

Chemical Interactions at the Interface Between a Carbon Fiber and a Boron Trifluoride-Catalyzed Epoxy Matrix

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SYNOPSIS

The cure of a tetrafunctional epoxy resin (largely tetraglycidyl-diaminodiphenylmethane, TGDDM), cross-linked with diaminodiphenylsulphone (DDS) and boron trifluoride/ethylamine (BF₃EA) catalyst, is affected in a complex fashion by the presence of an oxidized carbon fiber surface. If the fiber is aged in a humid environment (25°C, 95% humidity) before coating with the matrix, the affinity of the oxidized fiber surface for water leads to destruction of the catalyst and retardation of the cure. This retardation is noticeable at lower humidities if the polymer content of the composite is reduced to < 20%. For oxidized fibers that are stored under ambient conditions (40% humidity), the retarding effect of water is overwhelmed by the catalytic effect of the acidic fiber surface. This activates the latent catalyst, increasing the rate of epoxy consumption and the proportion of the epoxy-epoxy reaction relative to the epoxy-amine reaction. For the low-humidity case, even though the rate of chemical reaction is increased, vitrification of the matrix is retarded, implying that there is less cross-linking and more extended epoxy-epoxy sequences in the network. The proposed chemical changes in epoxy/carbon fiber composites were confirmed by analysis of model reactions in solution. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

It is now accepted as inevitable that the interphase between a polymer matrix and the reinforcing fibers in a composite material will differ in composition and properties from the constituent materials. However, considerable speculation remains about the nature of this interphase and in particular about the relative importance of physical and chemical interactions between the matrix and the reinforcement.¹⁻⁵ This paper is intended to establish the magnitude of chemical interactions between an oxidatively treated carbon fiber surface and a technologically important epoxy matrix material.

We have demonstrated previously that the cross-linking processes of epoxy resins can be modified extensively when adjacent to polar surfaces such as

metal oxides, aramid fibers, oxidized carbon blacks, and oxidized carbon fibers.⁶⁻¹⁰ This modification is due to the effects of adsorbed water, the selective adsorption of polar components of the resin mixture (particularly catalysts), and the catalytic effect of acidic surface species on epoxy cross-linking reactions. The localized chemical changes result in changes in the performance of adhesive bonds or composites made with these materials. For the most part, this work was restricted to relatively low performance epoxy systems, such as diglycidyl epoxies (DGEBA) cross-linked with *m*-phenylenediamine (MPDA) or nadic methyl anhydride (NMA), because such systems are well characterized and so make good models with which to demonstrate mechanistic principles.

We examined recently the effect of an oxidized carbon black surface on the cross-linking of a more technologically relevant system, viz. a tetrafunctional epoxy resin MY720 (largely TGDDM, structure below) cross-linked with the highly temperature stable amine DDS.^{11,12} Although there were kinetic differences in the early part of the reaction, the

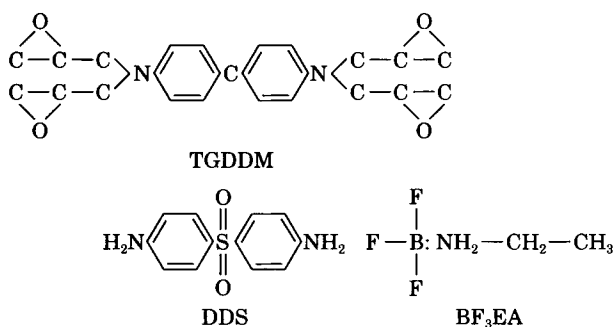
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chemical and physical state of the final cured polymer was not affected greatly by the presence of the carbon surface. As the final part of this project, we have now extended these earlier model studies to a realistic composite, viz. a BF_3 -catalyzed TGDDM/DDS matrix and a carbon fiber with an oxidative surface treatment, and will demonstrate that the fiber surface strongly influences the cure kinetics and final cure state of the matrix:



The TGDDM/DDS/ BF_3EA system has received extensive study (e.g., Refs. 13–17) and is thought to differ from the difunctional epoxy systems in that hydroxy–epoxy reactions are important in the later stages of the cure, while secondary amine–epoxy reactions are less important than in amine-cured diglycidyl epoxies. Many details of the mechanism remain unresolved. The thrust of this work is not to resolve the complete mechanism, but to determine how the cure is modified by a carbon fiber surface and to determine what effect this will have on the processing and properties of carbon fiber/epoxy composites.

