Chapter 7

INTRODUCTION

The issue of environmental-durability has become extremely important for fiber reinforced composite materials. As their use in industries such as civil infrastructure, transportation, and off-shore oil exploration increases, the need for an extensive database on their projected service lifetime must be developed. The environments in which these materials operate are harsh and dynamic. The loading is typically vibratory in nature and occurs in a wide range of ambient conditions. The physical environment is typically extreme with large variations in temperature and humidity. In certain applications, the composite will be completely immersed in either a fresh or a saltwater environment. It therefore becomes important to understand the effects of all these environmental factors on the performance of these composites.

Sizings, a thin coating applied to the surface of the carbon fiber before impregnation with the matrix, have been shown to affect the mechanical performance of the composite[7.1-7.4]. As was discussed in Part I of this series[7.5], the thermoplastic sizings (Phenoxy and K-90 PVP) were shown to improve static mechanical performance compared to the traditionally utilized oligomeric epoxy sizing, G'. All of the thermoplastic sized composites outperformed the standard sizing G' by at least 25% in static tensile strength, by at least 11% in longitudinal flexure strength, by at least 30% in short beam shear strength, and 31% in static compressive strength. The tensile, longitudinal flexure, and compressive modulus appeared to be unaffected by variations in the sizing. The purpose of this paper is to investigate the effect of moisture on the static tensile and fatigue-lifetime performance of these same composites with varying sizing agents.

The effect of the fiber-matrix interface on moisture absorption characteristics of a Twaron aramid fiber and Ciba epoxy matrix was studied by Janssens et.al.[7.6]. They observed that in a system in which both the matrix as well as the fiber absorbed water, although the maximum moisture content was not affected, the fiber surface treatment helped decrease the diffusivity in the fiber direction. Transverse tensile tests conducted by Bradely and Grant[7.7,7.8] indicated that the strength after saturation depended heavily on the properties of both the matrix and the shear strength of the interface. An environmental scanning electron microscope (ESEM) was used to facilitate in-situ damage evolution and propagation observation. Environments such as immersion in room temperature fresh and simulated seawater at atmospheric and 20.7 MPa pressures to simulate deep-water applications were investigated. Micro-indentation tests were also performed to evaluate the interfacial shear strength and to compare it to trends observed in the strength data. It was noted that composites made up of very brittle matrices promoted damage via matrix cracking leading to low strengths. Further, these composites showed an increase in strength after saturation because of the plasticization effect of the matrix. On the other hand, the strength of composites made up of matrices that were more ductile but develop poor fiber matrix interfaces remained unchanged after exposure since the damage was always restricted to the fiber-matrix interface region. Composites that did show significant changes in strength after saturation also indicated a change in damage mode, namely from being matrix dominated before aging to interfacial after saturation. The moisture uptake data also showed that saturation contents for salt water aged samples was less than their corresponding fresh water counter parts. This was attributed to the osmotic effect in the salt-water solutions. Little difference in strength was therefore seen to exist between the three exposure environments. Komai et al.[7.9] performed both quasi-static tension as well tension-tension (R = 0.06-1.0) fatigue tests at 5 Hz, on a “normal use” T-1 fiber and a “heat treated” MM-1 carbon fiber composite. In the case of the T-1 fiber the matrix was Epon 828 and in the case of the MM-1 composite it was an imide-modified resin system. It was noticed that after 7 months of exposure to water at 80°C, the moisture content increased dramatically for the MM-1 composite leading to a drop in fatigue strength. However, when exposed for only 2 months, the low moisture content led to a subsequent drop in interfacial strength and resulted in improved mechanical properties because of increased matrix ductility. For both the composites, fatigue tests performed in the air-water (specimen initially dry; tested in a fluid cell) environment yielded higher lives as compared to the air-air (always dry) case. This was attributed to the low uptake and resulting increases in ductility of the resin and moderate decrease in interfacial strength. For the case of the water-dry (initially saturated; tested dry) test, the resin degraded by the water was dried and became sensitive to cracks present. A similar observation has been made by Smith and Weitsman[7.10] on a AS4/3501, $[0/90_3]_s$ composite. They noticed that pre-saturated specimens tested wet with the help of a fluid cell had the shortest lives as compared to those that were saturated and then fatigued in air. In terms of modeling the moisture uptake process some of the pioneering work was done by Springer[7.11] who described the conditions under which Fick's law could be used to model the moisture uptake process. These were namely that the temperature equilibration process should be much faster than the moisture concentration, hence permitting a de-coupling of the energy and mass transfer equations and, the mass diffusivity is only a function of temperature and is not dependent on stress or concentration. Blikstad et al.[7.12] compared the effects of specimen aspect ratio (width to thickness) on the validity of using both the 1-D approximate and 2-D solutions. They found that only those aspect ratios higher than 20 yielded a close agreement between the two solutions. Anything less, resulted in a disagreement that only increased with decreasing aspect ratios. Similar solutions have been reported by Chateaumiois et.al[7.13] in their work on glass epoxy composites. They were able to reduce the complete 2-D solution by assuming that the diffusivities across the fibers and through the thickness were the same (namely D_x=D_z). This simplified form yielded a linear relationship between the experimentally evaluated D and h/l, where h is the thickness and l the specimen length. The intercept of such a plot yielded D_x and the slope D_y. The magnitude of this ratio, D_y/D_x was monitored for their composites and it was seen that substantial changes occurred when saturation was carried out in a 90°C water environment. The slope increased indicating that interfacial cracking and damage had increased the contribution of the diffusivity along the fibers (D_y).

Sheng and Springer[7.14] developed a technique for calculating the diffusivity from experimental moisture uptake data. The authors clearly explain the theoretical considerations for the 1-D diffusion process, because of which, the present contribution will only furnish some of the key equations that were used to make the necessary calculations. From the slope of the moisture content versus square root of time plot, the diffusivity through the thickness can be computed by using the following equation

$$D_z = \pi\left(\frac{h}{4M_m}\right)^2\left(\frac{M_2 - M_1}{\sqrt{t_2}-\sqrt{t_1}}\right)^2 \qquad (1)$$

In the above equation, D_z is the through the thickness diffusivity, h is the thickness of the specimen and M_m is the equilibrium moisture content taken at saturation.

