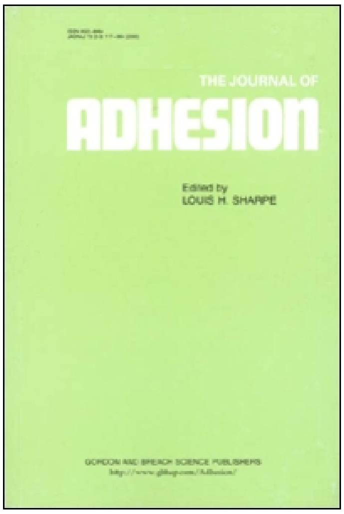

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G. R. Palmese[a]; R. L. McCullough[a]
[a] Center for Composite Materials and Department of Chemical Engineering, University of Delaware, Newark, DE, USA

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Kinetic and Thermodynamic Considerations Regarding Interphase Formation in Thermosetting Composite Systems

G. R. PALMESE and R. L. MCCULLOUGH

Center for Composite Materials and Department of Chemical Engineering, University of Delaware, Newark, DE, 19716, USA

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Thermodynamic and kinetic treatments are employed to analyze the role of preferential adsorption and diffusion in the formation of interphase regions in thermosetting composities. The thermodynamic analyses show that a driving force exists for the preferential adsorption of amines onto carbon fiber surfaces in amine-epoxy systems. Scaling analyses, based on kinetic considerations, lead to the identification of reaction-diffusion time regimes that control interphase formation in sized and unsized fiber systems. These considerations provide guidelines for the selection of material formulations and processing conditions that may be used to tailor behavior of the interphase region in thermosetting composites.

KEY WORDS scaling analyses; carbon fiber reinforced composites; adsorption of amines; surface influenced cure; fiber sizing; surface treatment; amine cured epoxy resins; mechanisms of interphase formation; reaction and diffusion.

INTRODUCTION

High performance composite materials typically consist of a high-modulus, fibrous reinforcing material imbedded in a thermosetting polymeric matrix. Graphite, glass, and aramid fibers are typical reinforcement materials. Amine and anhydride cured epoxy resins are common thermosetting systems. The behavioral characteristics of the composite depend on the properties of the matrix and reinforcing phases as well as on the interactions between them. Historically, one of the concerns associated with the use of fibers as reinforcing materials has been the low interfacial strength between the fiber and resin. Interfacial strength in glass fiber and epoxy matrix composites has long been enhanced by the use of coupling agents or sizings that are chemically grafted onto the fiber surfaces.[1] Under existing assumptions, the coupling agents are designed to bond chemically with the matrix during cure. Although early attempts to use this technique to aid the weak interface in carbon/epoxy composites were not successful, surface treatments that substantially improve the interfacial strength of epoxy/carbon composites have nonetheless been developed.[2] These treatments chemically and physically modify the fiber surfaces. Treatments typically in use are oxidation processes which tend to increase the specific area of the fibers and add oxygen-containing functional groups to their surfaces.[3] These surface and/or coupling agents are designed to alter the interactions of the fiber with the polymeric matrix and, in so doing, may alter the nature of the polymeric material in the vicinity of the fiber surface. The resulting interphase region may possess neither the properties of the reinforcement nor those of the homogeneous neat resin.

Surface-induced interactions may perturb only a monolayer of the matrix adjacent to the fiber surface, or a substantial portion of the matrix phase. In the latter case, the properties of the resulting interphase material can vary with distance from the fiber surface. The size and chemical and structural characteristics of the interphase are particularly important in determining composite behavior characteristics such as strength and fracture toughness.[4–6]

Possible causes for the formation of such an interphase region in thermosetting composite systems have been proposed.[7–9]. These explanations include:

(i) the formation of voids as material adsorbed onto fiber surfaces is volatilized;
(ii) direct chemical reaction between reacting prepolymers and curing agents with functional groups on the surface of fibers;
(iii) preferential adsorption onto fiber surfaces of one reacting species over another; and
(iv) the presence of thin monomer coatings known as sizings on the surfaces of fibers. Although these explanations are qualitative in nature, they have served to rationalize observed phenomena.

A more fundamental and quantitative understanding of the mechanisms for interphase formation in thermosetting systems in needed to enable tailoring of the interphase. A quantitative understanding of the thermodynamics of thermosetting resins in contact with fibers will elucidate the driving forces for interphase formation; and examination of the associated kinetic processes, such as chemical reaction and diffusion, will provide an understanding of the degree to which thermodynamic limits are approached. In this work, we will focus attention on carbon fibers in amine-cured epoxy resins and examine the influence of preferential adsorption and the presence of fiber sizings on interphase formation. Before proceeding with the thermodynamic and kinetic analyses, it will be useful to review some of the important factors that are involved in the formation of interphase regions.

REVIEW OF FACTORS INFLUENCING INTERPHASE FORMATION

Three important factors are involved in determining the nature and extent of interphase regions: (i) the total area of the fiber surface in contact with the polymeric phase, (ii) the nature of the fiber surface, and (iii) perturbations of the cure reaction and polymer structure induced by the fiber surface. Each of these factors are discussed below.

Surface Area

Typical fibers used in composite materials range between 6 and 10 μm in diameter. High performance composites usually have fiber loadings around 60 volume percent.

In such systems the ratio of fiber surface area to matrix volume is very high; therefore, even small interphase regions may represent a significant portion of the matrix phase. Equation (1) can be used to estimate the fraction of matrix phase occupied by interphase material (V_{mi}) as a function of interphase size (λ), fiber diameter (d), and fiber volume fraction (V_f). This relationship is applicable to a composite in which the fibers are arranged hexagonally and the interphase thickness is less than or equal to half the distance between fibers.

$$V_{mi} = 4\left(\frac{\lambda^2 + \lambda d}{d^2}\right)\left(\frac{V_f}{1 - V_f}\right) \tag{1}$$

Figure 1 is a plot of V_{mi} as a function of interphase size for several fiber diameters. For a 6 μm fiber composite having a 0.1 μm thick interphase, 10 percent of the matrix phase could be comprised of interphase material. Thus, from a geometric point of view alone, even small interphases may play an important role in determining composite behavior characteristics.

