CARBON FIBER-VINYL ESTER INTERFACIAL ADHESION IMPROVEMENT BY THE USE OF A REACTIVE EPOXY COATING

F. Vautard, L. T. Drzal
Composite Materials and Structures Center
Michigan State University, East Lansing, MI 48824, USA
Email:drzal@egr.msu.edu

SUMMARY

An engineered interphase consisting of a partially cross-linked epoxy coating that chemically bonds to the carbon fiber surface and forms an interpenetrating network with the vinyl ester matrix was found to sharply improve the interfacial adhesion and the mechanical properties of carbon fiber-vinyl ester composites.

Keywords: composites, carbon fiber, vinyl ester, epoxy, interfacial adhesion, cure volume shrinkage, interpenetrated networks.

1. INTRODUCTION

Since carbon fiber reinforced composites offer great mechanical properties with a low density, they have been of interest to many fields, such as military equipment, transportation, and sport and recreation goods. Carbon fiber composites are especially used in the aerospace and aeronautics industries when the required mechanical properties have to be outstanding. However, with the price of carbon fibers decreasing their uses increase, spreading into a wider range of applications. Specific demands related to mechanical properties, resistance to chemicals and environment, process and cost of manufacture have lead to an investigation of the use of different types of matrices. Vinyl ester resins are potentially very attractive, particularly because of their high resistance to moisture absorption and corrosion coupled with their simple processing requirements. Nevertheless, the mechanical properties of carbon fiber-vinyl ester composites currently do not complete well with the mechanical properties of carbon fiber-epoxy composites, due to their poor mechanical interfacial properties and low interfacial adhesion [1-3]. It has been established that the physico-chemical and mechanical properties of a composite material are not only dependant on the characteristics of the reinforcement material and the matrix, but also on the properties of the interface [4, 5], which depend on the conditions used during the manufacturing [6]. Factors influencing interfacial adhesion are mechanical interlocking [7, 8], physical [9] (dispersive [10], polar [11], acid-base [12, 13]) and chemical interactions [14, 15], the presence of defects [16] (lack of cohesion, voids) and remaining thermal stress [17]. Recently, the high cure volume shrinkage of vinyl ester resins was found to be a significant factor affecting interfacial adhesion with carbon fibers and the use of a lightly cross-linked epoxy coating applied to the carbon fiber surface was shown to lead to an improvement of interfacial adhesion [18, 19]. Evaluation in the case of unidirectional carbon fiber composites showed a significant improvement of

InterLaminar Shear Strength (ILSS) and flexural properties of composites utilizing this approach. The research reported here investigates the thickness of the reactive epoxy coating and the fractional conversion of the epoxy sizing in the fiber-matrix interphase and seeks to identify its role in this approach.

2. MATERIALS AND METHODS

2.1. Materials

The carbon fibers used in this study were surface treated and unsized high strength PolyAcryloNitrile (PAN) AS4 carbon fibers (Hexcel Inc). The vinyl ester resin was Derakane 510A-40, a bromated DiGlycidyl Ether of Bisphenol A (DGEBA) epoxy based vinyl ester provided by Ashland Co. The initiator was Cumene HydroPeroxide (CHP) and was supplied by Sigma-Aldrich. The epoxy coating was made of DGEBA cured by Jeffamine T-403, an aliphatic polyether triamine. DGEBA and Jeffamine T-403 were from Shell and Huntsman respectively. The formula of the chemicals that were used is given in Fig. 1.