In order to examine the validity of the Fickian diffusion mechanism, the above-calculated diffusivity is then substituted back into the following equation

$$G = \frac{M - M_i}{M_m - M_i} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{j=200} \frac{\exp\left[-(2j+1)^2 \pi^2 \left(\frac{D_z t}{s^2} \right) \right]}{(2j+1)^2} \qquad (2)$$

where M, M_i and M_m are the moisture content at time t, start of the experiment and final time respectively. ‘s’ is dependent on the nature of the exposure. If both sides of the specimen were exposed then it is equal to the thickness of the specimen. On the contrary, if only one side is exposed to the environment then s is equal to twice the thickness.

The objectives of the present work were to investigate and understand the role of the interphase on both the mechanical as well as enivronmental durability of unidirectional carbon fiber reinforced composites by applying different sizing polymers.

EXPERIMENTAL

Materials

The K-90 PVP sizing material (LUVISKOL lot # 20421501) (Figure 1 (a)) was obtained from BASF. The M_W of this material was 1,250,000 g/mol and it had a Tg of 180°C[7.15]. This material was dried at 110°C for 18 hours before being used.

The Phenoxy™ sizing material (PKHW-35 lot # 217013) (Figure 1 (b)) was obtained from Phenoxy Associates, Rock Hill, SC. This material was obtained as a 35 weight percent dispersion of approximately 1-micron diameter particles in water. The M_n of the Phenoxy was 19,000 g/mol (GPC) and it had a T_g of 97°C (DSC).

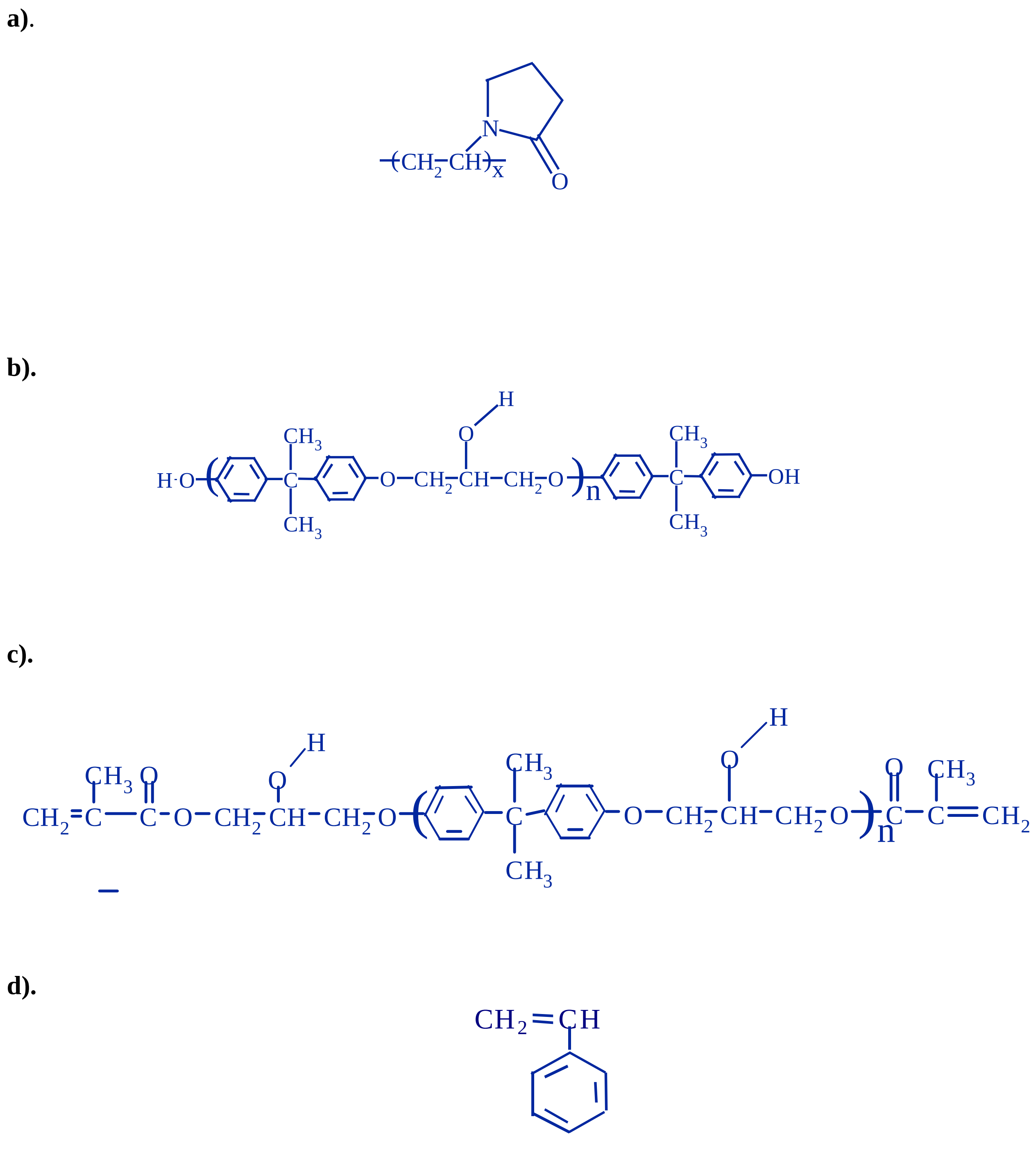


Figure 1 a). Chemical structure of poly(vinylpyrollidone) (PVP) sizing material. b). Chemical structure of poly(hydroxyether) sizing material. c). Chemical structure of vinyl-ester. d). Chemical structure of styrene monomer.

