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### **The Temperature Dependence of Interfacial Shear Strength for Various Polymeric Matrices Reinforced with Carbon Fibers**

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# The Temperature Dependence of Interfacial Shear Strength for Various Polymeric Matrices Reinforced with Carbon Fibers

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The influence of temperature on the interfacial shear strength between epoxy thermoset matrices and surface treated, carbon AS4 as well as with surface treated and sized AS4-C carbon fibers was investigated. The thermoset matrices all consisted of DGEBA epoxy resin cured with different amine curing agents resulting in matrices with a range of behavior from brittle, elastic to ductile, plastic. For all systems, the results indicate that the interfacial shear strength (ISS) decreases with increasing temperature and as the  $T_g$  of the matrix is approached, a large corresponding decrease in the interfacial shear strength is seen. Moreover, the AS4-C (epoxy sized) system revealed a distinct decrease in interfacial shear strength at temperatures lower than the bulk matrix  $T_g$  indicating the formation of an interphase layer of composition different from the bulk matrix. Linear superposition methods were used to generate a master curve for the different matrix materials reinforced with the AS4 fibers. These results allow the prediction of ISS at any temperature.

**KEY WORDS** Fiber-Matrix Adhesion; Single Fiber Fragmentation Test; Effect Of Variable Stoichiometry on Interfacial Shear Strength; Effect of Interphase Composition on Interfacial Properties; Effect of Temperature on Interfacial Shear Strength.

## INTRODUCTION

A typical process for producing epoxy-carbon fiber composites involves drawing carbon fibers through a vat of epoxy resin and winding the epoxy coated fiber onto a mandrel. The mandrel containing the wound fibers and epoxy matrix is then subject to a thermal processing cycle which "cures" the matrix into the fully cross-linked state. The curing occurs in two stages. In stage one, the material is reacted to produce a lightly crosslinked structure at moderate temperatures. In stage two, additional crosslinking is completed at higher temperatures and longer times to produce a fully crosslinked structure.

There is a major problem associated with thick-section (>25 mm) epoxy-graphite fiber composites made in this fashion. The curing of thick section composites can generate large temperature gradients in the composite caused by the combination of heat transfer to the material through both the inner and outer surfaces of the

cylinder coupled to the exotherm of the curing reaction.<sup>1</sup> During processing, defects can be produced as a result of this non-uniformity of temperature resulting in the appearance of large wavy regions of fibers in the central interior of the composite.<sup>2</sup> It is believed that these defects, characterized by wavy regions of fibers, are formed during the curing process. Subsequently when the cured composite is exposed to high stresses it appears that these defects cause the composite to develop radial cracks and failure occurs in the direction normal to the wavy regions, due to local compression and shear stresses.

The ability of the matrix to transmit stresses from fiber to fiber at the microscopic level is responsible for internal stress development in the composite during processing which in turn, is responsible for generating defects. During the early stages of processing, the matrix is in a fluid state and cannot transmit stresses. As processing progresses, however, there is a simultaneous increase in modulus with time and temperature.<sup>3</sup> Interfacial properties are heavily dependant on the matrix modulus and the interactions at the fiber matrix interface.<sup>4</sup> Simultaneously the matrix properties, and consequently the interfacial properties, will vary throughout the thickness of the material because of this temperature non-uniformity. Hence it is critical that the mechanism by which the interfacial (and adhesive) properties are generated during composite processing is understood so that the mechanical properties can be known as a function of temperature and time in order to optimize composite processing.

Though authors<sup>4,5,6,7,8</sup> have studied how temperature and modulus itself affects the critical length of certain polymeric composites, the role that residual stresses<sup>9,10,11</sup> play in determining the final mechanical properties of composites as well as the dependence of temperature on mechanical strength of composites,<sup>12</sup> little work has been done to determine the alteration of interfacial shear strength as a function of processing conditions.

An added complexity results from the fact that in most cases an "interphase" exists at the fiber-matrix interface. This region, first introduced by Sharpe<sup>13</sup> is a three dimensional region of some finite thickness extending, depending on the system constituents, from within the fiber surface to some point in the matrix where local properties approach the bulk properties. Its size and composition can vary with each system and can include unreacted polymer components, polymer reaction byproducts, weak surface layers of the fiber, among other things. Throughout this work the term "interface" will mean the actual contact surface between the fiber and matrix while the term "interphase" will be the region near and on both sides of the interface. Numerous other publications referenced throughout this paper, have shown the effect of this interphase itself on fiber-matrix adhesion and composite performance.