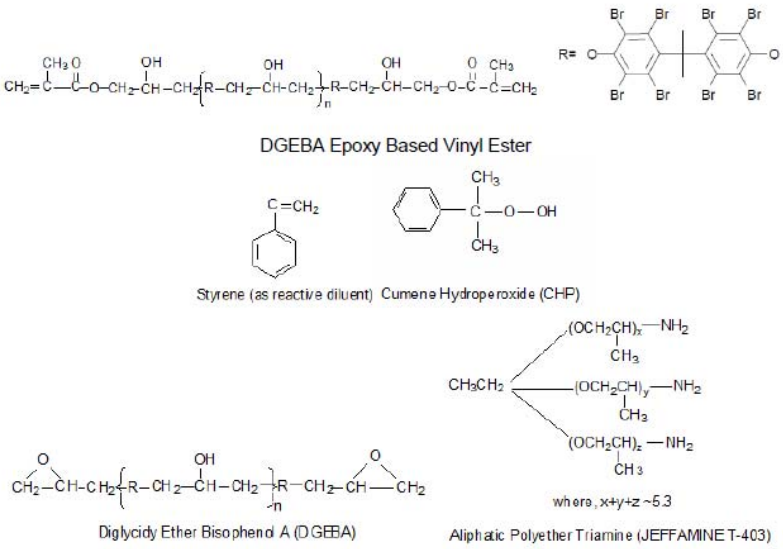

Fig. 1: Formula of chemicals used in this study.

2.2. Methods

FTIR

Fourier Transformed Infra Red spectra were carried out with a Perkin Elmer Spectrum One FTIR Spectrometer controlled by the software Spectrum v5.0.1. Each spectrum was the accumulation of 10 scans with a resolution of 4 cm^{-1}, from 650 to 4 000 cm^{-1}.

ThermoGravimetric Analysis (TGA)

A High Resolution TGA Thermogravimetric Analyzer (TA Instruments), controlled by Thermal Advantage software was used to measure weight loss as a function of temperature in nitrogen. The thermal program was made of three successive ramps, i.e.10 °C.min^{-1} from room temperature to 300 °C, 5 °C.min^{-1} from 300 °C to 500 °C and 10 °C.min^{-1} from 500 °C to 600 °C. The resolution was 4 °C. The data were analyzed using Universal Analysis 2000 software.

Environmental Scanning Electron Microscopy (ESEM)
A Philips Electroscan Environmental Scanning Electron Microscope (ESEM) was used for the observation of the quality of the carbon fiber coating. The acceleration voltage was 20 kV and the current in the filament was set to 1.83 A. No conductive coating was deposited at the surface of the samples.

ILSS and flexural tests with unidirectional carbon fiber composites
Unidirectional composites were manufactured using a Vacuum Assisted Resin Transfer Molding Process (VARTM). The volume fraction of carbon fibers was 60%. It has already been reported that the VARTM process enabled the manufacture of unidirectional carbon fiber composites with a high volume fraction of fibers and good quality [20]. The concentration of initiator in the resin was 1.25 wt%. The thermal program used for the cure was 2 hours at 150 °C + 2 hours at 170 °C.
InterLaminar Shear Strength tests were done according to ASTM D2344/D 2344M-00 and flexural tests were conducted according to ASTM 790-92. A United Testing Systems SFM-20 twin screw load frame was used with 1000 lb and 100 lb load cells. The testing device was controlled by the software DATUM version 3.0.

3. DISCUSSION AND RESULTS

3.1 Carbon fiber with an epoxy coating of controlled properties

A fiber sizing tower system was used to coat the carbon fibers with epoxy. The epoxy coating was a mixture of DGEBA and Jeffamine T-403 (30 wt%). The mix was cured for 30 min at room temperature in order to produce oligomers. The fraction conversion of the epoxy was then 0.01 (Fig.8). A spool of AS4 carbon fibers was unwound and the tow went through a bath of the epoxy mix dissolved in acetone and was dried by successive exposure to two tower-shaped furnaces. The temperature inside the furnaces was fixed at 60 °C and the time spent by the fibers in the furnaces was roughly 1 min.

3.1.1 Control of the thickness of the coating

The thickness of the coating was measured by TGA. The coating started to burn at 350°C and the mass of the system was stabilized at 550°C (Fig. 2). The difference in mass of the coated carbon fiber before and after the 600 ^{o}C exposure corresponded to the mass of the epoxy coating, which enabled the calculation of its thickness, assuming that the fiber and the coating were perfect cylinders and that the thickness of the coating was constant.

