MODELING OF INTERPHASE FORMATION ON UNSIZED FIBERS IN THERMOSETTING COMPOSITES

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ABSTRACT
The interphase is the region between the fiber and matrix whose properties strongly influence the overall composite behavior in terms of mechanical strength, chemical and thermal durability. The composition and thickness of the interphase region is governed by the processing conditions, in addition to the fiber surface treatments and other characteristics of the fiber and the resin materials. One of the strong contributing mechanisms to interphase formation is the preferential adsorption of matrix components onto the fiber surface, which takes place on the order of molecular scales. Chemical reaction in the matrix also happens simultaneously with the adsorption process. In this paper, a multi-layer adsorption-desorption-reaction model for a binary fluid mixture in contact with a solid surface is implemented to study the kinetics of interphase formation near bare fiber surfaces in thermosetting composite systems. Composition and thickness evolution of the interphase are predicted as functions of time. Conditions that lead to interphase formation upon vitrification are identified. Parametric studies are presented to investigate the effects of various nondimensional groups on the interphase region development.

NOMENCLATURE

\( E_{a,A} \) adsorption activation energy of amine molecules, [J/kg]
\( E_{a,E} \) adsorption activation energy of epoxy molecules, [J/kg]
\( E_{d,A} \) desorption activation energy of amine molecules, [J/kg]
\( E_{d,E} \) desorption activation energy of epoxy molecules, [J/kg]
\( k_{a,A} \) adsorption rate of amine molecules \([s^{-1}]\)
\( k_{a,E} \) adsorption rate of epoxy molecules \([s^{-1}]\)
\( k_{d,A} \) desorption rate of amine molecules \([s^{-1}]\)
\( k_{d,E} \) desorption rate of epoxy molecules \([s^{-1}]\)
\( N_0 \) number of adsorption sites available for adsorption on the fiber surface
\( N_0 \) dimensionless variable \( \frac{N_0}{N_E,0} \)
\( N_i \) total number of adsorbed resin molecules in \((i)th\) layer
\( N_{i,0} \) total number of resin molecules in the bulk state in \((i)th\) layer
\( N_{A,0} \) initial number of amine molecules at any layer
\( N_{A,i} \) number of adsorbed amine molecules in \((i)th\) layer
\( N_{A,i} \) dimensionless variable \( \frac{N_{A,i}}{N_{E,0}} \)
\( N_{A,\infty} \) number of amine molecules in the bulk state in \((i)th\) layer
\( N_{A,\infty} \) dimensionless variable \( \frac{N_{A,\infty}}{N_{E,0}} \)
\( N_{E,0} \) initial number of epoxy molecules at any layer
\( N_{E,i} \) number of adsorbed epoxy molecules in \((i)th\) layer
\( N_{E,i} \) dimensionless variable \( \frac{N_{E,i}}{N_{E,0}} \)
\( N_{E,\infty} \) number of epoxy molecules in the bulk state in \((i)th\) layer
\( N_{E,\infty} \) dimensionless variable \( \frac{N_{E,\infty}}{N_{E,0}} \)
\( N_{P,i} \) number of product segments in \((i)th\) layer due to the reaction in the adsorbed state
\( N_{P,i} \) dimensionless variable \( \frac{N_{P,i}}{N_{E,0}} \)
\( N_{P,\infty} \) number of product segments in \((i)th\) layer due to the reaction in the bulk state
\( N_{P,\infty} \) dimensionless variable \( \frac{N_{P,\infty}}{N_{E,0}} \)

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The objective of this paper is to develop a theoretical model for the prediction of the interphase growth with time during thermosetting composite processing, accounting for the simultaneous cure reaction. The model describes the mass transfer of the monomer coating on the fiber surface; the presence of thin monomer coating on the fiber.

Adsorption from a mixture of polymer chains and solvent molecules near a surface was presented by Scheutjens and Fleer [7] using a statistical approach. The partition function for the mixture was evaluated using a quasi-crystalline lattice model, which in turn gave the number of chains in each conformation in equilibrium. The focus of the work was on polymer adsorption, whereas the interphase formation in thermosetting materials is based on monomer transport.

