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Relationship Between Interphase Composition, Material Properties, and Residual Thermal Stresses in Composite Materials

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A methodology for predicting the formation and influence of interphase regions in composite materials is illustrated through an investigation of the relationship of sizing-induced interphase regions to the development of residual thermal stresses in a carbon fiber epoxy-amine composite. Fiber surface and sizing induced concentration gradients in the epoxy-amine system were predicted. Material property data was measured for bulk epoxy-amine systems corresponding to the predicted interphase concentrations and the properties mapped into property profiles in the vicinity of the fiber surface. Micromechanical models were used to predict residual thermal stresses for carbon fiber epoxy-amine composites with these interphase properties. The analyses predict that the thermal stress state is significantly affected by modulus variations in the interphase region. The variations in the properties of the interphase material can be affected through processing conditions and/or material selections.

KEY WORDS Interphase; material property gradients; composition profiles; micromechanical behavior; residual thermal stresses; sizings.

INTRODUCTION

Chemical and physical interactions between the fibers and matrix of a composite have been suspected to cause the formation of interphase regions which possess neither the properties of the reinforcement nor those of the neat matrix.¹ Composite behavior characteristics such as strength and fracture toughness are believed to depend on interphase composition and size.²⁻⁴ Over the years, expectations have been that interphases may be tailored to control, appropriate behavioral characteristics. To do

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so, however, requires not only an understanding of the chemical and physical mechanisms for interphase formation, but also an understanding of the relationship between the properties of the interphase and composite behavior.

Control variables associated with processing conditions and materials selection can determine the type and degree of reinforcement-matrix interactions which affect interphase development. Processing variables include time, temperature and pressure. Material selection includes the choice of fibers, surface treatments, surface coatings (sizings) and resin. A principal aim of this work is to illustrate a methodology which should allow tailoring the interphase structure by manipulating control variables to achieve desired composite behavior characteristics.⁵ In this approach, control variables are linked to reinforcement-matrix interactions and to the associated chemical and physical processes which lead to the formation of interphases. A key feature of this initial analysis is the determination of the chemical composition of the interphase region. Secondly, interphase composition is related to interphase material properties. And, thirdly, interphase material property information is linked to micromechanical characteristics which will affect overall composite behavior. In this fashion, composite behavior characteristics affected by an interphase can be predicted as a function of the material system and processing conditions.

In this paper the methodology summarized above will be applied to interphase regions resulting from the diffusion of amine species from the bulk into an epoxy-rich sizing. Predicted interphase composition profiles are presented, the composition profiles are related to material property profiles, and the effects of predicted property profiles on local residual thermal stresses are presented.

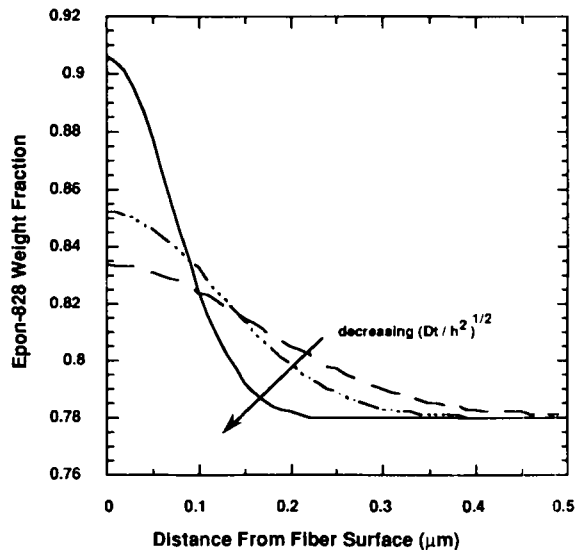


FIGURE 1 Interphase composition profiles resulting from the presence of $0.05\ \mu\text{m}$ sizings. $[(Dt/h^2)^{1/2} = 0.894$ (.....); $(Dt/h^2)^{1/2} = 1.67$ (-.-.-.-); $(Dt/h^2)^{1/2} = 2.28$ (—)].