The isopropanol used to break the Phenoxy™ emulsion was HPLC grade (lot # B5417) obtained from Burdick and Jackson.

The Derakane 441-400 vinyl-ester resin (Figure 1 (c)) was obtained from the Dow Chemical Company. The resin consisted of 70wt% vinyl-ester oligomer and 30wt% styrene monomer (Figure 1 (d)).

The sizing/Derakane™ blends were cured with benzoyl peroxide (BPO). The BPO utilized for this purpose was obtained from Aldrich. The material was 97% pure (lot # ES 03918CS).

Processing and Characterization of Sized Fiber and Composites

Details regarding the processing of the sized fiber and composites as well as their characterization were discussed in Part I[7.5].

Environmental Aging of the Composites

The composites were saturated with water at 65°C to determine the kinetic and thermodynamic parameters associated with water absorption. In addition, the saturated composite specimens were characterized for static tensile properties to elucidate the effect of moisture ingression. The composites were cut into 15.24 cm X 1.27 cm X 0.04 cm rectangles. This specimen geometry minimized the diffusion resistance in one direction while maximizing it in the other two. Therefore, the diffusion phenomena being monitored could safely be classified as one-dimensional. The specimens were then immersed in a 65°C tap water bath. The specimens were held in place by Plexiglass™ racks that provided support at two points. The samples were removed periodically to record the weight change. This was accomplished by removing the specimen, patting it dry, and allowing it to reach room temperature before recording it's weight. A Mettler balance was used to record the weights. In addition to the weights, the level of the water in the container was also checked in order to prevent any drying.

Preparing blends for moisture uptake determination

A set of K-90 PVP/Derakane™ 441-400 vinyl-ester blends were prepared at compositions of 0.25, 1.00, 3.00, and 5.00 wt% K-90 PVP. The Derakane™ was added to a one quart mason jar. An Arrow 850 high torque stirrer was placed into the Derakane™ and stirring was set at the maximum speed. The K-90 PVP was slowly added to the Derakane™ at a point where the vorticity appeared to be the greatest. If the K-90 PVP was added to quickly, then the PVP would clump and not dissolve. However, if the K-90 PVP was added to slowly, then the PVP would start to significantly dissolve before all the PVP had been added. This greatly increased the solution viscosity and made the adding of additional PVP impossible. After all the K-90 PVP had been added to the Derakane™, the mixture was allowed to rapidly stir until all of the K-90 PVP had been dissolved (approximately 24 hours for the 5.0 wt%). Some of the resulting K-90/Derakane™ blends were utilized for dielectric analysis and density determination (note: after the blend had been catalyzed then the density was determined). Some of the blends were also used for the preparation of cured K-90 PVP/Derakane blends. The curing procedure is discussed later in this paper.

Whatman Qualitative filter paper (Cat. # 1001 070) was used to filter the separated Phenoxy™ particles from the broken suspension. A 6.95 wt% Phenoxy™ in Derakane™ blend was prepared. Approximately 360g of the Derakane™ was added to a quart size mason jar. An Arrow 850 high torque stirrer was placed into the Derakane™ and stirring was set at the maximum speed. The Phenoxy™ was slowly added to the Derakane™. After several hours of rapid stirring, the optical appearance of the mixture remained very turbid. In addition, the viscosity of the mixture did not change significantly during the process. This was a strong indication that the Phenoxy™ was not dissolving into the Derakane™. Because the Phenoxy™ would not dissolve in the Derakane™, the density could be obtained on this blend. However, this blend was cured and tested for cured blend density and other mechanical properties.

Curing of the blends

The K-90 PVP/Derakane™ and the Phenoxy™/Derakane™ were cured utilizing benzoyl peroxide. A BPO concentration of 1.1 wt% in Derakane™ was utilized (or a .011:1 weight ratio of BPO to Derakane™). In order to keep the material systems somewhat similar, the same ratio of BPO to Derakane™ was utilized in these experiments. However, because the amount of sizing material varied from blend to blend, so did the actual concentration of BPO. The blend was added to a suitable glass container. An Arrow 850 high torque stirrer was placed into the blend and stirring was set at the medium speed. The BPO was slowly added to the stirring mixture. After the BPO had dissolved (approximately 1 hour), the blend was degassed utilizing approximately 24 in Hg vacuum. The blend was allowed to degas for approximately 30 minutes. The K-90 PVP/Derakane™/initiator blend was used for the density determination.

The K-90 PVP/Derakane™ and Phenoxy™/Derakane™ blends containing the initiator were cured in the following procedure. A 20.34 cm X 15.24 cm X 0.635 cm vertical mold was utilized for the curing process to prevent the formation of air voids. The mold was treated with mold release and then assembled. The blend was added very slowly to the mold. Because the viscosity of some of the blends was so high, it was difficult to prevent air from being trapped in the mold. In addition, the high viscosity prevented some of the blends from flowing into the corners of the mold. This was counteracted by heating the mold to above room temperature but below the initiation temperature of the Derakane™ and holding it there for a period of time. After the top had been secured onto the mold, it was then placed in a Fisher Isotemp forced convection oven. The material was cured utilizing the following cure cycle: 1 hour hold at 65°C → heating at 10°C/min to 150°C → 20 minute hold at 150°C. After the mold had cooled to room temperature, the cured blend was removed.

Glass transition temperature determination of the cured blends

The as prepared, "dry" glass transition temperature of the blends was determined using a Seiko Differential Scanning Calorimeter (DSC). First and second heat data were generated for pure Derakane™ and the K-90 PVP/Derakane™ blends. The second heat data was generated by holding the system isothermally at 250°C for 10 minutes.