The objective of this paper is to develop a theoretical model for the prediction of the interphase growth with time during thermosetting composite processing, accounting for the simultaneous cure reaction. The model describes the mass transfer of the monomer components in the composite system before the formation of the polymer macromolecules. Clearly, the intention is not to study all of the above-mentioned mechanisms contributing to interphase development. Rather, focus is placed on the mechanism of preferential adsorption of the resin components. The model development and analysis presented is based on the

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### INTRODUCTION

It is commonly realized that thermosetting composite materials are not just made up of two components, namely, resin and fiber. Due to the physical and chemical interactions between the matrix and the fiber, an intermediate layer—interphase—forms which has different composition and mechanical properties from the bulk matrix and fiber. The layer serves as a buffer between the original components, and it must be well designed to take the full advantages of the reinforcing fibers. Since the properties of the bulk resin and fiber for common composite system are well known or easily to be determined, the mechanical, thermal and chemical properties of the interphase are therefore the major issue to be investigated.

Prediction of the overall composite properties in the presence of the interphase region involves the following steps [1]:

- First, the manufacturing parameters must be linked with the interphase structures. For example, given a cure temperature and pressure cycle, the chemical composition of the interphase should be determined. In this step, physical and chemical mechanisms must be identified and modeled to give the interphase structure prediction.
- In the second step, the known interphase structure is related to the interphase material properties such as glass transition temperature, flexural modulus or the thermal expansion coefficient. This step is primarily based on experimental correlation of the interphase chemical composition to the measured interphase material properties.
- The last step is then to link the interphase material properties to overall composite properties such as the strength, fracture and environmental resistance.

A majority of the studies in the literature focus on the experimental determination of the influence of interphase layers on the behavior of composite materials [2–5, for example], i.e., steps 2 and 3 above. Surface treatment and sizing parameters are widely varied to tailor the structure of the interphase region and to examine the effects of different interphases on the mechanical behavior of the composite materials. Several studies have been conducted in this step using experimental approaches or numerical calculations such as finite element methods [4, 6]. The studies so far have provided insights into qualitative descriptions of the interphase regions and their influence on the composite properties for typical material systems used in practice.

The first step, i.e., the prediction of the interphase structure as a function of the process parameters forms the basis of the other two steps. However, due to the great mechanistic complexities involved, few investigations have been conducted in this area. The overhead comes from the fact that a dozen of physical and chemical mechanisms contribute simultaneously to the formation of the interphase region and only few of these mechanisms can be rigorously described in a mathematical manner. Some examples of the possible mechanisms are [4]: the skin area of the fiber might have morphological deviation from the bulk fiber; surface roughness of the fiber causes non-uniform deposition of the resin; surface proximity of the fiber changes the structure of the resin in the interphase; surface treatments give rise to chemically and structurally different regions near fiber surface; exposure to air before composite processing results in adsorption of impurities which are desorbed at elevated temperatures; the adsorption of the resin components onto the fiber surface; the presence of thin monomer coating on the surface of the fiber.

Palmese [1] presented a model to predict the interphase composition under the condition of thermodynamic equilibrium of the constituent resin and catalyst systems. Based on a Flory-Huggins type formulation of the Gibbs free energy [1], phase equilibrium was setup accounting for enthalpy interactions between fiber surface and resin monomers. The model did not take the chemical reactions into account and was reported to be useful in describing the composition of thin interfaces. Further, owing to the assumption of equilibrium state, the model can not describe the evolution of the interphase with time.
INTERPHASE FORMATION MODEL

During the manufacture of thermosetting composites, the prepolymer (or monomer) molecules react with a curing agent (or hardener) to form a crosslinked network that can not flow upon vitrification. The presence of the reinforcing fibers has been found to significantly alter the resin composition near the fiber surface [1] and in turn the cure characteristic of the fiber-resin mixture. The main goal of the present study is to predict the concentration profiles of the constituent species in the vicinity of the fiber surfaces. In the following discussion, we consider the graphite fiber/epoxy-amine thermosetting system as an example; however, all the model development and the results presented are applicable to a general two-component thermosetting system.

The geometry considered is the inter-fiber domain in a typical staggered arrangement of fibers in a composite [Fig. 1(a)]. In the model development, this domain is idealized as the region between two identical infinite planes which represent the fiber surfaces, as illustrated in Fig. 1(b). The epoxy (E) and amine (A) molecules are distributed uniformly between the two surfaces at \( t = 0 \); corresponding to a system without sizing applied to the fiber surfaces. The two species begin chemical reaction after \( t = 0 \); simultaneously, mass transfer of epoxy and amine molecules in the direction towards the surfaces occurs via adsorption and desorption processes caused by a “force field” of the fiber surfaces. The mass transfer causes the aggregation of the epoxy and amine molecules near the surface and forms a concentration profile which is “frozen” in space upon gelation of the thermosetting system.