Surface Treatments

Carbon fibers are the predominant reinforcing agents for high-performance thermosetting composites. The most common type of carbon fibers is manufactured by the controlled pyrolysis and graphitization of polyacrylonitrile (PAN) fibers. Two types of fibers are commonly produced: high modulus (HM-type) and high strength (HS-type). The difference in properties depends on the final processing temperature. HM-type fibers are processed at higher temperature; these have a higher degree of axial alignment of the graphitic ribbons that form the fibers and, therefore, possess a higher modulus

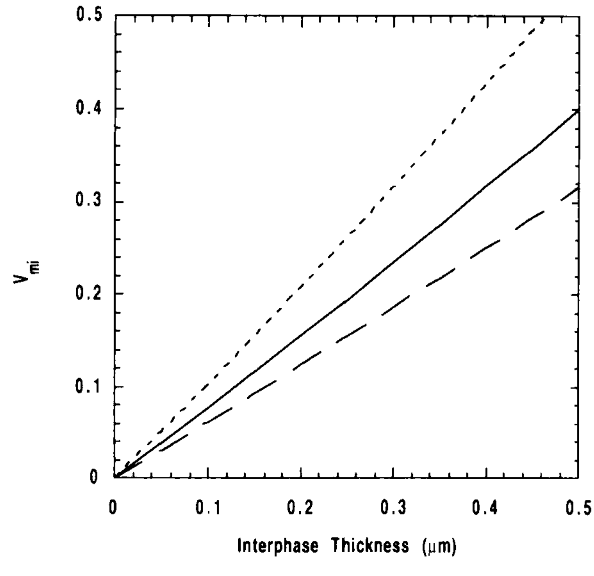

FIGURE 1 Volume fraction of matrix phase comprised of interphase material (V_{mi}) as a function of interphase thickness for hexagonally-arranged 60% fiber volume fraction composites of various diameters: 10 μm (— —), 8 μm (——), 6 μm (-----).

with respect to the HS-type fibers. Commonly-used HS and HM-type PAN-based graphite fibers are manufactured by Hercules and are designated as A and HM type fibers, respectively. The symbols "S" and "U" are appended to these designations to distinguish between sized and unsized fibers. The structure of these fibers has been investigated extensively and the results have been reviewed by several authors.[10,2]

The surface of the carbon fiber may be treated to improve adhesion between the fiber and matrix. Treatments typically in use are oxidation processes which tend to increase the specific area of the fibers and add oxygen-containing functional groups to their surfaces.[3] Commonly-used surface treatments include: wet oxidation, dry oxidation, electrolytic oxidation, and plasma treatments.[10,11] Dry oxidation treatments are gas phase oxidations which utilize air, pure oxygen, or gas mixtures containing oxygen-rich molecules (such as carbon dioxide, carbon monoxide and ozone) and are typically carried out between 200 and 500°C. The temperature and the composition of gases can be varied to modify resulting surface compositions. Treatments at high temperatures can cause severe degradation by pitting of the carbon fiber.

Wet oxidations are carried out in the liquid phase. Oxidations with solutions of nitric acid are common. The degree of oxidation can be controlled by varying the length of treatment, the temperature of treatment and the concentration of acid. Compared with dry oxidations, wet oxidative treatments are "gentler" and produce less pitting of the fiber surfaces.[10,2]

Electrolytic or anodic oxidations are most commonly used on an industrial scale. Electrolytes commonly used in this process are sulfuric acid, nitric acid and sodium hydroxide. The surface composition in this case can be varied by changing the electrode potential and the length of treatment.

Oxygen-containing surface groups which have been grafted onto carbon or graphite fiber surfaces during treatment include phenolic and aliphatic hydroxyl groups, carboxylic acid groups, carbonyl groups and quinones. Surface treatments have also been developed to add nitrogen-containing groups such as amines onto fiber surfaces.

These treatments have a pronounced effect on the mechanical behavior of the composite. A mechanical test often used to measure interfacial strength in composites is the interlaminar shear stress (ILSS) test. Following oxidative surface treatments, values of composite ILSS are typically higher which indicates a stronger interface.[12,13] Possible explanations for this behavior include:

(i) enhanced mechanical bonding due to the increase in surface area and rugosity;
(ii) enhanced physical and chemical interactions between the fibers and matrix *via* the added surface functionality; and,
(iii) the stripping of a weak, defect-laden layer of material from the fiber surface by the surface treatment.

All of these explanations are, in part, responsible for the observed behavior and it has been difficult to assess the relative importance of each mechanism. Nevertheless, the importance of fiber-matrix interactions on a molecular level in determining ILSS is clear. Investigators[3] have shown that by selectively masking oxygen-containing surface functional groups, the interfacial strength of graphite epoxy composites is decreased. Some workers have attempted to decouple the effects of surface functionality and surface area by removing the oxygen functionality without appreciably changing rugosity of the surface.[12,13] Their work demonstrates that chemical interactions arising from the presence of surface groups on the surface of the fibers play an important role in modifying interfacial strength of carbon fiber-epoxy composites.

Effect of Fiber Surface on Cure Behavior

The results discussed above indicate that there is evidence to support the contention that some of the chemical interactions which take place are reactive in nature. It is well known that the chemical structure of neat thermosetting resin depends on the extent of cure and, in some cases, on the cure history. Consequently, fiber-induced modifications of the cure reactions may perturb the structure of the polymeric matrix and alter the local mechanical behavior.

Figure 2 illustrates possible chemical reactions between the functionalities on the surface of fibers and epoxy and amine groups which have been proposed by Fitzer *et al.*, and others.[3,14,15] Reactions between acidic groups such as carboxylic acids and phenolic hydroxyls and epoxide rings and amines are possible. On the other hand, it is more likely that aliphatic or non-acidic hydroxyls react with epoxides while quinone and carbonyl surface groups react with amines.

Garton *et al.*,[8,9] have investigated the effects of carbon fibers and carbon blacks on the cure of several epoxy systems. Among these are Epon-828®/MPDA (*a diglycidyl ether of bisphenol A-based epoxy/metaphenylene diamine*) and the TGDDM/DDS (*a tetraglycidyl-4,4' diaminodiphenyl methane-based epoxy/diamino diphenyl sulfone*) systems. For the Epon-828/MPDA system containing carbon fibers, a marked increase of the reaction rate in the initial stages of cure was found with respect to the neat system.[8] In addition, the final extent of conversion and the glass transition temperature were found to be lower for the Epon-828-MPDA system containing carbon fibers.

A similar relative decrease in final conversion has been observed in our laboratories for the Epon-828/PACM-20 (*a diglycidyl ether of bisphenol A-based epoxy/bis (para-amino cyclohexyl) methane*) system modified with ground Hercules AU-4 carbon fibers

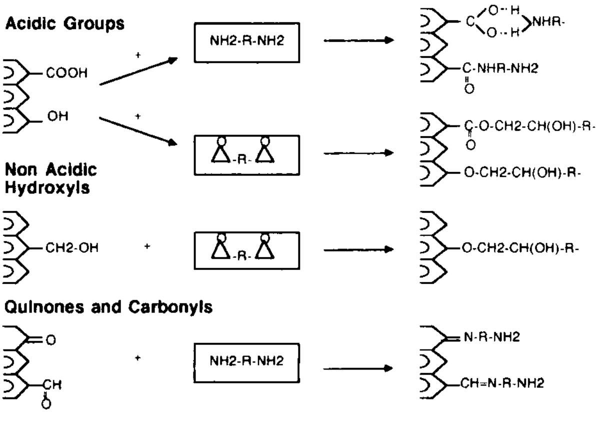

FIGURE 2 Possible reactions of epoxide and amine functional groups with the functionalities found on graphite fiber surfaces (after Fitzer *et al.*[3]).

oxidized using nitric acid wet oxidation. Transmission Fourier transform infrared spectroscopy (FTIR) was used to monitor the cure of the neat resin and a mixture containing 25% by weight carbon fiber. The results are shown in Figure 3 as plots of dimensionless epoxy concentration as a function of time for isothermal processing. The final extent of cure for the unmodified or "neat" system is about 3% greater than that of the carbon-modified system.

