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# Fatigue performance of carbon fibre/vinyl ester composites: the effect of two dissimilar polymeric sizing agents

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Carbon fibre/vinyl ester composites were made from sized carbon fibres. The carbon fibres were sized with an in-house sizing process and then formed into a unidirectional fabric. This fabric was processed into composite panels by a resin film infusion (RFI) technique. The effects of two dissimilar sizing agents—a brittle thermoplastic K-17 poly(vinyl pyrrolidone) (PVP) and a ductile thermoplastic polyhydroxyether (phenoxy resin)—on notched fatigue, short-beam shear, transverse flexure properties and compression properties were studied.

The fatigue properties of carbon fibre/vinyl ester composites were influenced drastically by the type of sizing agent used. A 20-fold increase in lifetime was demonstrated at a loading level of 207 MPa for the ductile phenoxy-sized composite compared with the unsized composite. The brittle PVP-sized composite panel showed a sixfold increase in lifetime compared with the unisized case. The phenoxy-sized composite panel showed a 40% increase in flexural modulus and the PVP-sized panel showed a 20% increase compared with the unsized composite panels. Negligible differences in the shear strength, flexural strength and static compressive strength were observed for the different interphase agents. The implications of these results for tailoring polymeric interphases in vinyl-ester-matrix composites are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: interphase; carbon fibre; vinyl ester)**

## INTRODUCTION

Fibre-reinforced polymer-matrix composites for structural applications comprise continuous or long chopped fibres embedded in a polymer matrix (usually a thermoset material). Such composites have high strength-to-weight ratios and excellent corrosion resistance relative to steel[1]. The function of the matrix is to protect the brittle reinforcing fibres and to transfer load to the fibres. Commonly employed polymer-matrix materials include thermosets such as epoxies, unsaturated polyesters and vinyl esters, and also selected thermoplastics such as poly(ether ether ketone), poly(ethylene terephthalate) and poly(phenylene sulfide). Carbon fibres, primarily derived from pyrolysis of poly(acrylonitrile), can provide high modulus or stiffness with a density of 1.8 g $\mathrm{cm}^{-3}$. In many aerospace and civil applications, other fibre types include ceramics, E-glass, aramids (Kevlar) and high-molecular-weight polyethylene (Spectra). A third constituent, the 'interphase', is now known to affect composite performance drastically[2]. The interphase is a region of finite mass located at the fibre/matrix interface. This region has gradients in physical properties that greatly influence the performance of the final composite. One method to modify and control the physical properties of this interphase region is by applying a coating (sizing) material to the surface of the carbon fibre prior to impregnation with the matrix material. The process of applying a sizing to a carbon fibre surface is referred to as sizing.

Recent research has demonstrated that thermoplastic sizings in carbon-fibre-reinforced epoxy-matrix composites can improve composite performance, especially durability and lifetime. Lesko *et al.* compared the mechanical properties of epoxy-matrix composites reinforced with carbon fibres sized with two different materials[3,4]: an epoxy and a low-molecular-weight poly(vinyl pyrrolidone) ($M_n$ = 14 000) thermoplastic sizing. The matrix was untoughened 3501-6. They compared several mechanical properties at two different sizing levels. The most significant interphase material effects were in the composites' dynamic performance. The composites had a $[0°/90°]_{8s}$ cross-ply lay-up. Quasistatic notched compression strength for both sets of composites were found to be almost equal at 314 and 313 MPa, respectively, for the poly(vinyl pyrrolidone) (PVP)- and epoxy-sized composites. In spite of their almost identical compression strengths, the compression–compression, $R = 10$ fatigue tests showed marked differences. For example, at an applied load of 70% of ultimate compression strength (UCS), the PVP-interphase composite was found to have an order of magnitude higher life compared with the epoxy-interphase composite. This is remarkable considering the fact that the quasi-static compression strengths were nearly identical. The transition from low-cycle fatigue to high-cycle fatigue characteristics in both cases was, however, seen to occur over a very narrow load range. In order to study the role of the

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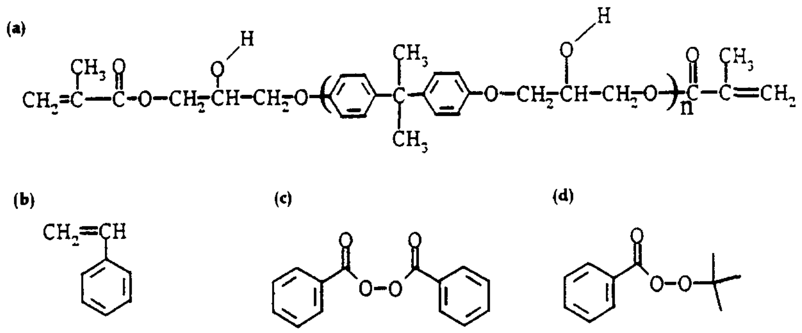

**Figure 1** Chemical structures of charged Derakane resin: (a) vinyl ester resin, (b) styrene, (c) benzoyl peroxide and (d) t-butylperoxybenzoate