SIZING LAYERS AND INTERPHASE FORMATION

Coatings are often applied to graphite fibers to protect their surfaces and 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 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 .⁶ 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.⁷

In a previous communication⁸ an analysis of reaction and diffusion kinetics for sized systems was presented. Diffusivity equations decoupled from reactive processes were solved to predict composition profiles in the vicinity of a fiber surface. This work indicated that the presence of sizings may result in interphase regions of variable composition provided that the sizing thickness and processing conditions (particularly temperature) are such that the characteristic times for reaction and diffusion are of the same order. Figure 1 displays calculated epoxy concentration profiles for an Epon 828/PACM-20 system as a function of distance from the fiber surface for a fiber separation of 1 μm and a pure epoxy sizing layer thickness of 0.05 μm . The initial matrix composition corresponds to that of a stoichiometric mixture of Epon 828 and PACM-20. The composition profiles depend on the group $(Dt/h^2)^{1/2}$ where D is the average diffusivity, h is the difference between one-half the distance between fibers and the sizing thickness, and t is time. Lesser values of this group result in smaller and more pronounced profiles. Therefore, for a fixed value of diffusivity, more time available for diffusion results in a broader and less-pronounced interphase region. These profiles serve as a guideline for the types of interphasial composition profiles that can develop in sized systems. It was concluded⁸ that the size of the interphase will depend on resin reactivity and diffusivity, which are affected by processing conditions, and on sizing thickness. The composition profiles shown in Figure 1 will be used as a basis for predicting interphase material properties.

PREDICTION OF INTERPHASE MATERIAL PROPERTIES

Material properties which affect interphase and overall composite mechanical behavior characteristics include the elastic modulus, the thermal expansion coefficient, and the glass transition temperature. To date, it is not possible to measure directly the interphase material properties in such a way as to map the material property profiles which may exist in this region. In light of this, two approaches can be followed to predict the material property variations which may result from epoxy-amine interphasial composition profiles such as those in Figure 1. These are discussed in detail elsewhere.⁵ Generally, one approach uses structure-property models to predict values for material properties as a function of chemical composition. However, for temperatures below the glass transition temperature (T_g), the elastic behavior of a crosslinked polymer is difficult to model, and reliable structure property models are not available.

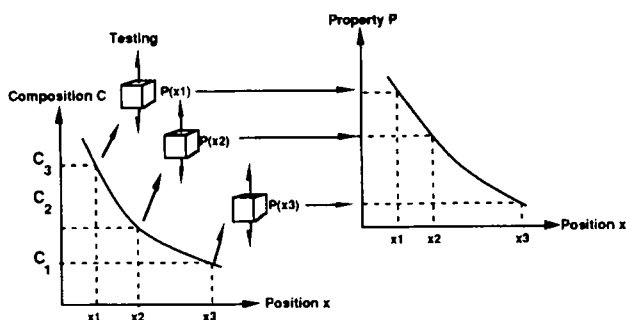


FIGURE 2 Schematic illustrating the synthesis and characterization of samples designed to match the chemical structures corresponding to predicted local interphase compositions in order to establish the material property variations of the interphase region.

An alternate approach, employed herein, is based on the notion that the properties of large homogeneous samples can be associated with local interphase compositions. In order to establish local interphase material properties, this approach entails the synthesis and characterization of a series of materials designed to match the predicted local interphase compositions. Figure 2 is a schematic representation of the process. This method may be used for most epoxy-amine systems.

The interphase composition profiles in Figure 1 are based on monomer concentrations. It has been assumed that the final interphase network structure is a result of complete reaction, given those compositions. For epoxy-amine systems which exhibit negligible amounts of etherification side reactions, the task of relating initial monomer composition to final structure is relatively simple. For such cases, given a specific initial composition, cross-linked structure should be determined by the degree of conversion. Thus, under these circumstances, the local compositions defined by the predicted profiles can be matched with the material properties of fully-cured samples prepared at the given local interphase compositions.

It is important at this point to indicate the shortcomings associated with this method. The physical effects the surface may have on the cured resin are neglected, and axial homogeneity has been assumed throughout the interphase region. In addition, it has been assumed that the material properties measured on a macroscopic level describe the microscopic state. Nevertheless, in the absence of direct measurement techniques or refined structure property models this methodology proves useful.

