The Effects of POSS on the Interlaminar Shear Strength of Marine Composites under Various Environmental Conditions

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ABSTRACT

The fiber/matrix (F/M) interface of carbon/vinyl ester composites has been modified by surface treating the carbon fiber with polyhedral oligomeric silsesquioxane (POSS). The objective was to improve the durability of the F/M interface in various environments. Two POSS systems with different functionalities, namely octaisobutyl and trisilanolphenyl, have been investigated. Carbon fibers were soaked in a sonicated dispersion of POSS in a compatible solvent, then fabricated into layered composites using Derakane 8084 vinyl ester resin. Treated and untreated composite samples were immersed in three different environments: seawater at room temperature (SWRT), seawater at 40°C (SW40), and in 85% relative humidity at 50°C (HM50). After six weeks, POSS modified samples reduced water absorption by 20-32% and there was no degradation of the interlaminar shear strength.

Keywords: nanocomposite, POSS, carbon fiber, vinyl ester, and F/M interface

1 INTRODUCTION

Increasing maintenance costs, fuel consumption, and warfare vulnerabilities of conventional steel vessels has raised Naval interest in the technological advances in composite fabrication [1]. Initial design studies indicate that the high specific modulus and strength, low weight, and corrosion resistance properties of composites decreases the life-cycle cost by 7% and the structural weight by 50% depending on the type of ship [2-4]. However, the durability of composites in moist environments has been a limiting factor in capitalizing on the structural advantages of composite vessels.

Several studies have been conducted investigating the effects of water on the mechanical properties of carbon/vinyl ester composites [5-8]. The mechanical and thermal analysis of all these studies indicated that the primary area of failure was the F/M interface due to water degradation. Structurally, poor interfacing of the F/M compromises the overall performance of the material system. Studies by Langston [9] and Verghese et at. [10] have shown that fiber surface modification improves the interface properties of carbon/vinyl ester components. However, an improvement across the range of mechanical, thermal and hygrothermal behavior of composites was not observed.

To address this issue, we are proposing the introduction of nanotechnology to the composite material system. POSS is an inorganic-organic hybrid nanosilica engineered to strengthen composites, as well as, promote hydrophobicity, which is ideal for marine applications. POSS are nano sized inorganic cage based structures of silica comprised of eight silicon atoms linked to twelve oxygen atoms. The silicon atoms can be linked to almost any unreactive and/or reactive organic groups creating the innovation of a hybrid inorganic-organic composition. It is therefore expected that if POSS particles, with appropriate functional groups, can be installed on the fiber surface, they would provide a stable and strong F/M interface. Recent studies by Zhang [11] have demonstrated 25-27% improvement of the interlaminar shear strength with various POSS products. Earlier work in this study showed that POSS improved the shear strength by 17-25%, impact by 38%, tensile properties by 8-10% and glass transition temperature by 8% in dry conditions[12].

In this investigation, composites treated with POSS systems, octaisobutyl and trisilanolphenyl, have been exposed to various moist environments. Over a period of six weeks the rate of water absorption was monitored in seawater at room temperature (SWRT), seawater at 40°C (SW40), and in 85% relative humidity at 50°C (HM50). Short beam shear testing was conducted on samples before and after exposure to determine the interlaminar shear strength (ILSS) of moisture exposed composites.

2 EXPERIMENTATION

2.1 Fabrication

Prior to surface treatment, unidirectional carbon fibers were soaked in acetone (Sigma Aldrich) and dried to remove the sizing. A liquid media was produced by de-agglomerating POSS (Hybrid Plastics Inc.) in a compatible solvent (hexane or ethanol) using homogenization followed by 90 minutes of sonication. The concentration for each POSS system was 1.0 wt% and 0.2 wt%, respectively, for octaisobutyl and trisilanolphenyl. Carbon fibers (Vectorply, Inc.) were first soaked for three hours in the liquid media dispersed with POSS. Once soaking was complete, fibers were dried in an oven to evaporate the solvent. POSS-coated fibers were then used with vinyl ester resin, Derakane 8084, (J.I. Plastics) to fabricate layered composites following the standard wet lay-up and compression molding method. The resin was cured at ambient temperature for 24 hrs.

2.2 Short Beam Shear

To determine the interlaminar shear strength (ILSS), at least 5 samples from each composite were tested by short beam shear. In accordance with ASTM standard D2344 the sample span/thickness ratio was maintained at 4 to ensure shear failure: 30 mm (length) × 10 mm (width) × 5 mm (thickness). Testing was conducted in ambient conditions on the Z050 Zwick/Roell machine at 1.3mm/min.

2.3 Hygrothermal Conditioning

The specimens were prepared according to ASTM D2344 [45] requirements: 30 mm × 10 mm × 5 mm, in order to conduct interlaminar shear strength testing of the moisture conditioned F/M interface. Twelve specimens from each type of panel were weighed under dry conditions prior to immersion in saltwater at room temperature, saltwater at 40°C, and an 85% humidity chamber at 50°C. For six weeks the rate of water absorption was observed by weighing each specimen to the milligram and taking the average.