In the following description, the domain between the two fiber surfaces is divided into molecular layers where one molecule of epoxy or amine can occupy only one of these layers, and \( N_L \) is the total number of molecular layers in the half domain (Fig. 2). Due to the interactions between matrix molecules and the fiber surface, as well as those among matrix molecules themselves, epoxy and amine molecules can move from layer to layer. The molecular movements near an adsorbing solid surface have been described in a multilayer adsorption model developed by Brunauer, Emmett and Teller, referred to as BET theory. The BET model considers a balance between the adsorption and desorption processes caused by a “force field” of the solid surface.

The adsorption phenomenon is considered to be a two-species process, where the adsorption and desorption rates are given by the BET isotherm. The BET model is based on the assumption that the adsorption of molecules on the surface is a random process that follows the principle of mass conservation. The BET model is a powerful tool for predicting the adsorption and desorption behavior of molecules on solid surfaces. In the present study, the BET model is used to simulate the adsorption and desorption behavior of epoxy and amine molecules on the fiber surfaces.

The adsorption equilibrium is described by the BET isotherm, which relates the amount of adsorbed molecules to the pressure of the molecules in the bulk. The BET isotherm is given by the following equation:

\[
\frac{t}{t_0} = \frac{1}{1 + \alpha_b P} + \frac{\alpha_b}{\alpha_b + \frac{1}{P}}
\]

where \( t \) is the amount of adsorbed molecules, \( t_0 \) is the amount of molecules adsorbed at saturation, \( \alpha_b \) is the adsorption coefficient, and \( P \) is the pressure of the molecules in the bulk.

The BET model is used to simulate the adsorption and desorption behavior of epoxy and amine molecules on the fiber surfaces. The BET model is based on the assumption that the adsorption of molecules on the surface is a random process that follows the principle of mass conservation. The BET model is a powerful tool for predicting the adsorption and desorption behavior of molecules on solid surfaces. In the present study, the BET model is used to simulate the adsorption and desorption behavior of epoxy and amine molecules on the fiber surfaces.
may be regarded as a distinct phase with respect to the bulk. The adsorbed molecules can also be desorbed into the bulk as a reverse process. These two processes balance each other at equilibrium, and the concentration of the molecules in each layer can be obtained. In the present study, the equilibrium formulation is extended to include the time-dependent (transient) mass migration, and the simultaneous reaction among the species as encountered in thermosetting composite material processing, with the objective of determining the time evolution of the concentration profiles.

The scenario shown in Fig. 2 is formed as follows: The catalyzed resin surrounding the fiber is composed of two states—the bulk state and the “adsorbed” state near the fiber surface. All the analyzed resin surrounding the fiber is composed of two states—the bulk and the “adsorbed” state near the fiber surface. At the beginning of the process, some molecules are adsorbed from the bulk into the first layer and occupy the adsorption sites of the bare fiber surface. At the next time step, three mass movements could happen: molecules adsorbed in the first layer could be desorbed into the bulk, (2) the molecules in the bulk could be continuously adsorbed into the first layer at the remaining adsorption sites on the bare fiber surface, and (3) molecules in the bulk could be adsorbed on top of the molecules in the first layer, forming the second adsorption layer. Similar processes continue and result in a multilayer adsorption scenario as shown in Fig. 2.

Chemical reaction between epoxy and amine happens simultaneously during the adsorption and desorption processes. The reaction equation can be written as:

\[ n_1E + n_2A \rightarrow P \]  

(1)

where \( P \) stands for the product, \( n_1 \) and \( n_2 \) are number of moles of the reactants needed to produce one mole of product. The reactions within a thermosetting system form a product with a network structure, which is treated in the model simply as a product molecule.

