

IMPACT OF AQUEOUS ENVIRONMENTS ON PERFORMANCE OF PULTRUDED COMPOSITES

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ABSTRACT

In the recent years, Pultruded Fiber Reinforced Polymeric (PFRP) composites have been accepted by the construction industry and are being increasingly utilized in different applications. In many applications the composite can be fully or partially immersed in water. Changes in properties of composites in aqueous environments have to be understood and measures have to be taken to optimize performance in these environments. The influence of short-term water absorption on performance of pultruded FRP composites has been investigated in this study. Polyester and vinylester pultruded composites were aged in distilled water and salt-water environments. The pultruded composites were tested to determine short beam shear strength (SBSS) prior and subsequent to aging. The dynamic mechanical properties were investigated utilizing dynamic mechanical thermal analysis. The E-glass/vinylester pultruded specimens exhibited a water absorption rate lower as compared to the polyester pultruded specimens. Higher drops in glass transition temperature (T_g) were observed for polyester pultrusions subsequent to aging. In addition, low levels of SBSS were recorded for the aged polyester pultrusions. Re-dried E-glass/vinylester pultruded specimens exhibited full SBSS recovery. Results of this study highlight the importance of selecting the proper resin system based on environmental exposure conditions.

INTRODUCTION

There has been a growing interest in the utilization of pultruded FRP composites in the construction industry, particularly in harsh environments. The combination of corrosion resistance, high specific strength and modulus, and low thermal and electrical conductivity positioned pultruded FRP composites as a good substitute to traditional materials, such as steel, particularly in the construction industry. However, questions still remain on durability and performance of these composites in various environments.

In the past few years, several investigations on the effects of various environments on performance of FRP composites have been reported¹⁻¹³. Durability of FRP in aqueous environment has received a particular interest due to various applications where the FRP

is in direct contact with water. In 2001, Karbhari and Zhang¹ reported the results of an investigation on the durability of E-glass/vinylester composites fabricated using the resin infusion process subjected to aqueous environment. The study showed that aged specimens exhibited signs of fiber/matrix interphase debonding and degradation as well as cracking. These cracks resulted in a reduction in mechanical properties and an increase in water absorption. The study also showed that post-cure took place during aging, resulting in an increase in level of mechanical performance following the initial drop due to immersion in aqueous environment.

The effects of various environments on polyester and vinylester matrix resins were investigated by Chin *et al.*². Unreinforced resin specimens were characterized following exposure to water, saline and alkaline environments at ambient and elevated temperatures. An increase in glass transition temperature (T_g) was detected for both polyester and vinylester which was attributed to hydrolysis and subsequent dissolution of low molecular weight segments. Tensile strength degradation was observed for all specimens and it was most significant for the E-glass/polyester pultruded specimens that were exposed to elevated-temperature alkaline solution. The degradation of both tensile and short beam shear strength (SBSS) for E-glass/vinylester pultruded specimens that were aged in both water and alkaline solutions were investigated by Zhang *et al.*³. After 50 weeks water immersion at 60 °C, 52% reduction in tensile strength was observed while only 62% of the original SBSS was retained. More reduction in mechanical properties was detected for specimens aged in alkaline solutions. In 1998, Mosallam⁴ reported a field study on pultruded E-glass/polyester pultruded composite structure subjected to harsh mining environment. The study showed that improper choice of the resin system, deficient steel-like connection details as well as the lack of quality control during construction resulted in premature local failures of different pultruded members (*refer to Figure (1)*). Dutta *et al.*⁵ (2002) presented the results of an experimental study on the behavior of pultruded composites lap joints under different exposures, including water, freeze-thaw, and extreme temperature. Test results indicated that the behavior of both bolted and bonded joints is affected by the type and the duration of exposure. The impact of environmental exposures on the performance and design of pultruded composites joints is presented in the American Society of Civil Engineers (ASCE) Composite Joints Design Guide⁶.

Dynamic Mechanical Thermal Analysis (DMTA) has been used in a number of studies to investigate performance and evaluate properties of matrix and fiber/matrix interface under various conditions^{2,3,8,11-15}. Fraga *et al.*¹¹ employed dynamic mechanical measurement to study water absorption effects on hand-lay-up polyester and vinylester composites. Results of the study showed that after immersion in 40 °C water and subsequent drying, neat polyester resin specimens exhibited lower loss tangent peak than that for the vinylester neat resin specimen. That was attributed to the extraction of styrene or monomer. Results also indicated the T_g for polyester matrix increases, while the width of loss tangent peak decreases, due to lower molecular distribution. Vinylester neat matrix showed similar behavior, where T_g increases and the loss tangent decreases, though to a lesser degree compared to the polyester.