Garton *et al.*,[8,9] deduced that the decreased conversion caused by the presence of fibers is due to the preferential adsorption of amine curing agent onto the fiber surfaces. Such adsorption would produce a local modification in the epoxy-amine ratio of that region. It was further stipulated that the reduced mobility of the adsorbed materials might inhibit secondary amine reaction and also affect the final degree of conversion. The increased reaction rate during the initial stages of cure was attributed to the possible catalytic effect of the acidic surface groups on the primary amine-epoxy reactions.

Garton *et al.*,[9] and Mijovic *et al.*,[16] have observed accelerated rates in the initial stages of cure for the carbon fiber modified MY720®/DDS (*a tetraglycidyl-4,4'-diaminodiphenyl methane-based epoxy/diamino diphenyl sulfone*) system similar to those encountered with the Epon-828/MPDA system. However, unlike the difunctional epoxy system, the final extent of epoxy conversion for the MY720/DDS combination is not appreciably affected by the presence of fibers. This difference is probably due to the relatively important role that epoxy-hydroxyl etherification reactions play in the cure of the tetraglycidyl-4,4'-diaminodiphenyl methane-based MY720/MPDA epoxy

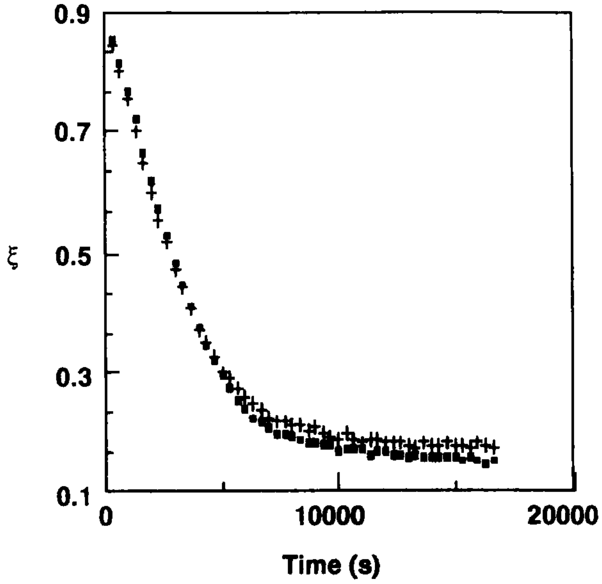

FIGURE 3 Dimensionless epoxide concentration (ξ) as a function of time for neat (■) and 25% by weight treated Hercules AU-4 fiber filled (+) Epon-828/PACM-20 resin. Samples were cured isothermally at 60°C and characterized using transmission FTIR.

system.[17–19] That is, epoxy groups not consumed by the amine-epoxy reaction, as a result of imbalances caused by the preferential adsorption of amine molecules, are consumed by the etherification reaction.

Concerning the initial reaction rates, the epoxy-amine ring opening reaction is not only enhanced by the presence of hydrogen donor species such as hydroxyl groups, but is also inhibited by proton acceptors such as carbonyls.[20,21] The oxidized surfaces of graphite fibers contain both types of these groups in significant concentration. Furthermore, the overall concentration of the catalyzing surface groups is small compared with the hydrogen donor moieties present in the resin systems.[20] Therefore, the explanation provided by Garton *et al.*,[8,9] whereby the acidic fiber surface groups catalyze the epoxy-ring-opening reaction, is not convincing.

An explanation that is perhaps more viable is that stoichiometric imbalances that form as a result of fiber-matrix interactions affect the reaction rate. For the initial stages of reaction of typical autocatalitic epoxy-amine systems[22] the rate of reaction (r_i) may be treated as first order with respect to epoxy and amine concentration:

$$r_i \propto C_E C_A \tag{2}$$

Figure 4 is a plot of the product $C_E C_A$ as a function of the initial molar ratio of epoxy to amine for the Epon-828/MPDA and the TGDDM/DDS systems. The stoichiometric molar ratios are indicated for each system. It is clear in both cases that amine, in excess of the stoichiometric ratio, causes a significant increase in the reaction rate. Therefore, the presence of an amine-rich layer near the fiber surface can explain the observed enhancement of reaction rate in the graphite fiber modified epoxy-amine systems.

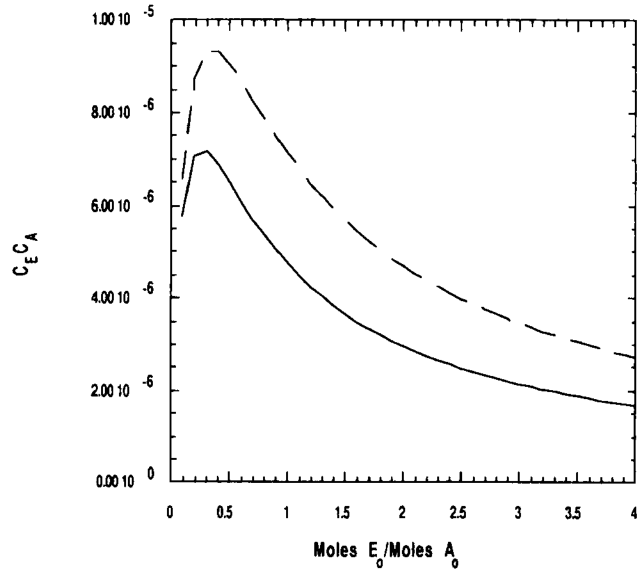

FIGURE 4 The effect of initial epoxy amine molar ratio (E_0/A_0) on initial rate of epoxide conversion ($C_E C_A$ (moles/cm^3)^2) for the Epon-828/MPDA (— –, Moles E_0/Moles A_0 = 2 at stoichiometry) and TGDDM/DDS (——, Moles E_0/Moles A_0 = 1 at stoichiometry) resin systems.

MECHANISMS OF INTERPHASE FORMATION

The foregoing discussions of the effects of reinforcement-matrix interactions on cure and behavior characteristics of carbon-fiber-modified amine-epoxy systems suggests that mechanisms exist for the formation of an interphase in such systems. On a molecular level, the reinforcement-matrix interactions may include physical interactions such as dipole-dipole, induced dipole and London dispersion forces as well as chemical interactions such as hydrogen bonding and chemical bonding. Collectively, these interactions provide a thermodynamic driving forces for interphase formation; the associated kinetic processes, such as chemical reaction and diffusion, establish the degree to which thermodynamic limits are approached. In the discussions which follow we firstly investigate the thermodynamic origin of the driving force for interphase formation and secondly, we analyze the kinetic processes associated with interphase development.

