

# Interphase Cure Characterization in Epoxy Composites by Fluorescence Technique

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Received 7 October 1995; accepted 15 September 1996

**ABSTRACT:** Monitoring the reaction of an aromatic diamine cure agent with epoxy by fluorescence technique was used for cure characterization of the interphase in epoxy/glass and epoxy/carbon composites. The effect of the various surface treatments was first studied by the model interphase obtained by using a quartz plate for glass or a modified quartz plate for carbon surface. Aminosilane treated quartz cured faster and showed increased cure extent, while water aging and air oxidation showed almost no effect on the cure kinetics in comparison to the untreated quartz surface. For a model carbon surface, air oxidation showed a faster reaction only at the early stage of cure.

The effects of the various surface treatments on glass or carbon fiber were also studied with the actual composites made by a thin coating of epoxy-diamine melt on glass or carbon fiber bundles. Epoxy/glass fiber composite showed a similar trend as the model interphase system. In the case of epoxy/carbon fiber composite, both air oxidation and water aging treatment showed a faster cure reaction at the early stage of cure. Furthermore, air oxidation treatment for the epoxy/carbon fiber composite showed somewhat increased cure extent. The reasons for these trends have been discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1769-1775, 1997

**Key words:** interphase; cure characterization; epoxy; diamine cure agent; fluorescence technique

## INTRODUCTION

High-performance epoxy composites have been widely used where high stiffness and strength as well as good environmental stability are required. Embedding high modulus fibers into epoxy matrix increases mechanical properties of the composites. Since stress is transferred through the in-

terphase, the ability of the interphase to transfer stress between the matrix and the reinforcement will influence the composite properties. It is speculated that there is a gradation of chemical and physical properties of the polymer at the interphase region,<sup>1</sup> possibly due to the preferential adsorption of curing agents. Surface treatments, which are commonly used to enhance the interaction of fiber reinforcements with polymer matrix, lead to additional complexity. As a result of these treatments, the nature of the polymeric material in the vicinity of the fiber surface may be altered or the local stoichiometric imbalance may occur, affecting the properties of the polymer at the interphase.<sup>2</sup> In the case of glass fibers, aminosilane coupling agents are often used for improved adhe-

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Contract grant sponsors: National Science Foundation, Polymer Program; Army Research Officer, DOD Instrument University Grant; Office of Naval Research; Institute of Materials Science, the University of Connecticut

Contract grant numbers: DMR 91-08060; DAAL03-92-G-0267

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sion,<sup>3,4</sup> whereas the oxidizing surface treatment of the carbon fibers is often carried out for similar purpose in the composite.<sup>5-9</sup>

Characterization of the molecular structure at the interphase is essential to understanding the performance of a composite in a given environment. Techniques such as dynamic dielectric analysis and differential scanning calorimetry only provide overall cure information, while it is important to characterize the chemical changes involved in interphase reactions. Information about the chemical functionality of the surface may be obtained by various techniques. X-ray photoelectron spectroscopy (XPS or ESCA)<sup>10-12</sup> is widely used for the surface with a great sensitivity. However, it is not suitable for cure chemistry monitoring at the interphase since the probed surface layer is less than 100Å. There are only few nondestructive and *in situ* monitoring techniques, while providing information about chemical changes during cure. Surface-oriented Fourier transform infrared (FTIR) techniques possess these capabilities. Several studies have been performed to study interphase cure kinetics of the epoxy composites by modifying the surface of internal reflection crystal.<sup>13-18</sup> But the modified internal reflection element surface may not be a satisfactory model for surfaces encountered in the high-performance composites. Reflection-absorption technique<sup>19</sup> is a sensitive technique for detecting the interphase between metal and thin polymer film. But the critical drawback of this technique is that the sample has to be coated on shiny metal surfaces, which are not frequently utilized in high-performance epoxy composites. These surface-oriented techniques requiring a model system to mimic the composite surface cannot be applied to the real composite system, such as glass or carbon fiber-reinforced composite.