After environmental exposure, specimens were tested by short beam shear and compared to the shear strength values under dry conditions. To maintain the exposed condition of the specimens, samples from the saltwater environment were transferred in Ziploc® bags containing saltwater from the testing environment. The humidity samples were transferred in portable humidity chambers established by mixing potassium bromide with distilled water in a sealed container [13]. For comparison, specimens were dried in ambient conditions and intermittently weighed to the milligram until the composite weight was consistent. Five samples from each category were tested under short beam shear.

3 RESULTS

3.1 Mechanical Analysis

The ILSS property of treated and untreated composites were compared to study the affects of POSS in dry conditions. Figure 1 shows that introduction of POSS the F/M interface improved the composite shear strength. Individually, POSS Octa improved the shear strength by 17%; however, POSS TriS increased to 25% as seen in Table 2. This difference is attributed to the respective chemical structures of the POSS systems. TriS is functionalized with silanol to promote chemical bonding specifically with vinyl ester; whereas, Octa is not functionalized.

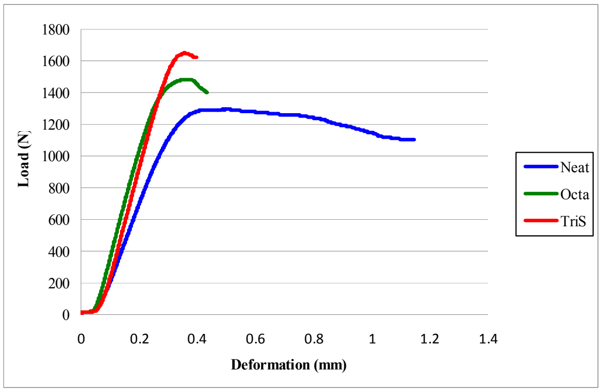


Figure 1. Short beam shear testing results

Panel Type	Carbon Fiber wt.%	Shear Strength (MPa)	Gain/Loss (%)
Neat	---	18.38 ± 0.72	---
Octa	1.0%	21.51 ± 0.73	17.03
TriS	0.2%	23.06 ± 1.82	25.48

Table 1. Comparison of interlaminar shear strength

3.2 Moisture Analysis

Having demonstrated that POSS improves mechanical performance in dry conditions, composites were exposed to moist environments. For six weeks, composite samples were immersed in three different environments: saltwater at room temperature (SWRT), saltwater at 40°C (SW40), and in 85% relative humidity at 50°C (HM50).

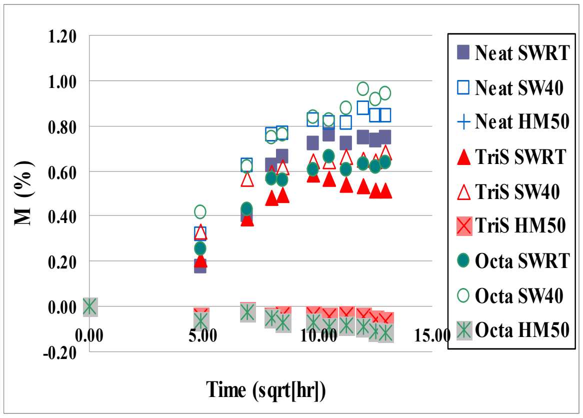


Figure 2: Percentage of weight change

	Percentage of Weight Change (%)				
Condition	**Neat**	**Octa**	**G/L (%)**	**TriS**	**G/L (%)**
SWRT	0.75	0.64	14.67	0.51	32.00
SW40	0.85	0.94	-10.59	0.68	20.00
HM50	-0.08	-0.11	-37.50	-0.06	25.00

*G/L is Gain/Loss

Table 2: Comparison of weight change

The moisture absorption of the composites shows that the effects of Octa and TriS improves the composite durability as observed in dry conditions. Figure 2 shows that the composites absorbed water at differing rates in saltwater; however, the carbon/vinyl ester composites exhibited negligible weight change in the humid environment. In the 40°C saltwater environment, the composites absorbed water at a higher rate suggesting that temperature is an influencing factor. Initially, Octa sizing reduced the absorption rate in the saltwater environment at room temperature by 15%. However, Table 2 shows that in 40ºC saltwater water absorption increases by 11% indicating that Octa is no longer reinforcing the F/M interface. On the contrary, introduction of TriS consistently reduced water absorption by 20% at 40°C and by 32% at room temperature.

