Aqueous-Based Emulsion Reactive Finishes for Improving Carbon/Vinyl Ester Interfacial Bonding

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Abstract

This study was undertaken to develop an aqueous-based finish (sizing) to improve the carbon/vinyl ester interfacial bond. A previously developed solvent-based finish for carbon/vinyl ester was modified to be applied as an aqueous emulsion. The finish is composed of a reactive coupling agent, a low viscosity vinyl ester resin, a free radical inhibitor, and a surfactant. Aqueous-based emulsions of the reactive finish components were successfully prepared and applied to unsized T700 fibers. Bromine analysis of the finished fibers showed the presence of the desired residual vinyl groups in the fiber surface coating that can chemically bond to the vinyl ester matrix during composite processing. Unidirectional laminates containing several types of fiber surfaces (unsized, Toray FOE sized, and reactive finishes of varying formulations) were prepared, characterized for microstructure, mechanically tested using interface sensitive test methods (transverse flexure, short beam shear) and a fiber dominated test (longitudinal flexure), and characterized for failure mode.

Results show that the reactive finishes substantially improve the carbon/vinyl ester interface-dominated mechanical properties compared to the unsized or FOE sized materials. In addition, the toughness of the interface in shear as seen in the area under the load-deflection curves is substantially increased as well. Failure mode analysis shows that interfacial failure dominates the unsized and FOE sized materials, whereas resin cohesive failure dominates the ATI finished materials. This is a strong indication that the desired chemical bonding is occurring at the T700/vinyl ester interface through the reactive finish. These data would also imply that, when the reactive finish is optimized, environmental durability in moisture and fatigue resistance would be greatly improved by the reactive finishes.

Key Words: Resins/Materials – Vinyl Ester, Sizing/Coupling Agent, Fiber Reinforcements - Carbon
INTRODUCTION

In this work, we distinguish a finish as an adhesion-promoting chemistry applied to a fiber surface as opposed to a sizing, which is applied as a handling aid. Enhanced interfacial properties are a direct result of forming chemical bonds with the fiber surface and matrix resin through the use of reactive coupling agents. These coupling agents will bond directly with the basal plane crystallites on the carbon-fiber surface in addition to edge and defect sites. Those bonds maximize interface environmental durability [1-3]. This approach has also been shown to improve the interface sensitive mechanical properties of carbon/vinyl ester composites [4]. Composite interfaces and the reactive finish concept for bonding to vinyl ester resins are presented in detail in Ref. 4.

When the finish is reacted with the carbon fiber, it leaves residual vinyl functional groups on the fiber surface that can subsequently chemically bond with the vinyl ester matrix resin during composite fabrication. These reactive finishes typically are composed of four or more ingredients including a reactive coupling agent, a film-forming polymer carrier, a surfactant, and a solvent. Mixtures of some of these ingredients are often necessary for solubility and processing reasons. Proper selection of the polymer or prepolymer carrier in the finish formulation results in a uniform nanometer scale (200-500 nm) coating on the fiber surface that is chemically bonded to both sides of the interface.

EXPERIMENTAL PROCEDURES

Materials Selection

Unsized T700 and T700 with Toray’s FOE vinyl ester compatible size were used as the fiber reinforcement. Derakane 510A-40 vinyl ester resin was obtained from Dow Chemical. Cobalt napthonate promotor was donated by Applied Poleramic, Inc. Trigonox 239 initiator was acquired from Akzo Nobel, and 2,4-pentanedione inhibitor was acquired from Sigma-Aldrich.

Emulsion Development

A survey of the patent literature for fiber sizings applied from aqueous emulsions was conducted to determine generalized ingredients for emulsion systems. Of the various systems surveyed [5-10], sizing systems typically consisted of the following:

- Coupling agent(s)
- Film-forming agent(s)
- Surfactant(s)
- Water.