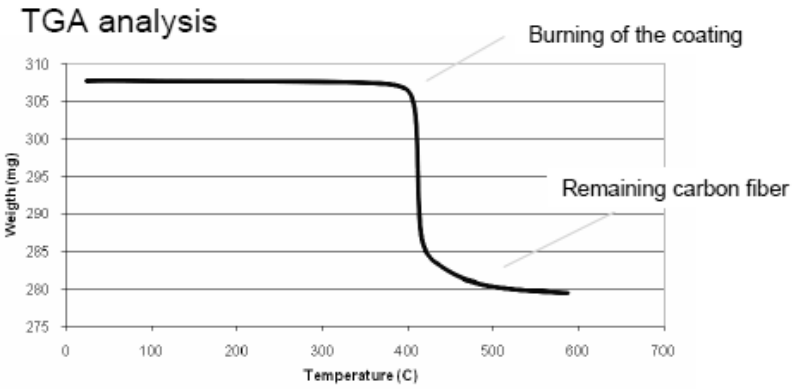

Fig. 2: TGA analysis of AS4 carbon fibers coated by epoxy (in nitrogen).

The thickness of the coating was directly proportional to the concentration of the sizing solution (Fig. 3). It was found that the time spent by the fibers in the bath, which was proportional to the rotation speed of the winding device, did not have a major impact on the thickness of the coating within the range of rotation speed studied. For each concentration, at least two batches of coated fibers were made. The deviation of the value of the thickness in function of the concentration of the sizing solution was low, which enabled a reliable control of the thickness of the epoxy coating (Fig. 4).

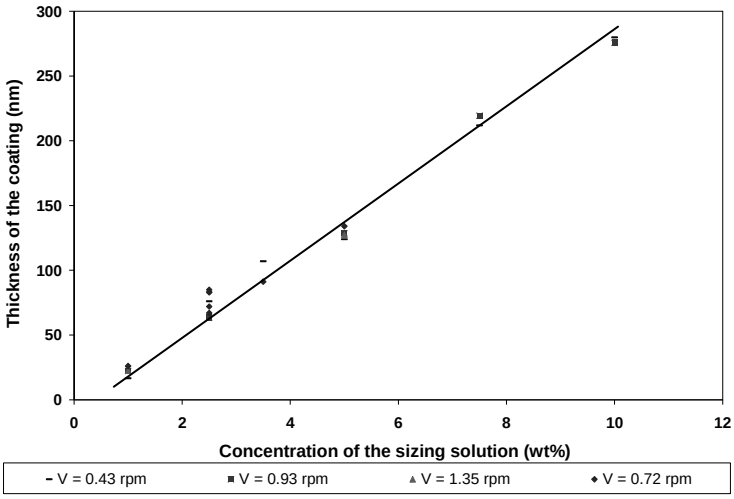

Fig. 3: Thickness of the coating as a function of the sizing solution concentration and the speed of rotation of the winding device.

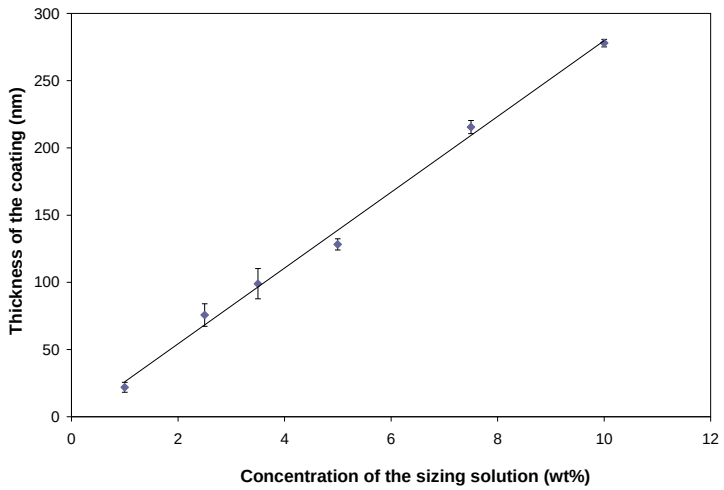

Fig. 4: Thickness of the coating as a function of the sizing solution concentration, regardless of the speed of rotation of the winding device.

3.1.2 Control of the uniformity of the coating

The quality of the coating (uniformity, absence of resin bridges between single fibers) was checked by ESEM. When the concentration of the sizing solution was ≤1 wt%, the surface of the fiber was not evenly coated, with some portions of the carbon fibers being uncoated. A concentration of 3 wt% gave a coating that appeared to uniformly coat the fibers, without any evidence of coating bridging between single fibers (Fig. 5). It was also found that a concentration higher than 4 wt%, which corresponded to a coating thickness greater than 100 nm, resulted in significant bridging between fibers within the tow, producing a tow that was hard and could not be processed after a certain time of curing (Fig. 6).

