IMPROVEMENT OF ADHESION BETWEEN VINYL ESTER RESIN AND CARBON FIBERS

Lanhong Xu and Lawrence T. Drzal

Department of Materials Science and Mechanics
Composite Materials and Structure Center, Michigan State University
East Lansing, MI 48824-1226, USA

SUMMARY: Free radical cured thermosetting vinyl ester resins have been extensively used for the manufacture of low cost high performance composites. The use of vinyl ester composites reinforced with carbon fibers requires an improvement in the fiber-matrix adhesion levels. Typical vinyl ester resins contain 35-50% styrene as reactive diluents. The effect of the vinyl ester, styrene, amount of catalysts and sizing thickness on the adhesion between AS4 carbon fiber and DERAKANE 411-C50 vinyl ester was investigated in this research. It was found that that the application of a lightly cross-linked amine-cured epoxy polymer to the carbon fiber surface creates a beneficial interphase between the carbon fiber and vinyl ester resin matrix resulting in a substantial increase in fiber-matrix adhesion. The vinyl ester and styrene components interact differently with the DGEBA-T403 sizing at the carbon fiber and vinyl ester interphase. Optimum fiber-matrix adhesion can be obtained by adjusting the amount of initiator and/or the thickness of sizing.

KEYWORDS: interphase (interface), adhesion, sizing, microindentation, nanoindentation, interfacial shear strength (IFSS), vinyl ester, carbon fiber

INTRODUCTION

The factors in the fiber-matrix interphase that influence adhesion between fiber and matrix are rather complex. As shown in Fig.1 [1-7], the interphase forms at the point where the fiber and matrix come in contact and are bonded together. The factors contributing to adhesion could be due to chemical reaction, van der Waals forces, electrostatic attraction, acid-base interaction including H-bond, or mechanical interlocking. For fibers with an organic coating (sizing) the situation is rather complex. Besides the interactions mentioned above, the entanglement between the molecules of the sizing and matrix and the interdiffusion [8,9] between a compatible sizing and the matrix polymer could also be an important contribution
to the adhesion. On the other side, voids, contaminates, etc., and thermal residual stress could be a negative contribution to the adhesion. The purpose of this study is to find the relationship between fiber-matrix adhesion and the interphase chemical and physical properties in this carbon fiber-vinyl ester system and to develop a solution for improving the adhesion.

Free radical cured thermosetting resin systems, such as vinyl ester resins, have been extensively used for the manufacture of low cost and high performance composites. Typical vinyl ester resins contain 35-50% styrene as reactive diluents. The copolymerization between styrene and vinyl ester is a heterogeneous, free radical, chain-growth, and crosslinking reaction. Different amount of initiators, promoters and accelerators produce different heats of reaction, crosslink density and degrees of microgel formation and/or phase separation [10-12] as well as a different interphase microstructure between the fibers and the matrix. A previous investigation by Weitzsacker, Drzal et al. [13] has investigated the reactions of the catalyst and/or promoters to determine if they were competing with the vinyl ester matrix resin for reactive sites at the carbon fiber surface. Cobalt was detected at 2.6% at the surface of the AS4 carbon fiber exposed to cobalt naphthenate (CoNap) and a minor change was also noted in the surface chemistry of the fiber exposed to dimethyl aniline (DMA) which are the promoters and accelerators for the free radical copolymerization respectively. Since removal of even a small amount of the initiator or promoter from the vinyl ester to the carbon fiber surface has the potential to greatly affect the polymerization reaction, one strategy is to prevent these constituents from getting to the fiber surface by applying a ‘coating’ or ‘sizing’ to create a beneficial interphase. The interphase between fiber and matrix could be controlled and designed by a suitable choice of fiber sizing. It was found that that the application of a lightly cross-linked, epoxy polymer onto the carbon fiber surface provides a beneficial
interphase between the carbon fiber and vinyl ester resin matrix resulting in an increase in fiber-matrix adhesion [14,15] while at the same time preventing the fiber from adsorbing the initiator and catalyst [15]. The effect of the reaction catalyst on the vinyl ester and styrene, which are the two components of DERAKANE 411-C50 vinyl ester (D411-C50), and the thickness and gradient of the amine-cured epoxy sizing on the adhesion between AS4 carbon fiber and the cured D411-C50 resin have been investigated and are reported in this research.