It is the objective of this work to determine the influence of processing temperature on the interfacial shear strength of various model, polymeric matrices reinforced with AS4 carbon fibers. An AS4-C fiber (embedded in a standard m-PDA/DGEBA matrix) was selected to investigate the effect of a low temperature epoxy sizing agent on the interfacial shear strength behavior at elevated temperatures. Single fiber adhesion studies, which allow the isolation and measurement of interfacial properties, were used to determine the interfacial shear strength as a

function of temperature for the various matrices. Linear superposition methods were used to generate a master curve (for the AS4 systems) from which the interfacial shear strength can be predicted as a function of the processing temperature of the composite material.

## EXPERIMENTAL MATERIALS AND METHODS

### Reinforcing Fibers

Two carbon fibers were chosen for this study. Both of the carbon fibers are the "A" type which are produced by high temperature inert gas graphitization of polyacrylonitrile (PAN) fiber. The morphology of the resulting carbon fiber is axially and radially symmetric composed of turbostatic graphitic layers which are formed into ribbons oriented almost parallel to the fiber axis as well as varying in orientation across the fiber diameter. Adhesion to these fibers in their untreated state<sup>14</sup> by a typical amine cured epoxy results in very low values of interfacial shear strength. Many surface treatments for improving the adhesion to carbon fibers have been proposed and various commercial ones are described in the existing patent literature.<sup>15</sup>

The PAN based carbon fibers chosen for this study are the A-4 (Hercules, Inc.) having a fiber tensile modulus of about 238 GPa and tensile strength 3.5 GPa when measured at a 25 mm gage length and are circular in cross section. The fibers used in this study had two different surface conditions: (1) "AS4" fibers—which are surface treated with an electrochemical oxidation process which optimizes the adhesion to epoxy matrices and (2) "AS4-C" fibers—which, in addition to being surface treated, are coated with a 100–200 nm layer of epoxy applied from an organic solvent directly onto the AS4 fiber surface. The surface energetics and surface morphology of PAN based carbon fibers have been studied and reported elsewhere.<sup>16</sup>

### Polymeric Matrices

A matrix system based on amine-epoxy chemistry was selected for this study. This chemistry is found in a majority of aerospace and submarine applications.<sup>17</sup> The reactants (a difunctional epoxy, diglycidyl ether of bisphenol-A (DGEBA) (EPON 828, Shell Chemical Co.) processed at stoichiometric conditions with any of a series of di-(or tri)functional amines) can be processed at low temperatures and the resulting properties of the matrix are typical of a high performance matrix. The amines were selected to provide a series with increasing molecular length and aliphatic and aromatic backbones between amine groups ranging from the small aromatic meta-phenylene diamine to linear polyether amines (Jeffamines, J-230, J-400, J-403, and J-700, Texaco Specialty Chemical Co.). This series of amine curing agents created an epoxy crosslinked network with an increasing degree of compliance. Table I below summarizes their final mechanical, interfacial and thermal properties.

It can be seen from Table I that the thermoset matrices used in this study have a wide range of mechanical and interfacial properties despite the fact that all formu-

lations listed above were cured using similar schemes. All of the Jeffamine formulations were cured at 80°C for 2 hrs followed by postcure at 125°C for 3 hrs; the mPDA formulation was cured at 75°C for 2 hrs followed by postcure at 125°C for 2 hours. The interfacial shear strength,  $\tau$ , is calculated by measuring the fragment distribution at the critical length and by using Equation (2). The brittle m-PDA system is seen to have a strain to failure of about 6% and a fully cured  $T_g$  of about 135°C while the compliant J700 system is seen to have a strain to failure of over 90% and a  $T_g$  of about 20°C. It can also be seen that lower adhesion results in systems with lower moduli; previous studies<sup>4</sup> have shown a reduction in interfacial shear strength when the modulus of the interphase is lowered. Finally, it can be seen that the AS4-C/mPDA/DGEBA system has a higher level of adhesion at ambient temperatures when compared to the same AS4 system.