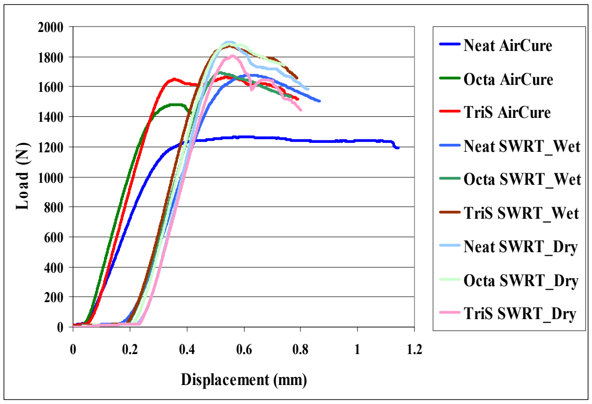


Figure 3: Comparison of seawater at room

	Shear Strength (MPa)		
Specimen	**SWRT**	**SW40**	**HM50**
Neat	26.08 ± 0.49	29.29 ± 1.35	31.66 ± 1.41
Octa	24.30 ± 0.81	28.02 ± 0.80	28.76 ± 0.32
G/L (%)	-0.29	14.98	18.01
TriS	26.60 ±1.58	28.64 ± 1.56	32.15 ± 1.91
G/L (%)	9.15	17.52	31.92

*G/L is Gain/LOSS

Table 3: Comparison of shear strength of wet moisture exposed composites

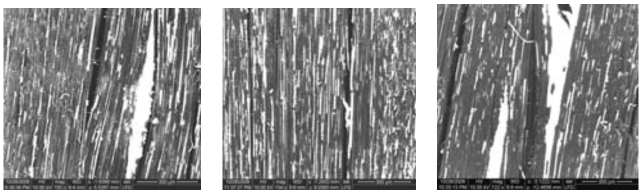
	Shear Strength (MPa)		
Specimen	**SWRT**	**SW40**	**HM50**
Neat	28.03 ± 1.12	29.58 ± 1.07	31.97 ± 0.99
Octa	26.19 ± 1.15	28.98 ± 1.03	30.03 ± 1.69
G/L (%)	7.47	18.92	23.23
TriS	26.06 ± 1.20	30.30 ± 2.16	31.33 ± 1.13
G/L (%)	6.93	24.33	28.56

*G/L is Gain/LOSS

Table 4: Comparison of shear strength of dried moisture exposed composites

Short beam shear testing of the composites indicated no degradation from moisture exposure, instead improvement of the F/M interface (Fig. 3). Under all three conditions: saltwater at temperature, saltwater at 40°C, and 85% humidity at 50°C, the shear strength of the wet and dry tested composites improved for both POSS systems. Table 3 shows that the shear strength values of the moist tested composites increased with the increase in temperature of the environment. Composites treated with Octa improved from approximately 0-18% in shear strength across the environments and TriS sizing gained 9-32%. This trend was also observed in Table 4 with composites dried after testing, where Octa improved from 7-23% in shear strength and TriS increased 7-29%. Even the shear strength property of the control samples increased from 8-14 MPa for both moist and dry testing. This behavior suggests that the varying temperature of the three aqueous environments is affecting the mechanical performance of the composites.

Based on this observation, ambient cured specimens were post cured for 2 hrs at 90°C as specified by Ashland, Inc., the manufacturer of Derakane 8084. Shear strength of the post cured composites was 33 MPa, which is nearly equivalent to 31-32 MPa shear strength of humidity exposed composites indicating that that composite were curing in the moist environments. A study conducted by Herzog et al. [14] with reinforced Derakane 8084 vinyl ester resin, demonstrated that curing the composites at room temperature as specified by the manufacturer does not achieve the advertised mechanical properties. The composites are not fully cured, which lowers the composites mechanical performance. For accurate mechanical characterization, post curing is required for complete crosslinking of the resin.



(a) Neat (b) Octaisobutyl (c) Trisilanolphenyl

Figure 4: Shear failure of composites exposed to saltwater at room temperature

Figure 4 shows SEM images of shear failure from composites that were dried after exposure to saltwater at room temperature conditions. Microscopic examination of the post fractured composites was required due to the overall reduction of failure propagation. After moisture conditioning, the shear failure seems to have reduced to a predominately intralaminar failure.

4 CONCLUSION

The following can be summarized from the above investigation:

1. Investigation of POSS systems, Octa and TriS, have shown that the nanosilica chemical structure influences the particle effectiveness. POSS systems, like TriS, functionalized with vinyl ester compatible silanol, promotes better adhesion with carbon fiber than unfunctionalized Octa.

2. In dry conditions, the composite shear strength property improved by 17-25% with POSS surface treatment of the carbon fibers.

3. Environmental exposure experiments have revealed that water uptake during a six week period of time was minimal. Although water absorption was insignificant at less than 1%, it has been shown that composites with trisilanolphenyl performed the best under each of the exposure conditions reducing absorption by 20-32% compared to neat specimens.

4. Short beam shear testing of samples after exposure to environmental conditions have shown that there is no degradation in interlaminar shear strength. Instead there was improvement of about 7-32%. This was true with neat as well as POSS reinforced composites. This observation suggests that while under environmental exposure, the resin was in fact curing rather than deteriorating within the six week time, especially at elevated temperature.

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