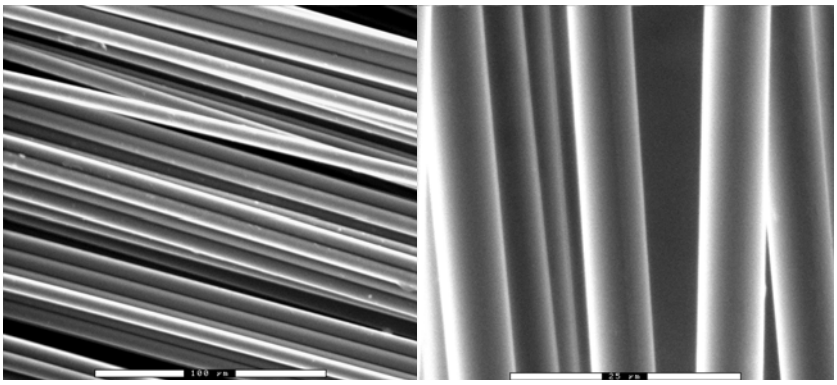

Fig. 5: ESEM picture of fibers coated with an epoxy coating (concentration of sizing solution = 3 wt%).

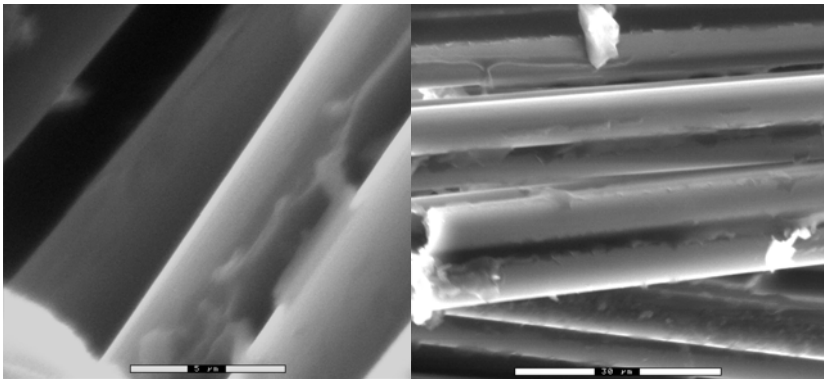

Fig. 6: ESEM picture of fibers coated with an epoxy coating presenting bridges between single fibers (concentration of sizing solution = 7.5 wt%).

3.1.3 Control of the conversion fraction of the epoxy

The kinetics of the cure of the coating at room temperature was monitored by FTIR spectroscopy. A droplet of DGEBA and Jeffamine T-403 was held between two pellets of potassium bromide at room temperature and a spectrum was collected within a determined amount of time. The fraction conversion of epoxy was assessed by measuring the area under the peak located at 914 cm^{-1} which corresponded to the asymmetric stretching of the epoxy ring (Fig. 7). The area of the peak decreased as epoxy groups were consumed by the polymerization reaction. The peak located at 1184 cm^{-1}, characteristic of the C-H aromatic stretching, was used as an internal reference. The fraction conversion of epoxy α was calculated with equation 1

$$\alpha = 1 - \frac{\left(A_{916} / A_{1184}\right)_t}{\left(A_{916} / A_{1184}\right)_{t=0}} \tag{1}$$

where A_{916} and A_{1184} were the area of the peaks located at 916 cm^{-1} and 1184 cm^{-1} respectively (Fig. 8).