Side reactions do not play a significant role in the cure of the Epon 828/PACM-20 resin system. In a previous communication,⁹ material property data, including modulus, glass transition temperature and coefficient of thermal expansion, were obtained for this system as a function of initial epoxy-amine composition. Figure 3 shows the effect of initial composition on modulus (note that the stoichiometric point for this system is 28 pph PACM-20). The behavior of modulus with respect to initial composition and temperature is complex and has been investigated by Palmese and McCullough.⁹ Not only is the modulus affected by the decrease in T_g away from the stoichiometric point, but also by the "antiplasticisation" effects associated with low

molecular weight species resulting from off-stoichiometric cure. The former effect results in the sharp drops of modulus far from the stoichiometric point while the latter effect accounts for the observed increases in modulus.

We illustrate the material property mapping procedure described above by using the modulus data of Figure 3 to predict modulus profiles resulting from the interphase composition profiles of Figure 1. Figure 4 shows modulus profiles at 30°C corresponding to selected interphase composition profiles from Figure 1. The profiles are dramatically different. For the broader interphase, the modulus is higher than the bulk value at the fiber surface and decreases monotonically to the bulk matrix value. On the other hand, the sharper interphase is characterized by a very low modulus near the surface and a maximum within the interphase region with a value of modulus greater than that of the bulk. The reason for this behavior is that the modulus of the Epon 828/PACM-20 system attains a maximum value 50% greater than that of the bulk when excess epoxy is used for cure.

Drzal *et al.*,⁷ have predicted that the interphase region of epoxy-sized systems have a higher modulus. Our results suggest that, depending on the processing time, the nature of modulus variations in the interphase region may drastically be affected: for the same sized system, interphases having higher or lower moduli than the bulk value are possible.

Similar mappings for the glass transition temperature and the coefficient of thermal expansion have been obtained and are discussed elsewhere.⁵

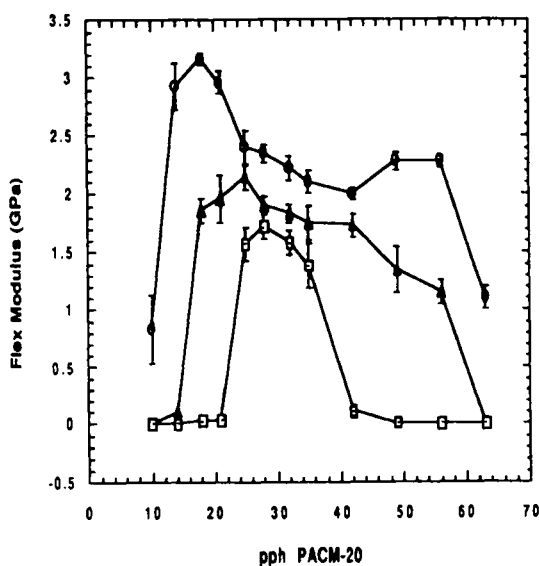


FIGURE 3 Flexural modulus measured for several temperatures as a function of stoichiometry for the Epon 828/PACM-20 system. Measurements obtained using DMA at 1 Hz. [30°C (—●—); 105°C (—▲—); 135°C (—□—)].

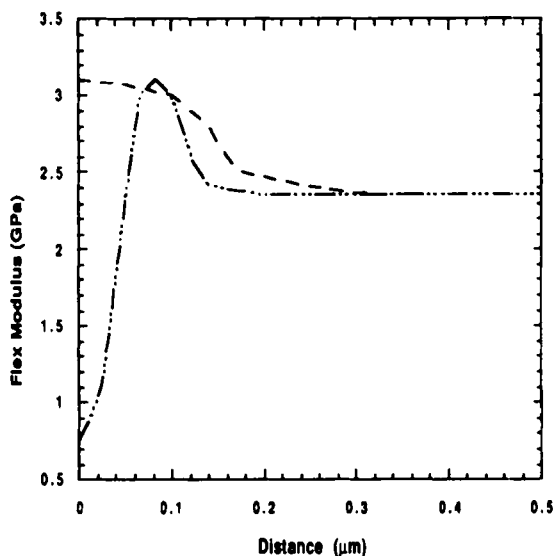


FIGURE 4 Modulus profiles at 30°C corresponding to the composition profiles in Figure 2. [$(Dt/h^2)^{1/2} = 0.894$ (---); $(Dt/h^2)^{1/2} = 1.67$ (-.-)].

RELATIONSHIP TO LOCAL RESIDUAL THERMAL STRESSES

In the foregoing discussion, the relationship between material properties and interphase composition was established. It was observed that dramatic changes in interphase material properties can be achieved by altering interphase composition. In this section, we link the predicted interphase modulus profiles to the local residual thermal stress state of a composite.