Considering the mass balance for the epoxy molecule in the \((i)th\) adsorbed layer in Fig. 2, we obtain the following equation:

\[
\frac{dN_{E,i}}{dt} = k_{a,E}S_{i-1}e^{-\frac{E_a,E}{RT}} \frac{N_{E,\infty}}{N_i} - k_{d,E}S_{i+1}e^{-\frac{E_a,E}{RT}} \frac{N_{E,i}}{N_i} - n_1k_r \frac{N_{E,i}}{N_i + N_{\infty} + N_{P,1} + N_{P,\infty}}
\]

(2)

In Eqn. (2), \( dN_{E,i} \) is the rate of change of the total number of epoxy molecules adsorbed in the \((i)th\) layer, and the subscripts \( E \) and \( i \) denote epoxy and \((i)th\) layer, respectively.

The parameter \( k_{a,E} \) in the “adsorption” term in Eqn. (2) is defined as the adsorption rate of epoxy molecules, and \( S_{i-1} \) is the number of available sites in the \((i-1)th\) layer which are open for adsorption. From a physical point of view, the parameter \( k_{a,E} \) should vary from layer to layer, corresponding to a progressively decreasing adsorption “force field” away from the fiber surface. Since the variation of \( k_{a,E} \) is not readily obtained from existing theoretical or experimental means, the adsorption rate, \( k_{a,E} \), is assumed to be constant as in the BET theory [9, 10]. The same assumption is made to the other adsorption/desorption rates in the following discussion. Because a molecule adsorbed into the \((i)th\) layer must adjoin an epoxy or amine molecule in the \((i-1)th\) layer, \( S_{i-1} \) can be found as \( S_{i-1} = N_{i-1} - N_i \), where \( N_i \) is the total number of molecules adsorbed into the \((i)th\) layer, i.e., \( N_i = N_{E,i} + N_{A,i} \). The exponential term \( e^{-\frac{E_a,E}{RT}} \) includes the activation energy of adsorption \( E_a,E \) for the epoxy molecules, which defines the energy barrier for an epoxy molecule to be adsorbed. The parameters \( N_{E,\infty} \) and \( N_{A,\infty} \) are the number of epoxy and amine molecules in the bulk state in the \((i)th\) layer, and \( N_\infty = N_{E,\infty} + N_{A,\infty} \). Considering the molecular distribution of a bulk state to be uniform over the whole geometric domain, a subscript \( i \) is not necessary for \( N_\infty \), \( N_{E,\infty} \) and \( N_{A,\infty} \). The fraction \( \frac{N_{E,i}}{N_\infty} \) in the “adsorption” term denotes the probability (taken to be equal to the epoxy mole fraction in the bulk) that a site can capture an epoxy molecule from the bulk.

The parameters involved in the “desorption” term in Eqn. (2) follow a similar definition as their counterparts in the adsorption rate expression. The reader is referred to the nomenclature section for the parameter definitions. It is worth noting that the fraction \( \frac{N_i}{N_\infty} \) in the “desorption” term arises from the fact that among all the molecules desorbed from the \((i)th\) layer, the probability of finding an epoxy molecule is its mole fraction in this layer. The “depletion” term is determined by the crosslinking chemical reaction between epoxy and amine, where \( k_r \) is the reaction rate and \( \frac{N_{E,i}}{N_i + N_{\infty} + N_{P,1} + N_{P,\infty}} \) is the mole fraction of epoxy in the \((i)th\) layer. The parameter \( N_{P,j} \) is the number of product molecules in the \((i)th\) layer which results from the chemical reaction in the adsorbed state, while \( N_{P,\infty} \) originates from the reaction in the bulk.

Following a similar mass conservation analysis for the amine and the product molecules, we obtain the rate equations for these species as follows:

\[
\frac{dN_{A,i}}{dt} = k_{a,A}(N_{i-1} - N_i)e^{-\frac{E_a,A}{RT}} \frac{N_{A,\infty}}{N_i} - k_{d,A}(N_i - N_{i+1})e^{-\frac{E_a,A}{RT}} \frac{N_{A,i}}{N_i} - n_2k_r \frac{N_{E,i}}{N_i + N_{\infty} + N_{P,1} + N_{P,\infty}}
\]

(3)
\[
\frac{dN_{P,i}}{dt} = k_r \frac{N_{P,i}}{N_i + N_{\infty} + N_{P,i} + N_{P,\infty}} \tag{4}
\]

Note that the right hand side of Eqn. (4) has only the reaction term since the product molecules are assumed to have no mobility, and will stay in their space of formation.