An important factor to note in selecting these curing agents to increase the polyether amine length as opposed to the epoxy length is the preservation of epoxy-amine chemistry throughout the series by the use of polyether diamines. If epoxy oligomers are selected, additional hydroxyl functional groups are present along the oligomer backbone. These hydroxyls, could in fact interact (e.g. hydrogen bonding) with each other as well as the fiber surface and unnecessarily complicate the analysis. A Dynamic Mechanic Analyzer (TA instruments model 9900; amplitude 0.8, frequency 1 Hz) was used to gather the storage modulus data as a function of temperature for the matrix materials studied.

### Single Fiber Fragmentation Test

Because of the complexity of the state of stress applied in most composite testing protocols,<sup>18</sup> a single fiber method was selected to evaluate adhesion at the fiber-matrix interphase. In this technique, preparation of the thermoset matrix coupons<sup>19</sup> involves mixing of the curing agent and resin in proper proportions and pouring into a mold with a fiber aligned axially within it followed by appropriate curing.

After the fiber is totally encapsulated in the matrix coupon, a tensile load is applied to the coupon, and an interfacial shear stress transfer mechanism is relied upon to transfer the coupon tensile forces to the encapsulated fiber through the interface. As the load is increased on the specimen, shear forces are transmitted to the fiber along the interface. The fiber tensile stress increases to the point where the fracture strength ( $\sigma_f$ ) is exceeded and the fiber breaks inside the matrix. This process is repeated producing shorter and shorter fragments until the remaining fragment lengths are no longer sufficient in size to produce additional fracture through this stress transfer mechanism. The fragment critical length-to-diameter ratio ( $l_c/d$ ) is measured. A shear lag analysis is completed on the fragments in order to calculate in interfacial shear strength,  $\tau$  according to:

$$\tau = \frac{\sigma_f d}{2 l_c} \quad (1)$$

Recently, Dave et al.<sup>20</sup> has suggested that a correction factor should be included in Equation (1) to account for thickness of the interlayer between fiber and matrix. In

practice, there is a distribution of critical lengths and Weibull statistics are used to fit the data according to:

$$\tau = \frac{\sigma_f}{2\beta} \Gamma(1 - 1/\alpha) \quad (2)$$

Equation (2) above was used for all the analysis done in this study. This embedded single fiber technique has several advantages. A large number of data points can be gathered in each observation, the failure process itself can be observed in transmitted (polarized) light, the locus of failure is identified and the process replicates the in-situ events in the actual composite itself. A plethora of experimental data has been generated with this method and published elsewhere.<sup>21,22</sup>

### Elevated Temperature Interfacial Shear Strength Measurements

A specially designed heated cell was constructed to conduct single fiber measurements at elevated temperature. The dimensions of the cell (2" × 1.25" × 1") are such that it fits snugly on the straining device used to conduct the fragmentation test described above. The cell is constructed entirely out of teflon which has thermal capabilities up to 300°C. Two aluminum blocks, which house the "firerods" (1/4 × 1" and 40 Watts—Watlow Co.) used for heating the interior of the cell, are built into the two outside teflon walls. Quartz glass windows above and below the specimen allow for experimental observation under an optical microscope. Elongated dog-bone shaped specimens (2.00" gage length) are inserted and the entire cell sealed with insulating material before the gage length is heated to the desired temperature and the tests conducted as mentioned above. Temperature calibration runs revealed that the entire gage length attains constant temperature to within 5% of the set-point temperature after equilibration. The time for equilibration is dependent upon the set point temperature and ranges from 5 to 15 minutes. Even at the highest temperatures used in this study (about 120°C), the equilibration time is less than 15 minutes.

## RESULTS AND DISCUSSION

### Chemical Bonding

New surface analytical techniques allow the chemical nature of the carbon surface to be determined. Xray photoelectron spectroscopy (XPS) provides not only atomic information but also molecular information about the surface characteristics and can be used to determine the extent of chemical bonding between matrix and reinforcing fiber.

To determine the extent of chemical bonding, a series of experiments were performed with model monofunctional epoxy compounds, amines and epoxy-amine adducts whereby these components were dissolved in an inert aromatic solvent and placed in contact with carbon fibers under the same temperature conditions

experienced in the processing of the composite.<sup>23</sup> Afterwards, the fibers were extracted with pure solvent, dried and then their surface composition determined with XPS. Subsequent comparison of the carbon fiber spectra before and after this exposure to the matrix components confirmed that chemical adsorption had taken place. Both the epoxy group and the amine group can chemically react with the surface oxygen present. Surprisingly, on an absolute basis only about 4–5% of the surface sites of the carbon fiber were found to be involved in chemical bonding. One would expect chemical bonding to create a stronger interaction than physical bonding.