Environmental Aging of the Blends

The blends were saturated with water in order to determine the kinetic and thermodynamic parameters associated with water absorption. The blends were machined into 15.24 cm X 1.27 cm X 0.04 cm rectangles. This specimen geometry minimized the diffusion resistance in one direction while maximizing it in the other two. Therefore, the diffusion phenomena being monitored could safely be classified as one-dimensional. The specimens were housed in a glass vial with a screw cap and placed in a convection oven at 75°C. The samples were removed periodically to record the weight change. This was accomplished by removing the specimen, patting it dry, and allowing it to reach room temperature before recording its weight. A Mettler balance was used to record the weights. In addition to the weights, the level of the water in the vial was also checked in order to prevent any drying.

MECHANICAL TESTING

Quasi-static Tension

The aged composite specimens were characterized for static tensile performance. The procedure utilized for completing the tensile testing was discussed in Part I[7.5] of this series.

Cyclic Fatigue

In order to determine the affect of the sizing on performance under cyclic tensile loading, composite specimens, 15.24 cm X 1.27 cm X 0.04 cm were prepared and test on a servo-hydraulic MTS test frame. Load was applied in a sinusoidal, tension-tension (R=0.1) manner at a frequency of 10 Hz. The selection of the applied the applied load was based on a percentage of the ultimate tensile strength of the material. A Microprofiler™ was used to control the programmed loading cycle and a test controller was used to monitor the number of cycles. An extensometer was used to measure the strain in the sample during fatigue. In order to prevent the specimen from being damaged, glass-epoxy end tabs were adhesively bonded to the grip section of the specimens using a 3M-epoxy adhesive. Labview®, a data acquisition software developed by national Instruments was used to aquire the data.

RESULTS AND DISCUSSION

Glass transition temperature determination of the cured blends

There was a single T_g for all the sizing/matrix blend compositions tested, which was an indication of miscibility. The Fox equation can be used to predict the blend glass transition as a function of the pure component glass transitions and is accurate for miscible systems without strong secondary bonding or interactions[7.16]

$$\frac{1}{T_g^{blend}} = \frac{\omega_1}{T_{g,1}} + \frac{(1-\omega_1)}{T_{g,2}} \tag{3}$$

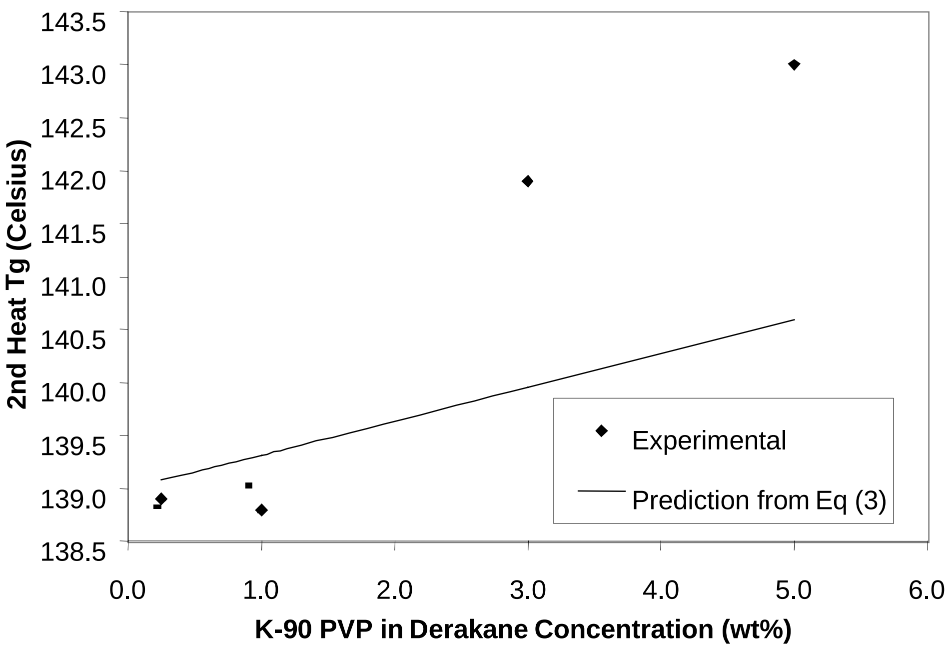
where T_g^{blend} is the blend glass transition, ω_1 is the weight fraction of component one in the blend, $T_{g,1}$ is the pure glass transition of component one, and $T_{g,2}$ is the pure glass transition of component two. The first and second heat glass transition temperatures were compared to those predicted by the Fox equation (Figure 2 a&b). The data showed a deviation from the Fox equation that was indicative of the hydrogen bonding present in this system. Between the first and second DSC heats, there was a consistent difference of approximately 9°C in the blend glass transition temperatures for all blend compositions. This was an indication that all the K-90 PVP in Derakane™ blends had the same degree of cure and that none of the variations in matrix shrinkage discussed previously were due to differences in matrix cure between the blend compositions.

Moisture Absorption

Moisture Uptake of Composites

Figure 3 shows the moisture uptake curves for the individual composites. The composites with the G' sizing absorbed the highest amount of water. This result, although not completely surprising, did initially prove to be difficult to understand especially when compared against the PVP K90 sizing which is known for its hydrophilicity. Data obtained from BASF[7.17] indicates that the PVP K series of polymers can absorb anywhere between 7% by weight at 20°C and 20% relative humidity to 60% at 20°C and 90% relative humidity. The literature also reports little effects of molecular weight or 'K' value on moisture uptake. The relatively poorer processability of the G' sized composites that resulted in void formation could be a cause for this large uptake. The moisture uptake data was input into a code written in Mathematica™ to evaluate the diffusivity (Table 1).

a)