Equations (2)–(4) pertain to the mass transfer rates of the molecules in the adsorbed state. As pointed out earlier, the adsorbed materials exchange mass with the bulk resin, which indicates that the rate equations for species in the bulk state must be solved simultaneously with those corresponding to the adsorbed state. Considering the rate of change of the number of epoxy molecules in the bulk state (i.e. \( \frac{dN_{E}}{dt} \)), three contributions are identified: (1) epoxy molecules being desorbed from each of the adsorbed layers which increases the number of epoxy molecules in the bulk [i.e., the “desorption” term in Eqn. (2)], (2) epoxy molecules being adsorbed from the bulk to the adsorbed state which decreases the number of epoxy molecules in the bulk [i.e., the “adsorption” term in Eqn. (2)], and (3) chemical reaction in the bulk. From its definition, \( N_{E,\infty} \) can be interpreted as an average value in each layer, therefore, the above-mentioned contributions from each layer are averaged in Eqn. (5) in the following way: (1) the chemical reaction rate is proportional to the mole concentration of epoxy in the bulk, which is determined by dividing the total number of epoxy molecules in the bulk, \( N_L N_{E,\infty} \) by the total number of reactant and product molecules in the bulk, \( \sum_i [N_i + N_{\infty} + N_{P,i} + N_{P,\infty}] \) and (2) the desorption and adsorption from each of the layers are summed and divided by the total number of molecular layers, \( N_L \).

\[
\frac{dN_{E,\infty}}{dt} = -n_1 k_i \sum_i \frac{N_{E,\infty} N_L}{N_i + N_{\infty} + N_{P,i} + N_{P,\infty}} + \sum_i [R_{d,E}(i) - R_{a,E}(i)] \tag{5}
\]

where \( R_{a,E}(i) \) and \( R_{d,E}(i) \) are identified in Eqn. (2). Similarly, we can get the rate equations for \( N_{A,\infty} \) and \( N_{P,\infty} \) as

\[
\frac{dN_{A,\infty}}{dt} = -n_2 k_i \sum_i \frac{N_{A,\infty} N_L}{N_i + N_{\infty} + N_{P,i} + N_{P,\infty}} + \sum_i [R_{d,A}(i) - R_{a,A}(i)] \tag{6}
\]

\[
\frac{dN_{P,\infty}}{dt} = k_i \sum_i \frac{N_{E,\infty} N_L}{N_i + N_{\infty} + N_{P,i} + N_{P,\infty}} \tag{7}
\]

The unknowns in Eqns. (2)–(7) are \( N_{E,i}, N_{A,i}, N_{P,i}, N_{E,\infty}, N_{A,\infty}, \) and \( N_{P,\infty} \). Additionally, the number of molecules at the \( (N_L + 1)th \) layer—\( N_{E,N_L+1}, N_{A,N_L+1} \), and \( N_{P,N_L+1} \)—are unknowns corresponding to the domain boundaries. Therefore, when \( i \) goes from 1 to \( N_L \), we have three more unknown variables than equations. The symmetry conditions at the middle plane provide three additional equations as

\[
N_{E,N_L} = N_{E,N_L+1}; \quad N_{A,N_L} = N_{A,N_L+1}; \quad N_{P,N_L} = N_{P,N_L+1} \tag{8}
\]

Equations (2)–(4) (where \( i = 1, 2, \cdots, N_L \)) with Eqns. (5)–(7) and the symmetry conditions [Eqn. (8)] constitute a complete ordinary differential equation (ODE) system for the \( 3N_L + 3 \) unknowns. The ODE system can be solved given the following initial conditions

\[
\begin{align*}
N_{E,i} &= N_{A,i} = N_{P,i} = N_{P,\infty} = 0; \\
N_{E,\infty} &= N_{E,0}; N_{A,\infty} &= N_{A,0}; (i = 1, 2, \cdots, N_L)
\end{align*}
\tag{9}
\]

The parameters in the ODEs are the kinetic rates (\( k_{a,E}, k_{d,E}, k_{a,A}, k_{d,A}, k_r \)) and the activation energies (\( E_{a,E}, E_{d,E}, E_{a,A}, E_{d,A} \)).