EXPERIMENTAL

The epoxy resin (MY720) was supplied by E. I. DuPont de Nemours (MY720, Batch 5083). We have shown previously¹¹ that the epoxy resin contained about 75% TGDDM. We also showed by liquid chromatography that the chemical composition of the resin did not change due to aging during this study. The DDS (Aldrich) was shown to be > 99% pure by liquid chromatography. The BF_3EA catalyst (Harshaw Chemicals) was used as received. Infrared (IR) spectroscopy showed that the catalyst contained \ll 10% of the hydrolysis product and the composition remained constant during the period of the study. The epoxy resin (100 parts), DDS (50 parts), and catalyst (1–2 parts) were mixed in ace-

tone solution to facilitate coating of the carbon fibers.

The carbon fiber used as the basis of this study was an intermediate modulus-type fiber (Hercules IM-6 U 12K), supplied in an untreated, unsized, state by Dr. W. B. Moniz of the U.S. Naval Research Laboratory. This fiber either was used as received or was subjected to surface oxidative treatment with nitric acid (concentrated nitric acid for 2 h at 105°C, followed by repeated washing with distilled water, and drying in vacuum for 18 h at 150°C). The surface chemical composition of the carbon fibers was examined by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5300 with monochromatized $\text{AlK}\alpha$ radiation), thermogravimetric analysis (DuPont 951 TGA), and IR spectroscopy (Mattson Cygnus 100 FTIR, operated at 4 cm^{-1} resolution, with 2000 scans, internal reflection [IRS] mode with the carbon fibers pressed as an oriented array against a 45° incidence germanium IRS element.^{18,19}). Some comparative data were also obtained with a nitric acid-oxidized carbon black specimen (14.6% oxygen, 157 m^2/g surface area) that we have described previously.¹¹

The epoxy matrix was coated onto the carbon fibers by immersion of an ordered array of the fibers (wound on a frame) in an acetone solution of the resin mixture, followed by removal of the solvent initially in air, then in vacuum for 24 h at 60°C. The loading of resin in the resultant composite was determined using TGA, by comparison of the mass loss characteristics of the composite with those of the carbon and resin alone. To test the effect of the extremes of humidity on the subsequent cure chemistry, freshly dried fiber specimens either were coated under standard laboratory conditions, immediately after drying, or were exposed to 95% humidity air at 25°C for 24 h before coating.

The reaction exotherm of the composite was followed by differential scanning calorimetry (DSC, Dupont 910) using a nitrogen atmosphere and a heating rate of 10°C/min. The chemical changes in the early stages of the cure were followed by extraction of soluble components with acetonitrile and examination of the extract and the residue by FTIR spectroscopy. The extract was dropped onto a sodium chloride disc and the solvent evaporated in vacuum at room temperature. The vitrification of the carbon fiber composites was followed by dynamic mechanical analysis (Polymer Laboratories DMTA-II, single cantilever bending mode) in a series of isothermal experiments. The vitrification time was taken as the time at which the curves of storage modulus and loss modulus cross.²⁰ The extent of re-

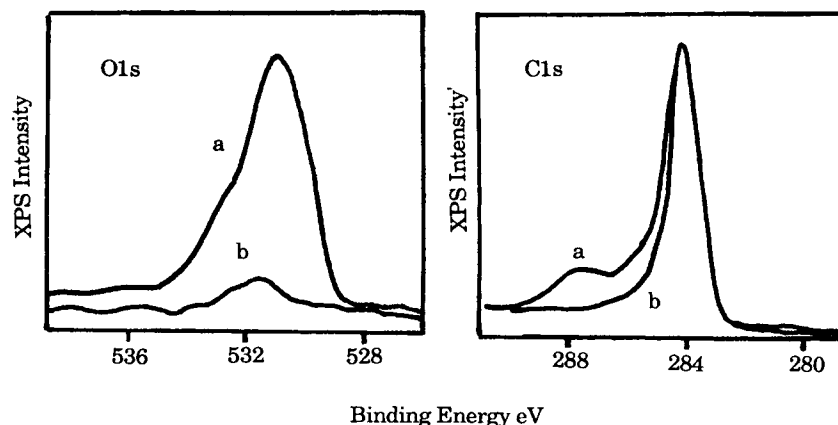


Figure 1 XPS spectra of carbon fibers: (a) after nitric acid oxidation; (b) original untreated. Note that the intensity axis of the O 1s peaks has been expanded to allow better visual comparison.

action at vitrification was determined by DSC using the residual exotherm of the vitrified sample and assuming the relationship

Extent of reaction

$$= (\text{total } \Delta H - \text{residual } \Delta H) / \text{total } \Delta H.$$

The glass transition temperature of the composite was determined by DMTA (10°C/min, 0.1 Hz).