This study investigates the short-term water absorption behavior of both polyester and vinylester pultruded composites. Changes in both SBSS and dynamic mechanical

properties as a result of exposure to elevated temperature distilled water and salt solution are investigated. Pultruded composite specimens were examined after exposure to assess the presence of permanent damage to matrix or fiber/matrix interface due to aging in aqueous environment.



Figure 1. A Premature Local Failure of the Web/Flange Junction of Thin-walled E-glass/Polyester Pultruded Composite Column Exposed to Harsh Environments⁴. (Mosallam 1998)⁴

EXPERIMENTAL PROGRAM

All pultruded specimens were supplied by Pultron Composites Ltd, New Zealand. The dimensions of the pultruded specimens evaluated in this program are 31 mm (length), 19 mm (width) and an average thickness of 5 mm. All specimens were cut to a length of 31mm and conditioned for 24 hours at 50 °C then weighed using an electronic scale with 0.1 mg accuracy to establish the specimen dry weight. Two sets of pultruded specimens were evaluated. The first set of specimens was then immersed in 60 °C distilled water, while the other was immersed in a 60°C solution composed of 0.6 mol/L NaCl in distilled water. Specimens were kept in the solutions for up to 17 days (408 hours). Periodically specimens were taken out, wiped with a dry cloth and weighed to determine weight gain. SBSS tests were then performed using test configuration described in ASTM D-4457-96. SBSS was also measured for re-dried specimens to establish the irreversible changes in interlaminar shear strength. The re-dried specimens were prepared by conditioning specimens taken out of the solution at 50 °C for 72 hours. The measurement of dynamic mechanical properties was carried out on (5 mm X 0.85 mm X 31 mm) strips in a

Rheometric Scientific DMTA V (New Jersey, USA) using a 28 mm span three-point bending configuration. The strips were cut from the edge of the 19.0 mm X 5.0 mm specimens. All specimens were heated at a rate of 3 °C/min from 30 °C to 300 °C and were cycled at a frequency of 1 Hz.

RESULTS AND DISCUSSION

Weight Gain: The weight gain for the vinylester and polyester pultruded specimens in water and salt solutions is shown in Figures 1 and 2, respectively. In both figures, vinylester specimens reached equilibrium prior to the end of the test. On the other hand, polyester specimens continued absorbing water and did not reach equilibrium within the duration of the test. This can be attributed to possible microcracking or crazing which commonly take place during accelerated aging tests performed at elevated temperatures². It is evident that the rate and the final level of weight gain for vinylester specimens are significantly lower than those for polyester specimens. This is in disagreement to results achieved by Chin *et al.*², which showed higher weight gain for the unreinforced vinylester compared to polyester. It is also shown in Figures 2 and 3 that the final levels of weight gain are higher for specimens immersed in distilled water compared to those immersed in a salt solution. This is likely to be a result of sorption retardation due to the presence of salt ions.