For the epoxy-amine-carbon fiber system studied here, it is expected that chemical bonding would be similar for all systems and because of the small number of chemical bonds formed, it is expected that the role of chemical bonding between fiber and matrix would be small and constant. At most, under the processing conditions of interest in this study (up to about 125°C), only 4–5% of the available carbon fiber surface sites can react with the epoxy matrix. Moreover, previous work has shown<sup>4</sup> that the bulk properties of the matrix and the interphase properties themselves play a much more significant role on fiber-matrix adhesion than does the chemical bonding between fiber and matrix itself. Since temperature significantly alters the bulk mechanical properties of the matrix, one would expect it to play a more important role than chemical bonding in affecting fiber-matrix adhesion in these systems.

### Interfacial Shear Strength

At ambient temperatures the interfacial shear strength was measured for all the systems and averaged according to Eqn. (2). The data is plotted in Figure 1 as interfacial shear strength vs. shear modulus of the bulk matrix (see Table I for the shear modulus of the various systems studied here) of the bulk matrix. Since the  $T_g$  of a material is related to the stiffness of the material, the differing compliance in the matrices studied can be seen by examining the  $T_g$ 's<sup>4</sup> listed for the various systems in Table I. A lower  $T_g$  is indicative of a material with a lower modulus. From Figure 1 it is seen that all of the matrix formulations fall on a single smooth curve showing an increasing interfacial shear strength with increasing shear modulus of the matrix.

For elevated temperature measurements, using the specially designed cell, measurements were made at 35°C increments up to the  $T_g$  for each of the different formulations. At each temperature replicate samples (a minimum of 5 samples were tested at each fiber/matrix/temperature combination) were tested to insure statistical significance. The interfacial shear strength,  $\tau$ , for all the matrix formulations reinforced with AS4 fibers, as a function of test temperature is shown in Figure 2. It can be seen that in all cases the interfacial shear strength slowly decreases with increasing temperature until at some point a significant decrease in the interfacial shear strength is noted. This point is near the bulk  $T_g$  of the matrix. These results are similar to those obtained by Wimolkiatsak and Bell<sup>6</sup> where it was shown that for uncoated carbon fibers embedded in a thermoset matrix, the interfacial shear strength decreased with increasing temperature slowly initially (where the interfacial shear strength is interface controlled) with a steep decrease at higher tempera-

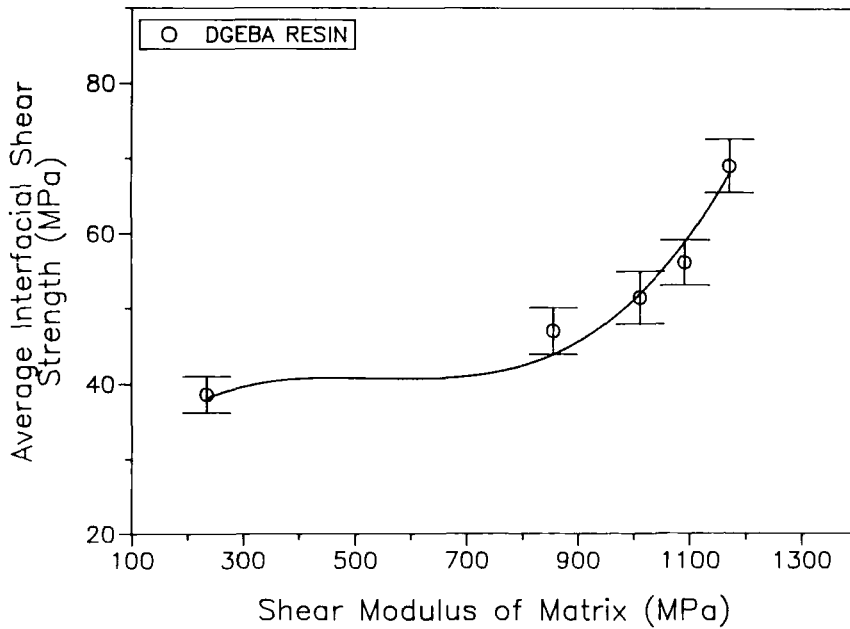


FIGURE 1 Shear modulus of bulk matrix versus interfacial shear strength.