Firstly, the importance of thermal and residual stresses for composite behavior is discussed and salient aspects of the computational model¹⁰ used to calculate residual thermal stresses for predicted interphase material property profiles are summarized. Secondly Local residual stress distributions are predicted and, thirdly, these are discussed in relation to interphase strength.

Thermal and Residual Stresses

Material properties such as modulus, thermal expansion coefficient, and T_g determine the thermomechanical behavior of a polymeric composite. An important thermomechanical phenomenon which occurs during the processing of such materials is the development of residual stresses. These stresses may develop for several reasons: a] differences in thermal expansion coefficients of the matrix phase and fiber, b] shrinkage of thermosetting resins as a result of cure, and c] volumetric changes upon crystallization of thermoplastic materials. Values for the thermal expansion coefficient of graphite fibers and a typical fully cured epoxy resin at temperatures below T_g are listed in Table I.

TABLE I
Transverse (*t*) and Longitudinal (*l*) Thermal Expansion
Coefficient for Graphite Fibers and Epoxy Resins

Property	Graphite Fiber	Epon-828/PACM-20
$\alpha_t(\mu\text{m}/\text{m}/^\circ\text{C})$	-1.0	65
$\alpha_l(\mu\text{m}/\text{m}/^\circ\text{C})$	10.1	65

The differences in thermal expansion coefficient between the fiber and the polymeric matrix can create large thermally-induced local residual stresses in the matrix phase surrounding the fiber surfaces. In many cases, the final residual stress state is sufficient to cause irreversible damage to a composite part even in the absence of externally applied loads. Such residual thermal stresses can cause the formation of microcracks in the vicinity of fiber surfaces which affect matrix and interfacial strength and, therefore, the ultimate structural performance of a composite part.

The local residual thermal stresses of the interphase region depend on the local values of the material properties, such as modulus and thermal expansion coefficient. Sottos¹⁰ has developed a computational model to predict residual thermal stresses for a variety of fiber configurations given the presence of a non-uniform interphase region. Parametric studies¹¹ have indicated that variations of the thermoelastic properties in the interphase region substantially affect the local residual thermal stress state of the matrix phase as well as the fiber. The computational approach adopted by Sottos is based on the Boundary Fitted Coordinates technique and details of the model are given elsewhere.⁹

All residual thermal stress predictions reported in this work have been obtained for 8 μm fibers arranged in a hexagonal array. Although calculations predict all components of the residual stress, we report only the radial residual thermal stress as a function of distance from the fiber center. The radial stresses (σ_r) are normalized by σ_o , where $\sigma_o = E_t \alpha_t \Delta T$. E_t and α_t are the transverse modulus and thermal expansion coefficient of the fiber in the transverse direction which are given in Table II and ΔT is -1°C . The radial distance is normalized by the fiber radius. A fiber loading of 72% corresponding to 1 μm fiber spacing was employed for the cases reported.

TABLE II
Transverse and Longitudinal Graphite Fiber Properties Used for
Micromechanical Calculations

Property	Longitudinal (<i>l</i>)	Transverse (<i>t</i>)
E(GPa)	214	13.8
$\alpha(\mu\text{m}/\text{m}/^\circ\text{C})$	-1.0	10.1
ν	.25	.20

Effect of Sizing-Induced Interphase on Local Residual Thermal Stresses

The effects of interphase material property profiles on residual thermal stresses is examined by using the interphase modulus profiles predicted in the foregoing analysis and shown in Figure 4. For the purposes of these discussions the matrix phase is defined as inhomogeneous if it contains an interphase and homogeneous if it does not. Stresses were computed for a 1°C decrease in temperature and results are plotted in terms of dimensionless radial distance. On this scale, 0 corresponds to the center of the fiber, 1 to the surface, and values greater than 1 to positions in the matrix.