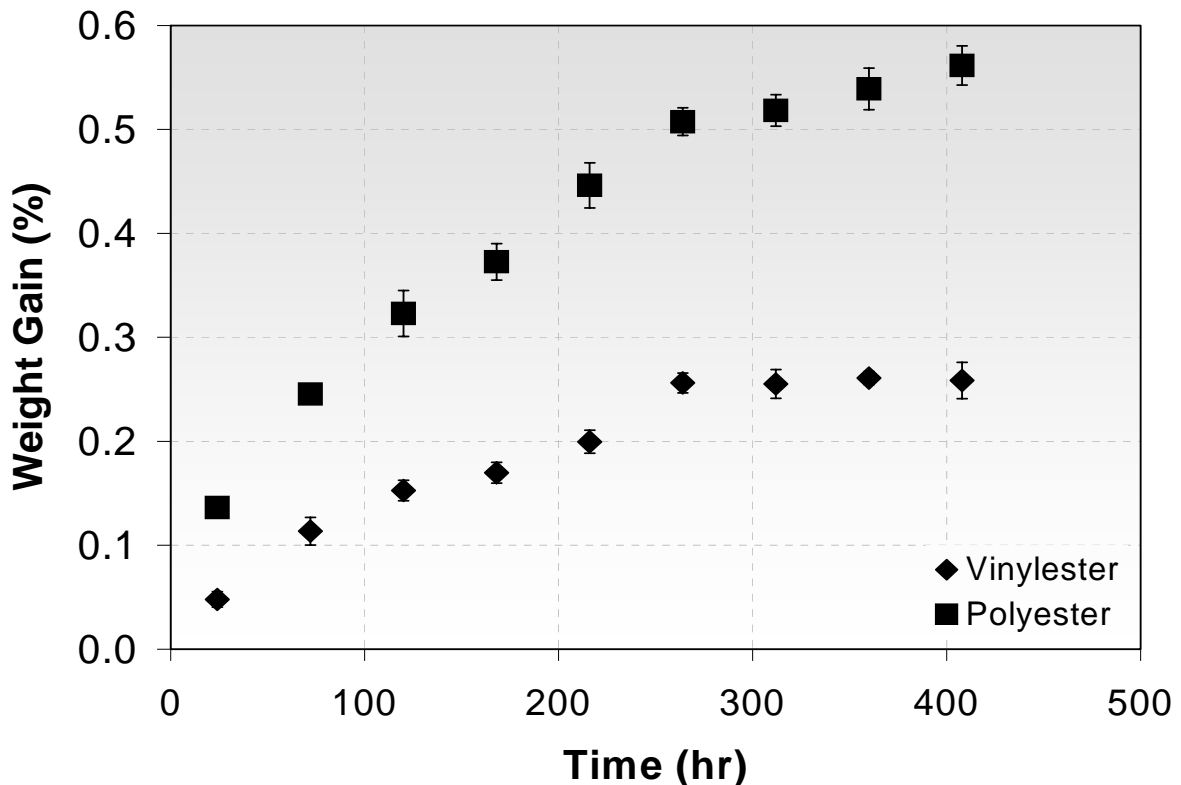


Figure 2. Weight Gain For Vinylester and Polyester Composite Specimens Immersed in 60°C Distilled Water.