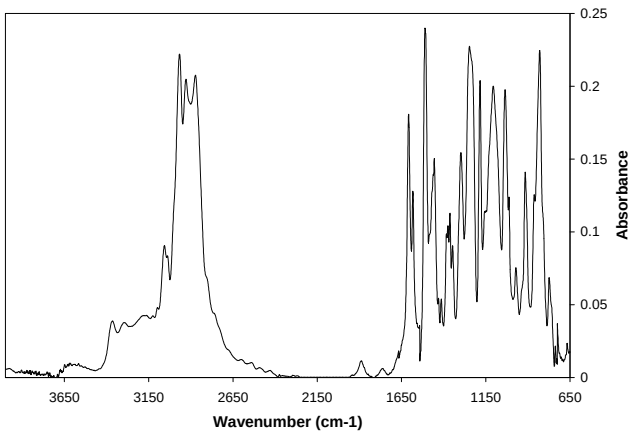

Fig. 7: FTIR spectra of the mixture DGEBA+Jeffamine T-403.

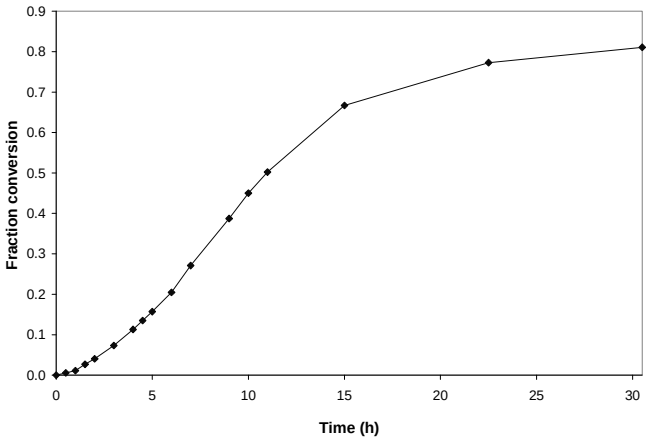

Fig. 8: Evolution of the fraction conversion of epoxy with time at room temperature.

3.2 Mechanical properties of unidirectional carbon fiber composites

The influence of the use of an epoxy coating was assessed for interlaminar shear strength and flexural properties, with regard to the thickness of the epoxy coating and its fraction conversion when in contact with the vinyl ester.

3.2.1 Transverse (90°) flexural properties

The transverse flexural properties of a unidirectional composite are sensitive to interfacial adhesion and they agreed with previous results assessing the carbon fiber-vinyl ester interfacial adhesion by the microindentation test [18]. Indeed, a sharp improvement of the flexural strength was observed with the use of an epoxy coating, an optimal value being obtained with a thickness of around 70 nm (Fig. 9). An optimal thickness was predicted by a finite element analysis reported elsewhere [19]. The increase of the flexural strength was 73% compared to uncoated fibers. The values of the modulus were statistically similar for all systems.

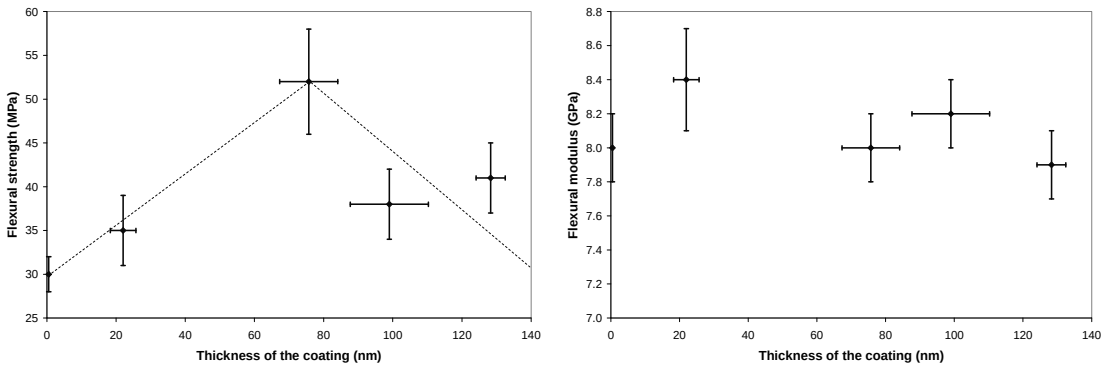

Fig. 9: Evolution of 90° flexural strength (left) and flexural modulus (right) with the thickness of the epoxy coating.