Recently, the nuclear magnetic resonance (NMR) imaging technique was used for the metal/epoxy interphase cure study.<sup>20</sup> Because of the magnetic attenuation, the thickness of sample has to be quite thick (0.5 mm). Therefore, the interphase-to-bulk ratio was too low to obtain a strong signal from interphase. Also, the quantification of the extent of cure was not obtained.

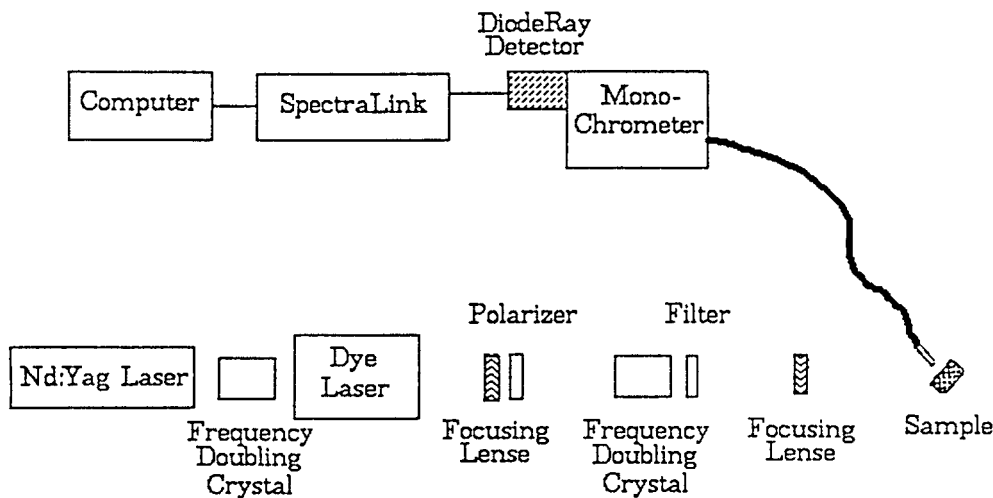
On the other hand, the fluorescence technique, which is well known as a sensitive nondestructive technique, can provide chemical information during cure. Recently, the research from our laboratory showed that the spectral shifts in the fluorescence can be used to determine the extent of

cure in epoxy composites cured with a commonly used aromatic diamine.<sup>21</sup> The problems encountered using a conventional fluorimeter, such as weak fluorescence and scattering from the fibers due to a very small amount of epoxy on the surface of fibers can be overcome by using a laser as an excitation source and collecting fluorescence by fiber optics. Therefore, in this study, we present the results on the interphase cure chemistry of epoxy cured with a diamine in glass or carbon composite by the laser-induced fiberoptic fluorescence technique and compare them with the results obtained on simulated surfaces by the conventional fluorescence method.

## EXPERIMENTAL SECTION

### Sample Preparation

A stoichiometric mixture of butyldiglycidyl ether (DGEb) and diaminodiphenyl sulphone (DDS) was prepared by mixing 2.98 g of DGEb with 1.825 g of DDS under constant stirring at 120°C for 2 min. For the interphase study on the model glass fiber, a very thin epoxy film was prepared by squeezing a small amount of DGEb/DDS melt between two quartz plates. The film thickness was measured by using the extinction coefficient of  $3.15 \times 10^4$  L/M cm for DDS, with the concentration of DDS in DGEb/DDS as 1.575M/L. This spectroscopic method can measure the thickness between 10 and 300 nm of very thin films with reasonable accuracy. For each sample, the absorbances at six different areas had been measured to check for uniform thicknesses. The cross-sectional area of light from a ultraviolet-visible (UV-Vis) spectrometer was about 1.5 cm × 0.1 cm. If the film absorbance measurements fluctuated more than 10%, the film was discarded, and another film was prepared. For the model surface study, the thickness of epoxy film was maintained to be about 200 nm. Very thin epoxy coatings were obtained either on glass or graphite fiber by dipping the fiber bundle into the DGEb-DDS melt and squeezing any excess resin out of the fiber. All glass or carbon fibers used in this study were obtained from Hexcel's F263™ glass or carbon epoxy prepregs. Fibers were cleaned by immersing prepregs in acetone for 24 h to dissolve the epoxy resins. Each fiber bundle was then heated in a furnace at 400°C for 24 h to remove any residual resin and subsequently exposed to the atmo-