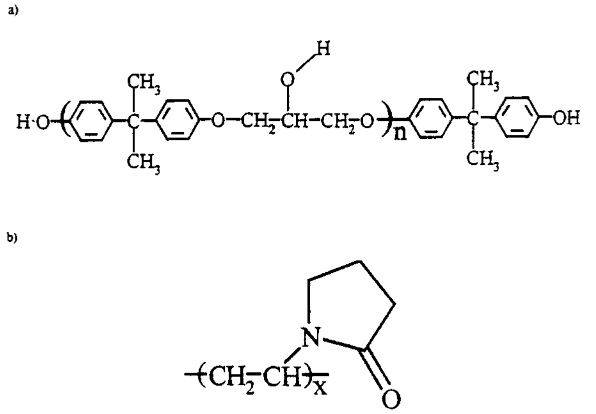

**Figure 2** Chemical structures of: (a) polyhydroxyether (phenoxy) and (b) poly(vinyl pyrrolidone) (K-17 PVP)

interphase in the fatigue failure process, extensive damage evolution and propagation studies were conducted. It was observed that the initiation and growth of longitudinal 0° splits that extended tangentially from the edge of the notch occurred at about the same rate for both the interphases. This was done by stopping the fatigue test at particular intervals and performing x-ray radiography. However, the ability of the PVP interphase to resist the other major form of damage, namely surface ply buckling (SPB), was far greater than that of the epoxy interphase. For example, at 70% UCS, the PVP-interphase composite initiated SPB at 10 000 cycles as compared with 3000 cycles for the expoxy interphase. In addition, once SPB initiated, the growth rate as measured through high-speed video monitoring was much slower for the PVP interphase. Finally, the length of SPB at which unstable growth occurred was greater for the PVP interphase composite as compared with the epoxy composite. All of the above are consistent with the longer lifetimes that the PVP interphase composites had over the epoxy composites for a given load level. From this study, it was concluded that the *apparent* critical $K$ (stress intensity factor) for the PVP interphase might have been higher. It is not merely the longitudinal splitting or the inherent material strength of the composite that controls the fatigue behaviour, but more precisely the toughness or damage tolerance of the interphase material. These results demonstrate that it should be possible to engineer an optimal sizing material to tailor selected composite properties.

The methodology followed in the present work involves comparing the effects of a relatively brittle polymeric sizing with a relatively ductile sizing material in a vinyl ester matrix. Fibres were sized with poly(vinyl pyrrolidone) and polyhydroxyether, which is a more ductile polymer. An unnotched fatigue test was found to distinguish quite well between the polymer sizing agents and an unsized fibre control. This work is a necessary starting point for further studies of the effects of polymer sizing agents on damage initiation and propagation.

## EXPERIMENTAL SECTION

### *Materials*

*Carbon fibre.* The fibres used in these experiments were Hercules AS-4 12K carbon fibre tow. AS-4 12K unsized but surface-treated (lot # 1187-4E) was used as a feedstock for the sizing process.

*Resin or matrix material.* The vinyl ester matrix material (Derakane 441-400) was obtained from the Dow Chemical Co. (*Figure 1*). Literature from the company indicates that the polymer has an ultimate tensile strength of 82.72 MPa and a strain to failure of 7 to 8%. The Derakane 441-400 matrix consisted of 70 wt% pure vinyl ester and 30 wt% styrene monomer. The vinyl ester component of the resin had a number-average molecular weight ($M_n$) of approximately 680 g mol$^{-1}$ [as determined with proton nuclear magnetic resonance spectroscopy ($^1$H n.m.r.)] and was terminated with methacrylate functional groups.

*Matrix initiators.* The benzoyl peroxide and t-butylperoxybenzoate initiators were obtained from Aldrich and Elf Atochem, respectively, and were used as received.

*Sizing materials.* The phenoxy polyhydroxyether (PKHW 35) sizing material (*Figure 2a*) was obtained from Phenoxy Associates, Rock Hill, SC. Data obtained from the company indicates that the polymer has an ultimate tensile strength of 55.16 MPa and a strain to failure of 40 to 100%. This polymer is therefore a tough polymer. This material was obtained as a 35 wt% dispersion of approximately 1 $\mu$m diameter particles in water. The $M_n$ of the phenoxy was 19 000 g mol$^{-1}$ [as determined by gel permeation chromatography (g.p.c.)] and it had a glass transition temperature ($T_g$) of 97°C [as determined by differential scanning calorimetry (d.s.c.)].

The Luviskol K-17 poly(vinyl pyrrolidone) (lot # 58-0978) sizing material (*Figure 2b*) was obtained from the BASF Corporation. Although the properties of K-17 are not known, K-90, a higher-molecular-weight version, as an ultimate tensile strength of 62.06 MPa and a strain to failure of only 0.9%. This indicates that it is an extremely brittle polymer. The $M_n$ of this material was 14 000 g mol$^{-1}$ (g.p.c.) and it had a $T_g$ of 121°C (d.s.c.).

Deionized water was used in the preparation of the aqueous sizing solutions used in the sizing process. The

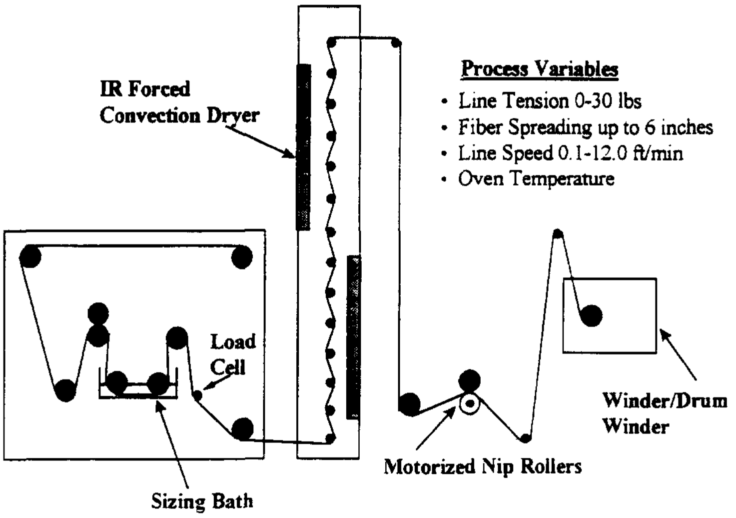

**Figure 3** Custom small-scale sizing line

deionized water came from a NanoPure II® unit equipped with a 0.2 $\mu$m filter and a resistivity typically of 15 M$\Omega$ cm or higher.

