-epoxide, secondary amine-epoxide, and epoxide-hydroxyl reactions with the primary amine reaction being an order of magnitude faster than the other

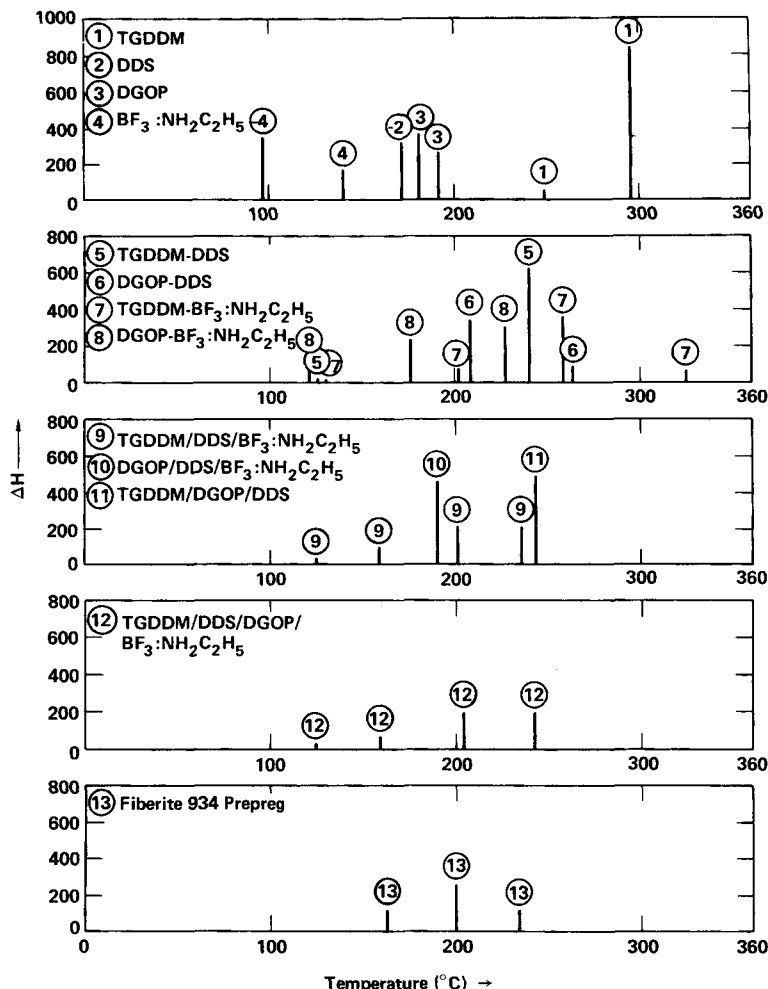


Fig. 3. DSC ΔH peak intensities (J/g) vs. the temperature associated with maximum peak intensity for one-, two-, three-, and four-component mixtures of TGDDM/DDS/DGOP/ $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ epoxies and commercial Fiberite 934 prepreg.

two reactions.^{6,7,9,10,14} However, we do not believe from our FTIR studies that the presence of $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ catalyst significantly modifies the relative rates of these cure reactions to such an extent that exotherm peaks associated with each cure reaction can be detected by DSC.]

The ΔH values associated with the α , β , and γ peaks are plotted as a function of $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ catalyst concentration in Figure 4. The α peak intensity associated with noncatalyzed cure reactions progressively decreases with increasing $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ concentration and approaches zero near 2 wt % $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$. The γ peak intensity progressively increases with $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ concentration, whereas the β peak intensity attains a maximum intensity at ~ 0.4 wt % $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ and then decreases with higher concentrations of $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$. The small δ peak intensity does not appear to be modified by increasing $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ concentration.

^1H , ^{19}F , and ^{11}B NMR studies of the catalytic activity and mechanisms of $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ towards TGDDM/DDS/DGOP prepreg mixtures and their

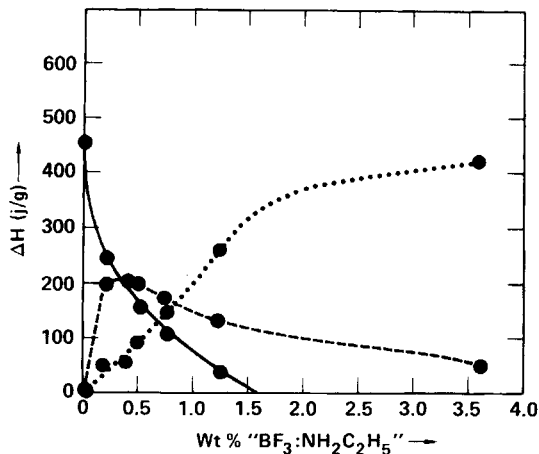


Fig. 4. ΔH values for the DSC (—) α , (- - -) β , and (· · ·) γ peaks in TGDDM (64 wt %)/DDS (25 wt %)/DGOP (11 wt %) epoxies as a function of $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ concentration.