In order to assess the influence of the fraction conversion of the epoxy coating when in contact with the vinyl ester resin on the mechanical properties, the epoxy coating was cured at room temperature for different times (7 h, 11 h, 15 h), which led to different values of fraction conversion (0.3, 0.5 and 0.7 respectively) (Fig. 8). A post cure of the epoxy coating (2 h at 75 °C + 2 h at 125 °C) led to a fraction conversion of 1. The

flexural strength was optimal for a fraction conversion of 0.5 and decreased significantly when the fraction conversion increased (Fig. 10). The interfacial adhesion was then worse with fraction conversion of the epoxy higher than 0.5. It is assumed that a higher fraction conversion prevented sufficient interpenetration of the epoxy and vinyl ester polymers, leading to poor mechanical properties. Indeed, the flexural strength of the composite made with an epoxy coating that was postcured was similar to the value obtained with uncoated fibers. The values of the flexural modulus were statistically the same for all fraction conversions (Fig. 10).

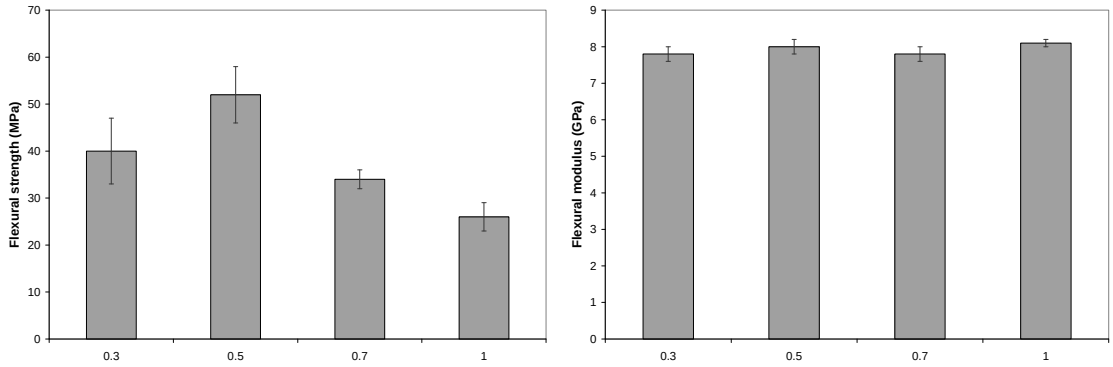

Fig. 10: Evolution of 90° flexural strength (left) and flexural modulus (right) with the fraction conversion of the epoxy coating.

3.2.2 0° Flexural properties (fiber axis)

The 0 degree flexural strength increased with the thickness of the epoxy coating to reach a plateau at around 60 nm (Fig. 11). This could be due to the protection of the fibers integrity by the epoxy coating during the process (winding, unwinding) and a potential change in the failure mode of the composite. The values of the modulus were statistically the same for all systems.

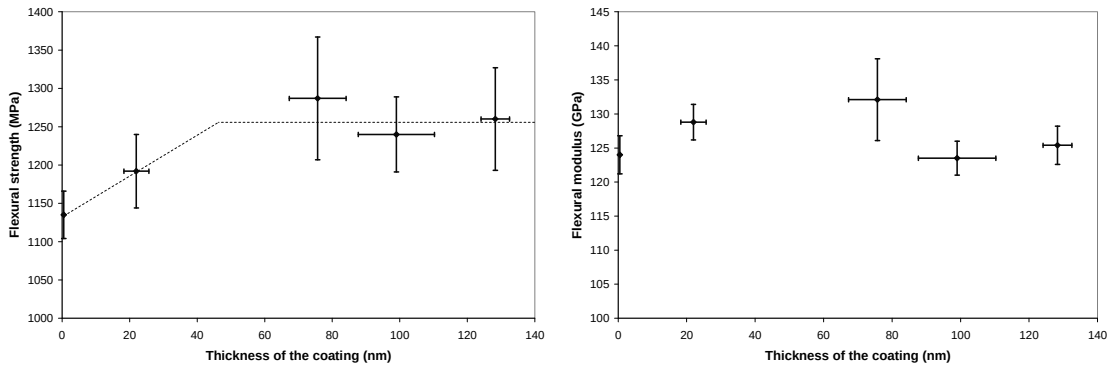

Fig. 11: Evolution of 0° flexural strength (left) and flexural modulus (right) with the thickness of the epoxy coating.