Further information was obtained about the nature of the chemical reactions by examination of the stability of the catalyst solutions in di-(2-methoxyethyl)ether (DME). The reactions of the catalyst with either TGDDM or DDS were also examined in DME solution, both in the presence and absence of oxidized carbon fibers. The primary tool for chemical analysis in this part of the study was FTIR spectroscopy. After filtration to remove the carbon fibers (when necessary), small amounts of solution were dropped onto a sodium chloride disc and the solvent removed in vacuum at room temperature.

RESULTS

Characteristics of Carbon Fiber Surface

Figure 1 shows the XPS spectra of the unoxidized and oxidized carbon fiber. Similar spectra have frequently been reported by others (e.g., Refs. 21–23) for nitric acid-oxidized carbon fibers and are included here only to demonstrate that the chemical nature of the surface is as would be expected from such a treatment. The XPS spectrum (after correction for atomic sensitivity effects) indicates a surface

oxygen content of about 28 atomic percent (discounting hydrogen) for the oxidized fiber, and following conventional practice, we assign the shoulder in the C 1s spectrum at 2.1 eV higher binding energy than graphitic carbon to C—O and at 3.5 eV higher to C=O.

The IR-IRS spectra of the untreated and oxidized carbon fibers (Fig. 2) are again consistent with earlier reports.^{18,19} The carbon fiber surfaces contain a complex mixture of oxygenated species including esters, acids, and quinones. The absolute amount of each species is not quantifiable from the IR-IRS technique (the “effective thickness” term is not defined for fiber specimens), although, clearly, there is a qualitative difference in the distribution of oxygenated species on the oxidized carbon fiber and on the oxidized carbon blacks we described previ-

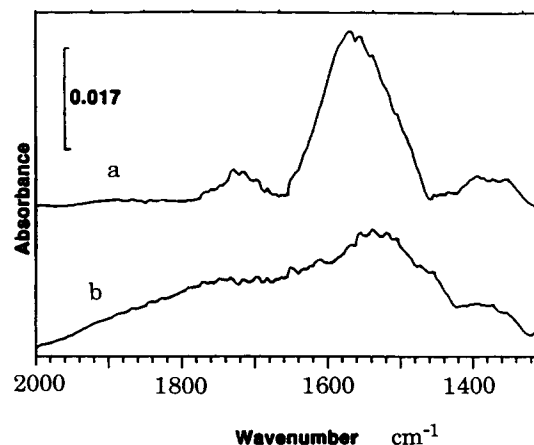


Figure 2 IR-IRS spectra of carbon fibers: (a) after nitric acid treatment; (b) original.

ously.¹¹ We felt that the quality of the carbon fiber spectra did not justify further band resolution, as has been carried out by others¹⁸ on similar spectra. Neither the XPS nor the IR data showed evidence of appreciable amounts of residual nitro functionality.

The TGA thermograms showed a mass loss of 20–30% in nitrogen at 1000°C for the oxidized carbon fiber, compared to 5–10% for the untreated control. The uncertainty in these numbers reflects the appreciable sample-to-sample variation of the 1–2 mg specimens used for TGA. The high-temperature mass loss can be used as a comparative measure of the extent of surface modification for the same base fiber with different surface treatments. A comparison with specimens of the same fiber that had been subjected to proprietary oxidative surface treatments showed that our nitric acid oxidation was somewhat more extensive than the commercial treatments (typically 10–20% mass loss under similar conditions), but was still within reasonable limits. The low-temperature TGA data showed that there was significant water sorption on the oxidized fibers, often amounting to more than 1% by weight, and the amount increased with increasing humidity history of the fibers. The data are not presented in a more quantitative fashion because of the large sample-to-sample variations in the small TGA specimens. Again, the amount of water sorption of our oxidized fibers is higher than for proprietary treatments, but

is consistent with literature values for carbon fibers with similar treatment histories.²⁴

Effect of Carbon Surfaces on Cure Exotherm

We anticipated that a BF₃EA-catalyzed system might be affected both by sorbed water and by the chemical functionality on the oxidized carbon surface. We therefore examined first the effect of fiber humidity history on the subsequent composite cure kinetics (30% polymer content of composite). As is clear from Figure 3, the oxidized fiber in a dry state accelerated the cure. The unoxidized fiber had little effect on the cure, while composites made from dried commercial fibers, with proprietary oxidative treatments, showed intermediate degrees of acceleration. However, if the fiber experienced a humid environment (24 h at 100% humidity and 25°C) before coating with the matrix, the cure was retarded. After humid aging of the fiber, the exotherm now resembles that of the uncatalyzed TGDDM/DDS system,¹¹ with the implication that fiber surface moisture had destroyed the catalyst. Composites made with unoxidized carbon fibers and with commercially oxidized fibers, after humid-aging, also showed retardation of the cure, but to a lesser and variable extent. At very low loadings of matrix (< 15%), the cure kinetics were even more sensitive to humidity history, which led to a lack of reproducibility in exotherms unless care was taken to ensure that the fibers remained in a dry environment before coating.