Thermodynamic Origins of The Driving Force for Interphase Formation

The preferential adsorption onto reinforcing surfaces of a component of a thermoset resin onto reinforcing surfaces has been reported by several investigators.[7,8] This phenomenon has been cited as a possible cause for the formation of the interphase in thermosetting composites. In amine-cured epoxy resins modified with graphite fibers, amine molecules are believed to adsorb preferentially onto the fiber surfaces during cure. A schematic representation of this process is illustrated by Figure 5. The preferential adsorption of amines during cure is assumed to cause transient gradients in chemical composition which are frozen in place at later stages of cure to form an interphase. Thus the preferential adsorption of one component over the other forms the basis of this mechanism for interphase formation. While Garton *et al.*,[8] used cure studies to deduce that amines preferentially adsorb onto fiber surfaces, a quantitative description of the phenomenon based on thermodynamic principles is required to assure the viability of the proposition.

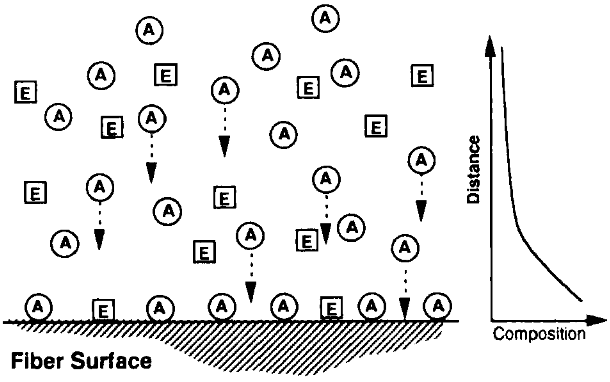

FIGURE 5 Schematic representation of preferential adsorption of amine monomer (A) onto graphite fiber surface from an epoxide/amine mixture. Such preferential adsorption forms the basis for an often-quoted mechanism of interphase formation. It is assumed that the preferential adsorption of amine causes the formation of transient gradients which are frozen in place at later stages of cure.

In the previous discussion, the extent of chemical interaction between fiber surfaces and epoxy matrices was highlighted by the fact that chemical bonding occurs between fiber surface groups and matrix components. However, covalent bonds may represent only a small part of interactions between fibers and epoxy matrices. Other interactions include hydrogen bonding, van der Waals interactions and polar interactions. The affinity of epoxy matrices for fiber surfaces depends on all of these factors. Furthermore, the relative affinity of epoxy prepolymers and amine hardeners for the fiber is a thermodynamic indication of the extent of adsorption of one component over the other, and provides the driving force for interphase formation. Thus, independent measurement of epoxy-fiber and amine-fiber affinity can provide support for the proposition that amine molecules are preferentially adsorbed onto the graphite fiber surfaces. Fitzer *et al.*,[23] compared the wetting behavior of amine hardener/graphite fiber and epoxy/graphite fiber systems by measuring contact angles and concluded that, because of the greater ease with which the amine wetted the graphite fibers, amine molecules are likely to serve as coupling agents between matrix and fiber. The following thermodynamic analysis of the results presented by Fitzer *et al.*,[23] demonstrates that a strong driving force exists for amine molecules to adsorb preferentially onto carbon fiber surfaces.

Comparison of changes in free energy associated with the spreading of pure liquids onto a surface can be used to rank their attraction for the surface. For a mixture of such liquids, this information can be used to predict the relative affinity of each component for a surface placed in contact with the mixture. The energetic interactions between two surfaces are described by the change in free energy associated with separating two unit surfaces of the material or materials in question to infinity in a vacuum. For a liquid (l) in contact with a solid (s), the change in free energy associated with spreading the liquid over a unit area of solid surface, known as the work of spreading (W_{sp}), is the difference between the work of adhesion between the solid and the liquid (W_{sl}) and the work of cohesion of the liquid (W_{ll}):

$$W_{sp} = W_{sl} - W_{ll} \tag{3}$$

The sign of W_{sp} for a liquid-solid system can be used to classify the attraction which exists between the components. If W_{sp} is negative, then the free energy of solid-liquid surfaces placed together is greater than the free energy of the separated surfaces. Hence, the latter configuration is preferred and the interaction can be considered repulsive. On the other hand, if W_{sp} is positive, then the free energy of solid-liquid contacting surfaces is less than that of the disjointed ones and the contacting configuration is preferred. This gives rise to a thermodynamically-attractive condition. Finally, if the work of spreading is zero, the two states will posses the same amount of free energy; neither state is thermodynamically favored and the interaction is defined as neutral. By comparing the values of W_{sp} of different liquids for the same substrate, an assessment can be made regarding the relative attractions of these liquids for the surface.

In order to apply this criterion to predict the adsorptive behavior of mixtures of amine hardeners and epoxy prepolymers on graphite fiber surfaces, the W_{sp} values for pure amines and pure epoxy prepolymers are needed. The work of spreading can be estimated from contact angle measurements by combining the Young-Dupre equation, *viz*,

$$W_{sl} = \tfrac{1}{2} W_{ll} (1 + \cos\theta) \tag{4}$$

with equation (3) to yield equation (5) which relates the contact angle and the work of cohesion of the liquid to W_{sp}:

$$W_{sp} = W_{ll} (\cos\theta - 1) \tag{5}$$

Many contact angle values have been reported for mixtures of epoxy resin and amine curing agents in contact with carbon fiber surfaces. Fewer contact angle measurements, however, have been reported for pure prepolymers and curing agents in contact with these fibers. Fitzer *et al.*,[23] have measured contact angles for pure Epikote 162® epoxy resin and Epicure 113® amine hardener in contact with HM-type graphite fibers which were treated to varying degrees by nitric acid oxidation. In order to obtain W_{sp} from such data, values for the work of cohesion (W_{ll}) for both the amine and the epoxy are required. The surface tension is related to the work of cohesion by the following expression:

$$\gamma = \tfrac{1}{2} W \tag{6}$$

Although values for surface tension for many materials are available in the literature, such values were not found for Epikote 162 and Epicure 113. Nevertheless, typical values for epoxy prepolymers range between 45 and 52 dyn/cm, and for amine hardeners between 23 and 26 dyn/cm.[20] Average values for these ranges have been used as estimates of the work of cohesion for Epikote 162 and Epicure 113. Estimated values of the work of spreading on HM carbon fibers (based on the contact angles measured by Fitzer *et al.*[23]) are reported in Table I.