*Microscopy materials.* Epoxide resin no. 20-8130-032 and epoxide hardener no. 20-8132-032 were obtained from Buehler for use in preparing composite specimens for scanning electron microscopy (SEM).

*RFI consumable materials.* Porous, Teflon-coated fibreglass release cloth was obtained from Airtech for use in the resin film infusion (RFI) process.

### *Materials characterization*

*Viscosity and glass transition temperature.* $^1$H n.m.r. spectra were collected with a Varian Unity 400 instrument operating at 400 MHz. G.p.c. was conducted on a Waters GPC/ALC 150-C chromatograph equipped with the differential refractometer detector (RI) connected in parallel to a differential viscometric detector (DV), Viscotek® model 100. The injector and column compartment, connecting line and DV detector were individually maintained at the same temperature (60°C). The signals from the RI and DV detectors permitted calculation of intrinsic viscosity and intrinsic viscosity distribution for universal calibration purposes by using Viscotek software Unical 4.04. This calculation assumed that the polymer concentration at the outlet of the size exclusion chromatography (s.e.c.) columns approached infinite dilution due to separation and column dispersion. *N*-methylpyrrolidone stirred over $P_2O_5$ was prepared according to the method of Cotts and co-workers[5,6]. HPLC-grade *N*-methylpyrrolidone and $P_2O_5$ were obtained from Sigma-Aldrich. The concentration of $P_2O_5$ was 0.02 M. D.s.c. was conducted with a DuPont 910 DSC instrument under a nitrogen purge, which was calibrated with indium, lead and poly(dimethylsiloxane) ($-123$°C). Samples of the polyhydroxyether and poly(vinyl pyrrolidone) sizing materials were scanned from 25°C to 300°C, then cooled quickly and scanned a second time. All scanning rates were 10°C min$^{-1}$. No melting endotherms were observed. Glass transition points were taken from the inflection points of the curves from the second scans.

*Sizing level determination.* The amount of sizing deposited on the carbon fibre was determined via pyrolysis in a nitrogen atmosphere. Approximately 8 g of sized carbon fibre were used for the analysis. This fibre was first dried in a convection oven above the $T_g$ of the particular sizing material for 8 h. The fibres were placed in a high-temperature Blue-M furnace with a slow nitrogen purge. The fibres were pyrolysed at 600°C for 30 min. In all cases, the pyrolysis cycle was found to be sufficient to completely volatilize the sizing while leaving the fibre unaffected. The amount of sizing material was computed from the differences in mass of the dry sized fibre and the pyrolysed fibre:

$$S = 100(M_1 - M_2)/M_1 \qquad (1)$$

where $S$ was the weight percentage of sizing on the fibre, $M_1$ was the dry sized fibre mass, and $M_2$ was the pyrolysed fibre mass.

*Sized fibre quality.* The quality of the sized fibre was determined by inspection of the fibres under scanning electron microscopy. The fibres were secured on a standard ESCA mount. The fibres were sputter-coated with gold for approximately 2 min. Analysis was conducted in an International Scientific Instruments model SX-40 SEM.

*Fibre volume fraction.* The fibre volume fractions of the composite panels produced in these experiments were calculated by measuring the density of the composite in air and in isopropyl alcohol. A 4 g sample of the composite was dried and weighed. The sample was then immersed in isopropyl alcohol and weighed again. The density of the composite was calculated by Archimedes' principle using the following equation:

$$\rho_c = \frac{W_{air}}{(W_{air} - W_{IPA})}\rho_{IPA} \qquad (2)$$

where $\rho_{composite}$ is the density of the composite, $\rho_{IPA}$ is the density of isopropyl alcohol. $W_{air}$ is the weight of the sample in air and $W_{IPA}$ is the weight of the sample in isopropyl alcohol.

The fibre volume fraction was then calculated by using the rule of mixtures

$$v = (\rho_c - \rho_{resin})/(\rho_{fibre} - \rho_{resin}) \qquad (3)$$

where $v$ is the fibre volume fraction, $\rho_{fibre}$ is the density of

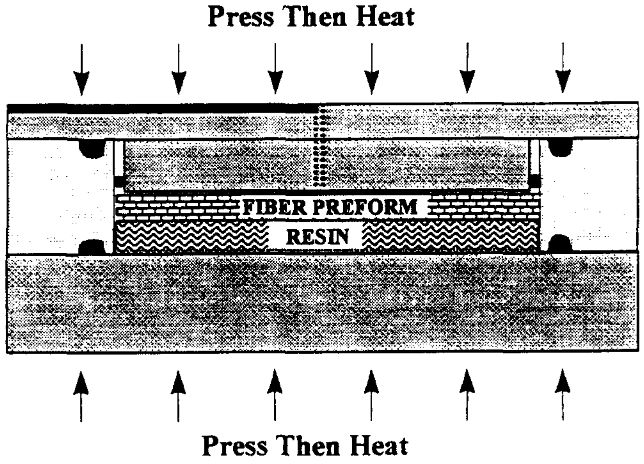

**Figure 4** Resin film infusion mould

the carbon fibre = 1.8 g cm$^{-3}$, $\rho_{\text{resin}}$ is the cured resin density = 1.162 g cm$^{-3}$, and $\rho_c$ is the composite density calculated from equation (2). The fibre volume fractions of the panels ranged from 0.55 to 0.58.