The patent literature supplied only extremely broad guidelines as to the relative concentrations of the various components in the sizing formulation. We followed the example of emulsion-based foam systems as discussed by Williams [10] for our finish emulsion development. The concentration of materials was reduced from the Williams example by 50% to generate something more suitable for use in fiber finish application.
Several surfactants were then tested with a lower viscosity vinyl ester resin system containing the reactive coupling agent. In this case, it was necessary to mix the emulsions hot to address several issues:

- To decrease resin viscosity to allow rapid stirring
- To melt and/or dissolve the surfactant
- To evenly disperse or dissolve the coupling agent in the resin/surfactant mix.

The resin and other solid components were heated to approximately 50°C after which boiling water was added with rapid stirring to form the emulsion. The emulsion was then further blended at room temperature. These experiments showed that emulsions made with Pluronic P105 surfactant were white in color and well mixed and showed no separation of ingredients after standing several days. Those emulsions were used in the balance of the study.

**Fiber Treatment Studies**

Several emulsion formulations were evaluated in fiber treatment processes. Ten-foot lengths of fiber were cut, weighed, and dipped into the emulsions to be evaluated. The fibers were air-dried and then heat treated at high temperature to activate the coupling agent. Next, the fibers were extracted in acetone to remove any unattached material. After drying, the samples were reweighed to determine the pickup of the finish agent on the fibers. We targeted finish pickup of one percent of the fiber weight.

There were several formulations that allowed for the desired pickup of one percent finish. Three formulations were selected for evaluation in finish line deposition. A bromine assay of remaining double bond functionalities was conducted on fibers treated with the three emulsions following the procedure given in Ref. 4. This assay indicated that significant unsaturated functionality remained.

**Finish Line Experiments**

Adherent Technologies’ fiber finishing line is discussed in detail in Ref. 4. In order to successfully deposit finish materials onto fibers from emulsions using the fiber finish line, two conditions must be met. First, the treated fibers must be dry and, second, a temperature high enough to activate the coupling agent must be reached during the line process. Initial trials indicated that the addition of flowing hot air into the 8-foot drying oven was necessary to facilitate drying. The following parameters were then used for the finish applications: 8-foot drying oven at 300°C, hot air injection at 220°C, 4-foot reaction oven at 350°C with helium blanket, and 10 ft/min line speed.

Weight pickup on the line-treated fibers was evaluated by measuring out known lengths of fibers and extracting with acetone as with the laboratory-scale experiments described above. Comparing the extracted weights with an average bare fiber weight, percentage weight gains were estimated. These results showed that the finish material was deposited onto the fibers at levels between one and two percent. Vinyl unsaturation in the surface finish was assayed using bromine addition to the remaining unsaturation followed by determination of unreacted bromine with visible absorption spectra.
The measured vinyl concentrations were in the 80-125 moieties per nm$^2$. That is substantially greater than the theoretical limit for a two-dimensional surface. This implies that the finish is forming a several hundred nm thick layer with an open structure that allows the bromine to diffuse in and react with additional vinyl groups. This is a significant variable that will be addressed in future work.

**Composite Fabrication**

Unidirectional plates of T700 carbon/vinyl ester were fabricated by filament winding on an "H-shaped" mold followed by resin infusion. This process was repeated to create panels with T700 12K carbon fiber tow with four finish conditions: (1) unfinished, designated U, (2) Toray FOE sizing, designated FOE, (3) ATI vinyl ester finish (2.31 w/o) with a measured 126 vinyl moieties per nm$^2$, designated 139 and, (6) ATI vinyl ester finish (1.06 w/o) with 80 vinyl moieties per nm$^2$, designated 142.

Table I shows the composition of the six sets of plates, the resulting resin fraction, and $V_f$. Resin content and $V_f$ were computed from the measured resin, determined by weighing the mold.