The negative sign of W_{sp} for the epoxy fiber combinations shows that the interactions between the epoxy resin and the fiber surface are thermodynamically repulsive. Surface oxidation, however, substantially reduces the non-attractive nature of these interactions. The amine-fiber interactions are non-attractive for the high modulus fibers treated for the shorter periods of time and become attractive as the surface treatment is prolonged. Comparison of W_{sp} for the epoxy and amine shows that the amine is relatively more attracted to the graphite fiber surface than the epoxy. Thus, the fact that W_{sp} is greater for the amine indicates that the free energy of an epoxy-amine liquid mixture forced in contact with a graphite fiber surface will tend to be lower if a greater

TABLE I
Calculated values of work of spreading on HM carbon fibers for epoxy and amine monomers based on data by Fitzer *et al.*[23]

Fiber oxidation time (hours)	Liquid	W_{ll} (dyne/cm)	W_{sl} (dyne/cm)	W_{sp} (dyne/cm)
0	amine	49	48.5	− 0.9
5	amine	49	48.9	− 0.1
24	amine	49	< 49	> 0
0	epoxy	97	93.1	− 3.9
5	epoxy	97	94.6	− 2.4
24	epoxy	97	95.6	− 1.4

number of amine molecules than epoxy molecules interact with the surface. In conclusion, this analysis shows that a driving force exists for preferential adsorption of amines onto the carbon fiber surface in epoxy composites. This tendency is predicted to exist regardless of the surface treatment.

Kinetic Considerations—Reaction and Diffusion

The existence of a driving force to promote the accumulation of amine in the vicinity of carbon fiber surfaces directs attention to issues related to the rates of accumulation as governed by diffusion and reaction. The significance of these kinetic effects is considered in this section. A discussion of the kinetic processes associated with interphase development is presented for sized and unsized fiber systems. For unsized systems, an adsorption and diffusion model for interphase formation is analyzed in light of kinetic considerations, while for sized systems a similar analysis will be used to delineate the conditions under which sizings may cause the formation of interphases.

Interphase Formation In the Absence of Sizings

For this analysis, the composite system has been idealized, as shown in Figure 6, by two parallel flat surfaces which sandwich a region of resin and are separated by a distance 2L. Since the epoxy-amine curing reaction is an addition polymerization reaction, a distribution of reacting species of different chain lengths but with similar reactive groups develops during cure. Thus, a large set of species continuity equations spanning the distribution is needed to describe this diffusing and reacting system completely. We simplify the problem by assuming the following equation for the epoxy amine cure

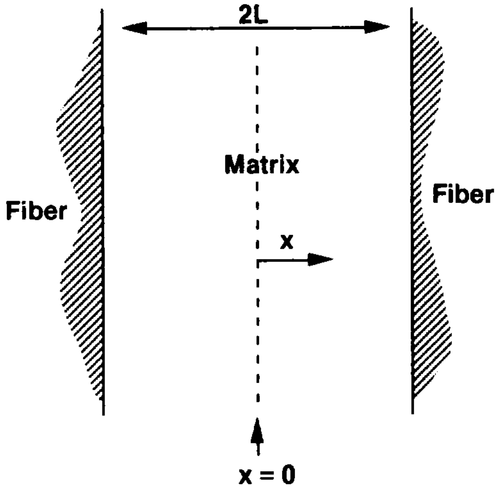

FIGURE 6 Idealized representation of the matrix region between two fibers. The fiber surfaces are represented by flat surfaces spaced a distance $2L$ apart. Distance, (x), is measured from the center-line between the two surfaces.

where the epoxy (E) and amine (A) can diffuse but the product (P) cannot.

$$E + A \rightarrow P \tag{7}$$

In essence, the epoxy and amine reacting groups have been lumped into two separate groups regardless of molecular weight or molecular association. The system is assumed to be stagnant and of constant density. Under these conditions, the one-dimensional species continuity equations are given by equations (8a–c). These describe the dependence of E, A, and P concentrations (c_E, c_A, c_P) on time (t), position (x), diffusivity ($D(\mathbf{c})$), and reaction rate ($R(\mathbf{c})$).

$$\frac{\partial c_E}{\partial t} = D_E(c)\frac{\partial^2 c_E}{\partial x^2} - R(\mathbf{c}) \tag{8a}$$

$$\frac{\partial c_A}{\partial t} = D_A(c)\frac{\partial^2 c_A}{\partial x^2} - R(\mathbf{c}) \tag{8b}$$

$$\frac{\partial c_P}{\partial t} = R(\mathbf{c}) \tag{8c}$$

These are three coupled differential equations with diffusivities and reaction rates as functions of composition ($\mathbf{c}$; the set of concentrations $\{c_E, c_A, c_P\}$). The characteristic length of interest is L. The problem is an internal one with fluxes of E and A set to zero at the center, and equated to the rate of adsorption at the surfaces. Equimolar counter-diffusion is assumed given the requirements of constant densities and no velocities. Therefore, the boundary conditions (B.C.) and initial conditions (I.C) are as follows.

$$\begin{aligned}
&\text{I.C. } t = 0: && c_E = c_{EO}, c_A = c_{AO}, c_P = 0\\
&\text{B.C. } x = 0: && \frac{\partial c_E}{\partial x} = \frac{\partial c_A}{\partial x} = 0\\
&x = L: && D_E(\mathbf{c})\frac{\partial c_E}{\partial x} = k_s c_E c_S(t)\\
& && D_A(\mathbf{c})\frac{\partial c_A}{\partial x} = k_s c_A c_S(t)
\end{aligned} \tag{9}$$

The rates of surface adsorption are assumed to vary with reactant concentration and surface site concentration (c_s); the sites are considered homogeneous. The surface site concentration is not constant since sites are not replenished as adsorption progresses. Hence the temporal vriation in site concentration is given by equation (10) and is a direct result of a site balance.

$$c_s(t) = c_s(0) - \int_0^t D_E(\mathbf{c})\left[\frac{\partial c_E}{\partial x}\right]_{x=L} dt - \int_0^t D_A(\mathbf{c})\left[\frac{\partial c_A}{\partial x}\right]_{x=L} dt \tag{10}$$

It is clear that due to extensive coupling and non-linearity, this system of partial differential equations (in conjunction with the initial and boundary conditions) is difficult to solve. A dimensional analysis conducted at this point would yield variable dimensionless groups. Therefore, some simplifications based on observations regarding epoxy-amine/graphite systems are helpful.