**Figure 1** Schematic showing laser-induced fiberoptic fluorescence spectrometer setup. (for details for the setup, refer to the Experimental Section.)

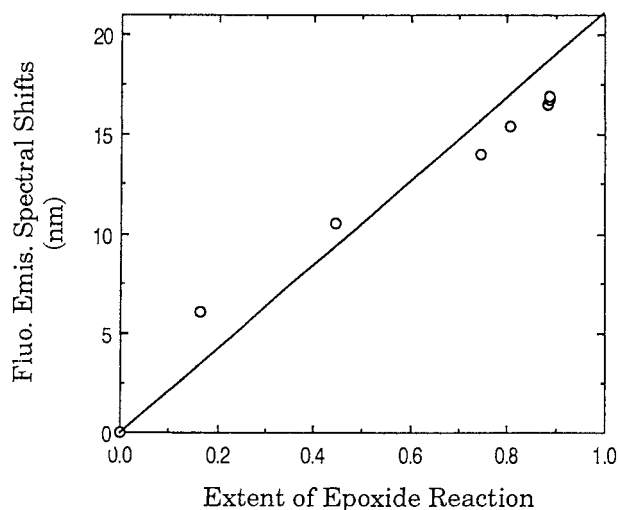
sphere for two months. The thickness of epoxy coating was less than  $1\ \mu\text{m}$  as checked by a microscope. The diameter of the glass fiber bundle was  $\sim 100\ \mu\text{m}$ .

### Surface Treatments

For the model carbon surface, a thin (about  $0.2\ \mu\text{m}$ ) polyacrylonitrile (PAN) film (purchased from Aldrich) was prepared by coating 2 wt % PAN in dimethyl sulfoxide (Aldrich) solution on a quartz plate, followed by drying in a vacuum oven at  $100^\circ\text{C}$  for removal of residual solvent. The PAN coating was then preoxidized to induce cross-linking and cyclization by heating the film in an air oven at  $175^\circ\text{C}$  for about 20 h. Carbonization was performed by heating this PAN-coated quartz plate at  $600^\circ\text{C}$  in an argon environment for 6 h. Three different surface treatments were performed on the model surfaces and fibers. Water aging was done by placing the quartz plate and fiber in a water bath without directly contacting water for 10 h. The air oxidation treatment was by heating the quartz plate and fiber in air between  $500\sim 550^\circ\text{C}$  for 45 min. The aminosilane-treated surfaces (applied only for the glass surface) were obtained by preparing a 1 wt % aqueous solution of 3-aminopropyltriethoxysilane (APS, purchased from Aldrich) and spraying onto the respective surfaces followed by vacuum drying for 2 h at  $90^\circ\text{C}$ .