Equations (2)–(7) are solved using a fourth order Runge-Kutta method [12]. Corresponding to the numerical range of the dimensionless groups introduced later in the paper, a dimensionless time step of 0.01 is found to yield converged results. Using this time step for a calculation case with 313 molecular layers (\( N_L = 313 \)) and a reaction rate \( k_r = 10 \), a typical CPU time of one minute is needed for the epoxy-amine system to reach its gelation point, which is defined as the minimum degree of cure among all of the molecular layers equals to 0.4, i.e., \( \min \alpha(i) = \min \frac{N_{E,i} - N_{E,\infty}}{N_{E,i}} = 0.4 \).

RESULTS AND DISCUSSION

The model developed in the previous section is used to simulate the interphase evolution under isothermal conditions, \( T = T_0 \). The main objective of the theoretical study is to illustrate the effects of different parameters on the interphase composition and thickness. A dimensionless form of Eqns. (2)–(9) is used to identify relevant non-dimensional groups that govern the process.

Introducing a dimensionless time, \( t' \), as \( k_{a,E} e^{-\frac{k_{d,E}}{RT_0}} t \), and dividing all the number of molecules (\( N_{E,i}, N_{A,i}, N_{P,i} \)) by the initial number of epoxy molecules \( N_{E,0} \) (e.g., \( N'_{E,i} = N_{E,i}/N_{E,0} \)), the dimensionless groups are identified as follows: (1) epoxy desorption ratio \( \beta_E = k_{d,E} a_{E,E} e^{-\frac{k_{d,E}}{RT_0}} \), (2) amine desorption ratio \( \beta_A = k_{d,A} a_{A,E} e^{-\frac{k_{d,A}}{RT_0}} \), (3) amine adsorption ratio \( \alpha_A = k_{a,A} a_{E,A} e^{-\frac{k_{a,A}}{RT_0}} \), and (4) adsorption Damköhler number \( \gamma = \frac{k_r a_{E,E} a_{E,A}}{RT_0} \) where \( T_0 \) is the isothermal temperature at which the process takes place.
The molecular layers may be related to physical dimensions in composites system as shown here in a sample calculation for the EPON-828/PACM-20 thermosetting system. First, the distance between fiber surfaces \( L \) is calculated based on a staggered fiber arrangement as shown in Fig. 1(a). The fiber volume fraction, \( v_f \), the fiber diameter, \( d \), and the distance between fiber centers \( R \) are related by the expression \( v_f = \frac{\pi}{2\sqrt{3}} \left( \frac{d}{R} \right)^2 \). The sizes of EPON-828 and PACM-20 molecules are estimated assuming the molecules to be spheres, and a uniform molecular weight distribution equal to the average molecular weight. Note that the calculation could be refined by accounting for a monomer molecular weight and shape distribution to arrive at better estimates of the sizes. The molecular volume \( v_m \) is found as \( v_m = \frac{M}{\rho \ N_A} \), where \( M \), \( \rho \) and \( N_A \) are molecular weight, density and Avogadro’s number, respectively. The thickness of each molecular layer is estimated as \( \frac{1}{3} \). Given the distance \( L \) as \( R - d \), and the molecular volume \( v_m \), the number of layers in the half domain is calculated as \( N_L = \frac{L}{v_m} \). The value of \( N_L = 313 \) used in the results presented in this section is based on the following parameters: \( v_f = 0.67 \), \( d = 6 \mu m \); for EPON-828 epoxy \( M = 382.4 \) and \( \rho = 142.26 \) kg/m\(^3 \) [1].