The primary intent of this analysis is to gain an understanding of the factors which influence the final composition of the region in the vicinity of the fiber surface. Once vitrification occurs, changes in chemical composition and structure are slow and represent only a small fraction of the changes that would have ocurred in the more "mobile" regime. Thus, the composition of the matrix just before vitrification is a good approximation to that of the final product and is all that is required for this treatment. With this in mind, constant and equal average diffusivities are assumed and the reaction rate is taken to be first order with respect to epoxide concentration. Furthermore, the fact that amines preferentially adsorb onto the fiber surfaces allows the flux of epoxy at the surface to be set to zero. Under these restrictions, equations (8a–c), (9) and (10) reduce to the following:

$$\frac{\partial c_E}{\partial t} = D\frac{\partial^2 c_E}{\partial x_2} - kc_E \tag{11a}$$

$$\frac{\partial c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x_2} - kc_E \tag{11b}$$

$$\frac{\partial c_P}{\partial t} = kc_E \tag{11c}$$

$$\text{I.C. } t=0: \quad c_E = c_{EO}, c_A = c_{AO}, c_P = 0$$

$$\text{B.C. } x=0: \quad \frac{\partial c_E}{\partial x} = \frac{\partial c_A}{\partial x} = 0$$

$$x = L: \quad \frac{\partial c_E}{\partial x} = 0$$

$$D\frac{\partial c_A}{\partial x} = k_S c_A\left[c_S(0) - D\int_0^t \frac{\partial c_A}{\partial x}\,dt\right] \tag{12}$$

The characteristic time for diffusion, t_d, is L^2/D^{25} where D is the average diffusivity for a specified isothermal cure temperature prior to vitrification, and the characteristic time for reaction in the bulk, t_{rb}, represents the time necessary for vitrification at a given isothermal cure temperature. By scaling time in equations (11a–c) and (12) with respect to the characteristic time for diffusion, position with respect to the characteristic length L, and concentrations with respect to the initial concentrations, it is apparent that for $t_d \ll t_{rb}$, the reaction terms drop out and diffusion equations for species E and A with no source terms survive. These results are summarized in Table II. The second order surface reaction cannot be faster than the rate at which reactants are supplied to the surface, thus the characteristic time for surface reaction, t_{rs}, should only be longer than, or nearly equal to, the characteristic time for diffusion. In the event that $t_d \approx t_{rs}$, then gradients will form on the time scale of diffusion. Yet, composition is desired at the time of vitrification. Since $t_d \ll t_{rb}$, at this later time no gradients survive; hence, the average concentrations will match the local concentrations and will depend on the amount of surface reaction that has occurred during that time.

TABLE II
Scaling of interphase diffusion equations

Scaling of equations (11a–c) and (12) with respect to t_d ($t_d \ll t_{rb}$)

$$\eta = \frac{x}{L} \quad \pi_E = \frac{c_E}{c_{EO}} \quad \pi_A = \frac{c_A}{c_{AO}} \quad \pi_{sP} = \frac{c_P}{c_{EO}} \quad \pi_S = \frac{c_S}{c_{SO}} \quad t_d = \frac{L^2}{D} \quad \tau = \frac{t}{t_d} \quad t_r = \frac{1}{k} \quad t_{rs2} = \frac{L}{k_S c_{SO}} \quad t_{rs1} = \frac{1}{k_S c_{AO}}$$

$$\frac{\partial \pi_E}{\partial \tau} = \frac{\partial^2 \pi_E}{\partial \eta^2} - \cancelto{0}{\left(\frac{t_d}{t_{rb}}\right)} \pi_E$$

$$\frac{\partial \pi_A}{\partial \tau} = \frac{\partial^2 \pi_A}{\partial \eta^2} - \cancelto{0}{\left(\frac{t_d}{t_{rb}}\right)} \pi_E$$

$$\frac{\partial \pi_P}{\partial \tau} = \cancelto{0}{\left(\frac{t_d}{t_{rb}}\right)} \pi_E$$

I.C. $\tau = 0$: $\pi_E = 1, \pi_A = 1, \pi_P = 0$

B.C. $\eta = 0$: $\dfrac{\partial \pi_E}{\partial \eta} = \dfrac{\partial \pi_A}{\partial \eta} = 0$

$\eta = 1$: $\dfrac{\partial \pi_E}{\partial \eta} = 0 \qquad \dfrac{\partial \pi_A}{\partial \eta} = \left(\dfrac{t_d}{t_{rs2}}\right)\pi_A - \left(\dfrac{t_d}{t_{rs1}}\right)\pi_A \displaystyle\int_0^{\tau} \dfrac{\partial \pi_A}{\partial \eta}\, d\tau$

Scaling of equations (11a–c) and (12) with respect to t_{rb} ($t_{rb} \ll t_d$)

$$\eta = \frac{x}{L} \quad \pi_E = \frac{c_E}{c_{EO}} \quad \pi_A = \frac{c_A}{c_{AO}} \quad \pi_P = \frac{c_P}{c_{EO}} \quad \pi_S = \frac{c_S}{c_{SO}} \quad t_r = \frac{1}{k} \quad \tau = \frac{t}{t_r} \quad t_d = \frac{L^2}{D}$$

$$\frac{\partial \pi_E}{\partial \tau} = \cancelto{0}{\left(\frac{t_{rb}}{t_d}\right)} \frac{\partial^2 \pi_E}{\partial \eta^2} - \pi_E$$

$$\frac{\partial \pi_A}{\partial \tau} = \cancelto{0}{\left(\frac{t_{rb}}{t_d}\right)} \frac{\partial^2 \pi_A}{\partial \eta^2} - \pi_E$$

$$\frac{\partial \pi_P}{\partial \tau} = \pi_E$$

I.C. $\tau = 0$: $\pi_E = 1, \pi_A = 1, \pi_P = 0$

B.C. No position dependence for $t_{rb} \ll t_d$

If, on the other hand, equations (11a–c) and (12) are scaled with respect to t_{rb} it becomes clear from Table II that for $t_{rb} \ll t_d$ the diffusion terms drop out and the surface characteristics of the fiber become unimportant as far as matrix reactions are concerned. Under these conditions, interphases will also not form.

The final possibility is that $t_{rb} \approx t_d$. In this case, scaling does not yield simplification of equations (11a–c) and (12) and complete solution is required. Therefore, it is under these conditions that interphasial gradients will form. The extent of the gradients will depend on the amount of preferential surface adsorption.

The foregoing considerations yield three reaction regimes for epoxy-amine composites which can shed light on the possibility of interphase formation. These are summarized in Table III. For the adsorption-diffusion model that is being considered, the possibility of interphase formation exists only when the characteristic time for diffusion and reaction are of the same order.

TABLE III
Reaction regimes for fiber-affected cure

Regime	Effect
$t_d \ll t_{rb}$	No interphase; fast rearrangement following adsorption
$t_d \approx t_{rb}$	Interphase; gradients frozen in place upon vitrification
$t_d \gg t_{rb}$	No interphase; not enough time for gradients to form before vitrification

Reacting epoxy systems can be categorized based on these regimes, and predictions of whether or not interphases will form based on the adsorption-diffusion model can be made without solving the above equations. We will illustrate such considerations for the Epon-828/PACM-20 system that has been characterized by Sanford.[26]

Figure 7 shows epoxy concentration curves for the Epon-828/PACM-20 system as a function of time for several isothermal cure temperatures. A kinetic analysis has shown that for the early stages of cure the reaction rate is first order with respect to epoxy concentration. The first order Arrhenius rate constant parameters reported by Sanford are $A = 97{,}000\,\mathrm{s}^{-1}$ and $E_a = 13{,}000\,\mathrm{cal/mol}$. The characteristic times for vitrification can be identified as the times at which the reaction rate becomes diffusion limited. Such values are reported in Table IV along with corresponding values for the reciprocal of the first order rate constant. Within a factor of order one, the time for vitrification can be estimated by the reciprocal of the first order rate constant (1/k).