*Quality of panels (voids).* Voids in the composite panels were analysed with an ISI model SX-40 scanning electron microscope at an acceleration voltage of 20 kV. Sections of the composite panel were cut and placed in a Buehler potting cup. Epoxide resin and epoxide hardener were mixed in a ratio of 5:1 by weight and poured into the potting cup. The mixture was cured a room temperature for approximately 6 h. The cured samples were polished with a Buehler Ecomet 3 (variable speed) polisher/grinder. The samples were placed in a carousel and attached to the spindle of the Automet 2 (power head). The power head ensured controlled loading of the specimens during polishing and resulted in specimens with a high gloss surface.

### *Materials preparation*

*Sized fibre preparation.* Fibres were sized on a custom-made small-scale sizing line[7,8] (*Figure 3*). Carbon fibre tow was pulled off a spool at a set speed ranging from 0.3 to 6.0 cm s$^{-1}$. The fibres were placed under tension by a nip roller connected to a particle brake in the range of 0 to 110 N. The fibres were then passed through the sizing solution where capillary forces provided the driving force for rapid tow wetting. The high fibre tension and extensive use of rollers after the sizing bath spread the tow bundle and also prevented the wet tow from clumping. The spread carbon fibre tow containing the sizing solution was dried online in an infra-red (i.r.) forced convection dryer.

The emitter surface temperature of the two i.r. heating panels embedded in the dryer was controllable from ambient temperature up to 500°C. The inlet air temperature was controlled at ambient conditions. The emitter surface temperature controlled directly the surface temperature of the carbon fibre. The surface temperature of the fibre was measured by a hand-held thermocouple. A time–temperature profile was generated by placing the thermo-couple on the fibre surface at various positions in the i.r. dryer.

The fibre that exited the dryer was wound onto a drumwinder to fabricate a 180 cm length of unidirectional single-ply fabric. The drumwinder operated by overlapping single tow strands onto a 60 cm diameter drum. The fibres were held in place via tape placed 19 cm apart. Areal weight (fibre mass per unit cross-sectional area) of the fabric was controlled by controlling the degree of tow overlap. The fibre on the drum was cut into individual 19 cm by 19 cm plies. The sized fabric produced by this process was stitched perpendicular to the fibre direction at 5 cm intervals to prevent fibre movement in the subsequent processing steps.

*Resin preparation.* The resin was prepared by dissolving 1.1 wt% benzoyl peroxide and 0.2 wt% t-butylperoxybenzoate in Derakane 441-400. The mixture was degassed under vacuum (0.5 atm) with rapid stirring at room temperature until styrene first appeared in the vacuum trap. The amount of styrene lost in this step was found to be negligible. This resin was used for laminate production immediately upon preparation.

*Laminate preparation.* The method utilized for composite panel production was resin film infusion (RFI) or matrix film infusion. A custom mould (*Figure 4*) was designed for the RFI process. The bottom of the mould was covered with a porous, Teflon-coated, fibreglass release cloth. Approximately 100 g of the initiator-charged resin was poured into the mould cavity. The stitched sized fabric produced by the process described earlier was cut to the exact size of the mould. After cutting to size, the stitched fabric weighed approximately 15 g per ply. Approximately seven plies or 105 g of fibre was placed on top of the resin. The orientation of the individual plies was varied to obtain either unidirectional or $[0°/90°]_{7s}$ cross-ply composite panels. The top surface of the fibres was covered with another piece of the porous Teflon release cloth. A hole was placed in the centre of the release cloth to allow resin to exit the cavity.

The piston plate (top of the mould) was placed on top of the fibres in such a way as to minimize pressure exerted on