Any cure exotherm experiment therefore represents a combined effect of acceleration by the carbon surface and retardation by water. Therefore, in the following series of experiments, we maintained a relatively high resin content (usually > 30%) and a low-humidity environment for the fibers (coated in a 25°C, < 40% humidity environment, immediately after drying), and our data followed the “dry” case in Figure 3.

With the above proviso concerning humidity history, we show in Figure 4 that oxidized carbon fibers have an accelerative effect on the cure exotherm similar to that of oxidized carbon black. However, equivalent degrees of acceleration are produced at much lower loadings of carbon black (e.g., 25% carbon black as compared to 61% carbon fiber in Fig. 4), as might be expected from the higher oxygen content and surface area of the carbon black. The exotherms of composites containing the unoxidized carbon fiber were similar to those of the fiber-free control, as was the exotherm for a composite made with a “basic” carbon black described in Ref. 11. These data are quantified in Table I and show that

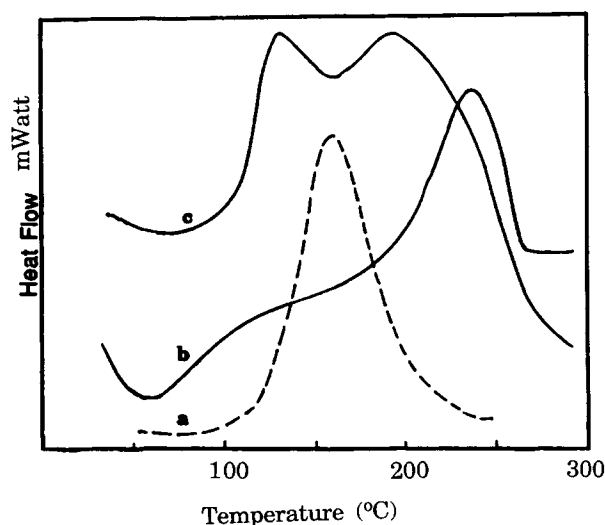


Figure 3 Cure exotherms by DSC at 10°C/min heating rate: (a) MY720/DDS/BF₃ (100:50:2) with no carbon fibers; (b) composite of humid-aged oxidized fibers and 30% matrix; (c) composite of “dry” oxidized fibers and 30% matrix.

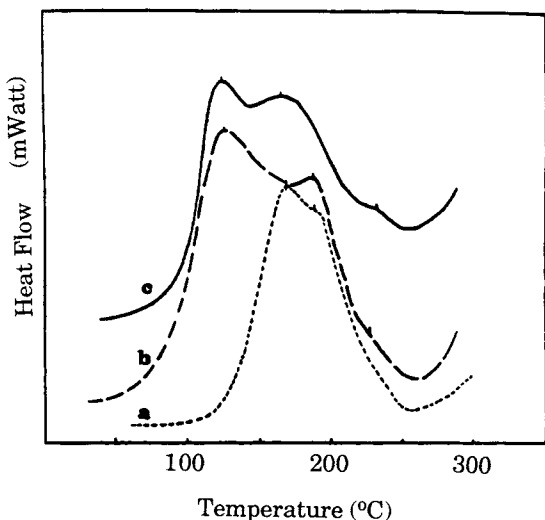


Figure 4 Cure exotherms by DSC at $10^{\circ}\text{C}/\text{min}$ heating rate: (a) control MY720/DDS/BF₃ (100:50:1); (b) composite of oxidized carbon black containing 75% matrix; (c) composite of oxidized carbon fibers containing 38% matrix.

the total exotherm (corrected to constant mass of polymer) was little changed by the presence of oxidized carbon black or carbon fiber. The most noticeable change is the introduction of a low-temperature exotherm, typically peaking at about 120°C . The mechanistic origin of this phenomenon is discussed in the final section.

Effect of Carbon Fiber Surface on Cure Reactions

As we demonstrated in our earlier study of the effect of carbon black on the uncatalyzed TGDDM/DDS system,¹¹ an examination of solvent-extractable components of partially cured composites can provide information about the early stages of the cure

Table I Reaction Exotherms MY720/DDS/BF₃ (100 : 50 : 1)