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>FOE</th>
<th>139A2</th>
<th>142A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon fiber, g</td>
<td>367</td>
<td>372</td>
<td>381</td>
<td>367</td>
</tr>
<tr>
<td>Measured resin, g</td>
<td>236</td>
<td>213</td>
<td>254</td>
<td>254</td>
</tr>
<tr>
<td>w/w resin, %</td>
<td>39.1</td>
<td>36.4</td>
<td>40.0</td>
<td>40.9</td>
</tr>
<tr>
<td>$V_f$, %</td>
<td>50.1</td>
<td>52.9</td>
<td>49.2</td>
<td>48.2</td>
</tr>
</tbody>
</table>

**Composite Characterization**

Laminate quality was examined using microscopic analysis of polished cross-sections. Void content and fiber distribution was evaluated visually by potting 1.25 cm. composite specimens end-on in epoxy buttons (100 parts Epon 826/50 parts T403 Jeffamine curing agent). The buttons were cured at 60°C overnight.

The buttons were ground with a Buehler Automet polishing adapter using 240, 320, and 400 grit emery paper, followed by 6-micron diamond paste. Composite ends were photographed under 10x magnification.

**Mechanical Testing**

Mechanical drawings showing the location of test specimens on the vinyl ester panels are given in Figure 1. Panels and mechanical drawings of test specimens were submitted to Automation
Concepts, Inc. (Albuquerque, NM) where the specimens were cut from the panels using a water jet.

![Cutting patterns for T700/vinyl ester composite plates from 2 sides of the mold](image)

Figure 1. Cutting patterns for T700/vinyl ester composite plates from 2 sides of the mold

Five specimens each were removed for the four types of panels for 0° flexure, 90° flexure, and short beam shear testing. The width and thickness of each specimen were measured at the midpoint and tabulated.

Flexural specimens of 0° and 90° were constructed and tested according to ASTM D 790–84a. Short beam shear testing was conducted according to ASTM D 2344–84. Specimen dimensions were based on a nominal value of 0.3 cm \((d)\) for panel thickness. Table II lists specimen dimensions for the three tests.

<table>
<thead>
<tr>
<th>Test Type</th>
<th>0° flexure</th>
<th>90° flexure</th>
<th>Short Beam Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Span, cm</td>
<td>10.0 ((l/d =32))</td>
<td>2.5 ((l/d = 8))</td>
<td>1.25 ((l/d = 4))</td>
</tr>
<tr>
<td>Width, cm</td>
<td>1.25</td>
<td>1.25</td>
<td>0.625</td>
</tr>
<tr>
<td>Length, cm</td>
<td>12.5</td>
<td>3.75</td>
<td>2.5 ((8 , d))</td>
</tr>
</tbody>
</table>

Crosshead velocities were 0.5 cm/min for 0° flexure and 0.125 cm/min for 90° flexure and short beam shear. The average value of the span calculated from the thickness of each specimen for a given test was used for all five specimens. Individual width and thickness measurements were used to compute stress for each specimen.
RESULTS AND DISCUSSION

Fiber Surface Characterization

The appearance of the unsized T700 surface is shown in Figure 2. Note that the micrograph
shown in Figure 2 was taken at high magnification. T700 is extremely smooth and nondescript.
The surface is so smooth that it was difficult to focus the electron beam on it due to a lack of
resolvable features. The slight texture seen in Figure 2 is not seen in general on the T700 fiber
surfaces. Clearly, mechanical interlocking is not an available adhesion mechanism with T700.

The appearance of T700 with the Toray FOE size is shown in Figure 3. The FOE size forms a
generally uniform coating on the fibers with an occasional small (<10 µ) clump.
Figure 3. Appearance of Toray FOE sized T700 carbon fiber

The ATI emulsion (142) showed few clumps and resulted in generally uniformly smooth coated fibers (Figure 4).

Figure 4. Appearance of ATI finish 142A on unsized T700 carbon fiber

Composite Microstructure

The microstructures of the T700/vinyl ester laminates obtained on polished cross sections are shown in Figure 5.
The microscopic analysis showed that the plates were of good quality, but with some resin rich layers, especially in the ATI finished laminates. The mechanical properties of those finished laminates should be reduced because of these features. The plate with the third ATI finish contained a high void content and was not tested.