Figure 5 compares the residual thermal stresses computed for the modulus profiles in Figure 4 with those computed for a homogeneous matrix. In general, the values of the radial stress in the matrix phase mirror the shapes of the modulus profiles. For the inhomogeneous case possessing an interphase with a lower modulus near the fiber surface ($(Dt/h^2)^{1/2} = 0.894$) the stress in the fiber is significantly lower than that found for the homogeneous case. The stress in the matrix phase, on the other hand, is for the most part significantly greater. There exists a stress concentration in the interphase region corresponding to the maximum in the modulus profile. The distribution of

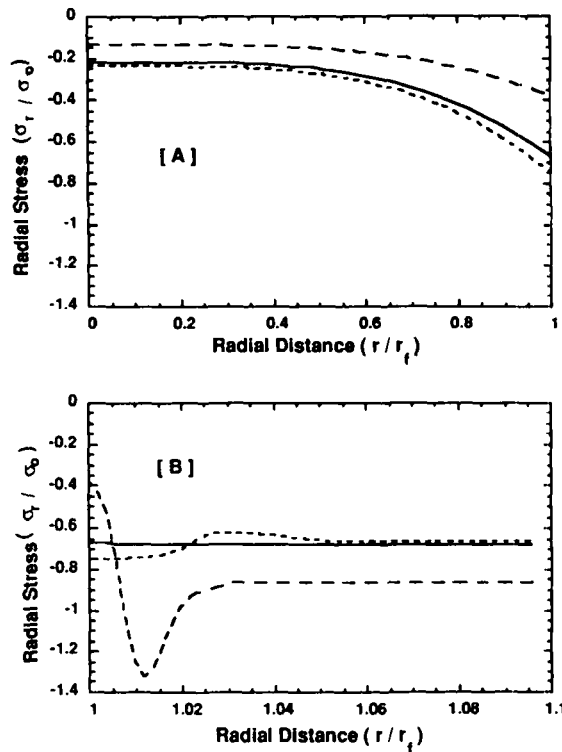


FIGURE 5 Radial residual thermal stress profiles in the fiber (A) and matrix (B) computed for the interphase modulus profiles of Figure 4 and the corresponding homogeneous matrix. [$(Dt/h^2)^{1/2} = 0.894$ (---); $(Dt/h^2)^{1/2} = 1.67$ (-.-.-); homogeneous (—)].

residual stresses for the interphase having a higher modulus near the fiber surface ($(Dt/h^2)^{1/2} = 1.67$) is dramatically different. For this interphase the compressive radial stress in the fiber is slightly higher than that of the homogeneous case and the matrix stresses are for the most part lower.

Figure 4 shows that the modulus is also dependent upon temperature. Accordingly, the property profiles of the interphase region will vary with temperature. Figure 6 shows modulus profiles for several temperatures associated with the interphase composition profile in Figure 1 labeled $(Dt/h^2)^{1/2} = 0.894$. These were obtained using the previously-described matching methodology and modulus information from Figure 4. Figure 7 shows normalized radial residual stress profiles for a -1°C temperature change calculated using the modulus profiles shown in Figure 6. For the higher temperature modulus profiles (135°C , 105°C), the material closer to the fiber surfaces is above T_g . The thermal expansion coefficient values were varied accordingly when calculating residual thermal stresses for such situations.

From these comparisons the following behavior of residual stresses as a function of interphase modulus profiles are recounted:

- (i) softer interphases decrease the residual radial compressive stresses of the fibers while they increase the overall stress state in the matrix phase of a composite;
- (ii) on the other hand, higher modulus interphase increase the radial stresses of the fibers while they decrease the overall stress state in the matrix phase of a composite;
- (iii) the smaller interphase sizes seem to accentuate the effects of a variation in modulus of the interphase region;

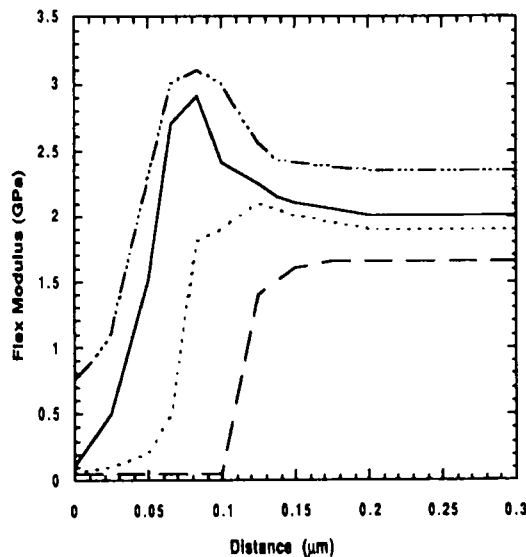


FIGURE 6 Modulus profiles associated with the interphase composition profile in Figure 4 labeled $(Dt/h^2)^{1/2} = 0.894$ for several temperatures. [30°C (.....); 70°C (—); 105°C (---); 135°C (-.-)].