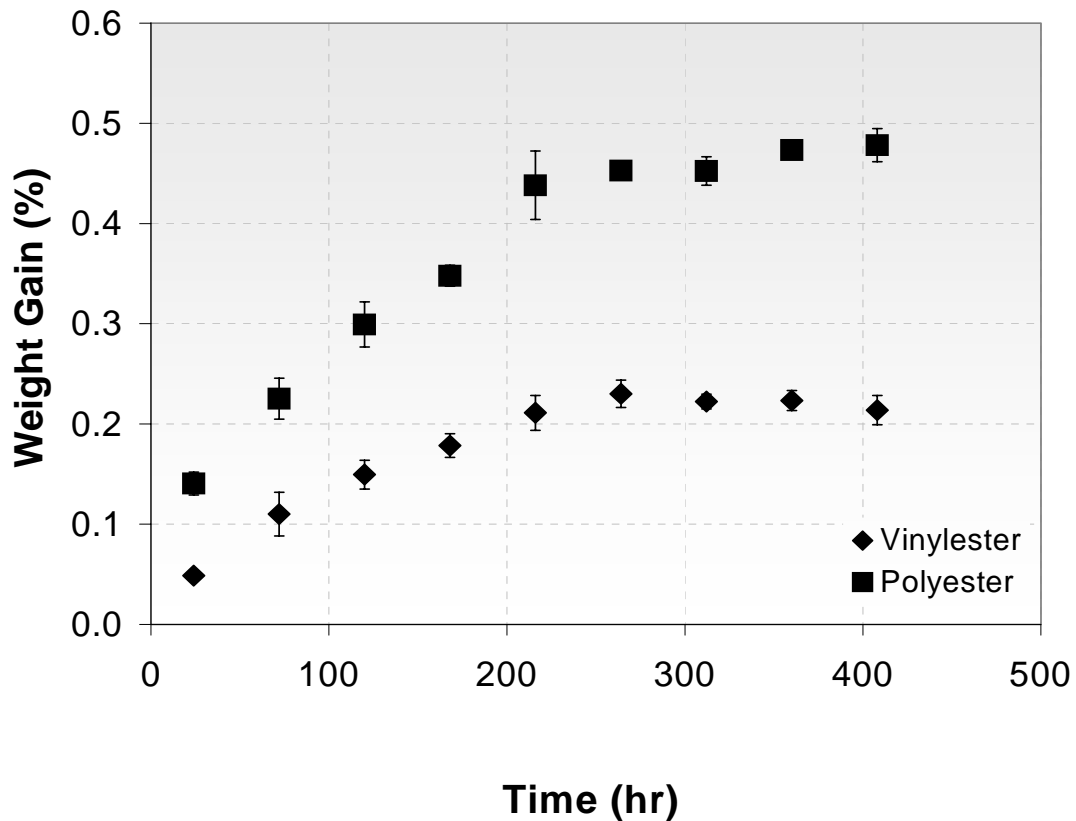


Figure 3. Weight Gain Percentage for E-glass/Vinylester and E-glass/Polyester Pultruded Composite Specimens Immersed in 60°C Salt Solution.

Short Beam Shear Strength Analysis: Measurement of SBSS provides valuable information on changes in physical properties of the matrix and fiber/matrix interface during aging treatment.

Figure 4 illustrates SBSS retention for the two composites in distilled water and salt solution environments after 72 hours and 408 hours (17 days). There is an increase in SBSS after immersion in distilled water for 72 hours for the vinylester composites. An increase in SBSS of over 5% was detected for vinylester specimens immersed in salt solution for 72 hours. During elevated temperature aging two competing phenomena take place: (i) post-cure and (ii) politicization. Enhancement in performance due to post-cure during aging in aqueous solution was reported by Karbhari⁶. Politicization results in a reduction in mechanical performance of the matrix, however it is reversible. Other processes can take place, such as hydrolysis, which can cause an irreversible damage to the matrix and fiber/matrix interface. The initial increase in SBSS for specimens aged for 72 hours can be attributed to post-cure effect. Test results indicated that specimens aged

for 408 hours exhibited a reduction in SBSS due to plasticisation that became more dominant than post-cure. It is noteworthy that while the drop in SBSS for polyester was significant, the change in SBSS for vinylester was not statistically significant. Figure 4 (b) demonstrate the role salt ions play in reducing the rate of water absorption that was evident in Figure 4, which showed lower weight gain for the vinylester and polyester composites in salt solution compared to distilled water. Higher SBSS values were achieved for all composites in salt solution compared to distilled water. Again, the highest level of SBSS retention after 408 hours was observed for the E-glass/vinylester pultruded specimens.

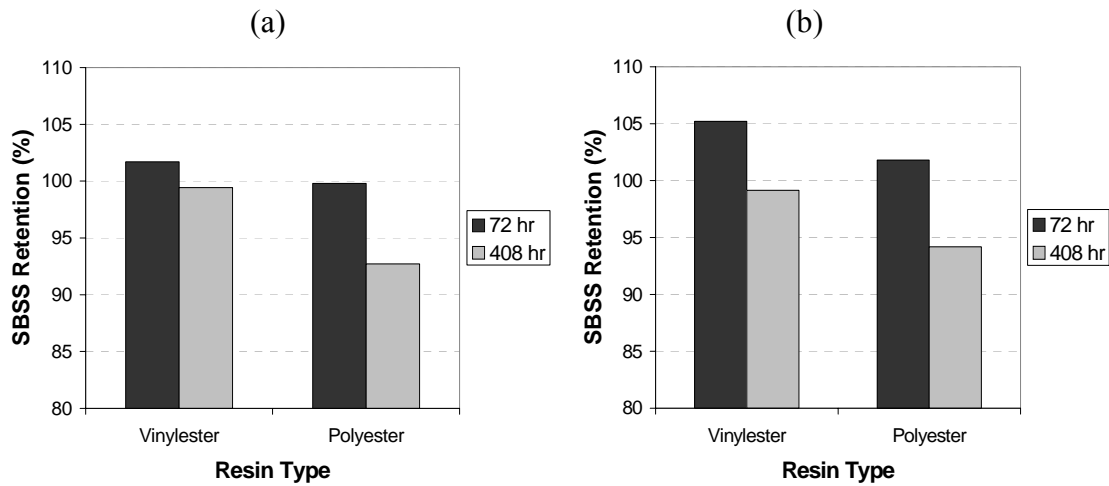


Figure 4. SBSS Retention for E-glass Vinylester and E-glass/Polyester Pultruded Composites after 72 Hours and 408 Hours of Immersion in (a) Distilled Water, and (b) Salt Solution.