![Figure 5. Microstructure of T700/vinyl ester composites (10X) of (a) unsized, (b) Toray FOE sized, (c) ATI 139 finished, and (d) ATI 142 finished laminates](image)

**Composite Mechanical Properties**

The longitudinal flexure specimens all exhibited linear load-deflection curves. Resultant average mechanical properties from five specimens and the coefficients of variation (standard deviation divided by the mean) for each data set are given in Table III.
Table III. Longitudinal (0°) Flexural Properties of T700/Vinyl Ester Laminates

<table>
<thead>
<tr>
<th>Laminate Type</th>
<th>Ultimate Strength (MPa)</th>
<th>Young's Modulus (GPa)</th>
<th>Deflection at Failure (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsized</td>
<td>960 ± 7.0%</td>
<td>105 ± 4.7%</td>
<td>0.513 ± 4.6%</td>
</tr>
<tr>
<td>Toray FOE Size</td>
<td>1052 ± 8.9%</td>
<td>104 ± 9.3%</td>
<td>0.521 ± 4.0%</td>
</tr>
<tr>
<td>ATI VE Finish 139</td>
<td>1135 ± 5.1%</td>
<td>102 ± 3.3%</td>
<td>0.602 ± 3.4%</td>
</tr>
<tr>
<td>ATI VE Finish 142</td>
<td>1127 ± 1.5%</td>
<td>97 ± 1.8%</td>
<td>0.597 ± 4.3%</td>
</tr>
</tbody>
</table>

The longitudinal properties nominally follow rule of mixtures behavior. Despite having a slightly lower fiber volume fraction (Table I), the plates containing the ATI finished fibers exhibited greater strengths and failure strains (deflections) in longitudinal flexure than those with the Toray FOE sized and unsized fibers. This is an indication of better shear transfer at the interface leading to increased translation of fiber tensile properties.

Properties in transverse flexure are given in Table IV. The data in Table IV are also average values for five specimens of each laminate type. Transverse flexure is extremely sensitive to interfacial tensile strength.

Table IV. Transverse (90°) Flexural Properties of T700/Vinyl Ester Laminates

<table>
<thead>
<tr>
<th>Laminate Type</th>
<th>Ultimate Strength (MPa)</th>
<th>Young's Modulus (MPa)</th>
<th>Deflection at Failure (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsized</td>
<td>24.4 ± 6.9%</td>
<td>4027 ± 8.6%</td>
<td>0.018 ± 6.9%</td>
</tr>
<tr>
<td>Toray FOE Size</td>
<td>23.2 ± 6.8%</td>
<td>4289 ± 12.4%</td>
<td>0.015 ± 11.6%</td>
</tr>
<tr>
<td>ATI VE Finish 139</td>
<td>59.8 ± 13.3%</td>
<td>5349 ± 2.6%</td>
<td>0.030 ± 14.4%</td>
</tr>
<tr>
<td>ATI VE Finish 142</td>
<td>74.6 ± 4.5%</td>
<td>5617 ± 4.6%</td>
<td>0.038 ± 3.5%</td>
</tr>
</tbody>
</table>

The strength data given in Table IV clearly show the improved performance imparted by the reactive finishes despite the stress concentrations caused by the resin rich regions. Deflection at failure in the ATI finished laminates was also 100% greater than in the unsized and FOE sized specimens and Young’s modulus of the samples containing the reactive finish is also nearly 50% greater, both of which indicate better load transfer to the fibers in this stress state.
Average short beam shear strengths and statistical variations for five specimens from each laminate type are given in Table V. The short beam shear tests were run using the method of Shivakumar [11] to avoid surface crushing.