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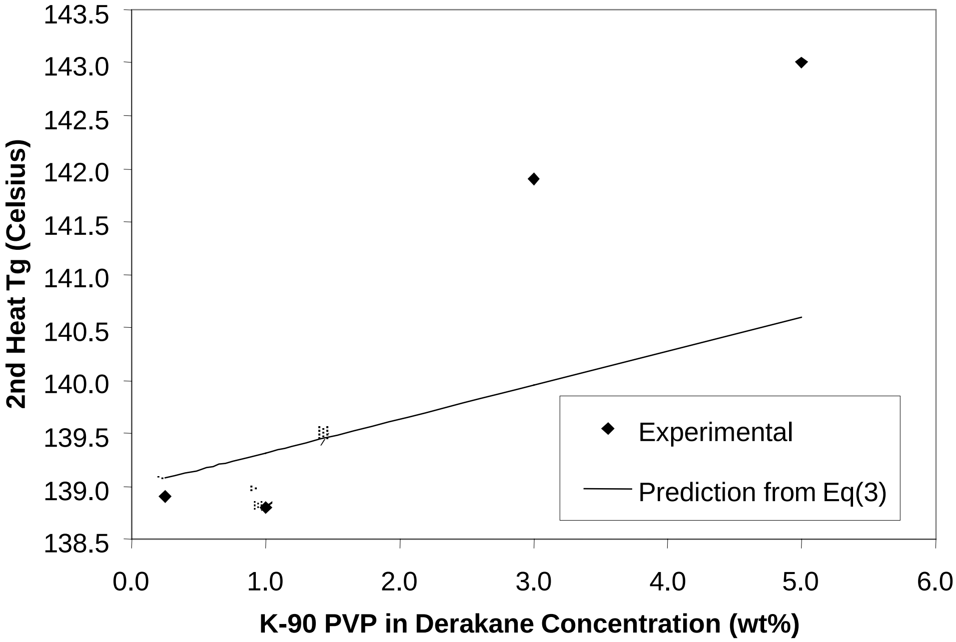

Figure 2: Glass transition temperature of cured K-90 PVP in Derakane™ 441-400 blends as measured by DSC (10°C/min). a). 1st heat b). 2nd heat (isothermal hold at 250°C for 10 minutes).

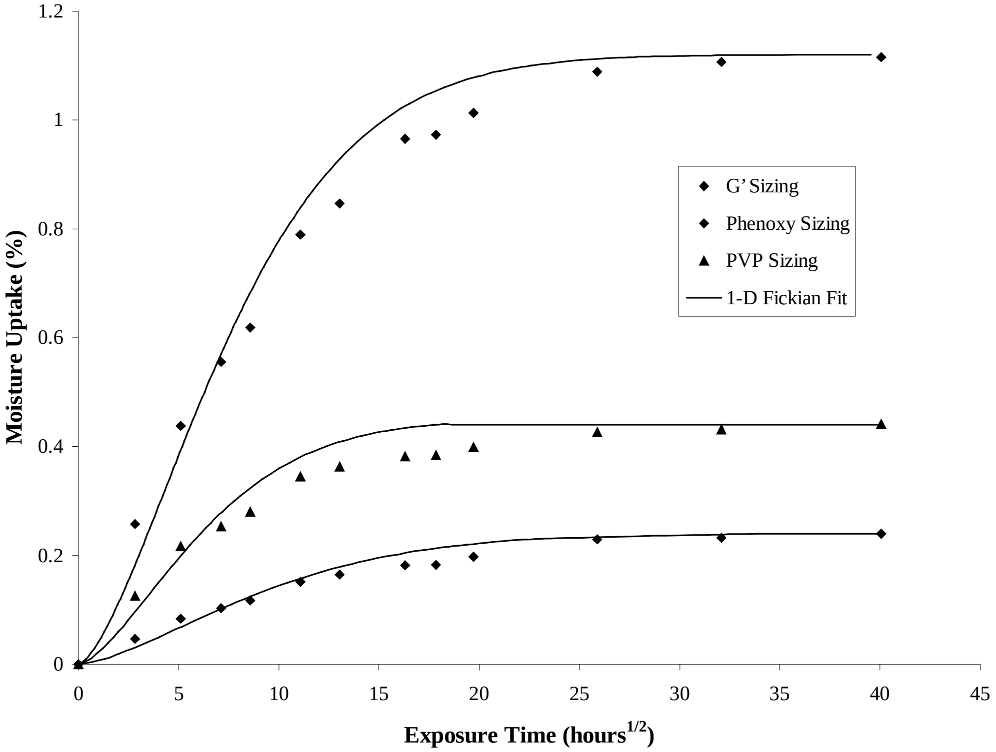

Figure 3: Moisture uptake curves for the individual unidirectional composites aged by immersion in a 65°C water bath. Comparison of data with the 1-D Fickian prediction.

Table 1: Equilibrium moisture content and diffusivities for the different sized fiber composites. These specimens were aged by immersion in a 65°C water bath

Specimen	**Diffusivity, D_z (in cm^2/sec)**	**Equilibrium Moisture Content, M_∞ (in %)**
Low Spread Phenoxy (LSP) Sizing	6.2×10^{-9}	0.24
PVP K90 Sizing	1.3×10^{-8}	0.45
G' Sizing	8.7×10^{-9}	1.12

Mathematica™ was used to evaluate both equations (1 and 2) for the individual composite systems. The solid line in Figure 3 is the 1-D Fickian fit to the absorption data. Although the curve seems to match the data fairly well, deviation is seen to exist at the "knee" for all the composites. Such an observation then implies that the 1-D Fickian equation may need to be extended for the 2-D case. An experiment similar to that performed by Chateaumiois et al.[7.13] must be carried out in order to ascertain the relative contributions of the two diffusivities for the different sizings.