components indicate (i) initially some of the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ reacts with the epoxide groups of the TGDDM and DGOP epoxides to form monofluoroborates and (ii) the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ in the prepreg converts to the $\text{BF}_4\text{-NH}_3^+\text{C}_2\text{H}_5$ salt and this reaction is complete near 160°C for the heating rate of $10^\circ\text{C}/\text{min}$ employed in the DSC studies.¹¹ From the DSC and NMR studies we conclude: (i) The δ peak is associated with $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ - or DDS-catalyzed TGDDM impurity reactions; (ii) the γ peak is associated with $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ and monofluoroborate catalyses of the cure reactions; and (iii) the β peak is associated with $\text{BF}_4\text{-NH}_3^+\text{C}_2\text{H}_5$ cationic catalyses of the cure reactions. The $\text{BF}_4\text{-NH}_3^+\text{C}_2\text{H}_5$ is the most stable of the catalytic species. However, with increasing $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ concentration at >0.4 wt % $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ progressively becomes the predominant catalytic species, catalyzing the cure reactions prior to its conversion to the $\text{BF}_4\text{-NH}_3^+\text{C}_2\text{H}_5$ salt (Fig. 4).

Our NMR studies¹¹ indicate that $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ will form the hydrated salt $\text{BF}_3(\text{OH})\text{-NH}_3^+\text{C}_2\text{H}_5$ upon exposure to $85^\circ\text{C}/100\%$ RH for 1 h. However, incorporation of this salt into an epoxy prepreg mixture does not modify the relative intensities of the DSC peaks, thus indicating that the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalytic activity is not irreversibly deteriorated by moisture. The hydrated salt presumably dehydrates back to $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ prior to a significant degree of cure.

We also studied a standard epoxy prepreg mixture that did not contain the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalyst but did contain 0.4 wt % H_2O . We found no detectable modification of the DSC α peak intensity within experimental error compared to a similar epoxy mixture that did not contain H_2O . These observations indicate that by itself H_2O does not catalyze these epoxy cure reactions.

Commercial Prepregs

The BF_3 :amine catalysts incorporated into Fiberite 934 and Hercules 3501 commercial prepregs were respectively identified by NMR studies as $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ and boron trifluoride piperidine ($\text{BF}_3\text{:NHC}_5\text{H}_{10}$).¹¹

We investigated the variability in catalyst activity within a Fiberite 934 lot and also between different lots by monitoring the magnitude of the ΔH values associated with the α , β , and γ DSC peaks. The ΔH values associated with each peak varied by only $\pm 5\%$ for samples within close proximity of each other (< 10 cm apart) within a prepreg lot. However, the variability in ΔH values was considerably greater (up to $\pm 30\%$) for samples investigated from (i) the same prepreg lot that were widely separated (> 20 cm apart) and (ii) between different prepreg lots.

From DSC ΔH peak intensities we ascertained that on the average Fiberite 934 prepreg cure reactions occur (i) 25% by noncatalyzed reactions (α peak), (ii) 50% by $\text{BF}_4\text{-NH}_2\text{C}_2\text{H}_5$ catalyzed reactions (β peak), and (iii) 25% by $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalyzed reactions (γ peak). In the case of Hercules 3501 prepreg resin DSC exotherm peaks were observed at 216°C ($\Delta H = 335$ J/g) and 152°C ($\Delta H = 152$ J/g). We suggest, based on our studies on Fiberite 934, that the lower temperature peak is associated with $\text{BF}_3\text{:NHC}_5\text{H}_{10}$ catalyzed cure reactions and the higher temperature peak with $\text{BF}_4\text{-NH}_2\text{C}_5\text{H}_{10}$ catalyzed cure reactions. However, we have not conducted systematic DSC studies as a function of $\text{BF}_3\text{:NHC}_5\text{H}_{10}$ catalyst concentration or detailed NMR characterization studies to confirm these peak assignments. If these peak assignments are indeed correct, then the Hercules 3501 prepreg cure reactions occur (i) 75% by $\text{BF}_4\text{-NH}_2\text{C}_5\text{H}_{10}$ catalyzed reactions and (ii) 25% by $\text{BF}_3\text{:NHC}_5\text{H}_{10}$ catalyzed reactions. In both commercial prepregs the δ peak is absent, because the BF_3 :amine-catalyzed DDS-TGDDM impurity reactions have already occurred during the epoxy mixing and C fiber-prepreg processing conditions.

Exposure of the Fiberite 934 prepreg to 85°C for 1 h at 100% RH does produce a significant shift in the intensities of the DSC peaks with the γ peak intensity decreasing by $\sim 50\%$ and the α peak intensity increasing by 50%. We suggest that during the environmental exposure conditions we may have leached a portion of the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalyst out of the prepreg, as we have observed the catalyst is readily soluble in H_2O .

CONCLUSIONS

In $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ -catalyzed TGDDM-DDS epoxy-C fiber commercial prepregs the epoxy cure reactions occur by (i) $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ -catalyzed reactions, (ii) $\text{BF}_4\text{-NH}_2\text{C}_2\text{H}_5$ -catalyzed reactions, and (iii) noncatalyzed reactions. There is considerable variation in catalytic activity within the same prepreg lot and between different lots. Moisture does not directly poison the $\text{BF}_3\text{:NH}_2\text{C}_2\text{H}_5$ catalyst activity or modify the cure reactions.

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