In order to examine reversibility of SBSS deterioration, re-dried specimens were tested and compared to wet specimens, which were tested without conditioning after removing from bath. Figures 5 and 6 show the results for specimens immersed in distilled water and salt solution respectively. All re-dried specimens aged for 72 hours in both distilled and salt solution exhibited SBSS higher than that for control specimens. Re-dried pultruded vinylester specimens aged in distilled water and salt solution for 408hr exhibited high SBSS retention levels. On the other hand, re-dried pultruded polyester specimens aged for the same period of time showed minor improvement in SBSS over wet specimens and SBSS retention was lower than that of vinylester. This suggests a permanent damage in the matrix or matrix/fiber interface caused by hydrolysis or microcracking.

Figures 7 and 8 show the loss tangent plots of control vinylester and polyester pultruded specimens. Figure 9 shows the loss tangent plots of control and aged polyester pultruded specimens. Aged specimens were re-dried subsequent to 408 hr immersion in 60°C distilled water.

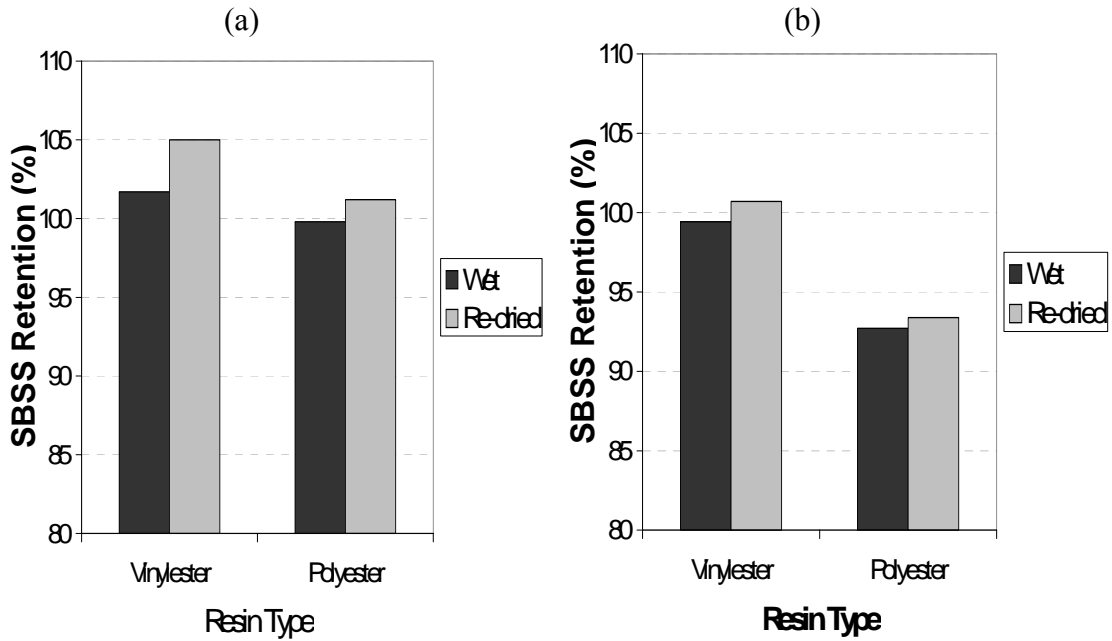


Figure 5. SBSS Retention for Vinylester and Polyester Composites in Wet and Re-Dried Conditions after Immersion in Distilled Water for: (a) 72 Hours, and (b) 408 Hours.