tures (where the interfacial shear strength is matrix controlled). Interfacial shear strength measurements could not be made at or above  $T_g$  due to the matrix being too ductile causing an excessive amount of necking and tearing upon tensile load application. Previous work by Rao and Drzal<sup>4</sup> has shown that decreasing the modulus of the matrix (and interphase) leads to lower values of interfacial shear strength for systems with constant interfacial chemistry. As the temperature is increased from room temperature towards  $T_g$  of the matrix, the modulus of the matrix decreases thereby reducing the ability of the matrix adjacent to the fiber surface to transfer stress.

The glass transition temperature for all of the different thermoset formulations used in this study are listed in Table I. In all cases it can be seen from Figure 2 that

TABLE I  
Interfacial, mechanical and thermal properties of the DGEBA system

DGEBA cured stoichiometrically with: (AS4 fibers)	TAU, $\tau$ at ambient conditions (MPa)	Bulk matrix shear modulus at ambient T (GPa)	$T_g$ of fully cured matrix ( $^{\circ}$ C)	Fiber
m-PDA	70.1	1.17	135	AS4
J-230	56.7	1.09	74	AS4
J700/J403	42.1	—	46	AS4
J-403	46.9	0.85	75	AS4
J-700	38.6	0.23	$\sim$ 20	AS4
m-PDA (AS4-C Fibers)	79.1	1.17	135	AS4C



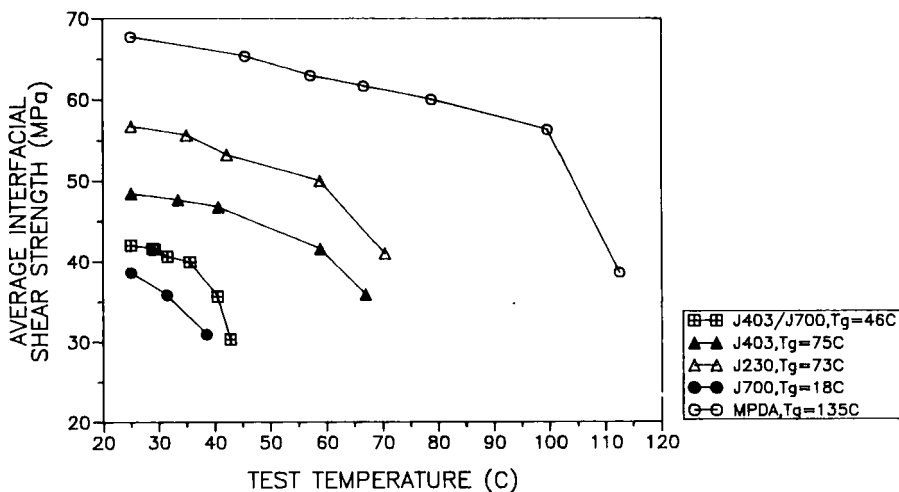


FIGURE 2 Interfacial shear strength versus temperature for the various polymeric systems.

the interfacial shear strength is seen to decrease as the  $T_g$  of each system is approached. It would be expected that at  $T_g$ , since the modulus of the matrix drops by orders of magnitude,<sup>24</sup> the interfacial shear strength would also rapidly decrease at that point. However, in all cases the interfacial shear strength is seen to decrease well before  $T_g$  of the bulk matrix is reached. For example, for the mPDA/DGEBA system the bulk matrix  $T_g$  is about 130–135°C, but the interfacial shear strength is seen to decrease well before this at a temperature of about 100°C. These results support the concept of the formation of an interphase whose glass transition temperature, and thus its mechanical properties, are different than that of the bulk matrix. Other authors<sup>25,26</sup> have also reported the formation of an interphase having mechanical and viscoelastic properties different from the bulk matrix material.