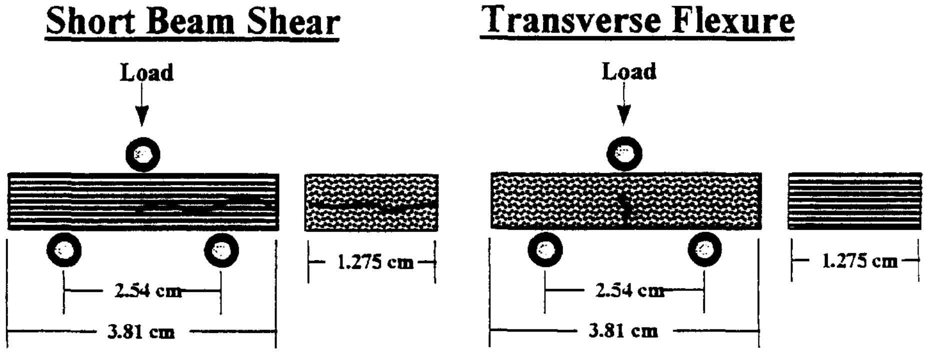

**Figure 5** Schematic of the short-beam shear and transverse flexure test specimens

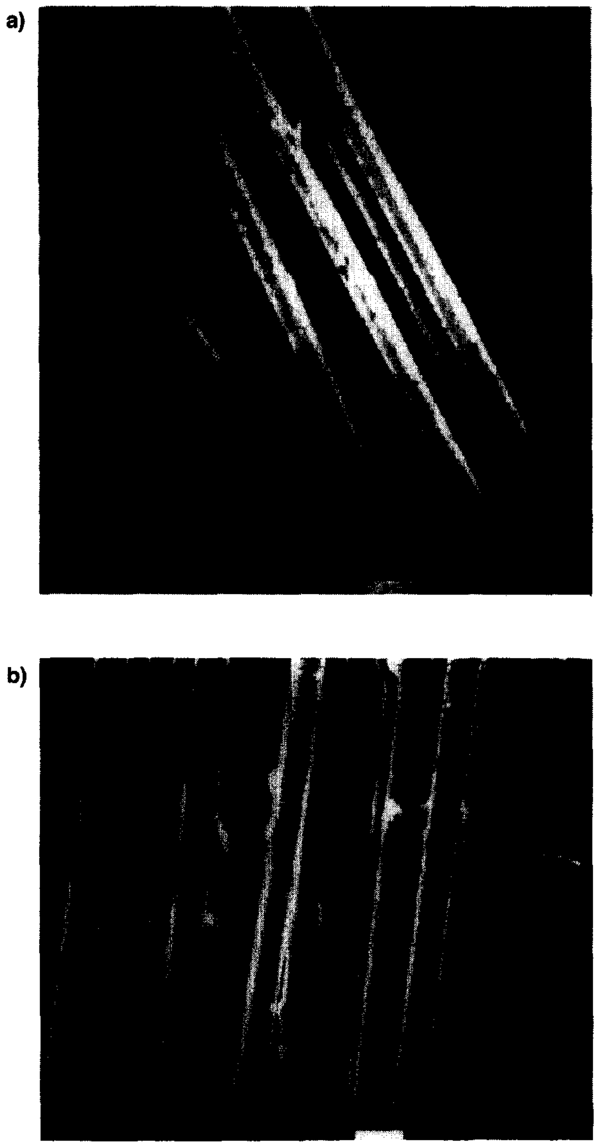

**Figure 6** SEM micrographs of: (a) sized AS-4 12K with 0.7 wt% poly(vinyl pyrrolidone) and (b) sized AS-4 12K with 0.6 wt% polyhydroxyether

the fibres. The piston plate was designed with three distinct features. First, an o-ring around the piston plate was used to minimize resin leakage from the sides of the mould. Second, a 3 mm diameter hole in the centre of the piston plate allowed excess resin to exit through the top of the mould. Finally, a trough was designed around the edges of the piston plate to allow excess resin to collect.

After the mould was assembled, it was placed in a Wabash (model 9112) 25 MPa vacuum hot press that had been covered with a 2 mm aluminium cover plate. The cover plate prevented excess resin from coming into contact with the press. The platens of the hot press were allowed to close at a rate of 6 mm min$^{-1}$. The slow platen closure rate allowed the resin to fully impregnate the individual fabric plies while allowing the air and excess resin to exit. The platen closure pressure was 4000 kPa. After the platens had fully compressed the mould, the platens were briefly opened to allow any trapped air to escape, then re-closed at a pressure of 10 MPa. The platens were then heated to 150°C at a rate of 15°C min$^{-1}$. The platens were held at 150°C for approximately 10 min then cooled to room temperature at a rate of −20°C min$^{-1}$. The platens were opened and the composite panel was removed from the mould. Each of the composite panels were produced under the same processing conditions to insure that the same time was available for sizing diffusion.

*Mechanical testing*

Short-beam shear (ASTM D2344-84) and transverse flexural (ASTM D790-90) tests were conducted on unidirectional composite samples. Specimens were cut in two stages in accordance with the ASTM standards. The first rough cuts were made with a Felker cutting saw. The final cuts were made with a Buehler Isomet low-speed cutting saw and a Buehler diamond wafering blade. The final specimen dimensions were 3.8 cm × 1.3 cm. The specimens were mounted in a three-point bend fixture and loaded at a rate of 1.3 mm min$^{-1}$ on an Instron 4104 instrument. A 5 kN load cell was used for both the short-beam shear and transverse flexural strength tests. LabView®, a National Instruments Corporation data acquisition software, was used to monitor load *versus* displacement. Failure was noted when cracking appeared along the length of the specimens in the short-beam shear tests and across the thickness in the transverse flexural tests (*Figure 5*).

Notched quasi-static compression and fatigue tests were conducted on notched, cross-ply $[0°/90°]_{7s}$ specimens. Specimens were rough cut with the Felker cutting saw and then ground to 15.2 cm × 2.54 cm. A 6.4 mm diameter hole was drilled in the centre of the specimen to create the notch. Aluminium extensometer tabs were attached to the specimen by using silicone grease such that the extensometer rested across the notch. An MTS model 632 extensometer with a gauge length of 2.54 cm and a maximum strain limit of 4% was used to monitor strain. Grit 100 sandpaper was wrapped around the specimen ends to protect them from being crushed by the test machine grips. An MTS instrument with a pair of model 647 hydraulic wedge grips, a 448.82 test controller, a 418.91 Microprofiler™, a 413.81 master controller and a 464.80 data display unit were utilized. An external Vishay Measurements Group model 2310 amplifier box was used to acquire the strain signals. A 5.08 cm test gauge length was used. The specimens were loaded into the grips at a grip pressure of 7 MPa and specimen alignment was ensured by the use of a spirit level. Quasi-static compression tests were conducted to evaluate the ultimate compression strengths of the materials. Compressive load was applied at a rate of 57 kg s$^{-1}$. This loading cycle was programmed in the Microprofiler™ which controlled the machine once a test was begun. The knife edges on the extensometer were made to rest in the aluminium tabs on the specimen and fastened via rubber bands. LabView® software was used to monitor the load, stroke and strain signals during the tests. The stroke interlocks on the machine were set tightly to prevent damage to the extensometer upon specimen failure.

Fatigue tests were conducted in a similar manner on the MTS test frame. Load was applied in a sinusoidal, fully reversed ($R = -1$) manner at a frequency of 10 Hz. The magnitude of the applied load was computed as a percentage of the ultimate compression strength for the material. The Microprofiler™ was used to control the programmed loading cycle and the test controller was used to monitor the number of cycles.