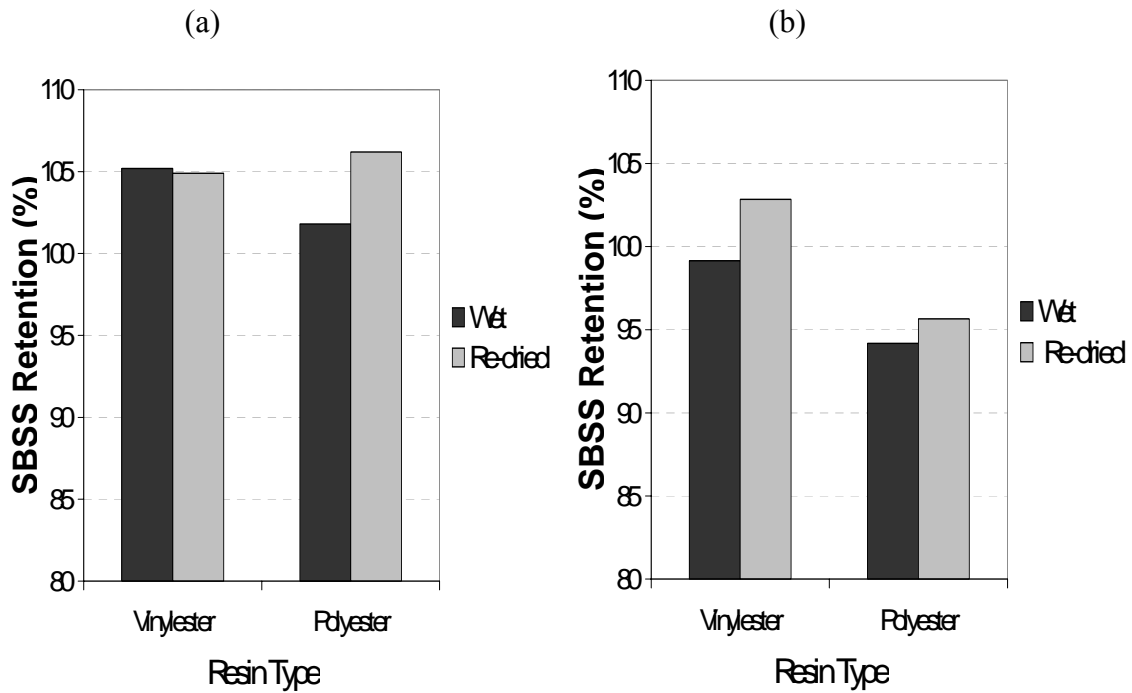


Figure 6. SBSS Retention for E-glass/Vinylester and E-glass/Polyester Composites in Wet and Re-Dried Conditions after Immersion in Salt Solution for: (a) 72 Hours, and (b) 408 Hours.

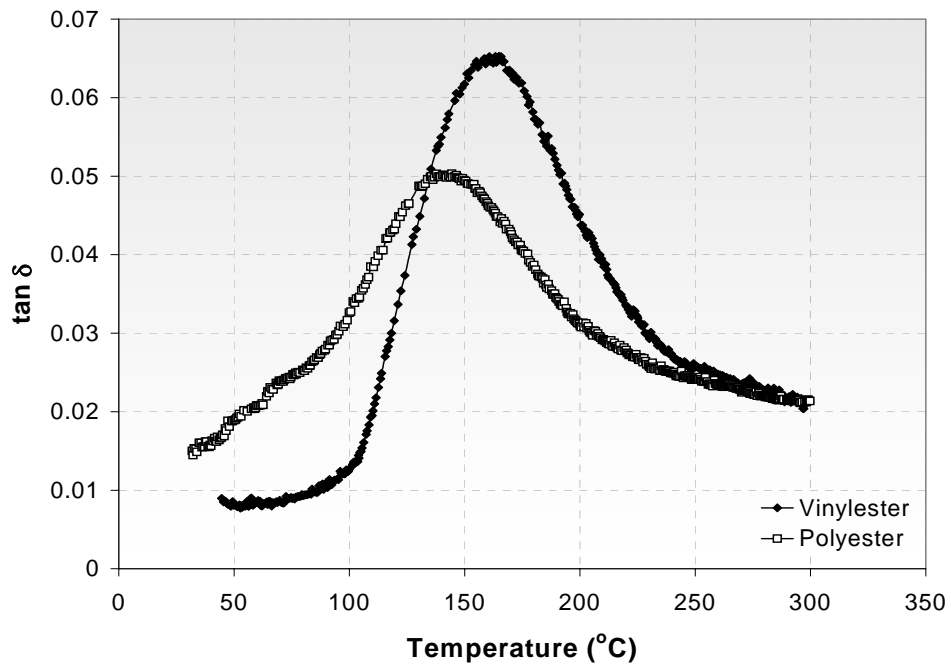


Figure 7. Loss Tangent Plots for Control E-glass/Vinylester and E-glass/Polyester Pultruded Specimens.