Moisture Uptake of Polymer Blends

The moisture uptake profile of the blends are shown in Figure 4. It is interesting to note that although there appears to be a trend in equilibrium moisture content with PVP K90 concentration, none of the blends appear to show a dramatic increase in the amount of water absorbed as compared to the neat Derakane™. This inspite of the highly hydrophilic nature of PVP K90[7.17] that has been alluded too earlier in the text. This is an interesting observation because it supplements the observations made earlier on the composites that showed a fairly low moisture content for the PVP K90 sizing in comparison with the G'. A possible reason for this could be the ability for the vinyl ester to hydrogen bond with the PVP K90. This hydrogen bonding is thought to be responsible for shielding the highly susceptible carbonyl and amide bonds

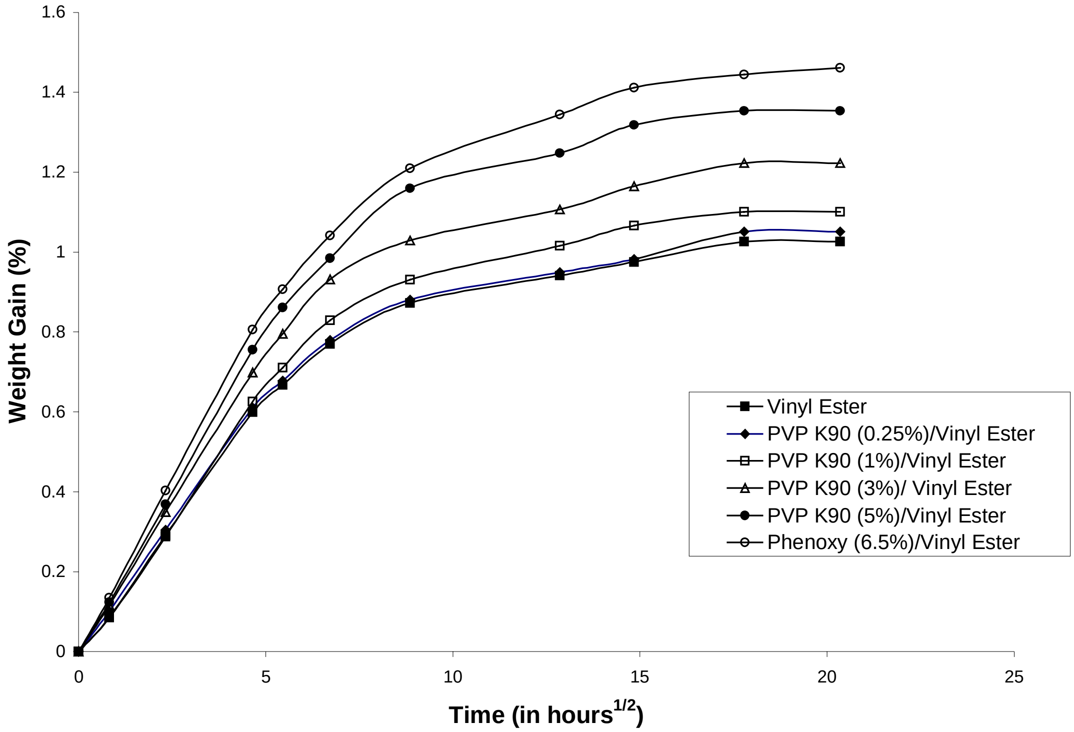

Figure 4: Moisture uptake plot for the unreinforced PVP K90 sizing/Vinyl Ester blends as well as Phenoxy sizing/Vinyl Ester blends.

(Figure 1 (a)) of the PVP polymer that are responsible for the polymer's hydrophilic nature. This interaction then limits the ability of the PVP to interact with the incoming water thereby reducing its hydrophilicity[7.18].

Table 2 indicates the maximum moisture content and diffusivities for the different blends. The diffusivity was calculated using equation (2). The diffusivity of the PVP K90/vinyl ester blends seem to decrease with increasing PVP concentration. The Phenoxy/vinyl ester blend on the other hand indicated the highest moisture content. It must be mentioned here that although the phenoxy polymer is considered to be hydrophobic, a carboxy-modified version of the polymer that is dispersible in water was used to make the blend specimens.

Table 2: Equilibrium moisture content and diffusivities for the different blends. These specimens were aged by immersion in a 75°C water bath

Specimen	**Diffusivity, D_z (in cm^2/sec)**	**Equilibrium Moisture Content, M_∞ (in %)**
Neat Derakane™ vinyl ester	7.83×10^{-8}	1.03
0.25% PVP K90/vinyl ester	7.93×10^{-8}	1.05
1% PVP K90/vinyl ester	7.96×10^{-8}	1.10
3% PVP K90/vinyl ester	6.20×10^{-8}	1.22
5% PVP K90/vinyl ester	6.04×10^{-8}	1.35
Phenoxy/vinyl ester	7.47×10^{-8}	1.44

During the uptake experiment in the unreinforced polymer blend, the appearance of the Phenoxy sample changed from a transparent golden yellow to an opaque milky white, suggesting moisture absorption. The clear golden yellow appearance then returned upon sustained drying at 100°C for approximately 24 hours. Upon cure, the Phenoxy is known to phase separate from the vinyl ester resin. As water absorption takes place, these globular domains are thought to swell giving the sample its turbid appearance and high moisture content. As reported earlier, the process is completely reversible. In the case of the composite however, the surface temperature of the Phenoxy sized fibers in the infra-red heating tower was set at 200°C. This facilitated excellent drying, melt coating of the fibers and some cross-linking of the carboxy modified polyhydroxyether (Phenoxy) polymer. It is believed that the crosslinking reduces the polymer's affinity towards water.

Mechanical Properties

Unaged Material

The tensile properties of the three different composites are indicated in Table 3.

Table 3: Tensile properties for the composites before and after moisture aging

COMPOSITE SYSTEM	**STRENGTH (MPa)**	
	Before Aging	**After Aging**
Phenoxy sized composite	2035±35	1728±30
PVP K90 sized composite	1964±71	1602±52
G' sized composite	1673±39	1408±25

The tensile strength seemed to very sensitive to the type of composite tested inspite of them all being unidirectional and having the same matrix and fiber. Explanations based on the prosessability of the fibers as well as interface have been alluded to by Broyles et al.[7.5] .