### Spectroscopic Analysis

For the model system, a conventional fluorimeter (Perkin-Elmer LS50B Luminescence Spectrometer) was used. The first derivative fluorescence emission spectra were used to identify the peak maxima because of the broadness of the fluorescence emission spectra. For the composite study, a fiberoptic fluorimeter with a laser source was used. Figure 1 shows a schematic diagram of the laser-induced fiberoptic fluorescence setup. A Quanta Ray DCR-3 pulsed Nd : Yag laser was used to pump a narrow-band Quanta-Ray PDL-2 pulsed dye laser. Solutions of a dye, DCM ([2-[2-[4-(dimethylamino)phenyl]ethyl]-6-methyl-4H-pyran-4ylidene]-propane dinitrile) in methanol at concentrations of 174 and 24 mg/L were used in the oscillator and amplifier, respectively. The excitation wavelength was 315 nm. This was accomplished by tuning the DCM dye laser to 630 nm and frequency-doubling the output with a KDP crystal (Inrad, Gimbal Mount). The output of the doubling crystal, which consists of the fundamental (630 nm) and second harmonic radiation (315 nm), is then passed through a cut-off filter (Oriol filter 51662, cut off between  $500\sim 700\ \text{nm}$  range) to block the fundamental radiation. Fluorescence emission from the sample was collected by a fiberoptic cable and delivered to the monochromator (Instrument SA, Inc.; Model HR320, which has 150 grating/mm), then analyzed by a diode array detector (Princeton Instrument, Inc.; Model IVY-512N/B), which is con-



**Figure 2** Correlation plot between the peak position in the first derivative emission spectra and the extent of epoxide reaction.

nected to a personal computer by Spectrum Link (Instrument SA, Inc.). The intensity of the dye laser used in this study was 0.5 mW. The fluorescence emission spectra were obtained by averaging five scans for each measurement.

The photodegradation was not a serious problem in this study because the exposure time of five seconds to the laser at each measurement did not cause significant photodegradation at a given laser intensity. Even if there is some degradation, it may reduce the fluorescence emission intensities, but it would not change the peak position of DDS that was used in this study.

## RESULTS AND DISCUSSION

### Estimation of the Extent of Cure

In order to study the cure kinetics by fluorescence technique, a correlation method that has been developed in our laboratory was used.<sup>21</sup> To obtain the extent of amine reaction, 25  $\mu\text{m}$  thick DGEb/DDS films were prepared and cured at 160°C in an air oven. In our previous study, a good correlation between the fluorescence excitation spectral shifts and the cure extent was demonstrated.<sup>21</sup> This is based on the red shifts of about 24 nm due to the conversion of the primary amine in DDS to the tertiary amine. In our laser-induced fluorescence setup, only fluorescence emission spectra can be obtained. As demonstrated by Song and

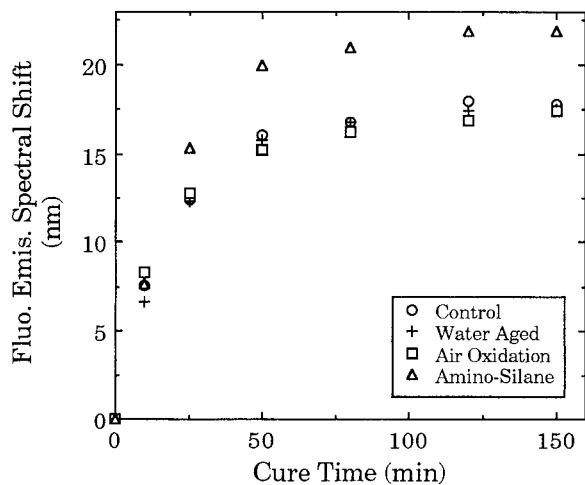
Sung,<sup>21</sup> the first derivative of the emission spectra also shows similar spectral shifts, with easier assignment of the peak position than the emission spectra. Therefore, the first derivative fluorescence emission spectra were taken as a function of cure time to develop a correlation between the spectral shift and the epoxy cure extent. The extent of epoxy reaction was measured by FTIR for thinner samples. Figure 2 shows a correlation plot of the spectral shift observed in the first derivative fluorescence emission spectra with the extent of epoxide reaction determined by IR for epoxy matrix cured at 160°C. The extent of amine reaction in any stoichiometric DGEb/DDS sample can be estimated by measuring the spectral shift in the first derivative of the fluorescence emission spectra using the correlation plot since there is one-to-one relation between diamine and the epoxy group reaction.