## RESULTS AND DISCUSSION

### *Sizing of carbon fibres*

*Processing.* An aqueous solution of 1.0 wt% K-17 PVP

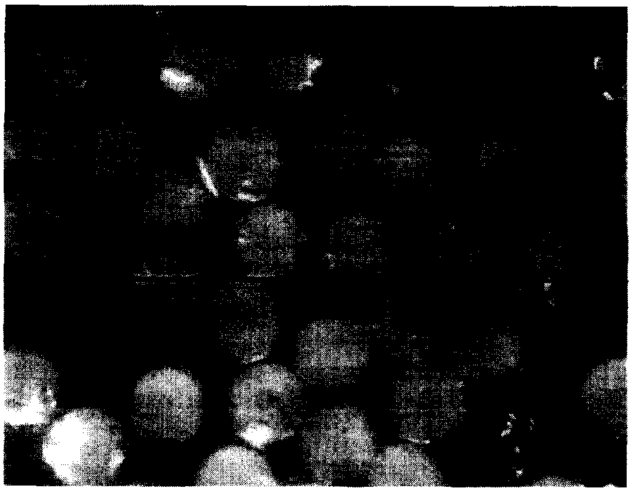

**Figure 7** SEM micrograph of representative cut and polished composite structure

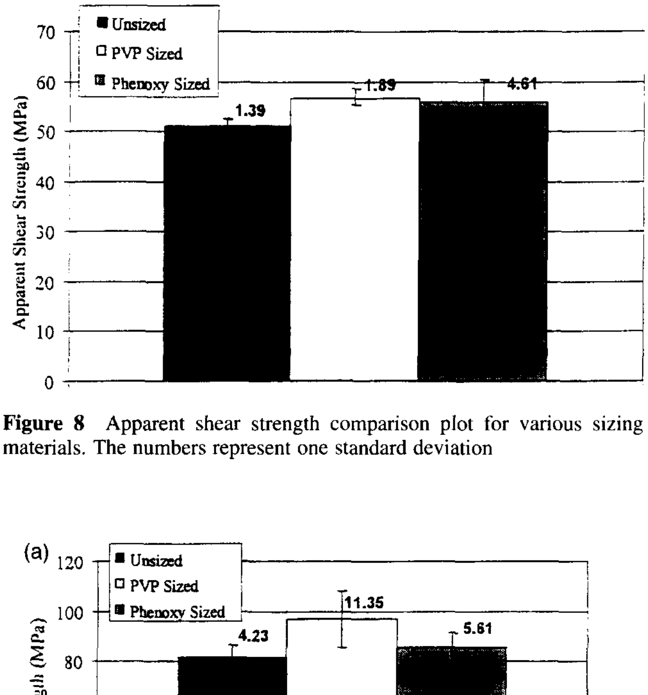

**Figure 8** Apparent shear strength comparison plot for various sizing materials. The numbers represent one standard deviation

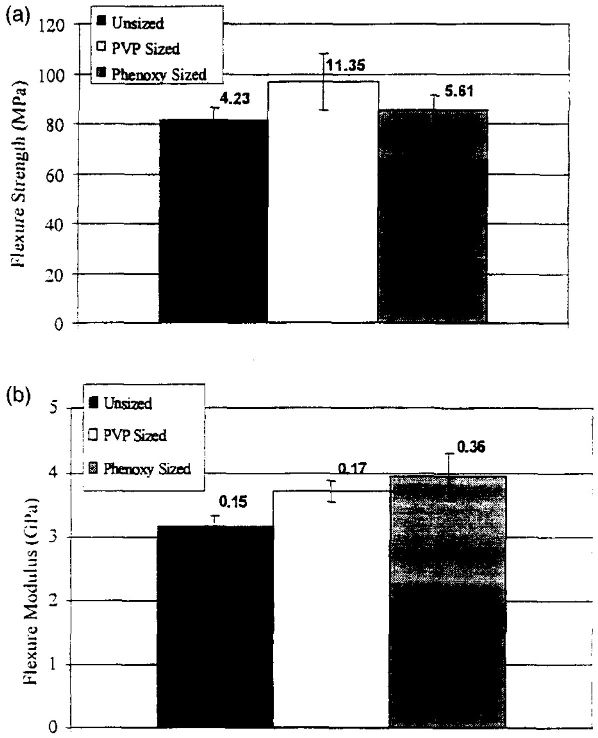

**Figure 9** (a) Flexure strength and (b) flexure modulus plot for various

and an aqueous dispersion of 1.0 wt% phenoxy were prepared and used in the sizing process to produce sized fibre.

The surface temperature history of the sized carbon fibre affected the handling characteristics of the final sized tow. It also affected the morphology of the sizing deposited onto the fibre surface. For each sizing material, an optimal time–temperature dryer profile was determined. For the case of fibre sized with PVP, the optimal fibre surface temperature was found to be above 150°C but below 200°C. The sized fibre was noticeably stiff and rigid when the fibre surface temperature did not exceed 150°C. On the other hand, fibre sized with PVP that had been processed above 150°C led to a pliable tow. This pliable tow was more suitable for the subsequent processing operations. Since the $T_g$ of K-17 poly(vinyl pyrrolidone) was 121°C, it was concluded that processing at or above 150°C allowed the poly(vinyl pyrrolidone) film to soften and thus evenly coat the individual filaments. Processing the poly(vinyl pyrrolidone) below 150°C did not allow the sizing to reach its $T_g$ and thus prevented the coated fibres from separating from each other owing to stresses experienced by the tow during handling in the drying tower. The fibres remained bonded together which resulted in a highly rigid sized fibre. Thus, the fibres sized with PVP were processed above their $T_g$ for the results presented later in this section. The resultant sized fibres showed an extremely smooth surface when examined under SEM (*Figure 6a*).

For the polyhydroxyether sizing, the sized fibres were not completely dried before they were stitched together to make preforms. These preforms were then dried in a convection oven between 150 and 200°C so that the polyhydroxyether sizing was in the form of films and particles on the fibre surface (*Figure 6b*).