Specimen	Exotherm (J/g)	Onset Temp ($^{\circ}\text{C}$)
Control	440	88
75% polymer/25% acidic carbon black	460	54
39% polymer/61% acidic carbon fiber	480	78
28% polymer/72% acidic carbon fiber	490	72
17% polymer/83% acidic carbon fiber	490	68

process. In particular, since TGDDM and DDS each have IR absorptions characteristic of their aromatic backbones (1517 and 1595 cm^{-1} , respectively), it is possible to compare the rates at which the two components were incorporated into the insoluble polymer. Epoxy-amine reactions should lead to equal depletion rates of the two monomers in the extract. Homopolymerization of the epoxy, as is expected here, should lead to a higher relative content of DDS-based structures in the extract. Figure 5 quantifies this phenomenon for carbon black composites and shows that for composites at $< 30\%$ loading of polymer the extract was rich in DDS-based structures, with the implication that the insoluble component was rich in TGDDM-based structures. Figure 6 shows that the same phenomenon occurred for carbon fiber composites, although the magnitude of the effect was not as great as in the carbon black case. The greater $1595/1517\text{ cm}^{-1}$ ratio from the extract of a composite made with oxidized fibers, compared to the untreated fibers, confirms that the presence of the oxidized fiber surface led to preferential incorporation of TGDDM-based structures into the insoluble polymer, i.e., the occurrence of homopolymerization of the epoxy.

The corollary of the above observation is that the IR spectrum of the insoluble component remaining on the carbon fibers should be rich in TGDDM-based structures, i.e., $1595/1517\text{ cm}^{-1} < \text{unity}$. Although this was found qualitatively true, the carbon

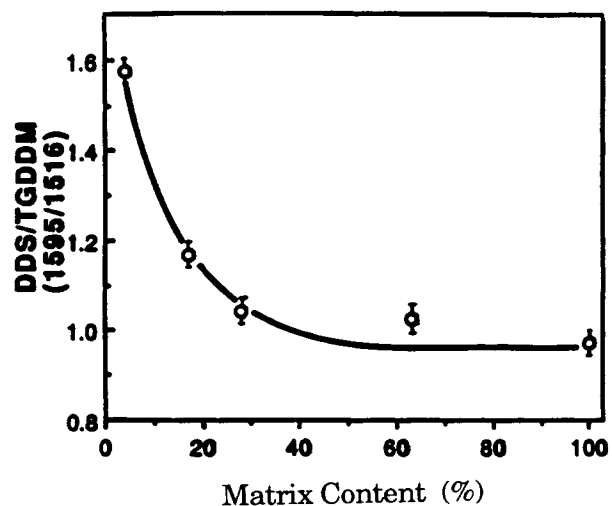


Figure 5 The ratio of DDS-based : TGDDM-based structures in the acetone-extractable components of composites made from MY720/DDS/BF₃ (100:50:1) and oxidized carbon black. Ratio based on the ratio of characteristic absorptions of aromatic structures of the two components.

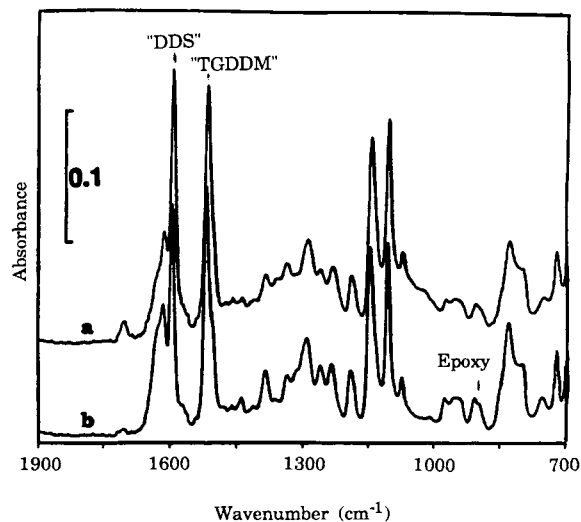


Figure 6 IR spectra of acetonitrile-soluble component of carbon fiber composites (MY720:DDS:BF₃ = 100:50:2) after 125°C cure. Acetonitrile removed by evaporation. (a) From oxidized fiber; (b) from untreated fiber.

fiber IR spectra were of insufficient quality to justify quantification.

Reactions of Catalyst in DME Solution

At temperatures below 60°C, the catalyst appeared to be stable for several hours in DME, as would be expected for a "latent" catalyst. However, when the catalyst solution was heated in the presence of either oxidized carbon fibers or carbon black, it decomposed rapidly. This effect is illustrated qualitatively in Figure 7, which shows the IR spectrum of the catalyst (on a sodium chloride disc) after decanting the catalyst solution from the carbon fiber and evaporation of the DME solvent. After heating the catalyst solution alone for 5 min at 75°C, the spectral changes were relatively minor. However, when the solution was heated in the presence of oxidized carbon fibers, the decomposition of the catalyst was almost complete after 5 min. The N—H bending