### Effect of Surface Treatments

Most fiber-reinforced composites are surface-treated for better performance; therefore, it is important to study the effects of surface treatments on cure kinetics and extent. First, model systems prepared from quartz or carbonized quartz were used in order to simulate glass or carbon, respectively. Then, a real composite system prepared with glass fiber or carbon fiber bundle coated with thin epoxy matrix was investigated. Three types of surface treatments (water aging, air oxidation, and aminosilane treatment) for glass surface and two types of treatments (water aging and an oxidation) on carbon surface were studied. These treatments were chosen because they are often used in the course of the real composite processing.

### Simulated Glass Surface

Two quartz plates were used as a model glass surface with very thin (about 200 nm) epoxy cured with DDS between them. The shape and the quality of the original fluorescence emission spectra were the same as in the case of bulk (about 25  $\mu\text{m}$  in thickness) DGEb/DDS sample. Figure 3 shows the spectral shifts in the first derivative emission spectra of DDS cured epoxy on simulated glass surface as a function of cure time at 160°C. The control sample was about 200 nm thick without any surface treatment. As one can see in Figure 3, water aging and air oxidation showed al-



**Figure 3** Plot of the first derivative emission spectral peak position as a function of cure time at 160°C for epoxy cured with DDS on simulated glass surface after various surface treatments.

most no effect on the extent of amine reaction when compared with the control sample. But the amino-silane treatment led to a faster reaction and a greater extent of cure compared with that of the control sample. The increase in crosslinking density could be obtained by using the correlation plot, such as in Figure 2, where the estimated spectral shift for 100% epoxide of reaction was about 21 nm. Since the aminosilane-treated sample showed a spectral shift 3.5 nm greater than that for control sample, the increase in crosslinking density was estimated to be about 10% greater for the aminosilane-treated epoxy/glass composite interphase. Chiang and Koenig<sup>22</sup> reported about 5 ~ 10% increase in the cure extent at the interphase in the aminosilane-treated anhydride-cured epoxy composite relative to the bulk resin. This trend of faster and greater cure may be the result of surface-induced initiation due to the amine group in the coupling agent.<sup>22</sup> When the glass surface is pretreated with aminosilane, a multilayer of aminosilane film is formed. Upon casting the uncured epoxy matrix over the aminosilane film, epoxy can diffuse into the aminosilane layer. The occurrence of interdiffusion between aminosilane and polymer matrices has been reported previously by Sung et al.<sup>23</sup> As a result of this diffusion, aminosilane not only acts like a catalyst but also participates in the crosslinking reaction.

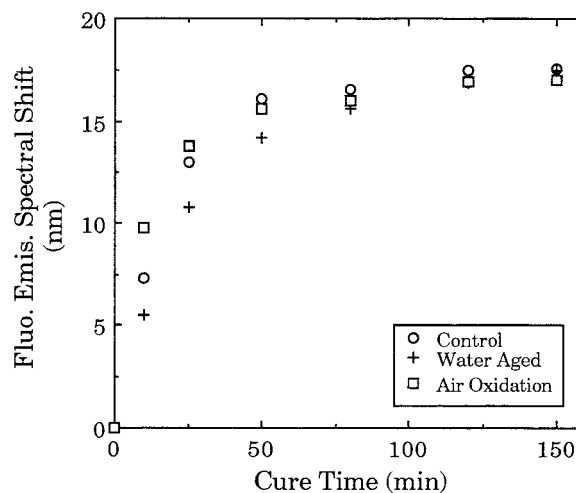
#### Simulated Carbon Surface

A simulated carbon surface was obtained by carbonizing poly(acrylonitrile) coating on a quartz