### Linear Superposition

Since all the matrices used in this study are cured with diamine type curing agents and the fiber-matrix chemical interactions would be constant, it should be possible to combine all of the data from Figure 2 into one curve. The interfacial shear strength data was analyzed using linear superposition in the same manner that the Williams-Landel-Ferry (WLF) equation of state<sup>24</sup> was used to describe polymer matrix temperature dependence. The J230 system was chosen as the reference system and all of the other data in Figure 2 were either shifted to the left or to the right to coincide with the chosen reference material. The shift factor was “best-fit” and optimized with temperature and the resulting plot is shown in Figure 3. These shift factors were then used to linearly superpose the data. The resulting plot is shown in Figure 4. The ordinate in Figure 4 is the “corrected” interfacial shear strength; the data has all been multiplied by the numerical factor  $T/T_o$ . In this notation  $T$  is the measured temperature and  $T_o$  is the reference temperature chosen, 346°K. This  $T/T_o$  factor is the standard factor used<sup>24</sup> for correcting data with the

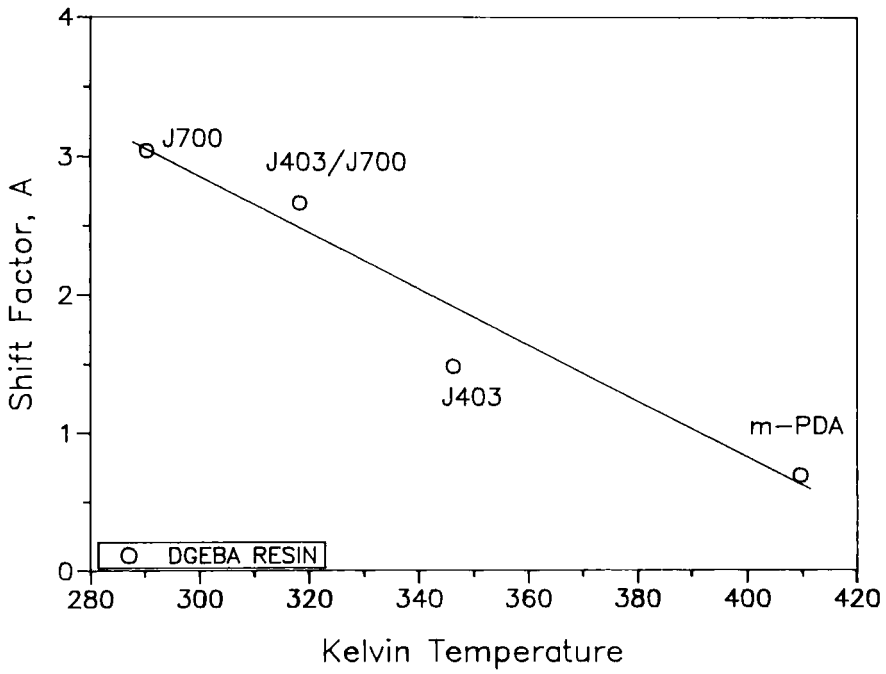


FIGURE 3 Optimized shift factor versus temperature.

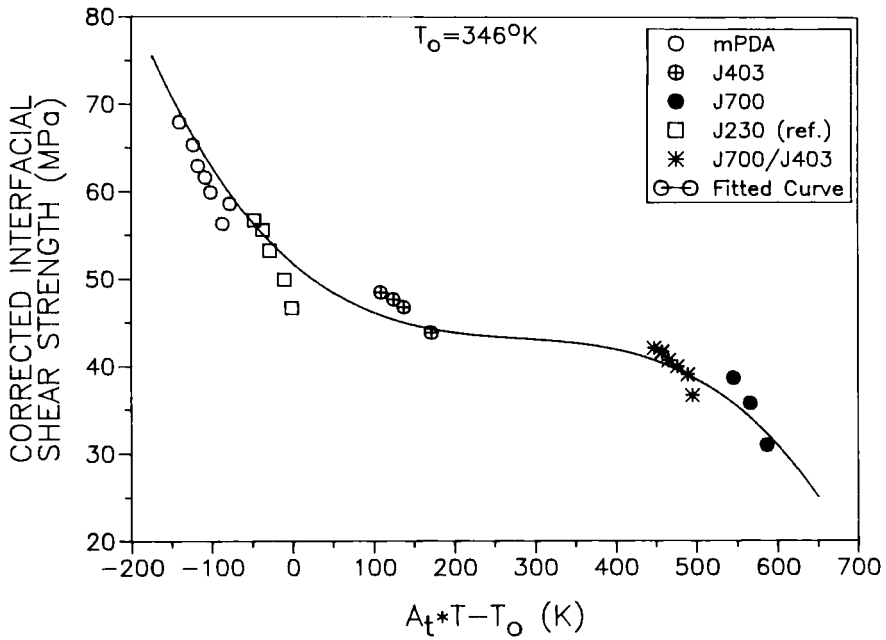


FIGURE 4 Master curve for interfacial shear strength for the various polymeric systems.