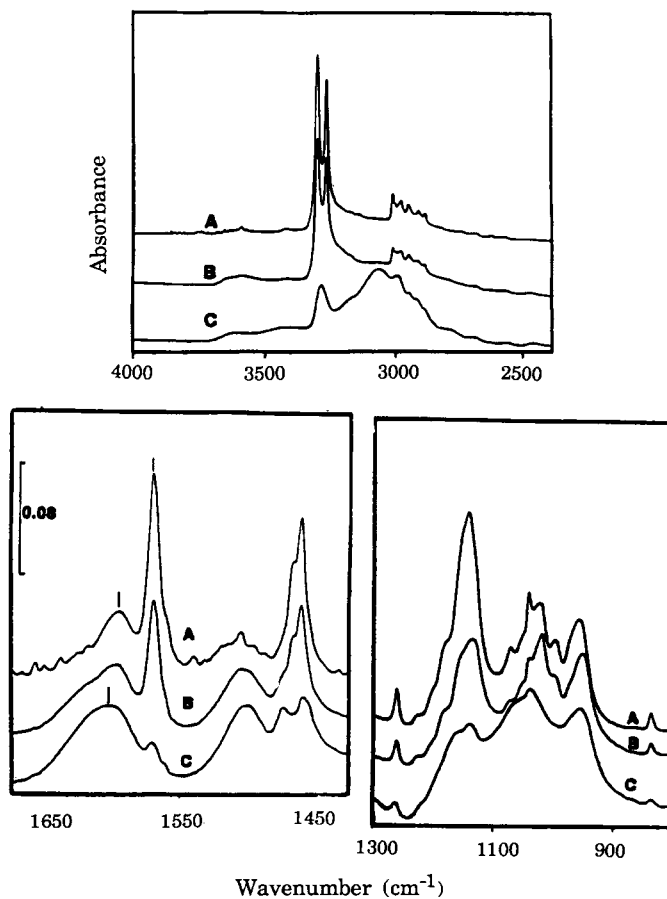


Figure 7 IR spectra of BF₃ catalyst after thermal aging for 5 min at 75°C in DME solution: (A) original; (B) 5 min at 75°C, no fiber; (C) 5 min at 75°C, in presence of oxidized carbon fiber.

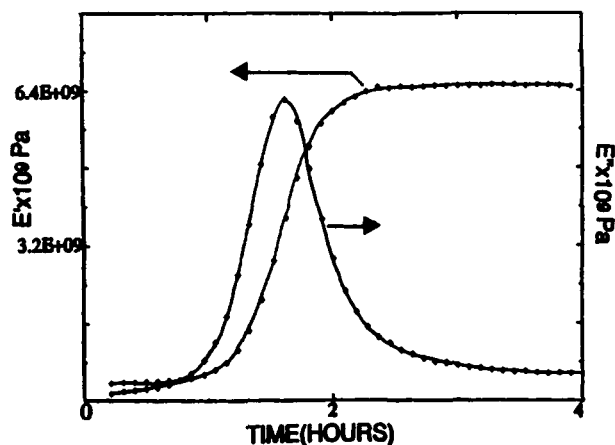


Figure 8 Isothermal DMA of carbon fiber composite (40% matrix) at 140°C and 0.1 Hz.

mode of the complexed amine was almost totally eliminated and replaced by a broad 1601 cm^{-1} absorption (uncomplexed amine?). The absorptions characteristic of the complexed BF_3 structure (1457 and 1144 cm^{-1}) were eliminated and replaced by the BF_4^- absorption at 1040 cm^{-1} . The oxidized carbon black and carbon fiber had the same qualitative effect on the catalyst decomposition, but the carbon black initiated decomposition at a slightly lower temperature. The unoxidized carbon fiber had a lesser accelerative effect on the catalyst decomposition.

In separate experiments on solution analogs of the epoxy resin mixture, the primary amine content

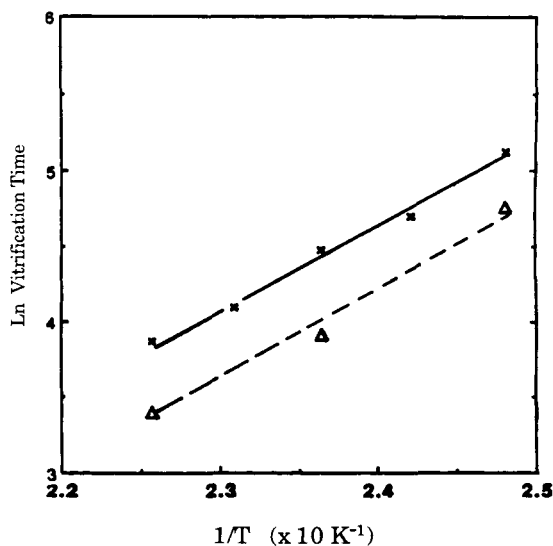


Figure 9 Vitrification time as a function of isothermal cure temperature: ($\Delta\Delta$) untreated carbon fibers; (xx) oxidized carbon fibers.