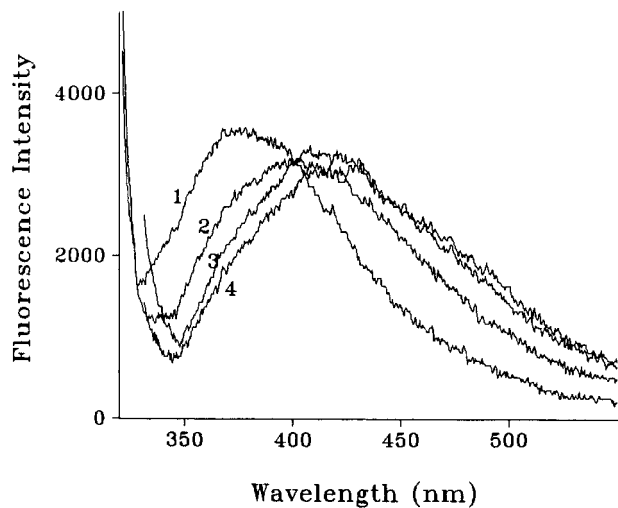
plate, as explained in the experimental section. The spectral shifts of DDS cured epoxy on the simulated carbon surface are shown as a function of cure time at 160°C in Figure 4. Water aging showed a retardation of epoxy cure during the early stage of cure but became similar to the control sample at the later stages of cure. This trend can be explained since water molecules may be tied up with epoxide to prevent the reaction of epoxide with DDS diamine at the early stage, but a prolonged cure at high temperature would remove water molecules from epoxide such that the final extent of cure does not change. In contrast, the air oxidation, which is known to introduce carboxyl, carbonyl, and acidic hydroxyl groups, resulted in a faster cure at the early stage only. This effect may be due to the catalytic effect of these surface oxidized species introduced by air oxidation.<sup>5-7,17,18</sup> These kind of acidic groups are well known as catalysts for the conventional epoxy cure.<sup>24</sup>

#### Epoxy/Glass Fiber Composite

Because of the limitations of the conventional fluorimeter, as mentioned in the introduction, a laser-induced fiberoptic fluorimeter was used for the study of composite with glass fiber bundle coated with a very thin film of epoxy (DGE/DDS) resin. With this fluorimeter, the quality of fluorescence emission spectra was improved, as

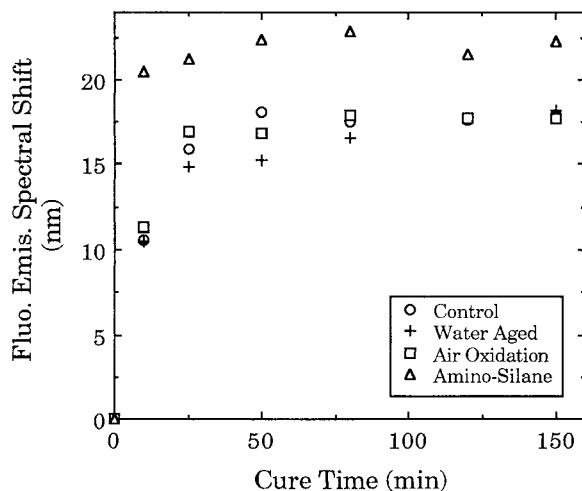


**Figure 4** Plots of the first derivative emission spectral peak position as a function of cure time at 160°C for epoxy cured with DDS on simulated carbon surface after various surface treatments.

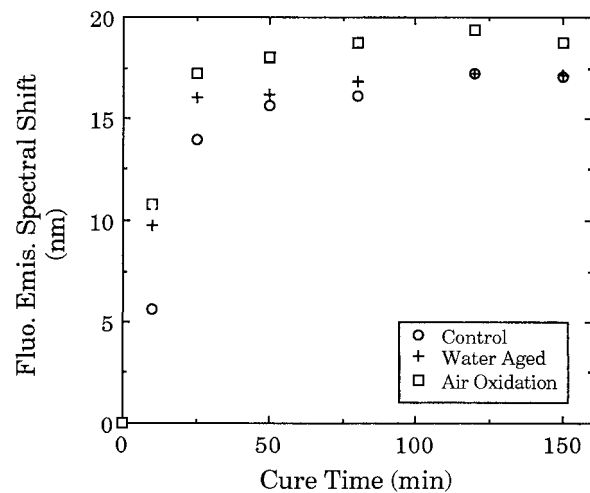


**Figure 5** Laser-induced fiberoptic fluorescence emission spectra obtained from epoxy/glass fiber composite as a function of cure time at 160°C (spectra 1, 2, 3, and 4 correspond to the cure time of 0, 10, 80, and 180 min, respectively).