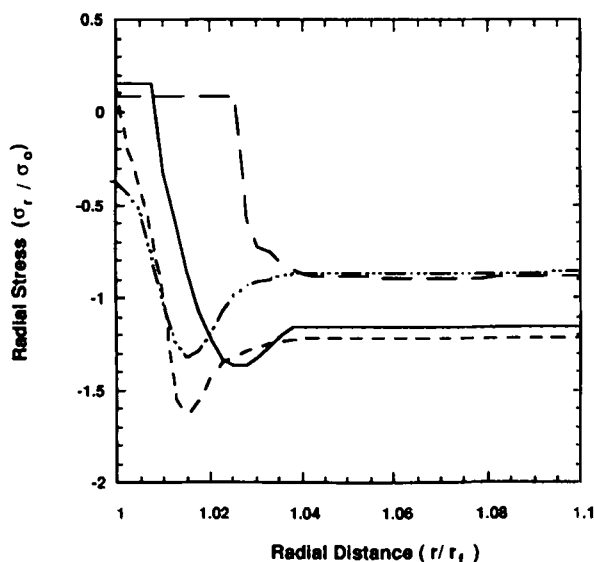


FIGURE 7 Radial residual thermal stress profiles in matrix computed for the interphase modulus profile in Figure 6. [30°C (.....); 70°C (---); 105°C (—); 135°C (—·—)].

- (iv) the stress profiles generally mirror the shape of the modulus interphase profile that was used to compute them.

We conclude that the local thermal stress state of a composite is very sensitive to material property variations of the interphase region.

Processing-Related Residual Thermal Stresses

The residual thermal stress data presented thus far represent normalized stresses caused by a -1°C change in temperature for modulus profiles typical of interphases in composites at various temperatures. During processing, and in subsequent application, composite parts sustain much greater temperature variations. For example, the Epon 828/PACM-20 system is typically cured at 150°C and then cooled to room temperature. When cooling from the cure temperature, however, the modulus profile depends strongly on temperature. The total stress incurred upon a large change in temperature is described by the integral of $\sigma_r/\sigma_o(T)dT$ where σ_r/σ_o is a function of temperature by virtue of the effects of temperature on the interphase modulus profiles.

The profiles of Figure 7 were used to approximate the integration numerically by applying the profile at each temperature over a temperature range of $\pm 15^{\circ}\text{C}$. The radial residual thermal stresses were computed as a function of temperature change given a 150°C initial temperature. Figure 8 shows the calculated radial stress state for a number of final temperatures. As the temperature decreases the stress throughout the matrix increases. Failure is expected when the residual thermal stress reaches the value of the ultimate strength of the material. The ultimate tensile strength of a fully-cured

stoichiometric mixture of Epon 828/PACM-20 is 72 MPa and is marked by a line in Figure 8. It has been assumed that the tensile strength equals the compressive strength. Typically, however, values of compressive strength are slightly higher.

Figure 8B shows local stress states of the matrix phase computed for a composite having a homogeneous matrix upon cooling from a 150°C cure temperature. The