of DDS (1625 cm^{-1}) in DME solution was shown to be unaffected by heating at 30–100°C with the BF_3EA catalyst, in the presence or absence of oxidized carbon surfaces. However, the epoxy absorption (915 cm^{-1}) of an MY720 solution in DME was decreased appreciably by heating with the BF_3EA catalyst, and the magnitude of the effect was increased by the presence of oxidized carbon surfaces. This model experiment demonstrates that, as expected, the principal reaction of the BF_3EA catalyst is with the epoxy resin, not with the amine curing agent, and that this effect is accelerated by the carbon surfaces.

Effect of Carbon Fiber on Resin Vitrification

When the coated fibers are cured in the DMTA oven, the progress of the resin cure can be monitored through the changes in storage and loss modulus (Fig. 8). Under favorable conditions, the gel point and vitrification point can be detected. However, the polymer data appear to be influenced by the nature of the fiber support, and resolution of the two transitions is not always possible.²⁰ In Figure 8, we observe only one transition, and we assign this to vitrification of the polymer matrix.

The vitrification time at various cure temperatures was measured for a series of specimens of constant polymer content. Figure 9 shows that fabrication of composites using oxidized carbon fiber produces a significant increase in vitrification time compared to the untreated fiber composite. There was only a slight difference in the activation energy associated with vitrification of the unoxidized and oxidized fiber composites (50.6 kJ/mol for oxidized fibers, 46.2 kJ/mol for unoxidized). The trend of increasing vitrification time with oxidized carbon fibers was supported by a separate series of experiments where the polymer content was varied (Table II). The vitrification time increased as the fiber content increased. This observation was surprising in view of accelerative effect of the oxidized fiber

Table II Vitrification of Carbon Fiber Composites at 140°C

Matrix % (by TGA)	Vitrification Time (by DMTA)	% Conversion at Vitrification (by DSC)
8	158 min	76
17	148 min	74
41	146 min	68
52	116 min	60

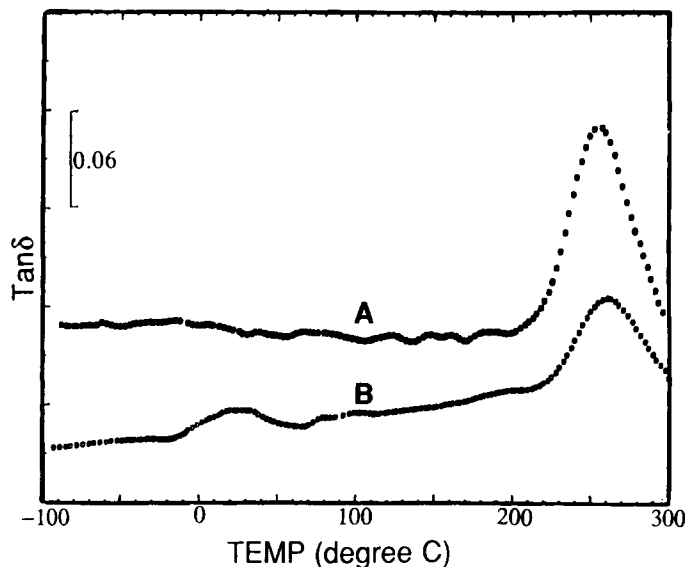


Figure 10 Loss tangent by DMTA for carbon fiber composites (15% matrix) after 2 h isothermal cure at 160°C. Data displaced vertically for ease of comparison: (A) untreated fibers; (B) oxidized fibers.

surface on the cure exotherm (Figs. 3 and 4), which might lead one to expect reduction in vitrification time. We therefore confirmed the change in extent of conversion required for vitrification by measurement of the “residual exotherm” of the vitrified specimens. Table II shows that there is an appreciable increase in the extent of conversion required for vitrification as the amount of oxidized fiber surface increases.

The physical properties of the cured composites also reflected the change in matrix chemistry. Figure 10 shows loss tangent data for composites made with oxidized and untreated fibers. The magnitude of the effect is enhanced by the choice of a low matrix content (15%), but the same qualitative features were observed at higher matrix contents. The composite made with oxidized fibers displays a marked low-temperature relaxation at about 30°C, possibly associated with the more flexible epoxy–epoxy structures in the network, which, in turn, are associated with the surface-catalyzed cure reactions as discussed below. The magnitude of the main alpha relaxation is reduced compared to the composite made with untreated fibers, consistent with the higher extent of reaction adjacent to the oxidized surface.