**EXPERIMENTAL**

*Materials:* The fiber is an AS4 carbon fiber from Hexcel, Inc. It is a type A, surface treated (S), 8 micron diameter, PAN based carbon fiber. The fiber tow size is 12K filaments. The matrix resin is Derakane 411-C50 vinyl ester resin from Dow Chemical which contain 50wt% of Bisphenol A Epoxy-based Vinyl Ester and 50wt% of Styrene. The components of D411-C50 are shown in Fig.2. CHP-5 (diluted cumene hydroperoxide (CHP)) from Witco Chemical is used as the initiator because it provided the best IFSS among the three initiators, CHP, MEKP (methyl ethyl ketone peroxide) and BPO (butanone peroxide) [14]. Both CoNap and DMA are from Aldrich Chemicals which are used as promoters and accelerators respectively. Diglycidyl ether of bisphenol A (DGEBA or Epon828) and Trimethylpropane Amine (JEFFAMINE T403) are from Shell and Huntsman respectively. Pure styrene monomer and pure bisphenol A epoxy based vinyl ester were kindly donated by Huntsman and Reichhold respectively.

*Fig. 2 Derakane 411-C50 and the catalysts*

![Chemical structures](image)

*Methods:* Since it was shown that adsorption of the catalysts of D411-C50 resin on the carbon fiber surfaces, it was expected that the vinyl ester in the interphase region would not have the stoichiometry of the bulk. Therefore, several off-stoichiometric compositions were prepared and their physical properties were measured. The curing recipes are listed in Table1. Data Set 1 refers to those samples cured with recipe 1-I, 1-II and 1-III a reduction in the
concentration of CHP-5. Data Set 2 and Data Set 3 are compositions with a reduction in the amount of CoNap and DMA respectively. A digitally controlled, programmable oven was used for specimen curing to make sure all the samples were processed in the same way. The curing process is shown in Fig. 3. Dynamic Mechanical Thermal Analysis (DMTA), DMA 2980 from TA Instruments, and physical testing, United Testing System (UTS), of the composite samples was conducted to measure the mechanical properties of the matrix resin formulations. Adhesion was evaluated as an interfacial shear stress (IFSS) measured with a microindentation system, Interfacial Testing System (ITS). The calculation of the IFSS from the ITS test is given by an experimental equation, Eqn. 1, which is based on a finite element analysis. In this equation, the \( d_n \), \( d_f \), and \( f_g \) are measured, while the other factors are input parameters. Fig. 4 shows a selected fiber before and after the ITS test.

\[
IFSS = A \frac{f_g}{d_f^2} \left\{ 0.875696 \sqrt{\frac{G_m}{E_f}} - 0.018626 \ln\left(\frac{d_n}{d_f}\right) - 0.026496 \right\}
\]

Eqn. 1

Where,
- \( f_g \) = Load on Fiber
- \( G_m \) = Shear Modulus of Matrix
- \( E_f \) = Tensile Modulus of Fiber
- \( d_n \) = Distance between the Nearest Fiber
- \( d_f \) = Diameter of the Fiber
- \( A \) = Conversion Factor

<table>
<thead>
<tr>
<th>Table 1 Curing Recipes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I</strong></td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>

**Fig. 3 Curing Process of Vinyl Ester/CHP**

**Fig. 4 ITS images**
The mixture of DGEBA (EPON828) and JEFAMINE T-403 is prepared and held for one half hour then added to acetone to form a 5wt% sizing solution. Fiber sizing is carried out by using a pre-impregnation machine to simulate the application of sizing and the prepregging of carbon fiber-vinyl ester prepreg tape in an industrial process. A Model 2020 ElectroScan Environmental Scanning Electronic Microscopy (ESEM) is used to investigate the uniformity of the sizing. Thermal Gravimetric Analysis (TGA) is used to measure the thickness of the sizing and a MTS nanoindentation instrument is used to figure out the gradient of the sizing and the interphase between the DGEBA epoxy and D411-C50 vinyl ester resin and test the mechanical properties of the materials as well.