shown in Figure 5. By comparing the fluorescence emission intensities, the film thickness in the composite was estimated and found to be comparable (around 200 nm) with those of the simulated interphase. Figure 6 shows the spectral shifts in the first derivative emission spectra in epoxy/glass composite as a function of cure time at 160°C. As in the cases of simulated glass interphases, the water aging and air oxidation



**Figure 6** Plots of the first derivative emission spectral peak position for the epoxy/glass fiber composite as a function of cure time after various surface treatments on glass fiber.



**Figure 7** Plots of the first derivative emission spectral peak position for the epoxy/carbon fiber composite as a function of cure time after various surface treatments on carbon fibers.

showed almost no effect on the cure kinetics of DDS reaction when compared with the control sample. But the amino-silane treated composite showed a much faster reaction even at very early stage (i.e., 10 minutes of cure at 160°C), which is faster than that for the simulated glass interphase. The total amount of spectral shift was about 22 nm. From this spectral shift, the estimated increase in crosslinking density was about 15% in comparison to the control sample.

#### Epoxy/Carbon Fiber Composite

The spectral shifts observed in carbon fiber composite with very thin epoxy resin is shown in Figure 7 as a function of cure time at 160°C. Water aging catalyzed the epoxy cure and led to faster reaction in the early stage of cure. But from the middle stage of cure, the extent of amine reaction was almost identical with that of control carbon composite. This catalytic effect may be due to the introduction of acidic hydroxyl groups from the water aging process. In the case of the simulated carbon interphase, water aging caused a small retardation of epoxy cure during early stages of cure. This discrepancy may be due to the oxidative carbon fiber surface introduced during fiber production, thus introducing a small amount of acidic hydroxyl groups that act as a catalyst on the fibers, but not on simulated carbon. Air oxidation lead to faster and higher percentages of DDS reaction throughout the whole cure process. In the

case of the simulated carbon interphase, air oxidation catalyzed only early stages of cure. But in real carbon fiber composites, air oxidation produced greater extents of cure as well. The estimated increase in extent of cure was a few percent. The reaction of surface oxides (carboxyl, carbonyl, hydroxyl, and quinones) on carbon fiber with epoxy and amine groups had been studied systematically.<sup>5</sup> These surface oxides act as reacting catalysts, which directly participate in the cure reaction and form a chemical bond with resin chains, leading to nearly complete cure. Bogoeva-Gaceva et al.<sup>26</sup> also observed an increased crosslinking density in the interphase region for surface oxidized carbon/epoxy composite by FT-IR. From these two (real carbon composite interphase and simulated carbon interphase) cases, it is clearly shown that the simulated surface cannot exactly mimic the real composite system.

## CONCLUSION

Laser-induced fluorescence technique was used to study surface treatment effects on interphase cure kinetics of epoxy composites reinforced with glass or carbon. Simulated surfaces (both glass and carbon) were also studied to compare with actual composites made with glass or carbon fibers.

Water aging or air oxidation did not show any effect on the extent of epoxy cure for glass interphase (for both simulated and actual composites). Aminosilane treatment showed not only faster cure reaction but also improved crosslinking density (about 10% for simulated glass and 15% for actual glass-fiber composite). For simulated carbon interphase, air oxidation showed faster cure at early stage without changing the extent of cure, while water aging showed retarded cure reaction. However, in the case of actual epoxy carbon-fiber composite, both water aging and air oxidation showed faster cure reaction in the early stage. Air oxidation also showed improved extent of cure (about 10%). From comparison of these results, it was concluded that the simulated surface could not exactly mimic the actual composite systems.

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