Sanford[26] also reports values of diffusivity as a function of composition and temperature for this system. Table V tabulates the minimum values of diffusivity, prior to vitrification, for specific isothermal temperatures along with values of the characteristic time for diffusion calculated assuming L equal to $1\,\mu\mathrm{m}$, and values of the characteristic

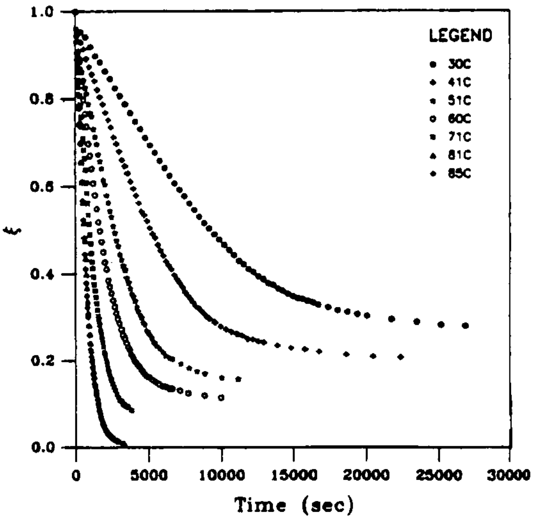

FIGURE 7 Dimensionless epoxide concentration *versus* cure time for isothermal cure of stoichiometrically-balanced mixtures of Epon-828/PACM-20 for isothermal cure at several temperatures (after Sanford[26]).

TABLE IV
Characteristic times for bulk reaction (t_{rb}) for the Epon-828®/PACM-20 system based on data from Sanford[26]

Temperature (°C)	$t_{rb} = t_{\text{vitrification}}$ (S)	$t_{rb} = \frac{1}{k}$ (S)
29	~ 15,000	26,410
60	~ 4,000	3,514
81	~ 1,500	1,096

TABLE V
Values of diffusivity and characteristic times for diffusion for the Epon-828®/PACM-20 system based on data by Sanford[26]

Temperature (°C)	Diffusivity (cm^2/s)	t_d(S) $L = 1\ \mu m$	t_{rb}(S)
29	$> .1$	< 100	15,000
60	> 10	< 1	4,000
81	> 100	$< .1$	1,500

time for reaction. In all cases $t_d \ll t_r$ and it is apparent without having to solve the continuity equations that interphases should not develop but that, rather, a homogeneous matrix having a composition affected on the average by the amount of amine adsorbed onto the fiber surface will form.

It was concluded in the previous section that a thermodynamic driving force exists for the amine component of an epoxy-amine resin mixture to adsorb preferentially onto graphite fiber surfaces. It had been postulated that the diffusion processes associated with the preferential adsorption might cause transient interphase composition gradients to form which are frozen in place upon vitrification. However, the foregoing kinetic scaling analysis indicates that in the absence of sizings such kinetic processes are not responsible for the formation of interphasial composition gradients. We conclude, therefore, that any interphase characterized by composition gradients are generated thermodynamically; that is, the interphase composition gradients will represent an equilibrium state of the region.

The thermodynamic analysis presented here takes into account only monomer-substrate interactions for the layer of molecules adjacent to the surfaces. A more sophisticated thermodynamic theory must be developed to relate monomer-monomer and monomer-substrate interactions to interphase equilibrium composition profiles spanning more than a monolayer. Such a theory will be the subject of a future communication.

Sizing Layers and Interphase Formation

Coatings are often applied to graphite fibers to protect their surfaces and to aid in processing. Such coatings are referred to as sizings. The manufacturers of fibers claim to design the thickness and composition of the sizings to enhance performance and they are not prone to divulging this information. However, it appears that typical fiber sizings designed for use with epoxy matrices are composed of low molecular weight epoxy monomers and range in thickness between 0.1 and 0.2 μm.[27] It has been proposed that during epoxy-amine cure of composites manufactured with epoxy-sized fibers, amine molecules diffuse into the epoxy-rich layer and form composition gradients which are frozen in place upon further reaction and vitrification.[28] The diffusion in this case is entropically driven. A schematic re- presentation of the process is given in Figure 8.

Figure 9 illustrates an idealized representation of the matrix region between sized fibers in a composite. The fiber surfaces are represented by flat parallel surfaces a distance $2L$ apart, and the sizing thickness is defined by h. The distance from the center-line to surfaces is given by x. In the absence of reaction, equation (13) describes the diffusion processes which may occur in this region for one species; *viz*

$$\begin{array}{lll} & & \dfrac{\partial c}{\partial t} = D\dfrac{\partial^2 c}{\partial x^2} \\ \text{I.C.} & t = 0 & c = c_0;\ \mathrm{x} \le h \\ & & c = c_{m0};\ x > h \\ \text{B.C.} & x = L & \dfrac{\partial c}{\partial t} = 0 \\ & x = 0 & \dfrac{\partial c}{\partial t} = 0 \end{array} \tag{13}$$

Solution of equation (13) quantifies the concentration of diffusing species (c) as a function of time (t), position (x), and diffusivity (D). The solution to this system has been reported by Crank [29] and is given by equation (14).

$$\frac{c(x,t) - c_{m0}}{c_0 - c_{m0}} = \frac{1}{2}\sum_{n=-\infty}^{\infty}\left\{\operatorname{erf}\frac{h + 2nL - x}{2(Dt)^{1/2}} + \operatorname{erf}\frac{h - 2nL - x}{2(Dt)^{1/2}}\right\} \tag{14}$$

Figure 10 displays epoxy concentration profiles as a function of distance from the fiber surface computed using equation (14) for a fiber separation of 1 μm and a pure epoxy

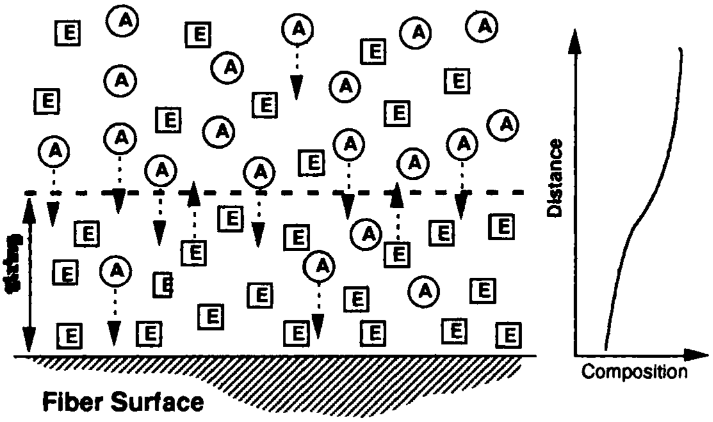

FIGURE 8 Schematic representation of diffusion of amine molecules from a mixture of epoxide and amine monomers into an epoxide-rich sizing layer coating a fiber surface. Such diffusion has been cited as a possible mechanism for interphase formation. Composition gradients which are set upon vitrification are assumed to form.