*Characterization of sized carbon fibres.* The fibres sized by the process were analysed via pyrolysis to determine the amount of sizing material present. The K-17-PVP-sized fibre coated from a 1.0 wt% sizing solution had a final sizing level of approximately 0.7 ± 0.05 wt%. The polyhydroxyether-sized fibre coated from a 1.0 wt% sizing solution had a final sizing level of approximately 0.6 ± 0.08 wt%.

The two systems described above were processed into stitched fabric plies by using a very fine thread with a spacing of about 5 cm between stitches. In addition, unsized fabric was stitched into plies using very light tension as a control. The resulting plies were used to make composite panels with varying interphase regions.

### *Composite panel production*

*Processing.* The three fibre systems described previously [unsized, poly(vinyl pyrrolidone) and polyhydroxyether] were processed into composites by means of the RFI technique. Four sets of unidirectional laminates were prepared for each of the three systems. In addition, four sets of $[0°/90°]_{7s}$ laminates were prepared. The resulting composite specimens were analysed for void content and fibre volume fraction. In these experiments, the composite processing cycle was fixed.

*Composite characterization.* The resin film infusion process produced consistent panels with a low void content as evident from the representative micrograph (*Figure 7*). The process allowed for the rapid production of numerous composite panels with varying interphase regions.

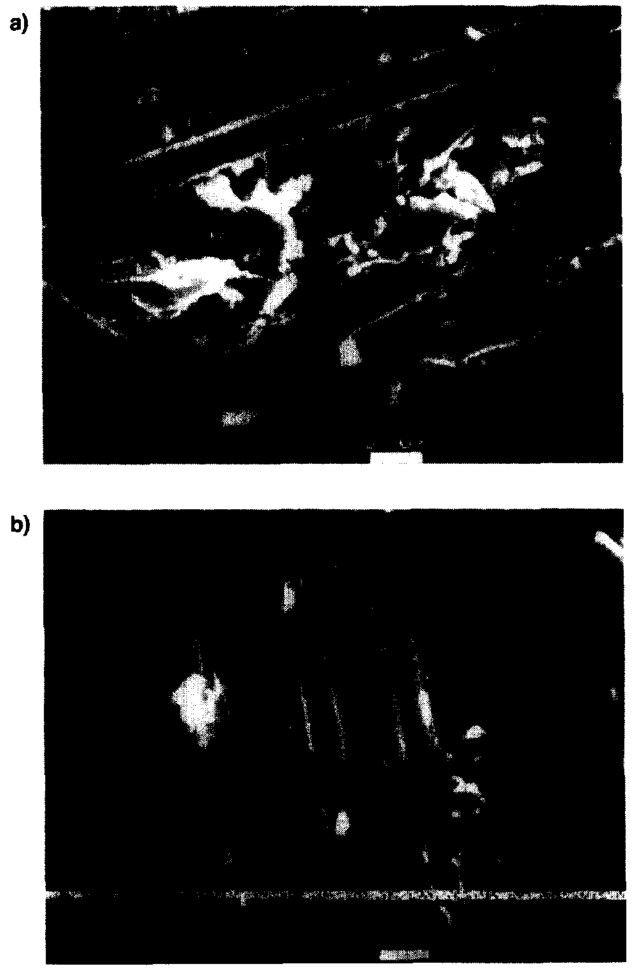

**Figure 10** Micrographs of (a) unsized and (b) PVP-sized fracture surfaces

Another strong point of the RFI process was the consistency of fibre volume fraction obtainable (i.e. 0.58–0.61). For each of the composite panels, fibre volume fraction did not vary significantly within any sizing set and also did not vary significantly between sizing sets. This consistency in fibre volume fraction between composite panels allowed for the direct comparison of mechanical property results without any normalization.

### *Mechanical testing*

*Short-beam shear and transverse flexure tests.* Apparent shear strengths were determined for the unidirectional composites produced from unsized, PVP-sized and phenoxy-sized fibre (*Figure 8*). There was no statistically significant effect of the sizing material on the apparent composite shear strength.

Flexure strength and modulus were determined for the unsized, PVP-sized and phenoxy-sized fibre composites (*Figure 9a* and *Figure 9b*). There was no statistical difference in the flexural *strengths* for the various sizings tested. However, the flexure *modulus* for the composites containing a sizing did show a marked increase over the composite produced from unsized carbon fibre. The polyhydroxyether showed a 40% increase in flexural modulus and the poly(vinyl pyrrolidone) showed a 20% increase compared with the unsized composite panels. The magnitude of the error bars is possibly due to some fibre misalignment that was noticed in the fracture surfaces of the specimens. The sized specimens (*Figure 10b*) showed a highly organized fibre arrangement wherein they remained stuck to each other by the matrix. In contrast, the fracture surfaces of the unsized specimens (*Figure 10a*) indicated more bare fibres caused by matrix debonding from the fibre probably due to poor fibre/matrix adhesion.

*Fatigue and compression tests.* The fatigue limit of the composites with poly(vinyl pyrrolidone), polyhydroxyether and unsized interphases was determined (*Figure 11*). The fatigue limit is defined as the highest load level that can be applied to a specimen in order to achieve a million cycles in fatigue. The stress on the plot was computed based on the ultimate compression strength. Stress levels of 75%, 65%, 55% and 45% were chosen based on the composite in order to get a good idea of the shape of the $S$–$N$ curve. Quasi-static compression strength was determined for the PVP-sized and phenoxy-sized composites (*Figure 12*). There