The G' sized carbon fiber tows were extremely bushy and formed a lot of fuzz in the dip bath as they passed through it. This fuzz consisted primarily broken fibers that were separated from the tow during its passage through the nip rollers in the dip bath. This phenomenon was however not only restricted to the resin bath but also continued as the fibers were drawn into the forming die. Because of which the surface of the composite always seemed to be rough and visual inspection indicated the presence of twists in the tows especially on the surface layers. The thermoplastic sized carbon fibers were stiff in comparison when coming off the spool. This enabled them to move through the nip rollers smoothly with minimum collection of fuzz. The final composite had an extremely smooth and glossy surface and the fibers were all generally straight.

The fatigue tests did not show a significant change in the slope of the 'S-N' curves of the Phenoxy and PVP K90 composites especially when plotted with respect to the normalized applied stress (Figure 5). Normalization was done by dividing the applied stress with the ultimate tensile strength of the composite in consideration. Changes did however exist between the G' and two thermoplastic sizings. This indicates that the damage mechanism in the G' composite is different. Dynamic stiffness data collected during the test is also shown in Figure 6.

Aged Material

Upon saturation, in order to minimize moisture loss, glass epoxy end tabs as well as extensometer tabs were attached to the specimen with the help of the M-Bond™ cyanoacrylate ester adhesive instead of the conventional epoxy. This process took a couple of minutes. Figure 7 shows the changes in tensile strength after saturation for the different composites. The abscissa in the figure has been normalized with respect to the particular composite's tensile strength prior to aging. As seen in the figure, although the G' composite has the highest diffusivity and moisture content it's tensile strength did not drop much as compared to the other two that had a lower moisture content. This result again leads the

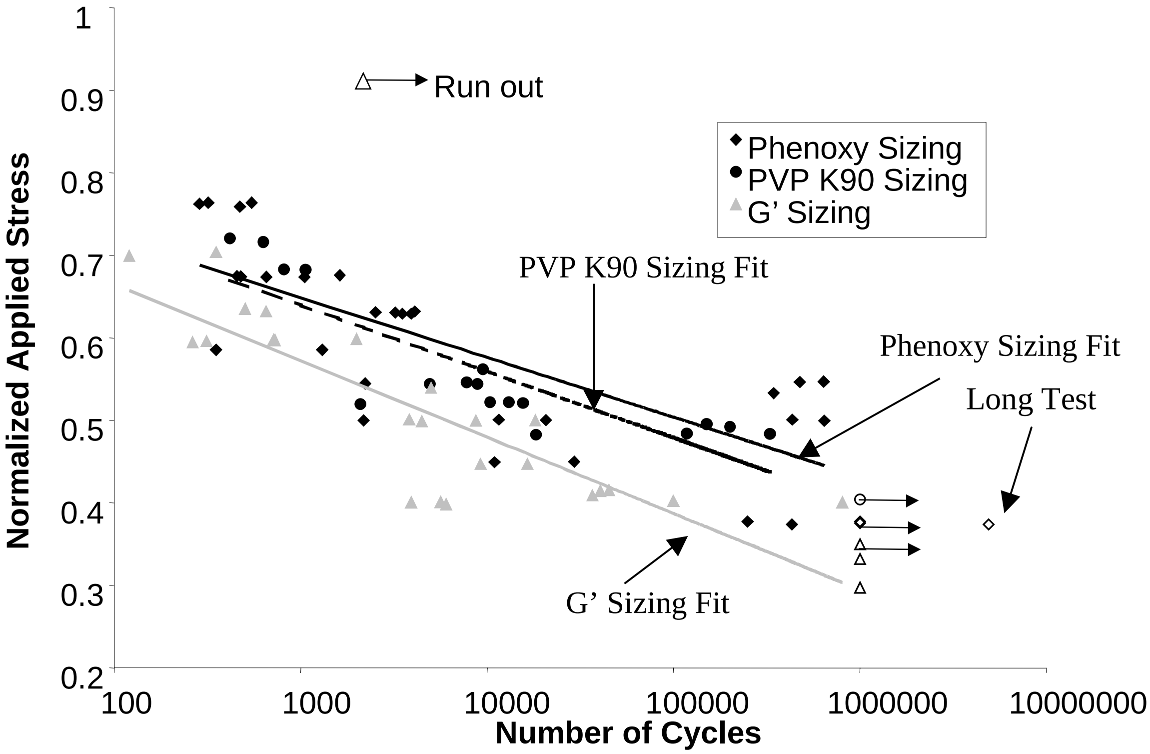

Figure 5: Stress normalized ‘S-N’ curves for the individual unidirectional composites tested in fatigue at 10Hz under an R = 0.1 condition. Also indicated is a run-out data point from a single Phenoxy sized composite specimen that was tested to 5 million cycles.