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WLF equation of state for superpositioning data. It can be seen that the shifted data is seen to cover a wide range of temperatures and interfacial shear strengths. This then allows for the prediction of interfacial shear strength by knowing just the modulus (or processing temperature at a given time) and the glass transition temperature.

### Residual Stresses

In addition to chemical and structural considerations, the state of stresses which result from the processing of the material itself can influence the degree of fiber-matrix adhesion. In the case of carbon fibers, the coefficient of thermal expansion is quite small and can actually be negative.<sup>9</sup> The fiber itself is anisotropic and the radial and longitudinal thermal expansions can be quite different. The matrix is isotropic but has a coefficient of thermal expansion a factor of thirty larger<sup>9,27</sup> than the fiber. This disparity becomes increasingly significant as higher processing temperatures are reached with the absolute difference between the glass transition temperature and the use of temperature determining the magnitude of these residual thermal stresses.

Epoxy matrices also reduce their volume as they begin to crosslink. This volumetric shrinkage also contributes to the state of stress at the fiber-matrix interphase. For fibers surrounded by matrix, the resulting cure shrinkage produces a beneficial compressive interfacial force while for matrix confined between a row of fibers, a net tensile interfacial state of stress may result. The resulting state of stress can reduce the level of adhesion attainable between fiber and matrix. Calculations of interfacial stresses have been made previously for these thermoset systems<sup>4</sup> and they show that although the radial component of the stress changes in the same manner as the measured interfacial shear stress, the magnitude of the radial compressive stress is small and is considered to be a minor factor. Thus, it is concluded that it is the changes in matrix material properties themselves, that are primarily responsible for the changes in the interfacial shear strengths in this study.

### AS4-C/mPDA/DGEBA System

The AS4-C/epoxy system was chosen as an example where an interphase of known composition different than the bulk is present. It has been proposed and indirectly verified<sup>28</sup> that this interphase consists of a low  $T_g$  epoxy material. The plot of interfacial shear strength versus temperature are shown in Figure 5. For comparison purposes, both the AS4/mPDA/DGEBA as well as the AS4-C/mPDA/DGEBA data is shown. At ambient temperatures, it can be seen that the AS4-C system has a 15% higher interfacial shear strength due to the interphase resulting from the coating placed on the fiber during processing. Its modulus is higher than the stoichiometric bulk epoxy modulus. As the test temperature is increased, however, the AS4-C system is seen to exhibit a measurable decrease in interfacial shear strength (indicating a lower level of adhesion) as the temperature is increased, culminating in a distinct decrease starting at about 70°C well before the expected decrease in interfacial shear strength when the  $T_g$  of the bulk matrix is approached. The drop