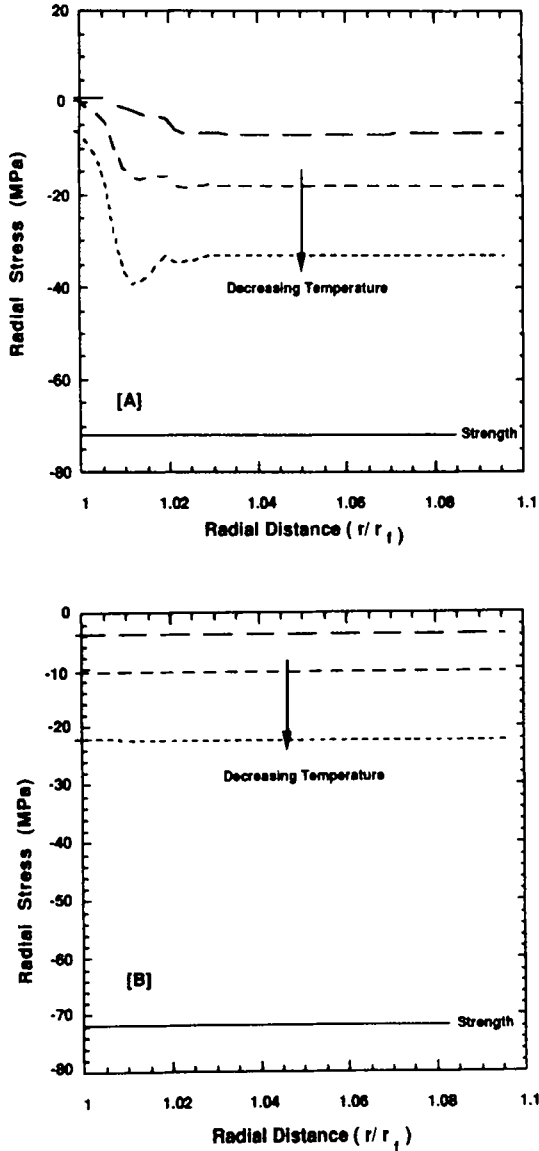


FIGURE 8 Radial residual thermal stress state calculated for a number of final temperatures using an initial temperature of 150°C for, (A) the interphase modulus profiles in Figure 7, [100°C (—); 25°C (- - -); -100°C (.....)] and, (B) a homogeneous matrix.

calculations were conducted analogously to those for Figure 8A. The values used for the moduli of the matrix are those for the bulk stoichiometric material at the corresponding temperatures. Except for the very thin layer of material closest to the fiber surface, the stress state of the inhomogeneous matrix Figure 8A is significantly higher than that of the homogeneous matrix: the inhomogeneous matrix maximum stress is 30% of the ultimate strength of the epoxy compared with 17% for the homogeneous case after cooling to 25°C.

Residual thermal stresses greater than or equal to the ultimate strength of the material may only be achieved for very large temperature changes. After cooling to room temperature, however, the local residual thermal stresses are large enough to affect significantly the apparent strength of the material upon external loading. Such loading includes forces placed on the composite as well as macroscopic scale residual stresses.

It should be noted that these predictions do not account for stress relaxation. Stress relaxation will mitigate the stress concentrations in the viscoelastic matrix as the residual stresses decay with time.

When investigating the failure of a composite at the microscopic level it is often found that failure occurs in the matrix phase and not at the interface. In such cases, it is typically argued that the interfacial strength is greater than the strength of the matrix material and that a good interfacial bonding exists for that system. The foregoing discussion indicates that this need not be the case since the distribution of residual thermal stresses in the interphase region may significantly reduce the apparent strength of the matrix phase. An interesting outcome of this analysis is that as a consequence of these complicated states of residual thermal stress in the vicinity of the fiber, past interpretations of results from tests used to measure interfacial strength directly may be flawed.

Particularly interesting is the local interphase stress concentration predicted for the inhomogeneous case shown in Figure 8. Such behavior can potentially influence the fracture mechanism of a composite. Intuitively, upon loading microcracks might be expected to originate in the high residual stress region. Hence the strength and fracture behavior of a composite material should be significantly influenced by the local residual stress state of the interphase region.

CONCLUSIONS

A methodology for predicting composite behavioral characteristics as a function of materials characteristics and processing conditions has been illustrated by investigating the influence of sizing-induced interphases on composite residual thermal stresses. Using this methodology, the effects of interphase composition on the local residual thermal stress state of a composite were investigated. These studies demonstrated that the thermal stress state is significantly affected by modulus variations in the interphase region. A lower modulus interphase causes an increase in the thermal stress state of the matrix phase, while a higher modulus interphase results in a decrease of the thermal stress state of that region. Furthermore, the shape of the interphase modulus profile influences the residual thermal stress distribution.

It was found that differences in the residual thermal stress state of the matrix as a result of interphase variations represent a significant fraction of the strength of cured epoxy resins. Hence these stresses are sufficient to affect significantly the performance of the material upon external loading.

In closing, it is felt that this work provides the necessary framework to investigate systematically the interphase behavior of other composite systems. We conclude that future theories and models developed to describe fracture and strength in thermosetting composite systems should take into account the thermomechanical properties of the interphase region.

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