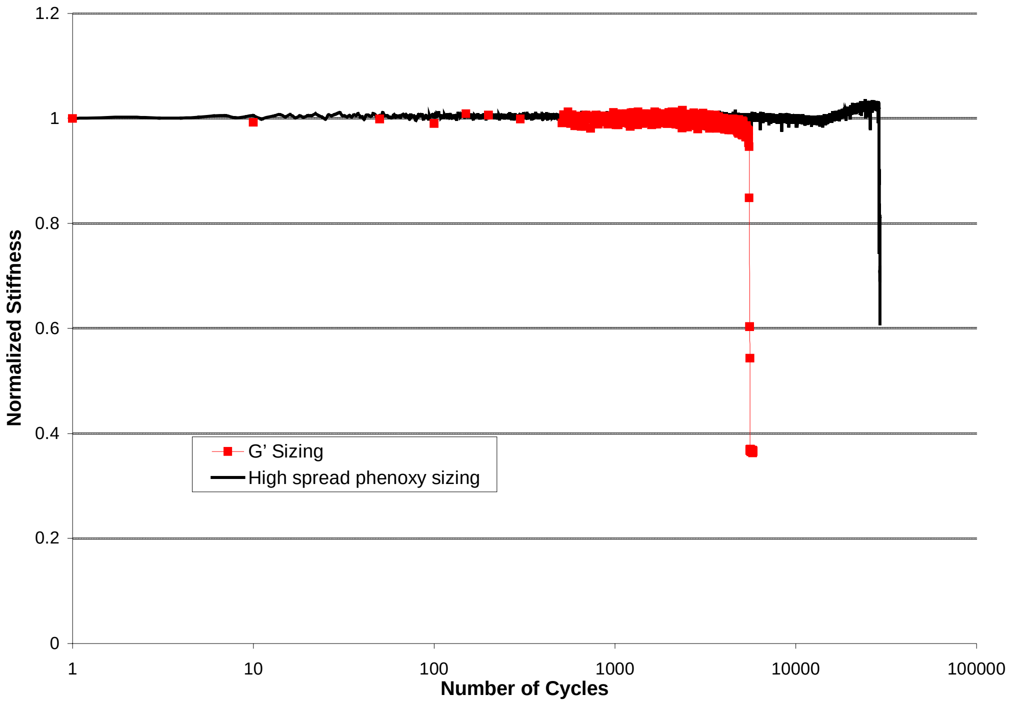

Figure 6: Stiffness reduction curves for the G' sizing and the High Spread Phenoxy sizing during fatigue at 50% of their respective ultimate tensile strengths.

authors to speculate that the poor processability of the G’ composites resulted in the formation of voids that acted as reservoirs for water entrapment during moisture uptake. Since these voids are randomly distributed throughout the composite, there was no preferential attack at the interphase that could have caused a change in failure mode. This, the authors believe was however true in the case of the two thermoplastic sized composites. In this case, since the processing was of superior quality, the nature of the sizing resin made all the difference. PVP K90 is an extremely hydrophilic polymer whereas Phenoxy tends to hydrophobic. This is the reason for the higher diffusivity as well as the moisture content in the case of the PVP K90 sized composite as compared to the Phenoxy. It is also clear from the location of the absorbed water namely at the interphase, that the residual strength of the PVP K90 composite should be lower than the Phenoxy, proof of which is shown in Figure 7.

CONCLUSIONS

The blend glass transition temperature was found to deviate from the Fox prediction due to strong hydrogen bonding interactions.

Fatigue tests performed on the unidirectional composites indicated that the slope of the two thermoplastic sized composites were similar when plotted on a normalized stress versus cycles to failure plot. The slope of the G’ sized composite was different indicating a change in damage progression. Large fiber waviness as well as damage to the fibers during pultrusion was thought to be responsible for this.

The interphase was also found to have a profound impact on the moisture uptake characteristics and residual strength of the composites. There seemed to be a larger amount of void formation in the G’ sized composites as compared to the two thermoplastic sized composites. This was speculated to be responsible for the higher moisture weight gain in the G’ sized composites. In the case of the Phenoxy and PVP-K90 sized composites, the role of the sizing and resulting moisture weight gain was responsible for the loss in tensile strength after saturation. Moisture uptake experiments conducted on the blends resulted in some interesting results. The diffusivity of the PVP-K90 blends were related to the concentration of the PVP in the blend however, the equilibrium moisture content was not significantly

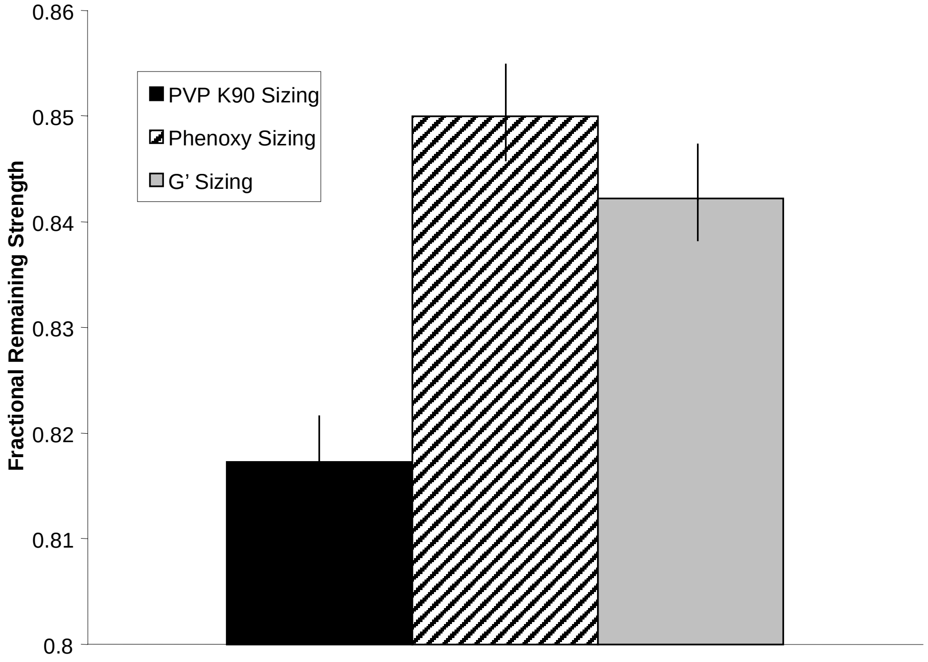

Figure 7: Residual tensile strength of sized unidirectional composites that were tested wet after saturation

larger than the pure Derakane™ vinyl ester resin. It was speculated that hydrogen bonding between the PVP and vinylester caused a shielding effect for the carbonyl and amide groups on the PVP resin thereby reducing its affinity for water. The phenoxy blend on the other hand, was seen to absorb a larger amount of water. This was however not true for the composite case in which the elevated drying conditions in the heating tower of the sizing line was thought to have promoted some crosslinking in the carboxy modified polyhydroxyether polymer. A further investigation however is suggested in order to understand this phenomenon completely.