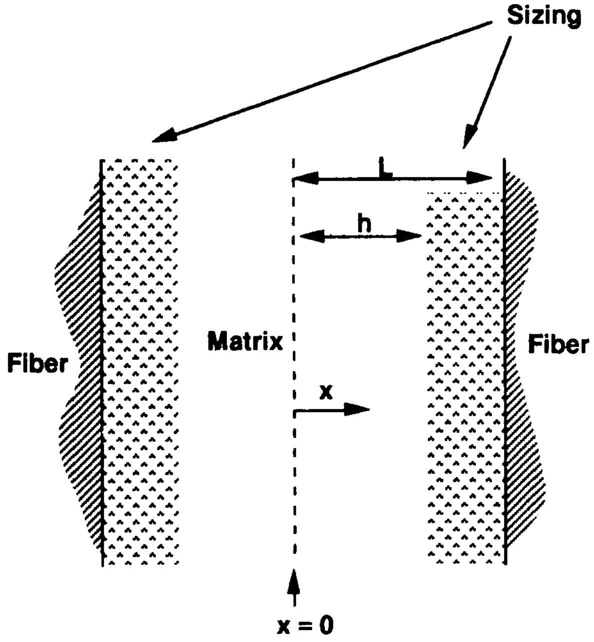

FIGURE 9 Schematic representation of the region between sized fibers. The distance from the fiber surface to the center-line between fibers is given by L, and h represents the distance from the surface of sizing to the center-line. Distance, *x*, is measured with respect to the center-line.

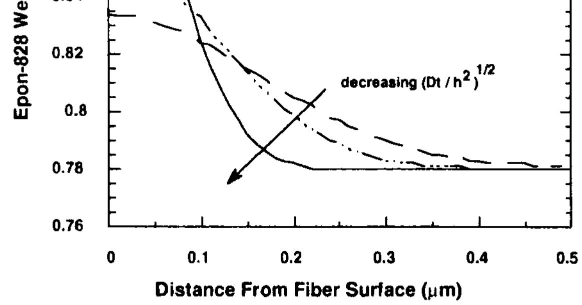

FIGURE 10 Calculated interphase composition profiles resulting from the presence of 0.05 μm sizings. $[(Dt/h^2)^{1/2} = .894$ (——); $(Dt/h^2)^{1/2} = 1.67$ (— --- -); $(Dt/h^2)^{1/2} = 2.28$ (— —)].

sizing layer thickness of 0.05 μm. It was assumed that the initial matrix composition corresponds to that of a stoichiometric mixture of Epon-828 and PACM-20. The solution of equation (14) depends on the parameter $(Dt/h^2)^{1/2}$. The smaller the value of this parameter the smaller and more pronounced the resulting profile will be. Therefore, for a fixed value of diffusivity, more time available for diffusion results in a broader and less pronounced interphase region.

The aforementioned solutions are meant to give an idea of the various types of interphasial composition profiles that can develop. As a first order approximation, the time is assumed to be the time for vitrification. Thus, for a particular resin system, the size of the interphase should be a function of the sizing thickness, reactivity and diffusivity.

In light of the scaling arguments presented in the previous section, three reaction regimes can be identified for the sized systems. These are summarized in Table VI. If the characteristic time for reaction is much less than the characteristic time for diffusion into the sizing, the matrix will react without interacting with the sizing, thus leaving the sizing layer unaffected. In this case, the original sizing becomes the interphase. On the other hand, for characteristic times of diffusion much less than that of reaction, complete diffusion will occur, resulting in a homogeneous matrix phase albeit with a different composition. The third possibility is that the characteristic times are of the same order of magnitude. In this case, interphasial gradients larger than the sizing thickness are expected.

Since typical sizings for carbon fibers are low molecular weight epoxies and cure is carried out at elevated temperatures, the analysis of Sanford's Epon-828/PACM-20 reactivity and diffusivity data [26] (Table V) is likely to apply to most sized systems. That is, typically, the characteristic times for diffusion are several orders of magnitude lower than the characteristic times for vitrification. Therefore, interphasial composition gradients are not expected to form as a result of the presence of sizings. Changes in composite mechanical behavior which may be observed as a result of the presence of a sizing layer are perhaps due to the homogeneous incorporation of the epoxy from the sizing into the rest of the resin phase. An epoxy sizing of modest thickness comprises a significant portion of the matrix phase for a high fiber volume fraction composite. For example, from Figure 1, a 0.1 μm sizing would constitute roughly seven percent of the matrix phase in a sixty percent volume fraction composite of 8 μm diameter fibers. This is sufficient to alter material properties significantly.

We conclude, based on this discussion, that it should be possible to tailor interphase structure using sizings, provided that the diffusivity of the sizing is such that the characteristic time for diffusion is of the same order of magnitude as the characteristic time for reaction. Control over the interphase structure could then be achieved by varying thickness and reaction conditions such as temperature.

TABLE VI
Reaction regimes for interphases in sized fiber systems

Regime	Effect
$t_d \ll t_{rb}$	No interphase; fast homogeneous incorporation of sizing material
$t_d \approx t_{rb}$	Interphase; gradients frozen in place upon vitrification
$t_d \gg t_{rb}$	Sharp interphase; not enough time for sizing material to diffuse

SUMMARY AND CONCLUSIONS

Two commonly-accepted mechanisms for interphase formation in epoxy-amine thermosetting composite systems have been analyzed in light of thermodynamic and kinetic considerations. These are: a), the diffusion of amine curing agent from the bulk resin into epoxy-rich sizings; and b), the preferential adsorption of amine curing agent onto carbon fiber surfaces.

It was shown that the cure of a sized system can be categorized in terms of the three regimes summarized in Table VI, and that for typical sizings and reaction conditions interphasial gradients are not expected to form as a result of the presence of sizings. The possibility exists, however, that interphases of varying structure can be formed by insuring, through proper selection of materials and processing conditions, that the characteristic times for diffusion and reaction are of the same order of magnitude.

A thermodynamic analysis was used to quantify the relative interactions of epoxy and amine monomers with graphite fibers. The results from this treatment show that there exists a thermodynamic driving force for the preferential adsorption of amines onto carbom fiber surfaces from epoxy-amine mixtures. However, kinetic analyses indicate that preferential surface adsorption of amine is not sufficient to explain either the existence of interphases larger than one monolayer or the relatively-pronounced effects observed in fiber affected cure of epoxy-amine resins. A more sophisticated thermodynamic treatment is needed to describe the formation of interphase composition profiles spanning more than a monolayer and resulting from monomer-monomer and monomer-substrate interactions. This will be the subject of a future comunication.

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