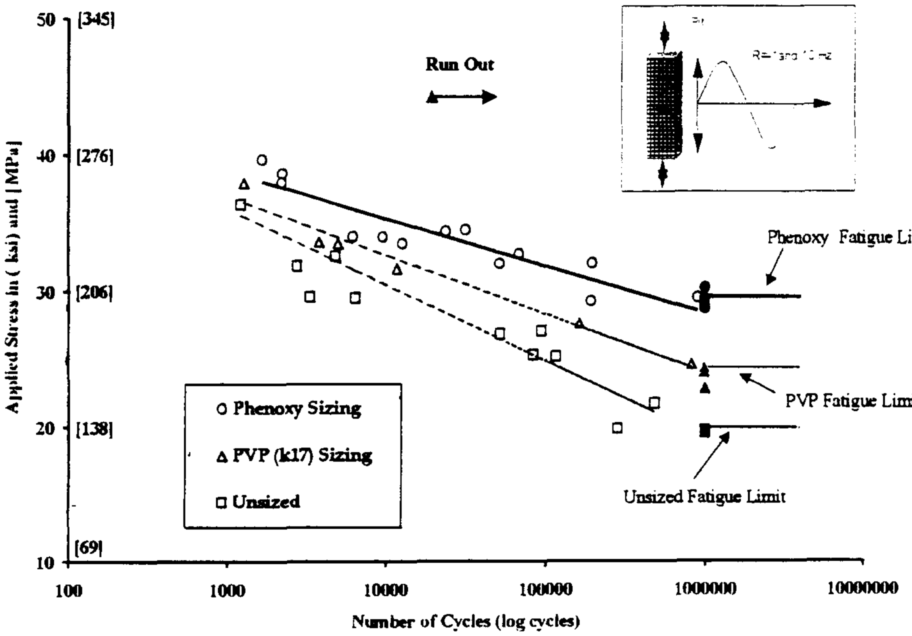

**Figure 11** Fatigue limit $S$–$N$ curve for various sizing materials

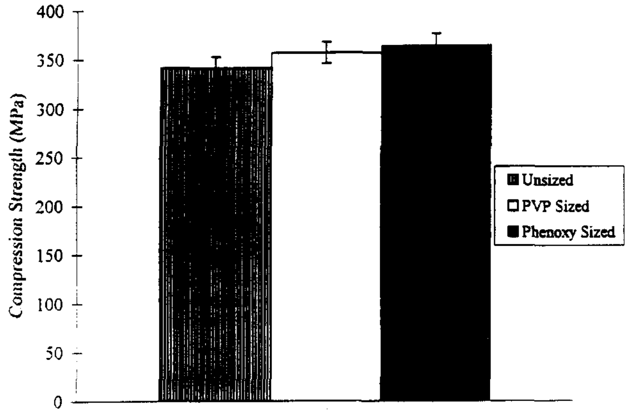

**Figure 12** Quasi-static compressive strength for various sizing materials

was no statistically significant effect of the sizing material on the compression strength.

Substantial differences in the fatigue limit were noted between the materials sized with polyhydroxyether and poly(vinyl pyrrolidone), and the unsized material. As seen in *Figure 11*, the fatigue limit for the phenoxy-sized material was about 210 MPa, a 60% improvement in the fatigue limit compared with that (130 MPa) for the unsized material. The fatigue limit for the poly(vinyl pyrrolidone)-sized material was about 160 MPa, about 20% higher than the limit for the unsized material.

At a given stress level, the type of sizing material had a significant effect on the lifetime of the composites. For example, at a 207 MPa stress level, the composite sized with polyhydroxyether lasted for 200 000 loading cycles, the composite sized with poly(vinyl pyrrolidone) lasted for 50 000 loading cycles, and the unsized material lasted for only 9000 loading cycles. This drastic difference in the fatigue and the lifetime limits can be explained by the physical nature of the sizings present in the interphase region. The polyhydroxyether was a relatively tough thermoplastic material compared with the more brittle poly(vinyl pyrrolidone). Experiments are underway to relate more precisely the sizing material properties to interphase effects at the micro- and macroscales.

## CONCLUSIONS

Carbon fibre/vinyl ester composites were made from sized carbon fibres that were formed into a unidirectional fabric. This fabric was processed into composite panels by means of a resin film infusion (RFI) technique. Two dissimilar sizing agents were studied—a brittle thermoplastic K-17 poly(vinyl pyrrolidone) (PVP) and a ductile thermoplastic polyhydroxyether (phenoxy resin). The processing conditions were shown to affect the handling characteristics of the fibre. Processing above $T_g$ for the poly(vinyl pyrrolidone) sizing resulted in a high-quality, pliable sized fibre. The polyhydroxyether sizing was processed in such a way as to coat the fibre with a mixture of films and particles. RFI provided a fast and easy way to manufacture consistently good panels with uniform fibre volume fractions and relatively low void content.

Fatigue tests demonstrated clear differences between the two polymeric sizings and the unsized fibre control. Large differences were noticed in the fatigue limit of the composites. The polyhydroxyether sizing resulted in a 60% improvement in the fatigue limit compared with the unsized composite. The fatigue limit for the material sized with poly(vinyl pyrrolidone) was about 20% higher than the limit for the unsized material. A 20-fold increase in lifetime was demonstrated at a 207 MPa loading level for the ductile phenoxy-sized composite compared with the unsized case. The brittle PVP-sized composite panel showed a sixfold increase in lifetime compared with the unsized case. Negligible differences in the shear strength, flexural strength and static compressive strength were observed for the different interphase agents. To understand the reason for these effects, it is necessary to understand how damage is initiated and propagated in these materials.

In future work, the interdiffusion of the sizing and matrix will be measured and used in a model to predict mechanical property gradients across the interphase. Micromechanical modelling[9,10] can then be used to predict both initiation and propagation of damage in a composite system under a particular loading scheme. It has been shown before[11] that the inelastic properties tend to have a larger impact on the micromechanical models than the elastic properties. Once this is done for the different interphases, laminate-level responses can then be addressed.

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