An optimal flexural strength was also obtained at a conversion fraction of 0.5 but the gain in comparison to other values of the fraction conversion was low (+15% compared

with a coating that was post cured, with a standard deviation between 3 and 7%) (Fig. 12). The values of the modulus were statistically the same for all systems.

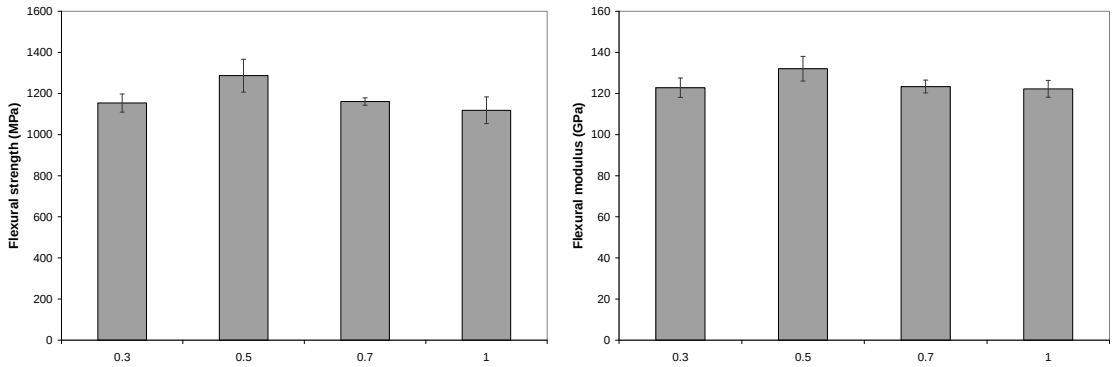

Fig. 12: Evolution of 0° flexural strength (left) and flexural modulus (right) with the fraction conversion of the epoxy coating.

3.2.3 Interlaminar shear strength properties

After coating the carbon fibers with epoxy, the value of ILSS increased from 65 MPa to reach a plateau at 75 MPa (Fig. 13). The increase was about 15%. No particular trend was found as a function of the fractional conversion of the epoxy coating except that the value obtained with a postcured coating gave a value identical to the one obtained with uncoated fibers.

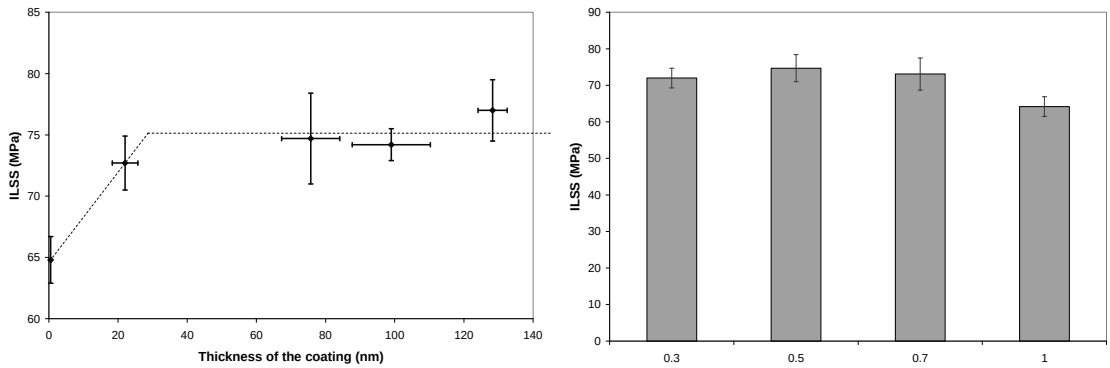

Fig. 13: Evolution of ILSS in function of the thickness of the coating (left) and its fraction conversion (right).

4. CONCLUSIONS

The use of a reactive epoxy coating applied to carbon fibers is a simple and cost effective method to improve the interfacial adhesion of carbon fibers to a vinyl ester matrix, composites and their overall mechanical properties (interlaminar shear strength properties, flexural properties, transverse properties). There is an optimum condition for the thickness and the fractional conversion of the epoxy coating. It provides the best interpenetration of epoxy and vinyl ester, which is essential for optimum mechanical properties.