DISCUSSION

We have demonstrated previously that acidic carbon surface functionality can accelerate primary amine–

epoxy reactions in the uncatalyzed TDDDM–DDS system.¹¹ The changes in cure kinetics we report here for the BF₃EA-catalyzed system are of an appreciably greater magnitude.

The detailed mechanism of BF₃ catalysis has been interpreted in several ways: Thermal dissociation of the complex and attack by the BF₃ on epoxy functionality is conceptually the simplest interpretation and explains many features of the catalysis by various BF₃ complexes.^{25,26} However, many authors have concluded that impurities or the hydroxyl functionality of the epoxy resin play an important part in the catalysis.^{25–31} For example, Mones et al.²⁷ showed that BF₃EA has a greater catalytic effect in commercial MY720 than in pure TGDDM. This implies that the BF₃EA complex may decompose to a variety of catalytically active species. Arnold²⁸ describes a proton transfer between the BF₃EA catalyst and an epoxy functionality to give an ion pair that can initiate cationic polymerization of epoxy groups. Harris and Temine²⁹ suggest the formation of an adduct between the BF₃ complex and the epoxy group that can decompose at elevated temperatures to give initiating species for cationic polymerization. Morgan et al.¹⁴ assigned a large fraction of the cure exotherm to reactions induced by ethylammonium tetrafluoroborate. Smith et al.^{30,31} provided spectroscopic data and model reaction studies to support the hypothesis that fluoroboric acid is the major catalytic species. Whatever the detailed mechanism, there appears to be a consensus that BF₃EA-based

species are responsible for the low-temperature peaks of the cure exotherm (Figs. 3 and 4). It also appears likely that homopolymerization of epoxy functionality is important in these early stages and competes with the normal epoxy-amine reactions.

A reasonable explanation for the catalytic effect we observe here from the carbon fiber surface is that acidic species on the fiber surface interact with the latent BF_3EA complex to produce catalytically active species. The evidence of the IR spectra obtained from DME solutions indicates the possible involvement of alkylammonium cations (3050 cm^{-1} , broad), uncomplexed amine (1601 cm^{-1}), and tetrafluoroborate anions (1040 cm^{-1}). The DSC evidence supports the enhancement of the low-temperature homopolymerization exotherm, a conclusion further supported by the deficit of TGDDM residue in the soluble extract. The vitrification time data and loss tangent characteristics of the cured specimens are consistent with a model where homopolymerization of the epoxy resin has produced a more flexible, less cross-linked, network than that which would be produced by epoxy-amine reactions.

The literature concerning the effect of moisture on the cure of MY72/DDS/ BF_3EA is conflicting. Morgan et al.¹⁴ report that BF_3EA can be hydrolyzed to $\text{BF}_4^-\text{NH}_3^+\text{C}_2\text{H}_5$ at 85°C and 100% humidity, but that when this salt is incorporated into the epoxy resin/curative mixture, the reaction kinetics are the same as those with the unhydrolyzed complex. Stark et al.³² show a suppression by water of the low-temperature components of the cure exotherm for TGDDM/Novolac/DDS/ BF_3EA and a similar commercial epoxy formulation (Hercules 3501-6) (Figs. 7 and 9 of Ref. 32), although this is at variance with the statement in their synopsis of that paper that "moisture was found to accelerate the cure, especially for formulations exposed to the vapor environment." In the classical chemical literature, it is well known that BF_3EA is prone to hydrolysis. For example, Wamser³³ measured the second-order rate constant for reaction of BF_3 and water and demonstrated that boric and fluoroboric acids were the major products. The data presented here clearly demonstrate a retardation in the cure when using humid-aged fibers, presumably due to the destruction of the catalyst. Possible factors that could explain the lack of consistency of the various studies could be differences in water concentration, differences in catalyst concentration, and, in this case, the simultaneous presence of both water and the acidic carbon fiber surface.

It is clear from the above that the matrix system MY720/DDS/ BF_3EA will be affected profoundly by

proximity to an oxidized carbon fiber surface. The relevance of this observation to commercial prepreg systems is obscured by the confidentiality that surrounds the nature of commercial fiber treatments. Only those who are privy to the exact fabrication history of their commercial fiber can assess the relevance of the oxidative treatment described here. However, we took several commercial carbon fibers with oxidative surface treatments and observed modifications to the cure exotherm of MY720/DDS/ BF_3EA qualitatively similar to those reported here (albeit usually of a lesser magnitude). The relevance of this work to other matrix systems will depend on their sensitivity to the chemical effects described here. A general conclusion from this 6-year project on the modification of epoxy matrices at interfaces is that those systems that rely on low concentrations of catalysts are particularly prone to interfacial modification. When that catalyst is sensitive to water and acidity, as in the present case, an appreciable interfacial modification is inevitable.

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