RESULTS AND DISCUSSION

1. Influence of the catalyst concentration on the properties of the matrix material

The data plotted as vertical bars in Fig. 5, Fig. 6 and Fig. 7 indicate the amounts of CHP-5, CoNap and DMA respectively used in the various formulations. For an isotropic material, \( G_m = E_m / (2(1+\nu)) \), where \( E_m \) is the Young’s modulus and \( \nu \) is the Poisson ratio of the matrix material respectively. The Poisson ratio of each formulation was assumed to be 0.36 (refer to reference 14) and insensitive to the amount change of the CHP-5. The shear modulus and the Young’s modulus then are related through the relationship \( G_m = E_m / 2.7 \). Fig. 5, Fig. 6 and Fig. 7 show that a small change of the catalyst could result in a detectable change in the glass transition temperature, but the change of the mechanical properties such tensile modulus from UTS measurement and storage modulus from DMTA measurement are rather small even in two extreme situations (no CoNap and no DMA), especially for
the calculated shear modulus which is about 1/3 of the tensile modulus. Also the change of
glass transition temperature is not proportional to the change of the mechanical properties.
Since the change in the tensile modulus is small, it is assumed that any changes of the
Interfacial Shear Strength (IFSS) are the result of change of the adhesion between the fiber
and the matrix.

2. The effect of catalyst concentration on the Interfacial Shear Strength (IFSS)
The percent numbers in Fig. 8, Fig. 9 and Fig. 10 are the amounts of CHP-5, CoNap
and DMA in each vinyl ester formulation respectively. The set of bars on the left side
in these figures correspond to the samples made of ‘as-received’ fibers and the data on the right side refer to
fibers ‘sized’ with the DGEBA-T403/ACETONE sizing solution. The coated fibers overall produce a greater
IFSS than the ‘as-received’ fibers. For as received fibers, it is clear that the
IFSS of the samples with different amount of CoNap and DMA are almost
the same, even for those without CoNap and DMA, see Fig. 9 and Fig.
10. Fig. 9 might indicate that although cobalt absorbs on the carbon fiber
surface, it does not result in a significant change in adhesion. The
same can be said for DMA in Fig. 10. It is interesting to see that slight
changes in the amount of the initiator cause a significant change of IFSS
(Fig.8). At a concentration of 1.5% of CHP-5, the greatest value of IFSS was
measured. Changes in the initiator concentration are responsible for a
change in the number of reactive
species in the vinyl ester system. It appears that at a certain concentration, the vinyl ester copolymer has a microstructure (phase separation or microgel formation) which produces good adhesion or at the carbon fiber surface, an excess of the styrene rich phase or vinyl ester rich phase optimizes the adhesion.

3. The contribution of vinyl ester and styrene monomer of the D411-C50 to the adhesion

Further investigation has been carried out to find the roles that pure styrene and pure vinyl ester play in forming the interphase between AS4 carbon fiber and D411-C50 vinyl ester resin. New composite specimens were prepared with the AS4 carbon fibers in either pure vinyl ester or pure styrene where the catalyst concentration was adjusted to maintain the same double bond concentration based on the standard recipe, recipe 1-I, in table 1. As an input parameter for the ITS test, as shown in Eqn. 1, the shear moduli of both pure materials are critical to get the IFSS. Pure bisphenol A epoxy-based vinyl ester is a solid and styrene monomer has a very high vapor pressure, which makes neither one very easy to process at room temperature. To obtain the in-situ mechanical properties, a nanoindentation test was used with the ITS sample. The nanoindentation testing area is far away from the fiber area to avoid other affects. DMTA tests and literature citations of mechanical properties are also used as references, Fig.11.