5. ACKNOWLEDGEMENTS

Ashland, Huntsman and Hexcel Co. are sincerely thanked for having donated samples of vinyl ester resin Derakane 510A-40, curing agent Jeffamine T-403 and AS4 carbon fibers respectively. Financial support for this research from the US Office of Naval Research (Y. Rajapakse) and Florida Atlantic University (R. Granata) is gratefully acknowledged.

6. REFERENCES

1. Kang HM, Yoon TH, Bump M, Riffle JS (2001) Effect of solubility and miscibility on the adhesion behavior of polymer-coated carbon fibers with vinyl ester resins. J Appl Polym Sci 79:1042-1053
2. Kim IC, Yoon TH (2000) Enhanced interfacial adhesion of carbon fibers to vinyl ester resin using poly(arylene ether phosphine oxide) coatings as adhesion promoters. J Adhes Sci Technol 14:545-559
3. Robertson MAF, Bump MB, Vergese KE, McCartney SR, Lesko JJ, Riffle JS, Kim IC, Yoon TH (1999) Designed interphase regions in carbon fiber reinforced vinyl ester matrix composites. J Adhes 71:395-416
4. Schultz J, Nardin M (1990) Interfacial adhesion, Interphase formation and mechanical properties of single fiber polymer based composites. In: Ishida H (ed) Controlled Interphases In Composites Materials. Elsevier, New York
5. Schultz J, Nardin M (1994) Some Physico-Chemicals Aspects of the Fibre-Matrix Interphase in Composite Materials. J Adhes 45:59-71
6. Nardin M, Asloun EM, Schultz J (1990) Physico-chemical interactions between carbon fibers and PEEK. In: Ishida H (ed) Controlled Interphases in Composite Materials. Elsevier, New York
7. Jennings CW (1972) Surface roughness and bond strength of adhesives. J Adhes 4: 25-38
8. Drzal LT, Sugiura N, Hook D (1997) The role of chemical bonding and surface topography in adhesion between carbon fibers and epoxy matrices. Compos Interfaces 5: 337-354
9. Schultz J, Lavielle L, Martin C (1987) The role of the interface in carbon-fiber epoxy composites. J Adhes 23: 45-60
10. Raghavendran VK, Drzal LT, Askeland P (2002) Effect of surface oxygen content and roughness on interfacial adhesion in carbon fiber-polycarbonate composites. J Adhes 16: 1283-1306
11. Owens DK, R. Went RC (1969) Estimation of the surface free energy of polymers. J Appl Polym Sci 13: 1741-1747
12. Fowkes F.M (1987) Role of acid-base interfacial bonding in adhesion. J Adhes Sci Technol 1:7-27
13. Fowkes FM (1984) Acid-base contribution to polymer-filler interactions. Rubber Chem Technol 57

14. Hook KJ, Agrawal RK, L. Drzal LT (1990) Effects of Microvawe Processing on Fiber-Matrix Adhesion. 2. Enhanced Chemical Bonding Epoxy to Carbon-Fibers J Adhes 32: 157-170

15. Pisanova E, Mäder E (2000) Acid-base interaction and covalent bonding at a fiber-matrix interface : contribution to the work of adhesion and measured adhesion strength. J Adhes Sci Technol 14: 415-436

16. Bikerman JJ (1961) The science of adhesive joints. Academic Press, New York

17. Paiva MC, Nardin M, Bernardo CA, Schultz J (1997) Influence of thermal history on the results of fragmentation tests on high-modulus carbon-fiber/polycarbonate model composites. Compos Sci Technol 57: 839-843

18. Vautard F, Xu L, Drzal LT (2009) Influence of cure volume shrinkage on interfacial adhesion in carbon fiber-vinyl ester composites. SAMPE 2009 (Baltimore May, 18th-21st). Technical paper.

19. Vautard F, Xu L, Drzal LT (in press) Adhesion of Carbon Fibers to Vinyl Ester Matrices. In: Accomplishments in Composite Materials and Sandwich Structures – An Anthology of ONR Sponsored Research. Springer.

20. Shivakumar KN, Swaminathan G and Sharpe M (2006) Carbon/Vinyl Ester Composites for Enhanced Performance in Marine Applications. J. Reinf. Plast. Compos. 25:1101-1116