Figure 3 shows the distributions of the number of epoxy and amine molecules from the fiber surface (Layer 1) to the middle plane (Layer 313) at different nondimensional times during the process. The results correspond to the parameter combination of \( \gamma = 0 \), \( \beta_E = \alpha_A = 0.5 \), \( \beta_A = 0.1 \), \( N'_{E,0} = N'_{A,0} = 1 \), \( N_0 = 0.25 \) (\( N_0 = \frac{N_0}{N_0} \)), where \( N_0 \) is the number of adsorption sites at the fiber surface. The adsorption Damköhler number (\( \gamma \)) is set to zero in order to examine the effects of the adsorption and desorption processes in the absence of chemical reactions. The desorption ratio \( \beta_A \) is chosen to be relatively small which indicates that the resin molecules are easily adsorbed onto the solid surfaces. In the vicinity of a fiber surface, we observe the number of molecules for both of the species increase due to adsorption onto the surface, resulting in a high concentration region near the fiber surface and a low concentration region near the middle plane. The “interphase thickness,” \( \delta \), is defined in a similar way as the boundary layer thickness in fluid mechanics, i.e., \( \delta \) equals to the number of layers where the number of epoxy molecules is within 1% of the number of epoxy molecules in the layer adjacent to the middle plane (Fig. 3). Note that the thickness defined in this way is an estimate and it could alternatively be defined based on the amine concentration profile or a combination of epoxy and amine concentration profiles. In this paper, all the thickness data are obtained from the epoxy profiles. The interphase is thin at an early time (\( t' = 100 \)) and grows as the process progresses (\( t' = 1000 \)). For the combination of parameters in Fig. 3, owing to the absence of the reaction and the relatively small desorption, the influence of the fiber surface propagates all the way to the middle plane leading to very thick or no distinct interphase formation at equilibrium. The number of epoxy molecules near the fiber surface is larger than that of the amine molecules owing to the larger epoxy adsorption rate (\( \alpha_A = \frac{k_{EA}}{v_m} = 0.5 \)). As an effect of mass balance, the number of epoxy molecules near the middle plane are smaller.

Figure 4 shows the interphase evolution for the same parameter setting as in the case of Fig. 3 except that the amine desorption ratio \( \beta_A \) was increased to 0.4; all other parameters retain the same values as previously stated. The interphase thickness increases from \( t' = 10 \) to \( t' = 300 \), and remains invariant afterwards (Fig. 4). An equilibrium state is thus reached, where the desorption and adsorption processes balance each other and a finite interphase region forms near the fiber surface. This scenario is in contrast to what was seen in Fig. 3, where a strong “force field” by the fiber surface penetrates the entire resin domain. By increasing \( \beta_A \), the desorption process is strengthened with respect to adsorption, which corresponds to a relatively weak...
“force field” by the fiber surface that can only penetrate into a few molecular layers.

The growth of the interphase is further influenced by the reaction. As mentioned earlier, the interphase is set in its thickness and composition profile upon the reactions reaching the gel point. Interphase thickness at the gelation point of the thermosetting system is an important parameter in the calculation of overall composite properties and performance. In Fig. 5, the interphase thickness is defined as number of epoxy layers where the number of molecules reaches within 1% of the bulk value and in the case of the epoxy-amine system the maximum value is 313. For \( \gamma = 0 \), i.e., no chemical reaction and an infinitely long gelation time, the thickness is the maximum value 313 when the epoxy desorption ratio \( \beta_E \) goes from 0 to 0.26 (Interval 1 in Fig. 5), which corresponds to strong “force fields” by the fiber surfaces whose influence can reach the middle plane. From \( \beta_E = 0.26 \) to 0.4 (Interval 2 in Fig. 5), the thickness decreases from 313 to a few molecular layers (around 10 in this case), which corresponds to moderate “force fields” by the fiber surfaces, and when \( \beta_E > 0.4 \) (Interval 3 in Fig. 5), the thickness approaches a small value due to weak “force fields.”

The curve corresponding to the adsorption Damköhler number \( \gamma = 0 \) sets an upper limit on the interphase thickness, since in the presence of the reaction, the interphase development is limited to time instants prior to gelation. For Interval 3, the influence of different \( \gamma \) values (reaction rates) is negligible because the upper bound of the interphase thickness \( \delta \) is small (around 5 this case) and \( \delta \) can only change in the small range from 0 to 5. However, in Intervals 1 and 2, \( \gamma \) emerges a strong control variable which can dramatically change the interphase thickness. As the value of \( \gamma \) increases (equivalently, as the reaction time scale decreases) the thermosetting system is quickly vitrified, leading to reduced time available for the adsorption and desorption processes, and the resulting interphase thickness is small.

Figure 6 presents the interphase thickness as a function of the amine adsorption ratio \( \alpha_A \) and the adsorption Damköhler number \( \gamma \) for fixed values of the other parameters. The parameter \( \alpha_A \) reflects the relative attraction strength of the fiber surface to the epoxy and amine molecules, with \( \alpha_A > 1 \) denoting a preferential adsorption of the amine molecules. By increasing \( \alpha_A \), surface attraction to amine molecules is strengthened, which leads to thicker interphases rich in amine concentration. The influence of \( \gamma \) can be discussed by similar consideration as above. In this case it is found that when \( \alpha_A > 1.0 \), the reaction rate \( \gamma \)
has significant influence on the interphase thickness, while for \( \alpha_A < 1.0 \), the thickness is smaller than or equal to 10 and does not change too much with varying \( \gamma \).