The ITS test results are very interesting, (Fig. 12). The data on the left side in Fig.12 corresponds to samples made with ‘as-received’ fibers and the data on the right side are for fibers coated with the DGEBA-T403/ACETONE sizing solution. Again, for ‘as-received’ fibers, there are slight IFSS differences between vinyl ester (~+20%), and styrene (~-10%) compared to the D411-C50 vinyl ester. Styrene gives the lowest IFSS because it is the softest material among these three. In contrast, the carbon fiber with the lightly crosslinked sizing, has the highest adhesion in the pure styrene matrix. This suggests that the styrene monomers (monomer molecular weight is 104g/mole while vinyl ester is about 900g/mole) diffuse into lightly-crosslinked DGEBA-T403 sizing and bring about a big change to the fiber/matrix
interphase. It might also create a gradient interphase compared to the bisphenol A epoxy-based vinyl ester.

4. The Influence of sizing thickness on the Interfacial Shear Strength (IFSS)

The thickness of the lightly cross-linked epoxy sizing was varied. Fibers were coated with a pre-impregnation machine and the thickness was measured using TGA. The weight loss measured by TGA is an average value of the sizing thickness. The uniformity of the sizing
was investigated by ESEM. The sizing thickness is linearly related to the concentration of the DGEBA-T403/ACETONE sizing solution, as shown in Fig. 13. ESEM examination of the sized fibers, Fig.14, shows that the sizing material is distributed unevenly. From the ESEM observation, the 5% sizing solution sized fiber gives the most uniform coating. The sizing applied from the 7.5% and 10% sizing solution creates fibers which have “sizing bridges” between them. There is no other detectable topographic phenomenon between the different sizing solution sized fibers except the so-called “sizing bridges”. ITS tests show that fibers with sizing thickness around 90nm give the maximum value of IFSS, Fig. 15. Sizing material by itself is normally softer than the matrix material. Therefore, it is reasonable that too much sizing makes the IFSS goes down.

CONCLUSIONS

Derakane 411-C50 vinyl ester resin is a mixture of vinyl ester and styrene monomer. The interface between this resin and AS4 carbon fiber is much more complex than that between epoxy and AS4 carbon fiber. From this study, several conclusions can be made.

1. Slight change of catalyst concentration does not make a major difference in the mechanical properties of the cured D411-C50 resin. The glass transition temperatures of the cured resin appear to be influenced by the catalyst concentration. The glass transition temperature is not necessarily related to the mechanical properties of the materials for this system.

2. Neither the promoter (CoNap) nor the accelerator (DMA) significantly influences the level of adhesion between AS4 carbon fiber and D411-C50 vinyl ester resin. Changes in the initiator (CHP-5) concentration cause changes in the polymerization of the vinyl ester system. Optimum fiber-matrix adhesion could be obtained by adjusting the amount of initiator.

3. A sizing selected for isolating the carbon fiber surface from the reacting polymer appears to be useful in improving adhesion. With DGEBA-T403 sizing, the interfacial shear strength between D411-C50 and AS4 carbon fiber can be increased indicating a strong interphase formed.

4. The contributions of styrene and vinyl ester in D411-C50 to the adhesion between the fiber and matrix are different especially for fibers with the lightly cross-linked DGEBA-T403 sizing. The styrene monomers diffuse into the DGEBA-T403 sizing material and provide a much smoother interphase than only pure vinyl ester.

5. The sizing thickness has an optimum value for best interfacial shear strength. A sizing that is too thick or too thin does not produce beneficial results.
ACKNOWLEDGEMENT

Support for this research was provided by the General Motors Corporation and the NSF State/Industry/University Cooperative Research Center at Michigan State University on Low-Cost, High-Speed, Polymer Composites Processing. The authors also wish to express their thanks to the Dow Chemical Company for supplying the vinyl ester resin.

REFERENCES