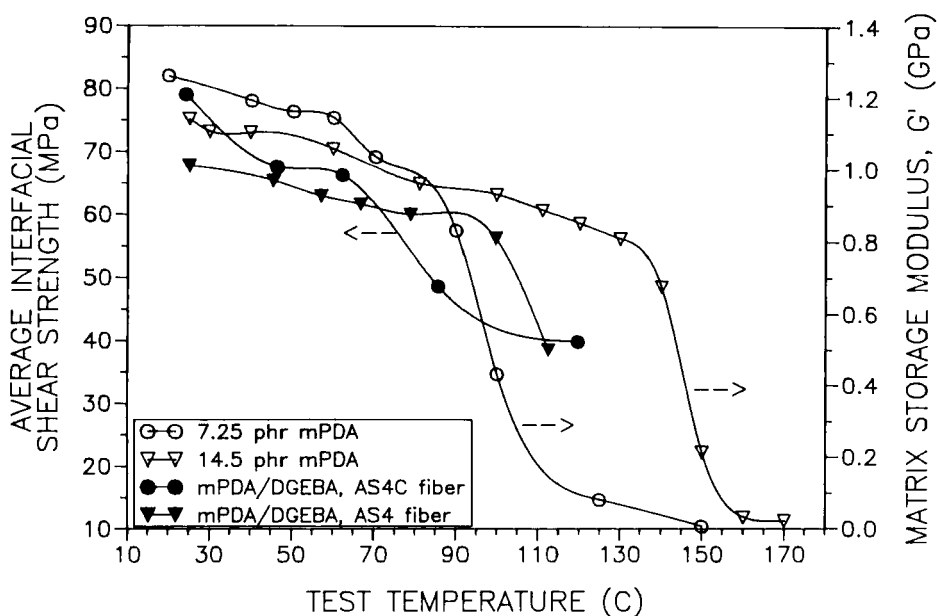


FIGURE 5 Interfacial shear strength and matrix storage modulus versus temperature for AS4 and AS4C fibers in DGEBA/mPDA matrix.

in the measured interfacial shear strength at 40°C may be attributed to the interphase epoxy softening thereby leading to a lower modulus in the interphase region causing a corresponding lowering of interfacial shear strength.

The interphase that results from the diffusion controlled interaction of the pure epoxy coating with the bulk stoichiometric matrix will produce a region around the fiber having less than the stoichiometric amount of amine curing agent. Separate measurements of the  $T_g$  and the modulus of this material<sup>29,30</sup> which is subject to the same curing schedule as the bulk matrix indicates that the glass transition temperature can decrease from the bulk value to about 75°C at 50% of the stoichiometric amine level. Netravali et al.<sup>8</sup> have also shown that the bulk modulus plays a lesser role than interphase interactions when using certain types of carbon fibers. They speculate, as Drzal et al.<sup>22</sup> did earlier, that the interphase region is more brittle due to migration of the curing agent into the interphase thereby leading to a stronger interfacial shear strength.

Figure 5 also shows the relationship between bulk matrix storage modulus and temperature for DGEBA resin cured with a stoichiometric amount (14.5 phr) of mPDA (open inverted triangles in Figure 5) as well as for DGEBA resin cured with a 50% of stoichiometric amount (7.3 phr, open circles in Figure 5) of mPDA. It can be seen that for the 14.5 phr system, the  $T_g$  of the matrix falls in the range of 130–150°C while for the 7.3 phr system the  $T_g$  is in the range of 70–90°C.

Since pure DGEBA monomer melts at about 40°C,<sup>31</sup> the first drop in Figure 5 at about 40°C may be due to melting of the unreacted excess DGEBA in this region. Following this decrease the interfacial shear strength remains higher than the AS4

system until about 70°C. At this point, a precipitous drop in interfacial shear strength is measured. The temperature at which this occurs corresponds to the  $T_g$  of a 50% of stoichiometric amine/epoxy mixture. This indicates that the interphase composition is approximately 50% of the stoichiometric (bulk matrix) amount. These results show that the composition of the interphase region plays a role in determining the final level of fiber-matrix adhesion.

## CONCLUSIONS

The dependence of the fiber-matrix interfacial shear strength on temperature for epoxy matrices reinforced with AS4 as well as AS4-C carbon fibers was studied. The results indicate that the interfacial shear strength decreased with increasing temperature because of the decreasing interphase modulus. At a temperature slightly below the bulk  $T_g$  of the matrix, a significant decrease in the interfacial shear strength was detected. This drop, seen in all the systems, is most likely related to the structure of the polymer and hence  $T_g$  of the polymer in the interphase region, whose composition can be different than that of the bulk matrix and whose mechanical properties control the level of fiber-matrix adhesion. Linear superposition was used to reduce all of the thermoset data into one master curve making possible the prediction of interfacial shear strength under any thermal conditions such as during temperature excursions encountered by the composite material. Additionally, the AS4-C system has been shown to exhibit a distinct decrease in interfacial shear strength at low temperatures (i.e., low  $T_g$ ) indicating the formation of an interphase layer with mechanical properties different than that in the bulk matrix. Overall the thermal response of the interfacial shear strength has been shown to be quite sensitive to the interphase composition.

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## NOMENCLATURE

- $\alpha$ : Weibull scale parameter  
 $\beta$ : Weibull shape parameter  
 $\Gamma$ : Gamma function  
 $\tau$ : Interfacial shear strength (MPa)