### Table V. Short Beam Shear Strengths of T700/Vinyl Ester Laminates

<table>
<thead>
<tr>
<th>Laminate Type</th>
<th>Shear Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Coefficient of Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsized</td>
<td>46.9</td>
<td>2.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Toray FOE Size</td>
<td>50.8</td>
<td>2.8</td>
<td>5.5</td>
</tr>
<tr>
<td>ATI VE Finish 139</td>
<td>73.6</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>ATI VE Finish 142</td>
<td>84.2</td>
<td>1.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The Table V data show the vinyl ester finish improved short beam shear strengths by up to 66% under room temperature, dry conditions compared to the FOE size. Considering the resin rich and void regions in the center line of the finished material seen in Figure 5, it is significant that interface modifications imparted by the reactive finish improve the shear strength to this degree. In addition, the improved interface reduced the scatter in the finished data. One would expect that shear strength will be greatly improved in better quality laminates with the reactive finish. Shear strengths of 100+ MPa were measured in the Ref. 4 study on AS4 fiber. It may also be that the very smooth surface of the T700 fibers may limit shear strengths under the value obtained in the Ref. 4 work.

Taken together, the data given in Tables III-V indicate that the improved interface produced by the reactive vinyl ester finishes would show an even greater effect after environmental stress such as moisture and fatigue on high-quality laminates. In addition, comparison of the load-deflection curves shown in Figure 6 shows that the ATI finished laminates exhibit increased toughness in shear compared to the controls, as evidenced by the much larger area under the curve, even though some of the finished laminates were of lower quality. As seen in Figure 6, the ATI 142 material failed at loads 90 kg (200 lb) greater than the FOE sized material.
Fracture Surface Analysis

The 90° flexure failure surfaces were examined to determine failure modes. The laminates containing the unsized T700 fibers are characterized by numerous loose fibers on the failure surface (Figure 7), a strong indication of poor interfacial bonding.
Failure surfaces of the FOE sized material show primarily loose fibers with some small areas of resin evident (Figure 8). At 500X, some small bits of resin adhering to the fibers are evident, but the fibers are mainly clean as determined under higher magnifications.
The $90^\circ$ flexure failure surfaces of the specimens containing the ATI emulsion finished T700 fibers displayed completely different behavior. They are characterized by flat resin-coated surfaces (Figures 9 and 10). These micrographs show that failure is dominated by cohesive failure in the resin caused by a strong fiber-matrix interfacial bond.
Figure 9. Fracture surface appearance of ATI 139 finished T700/vinyl ester laminate

As seen in Figure 10, what appear to be loose fibers at lower magnifications are coated with thin amounts of vinyl ester resin. When optimized, this approach should provide the most durable T700/vinyl ester composites.
CONCLUSIONS

This work was undertaken to evaluate the use of finishes with reactive coupling agents, tailored for bonding with vinyl ester resins, for improving interfacial properties in T700 carbon/vinyl ester composite laminates. Aqueous-based emulsions of the reactive finish components were successfully prepared and applied to unsized T700 fibers. Bromine analysis of the finished fibers showed the presence of the desired residual vinyl groups in the fiber surface coating that can chemically bond to the vinyl ester matrix during composite processing. Unidirectional laminates containing several types of fiber surfaces (unsized, Toray FOE sized, and reactive finishes of varying formulations) were prepared, characterized for microstructure, mechanically tested using interface-sensitive test methods (transverse flexure, short beam shear) and a fiber dominated test (longitudinal flexure), and characterized for failure mode. Results show that the reactive finishes substantially improve the carbon/vinyl ester interface-dominated mechanical properties. In addition, the toughness of the interface in shear as seen in the area under the load-deflection curves is substantially increased as well. Failure mode analysis shows that interfacial failure dominates the unsized and FOE sized materials, whereas resin cohesive failure dominates.
the ATI finished materials. This is a strong indication that the desired chemical bonding is occurring at the T700/vinyl ester interface through the reactive finish. These data would also imply that, when the reactive finish is optimized, environmental durability in moisture and fatigue resistance would be greatly improved by the reactive finishes.

ACKNOWLEDGMENTS

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REFERENCES