From Eqsns. (2)–(3) it follows that the amine desorption ratio \( \beta_A \) has the same parametric effect as the epoxy desorption ratio \( \beta_E \) in that large values of \( \beta_A \) and \( \beta_E \) weaken the “force field” of the fiber surface. This prediction is validated by Fig. 7 where interphase thickness is plotted as a function of \( \beta_A \) and \( \gamma \), presenting qualitatively similar trends as in Fig. 5. Again, the curve \( \gamma = 0 \)
in Fig. 7 gives the upper limit of the interphase thickness. When \( \beta_A < 0.25 \), the influence of the fiber surface can penetrate all the way to the middle plane, while increasing \( \beta_A \) results in smaller interphase region with less amine molecules being adsorbed. Although Figs. 5 and 7 give similar thickness variations with corresponding desorption rates, it must be pointed out that the interphase compositions in the two cases are different, i.e., large \( \beta_E \) value corresponds to an epoxy-deficient interphase while large \( \beta_A \) value corresponds to an amine-deficient interphase. Obviously, these two types of interphase will lead to completely different properties of the composite material.

The predicted interphase thicknesses are important input data to the models which calculate the overall composite material properties [1]. In this paper, interphase thicknesses ranging from a few molecular layers to a few hundred layers was found depending on the parameter combinations. Similar results were reported from the theoretical predictions of Palmese [1] and the experimental studies of Sergeyeva [8]. These studies provide preliminary validation of the present model predictions. However, direct comparison of interphase composition profiles with experimental measurements is imperative for a detailed validation. It is also common practice to apply a “sizing” layer to the fiber before composite fabrication. The influence of the “sizing” needs to be included in the adsorption model. Moreover, the size distribution of resin molecules and their shape effects are ignored in the present model. It is most likely that different sizes of molecules have different adsorption and desorption rates, also different molecular shapes yield different interphase structures.

Experimental determination of the parameters in the above model is on the following considerations. Because of the difficulties in directly inspecting the time variation of the small interphase region, the fiber surfaces are brought to contact with the resin components for a long period of time until equilibrium state is obtained. From the above model, the equilibrium composition profiles are determined by setting the storage terms in Eqsns. (2)–(7) to zero. Experimental techniques such as Attenuated Total Reflection (ATR) Fourier Transform infrared (FT-ir) spectroscopy and x-ray photoelectron spectroscopy (XPS) may be used to measure the concentration profiles near fiber surfaces [13–15]. By fitting the model predicted concentration profiles to experimental measurements, the rate and energy parameters in the model can be determined. Detailed implementation of the experiments is beyond the scope of this article, and will be reported in the future.

In the present study, the temperature is taken as a given constant, while the real temperature field needs to be solved by coupling to the energy equation written for the whole composite domain. The cure cycles in the manufacturing processes act as boundary conditions of the energy equation to influence the temperature field, which in turn controls the adsorption-desorption processes and interphase formation. Therefore, by optimizing the cure cycle, interphase can be tailored for specific material
system requirements. These issues are under present investigations toward enhancing the capabilities of the current model.

CONCLUSIONS

An adsorption-desorption-reaction model was developed to predict the interphase formation during thermosetting composite processing. Parametric studies reveal that when the influence of the fiber surface is strong, as indicated by large values of adsorption rates and small values of desorption rates, interphase thickness can be dramatically changed by chemical reaction rates. A rapid reaction freezes the interphase concentration profiles prior to reaching the equilibrium and forms a thin interphase region, while slow reaction gives sufficient time for the interphase to grow significantly, leading to no distinct interphase formation. Weak surface influence results in a interphase of a few molecular layer thickness and the reaction rates does not play an important role in this case. The model predicts similar interphase thickness results as previous theoretical and experimental works. However, a notable distinction is the ability to predict the time-evolution of the interphase. The model may be combined with macroscopic thermodynamical model to establish the influence of the cure cycle on the interphase formation. This, in turn, will lead to capabilities for tailoring interphase via cure cycle selection.

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