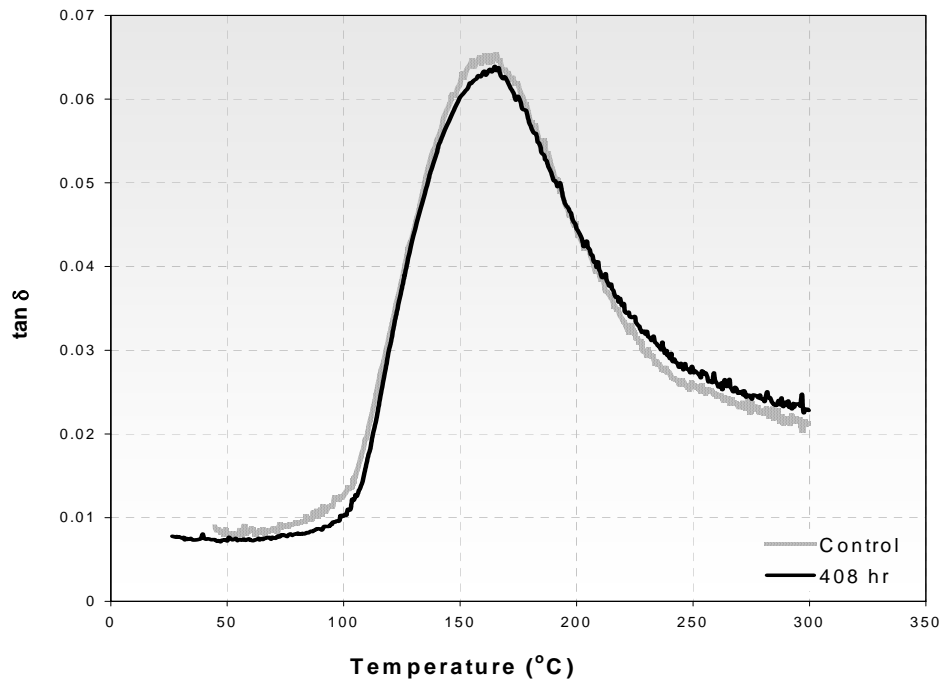


Figure 8. Loss Tangent Plots of Control and 408 Hours Aged E-glass/Vinylester Pultruded Specimens.

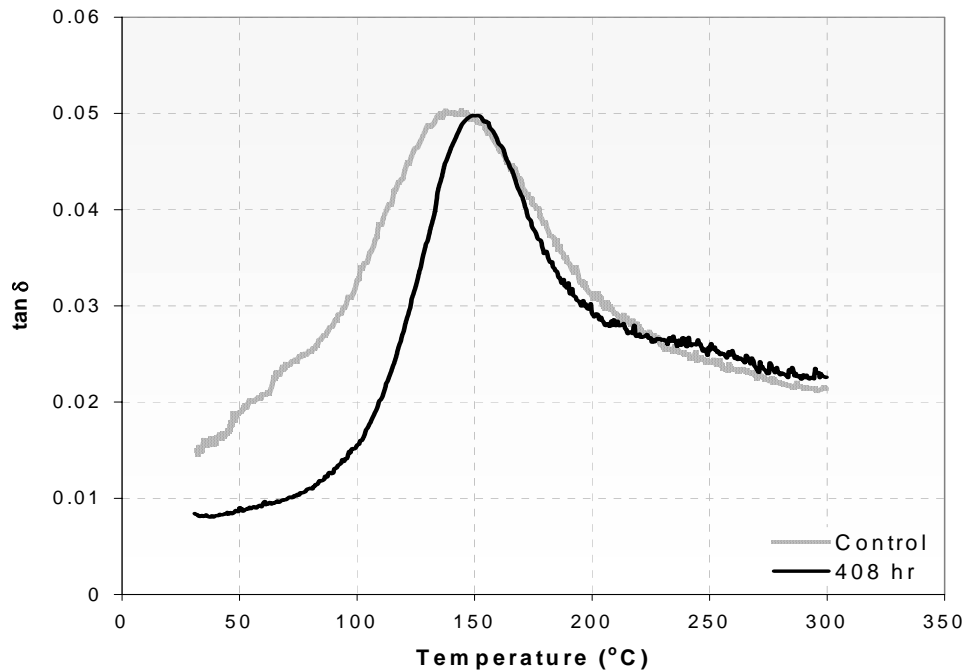


Figure 9. Loss Tangent Plots of Control and Aged E-glass/Polyester Pultruded Specimens.
(Aged Specimens were Re-Dried Subsequent to 408 Hours Immersion in 60 °C Distilled Water.)

The storage modulus behavior for vinylester and polyester pultruded specimens is shown in Figures 10 and 11. As temperature increased, approaching glass transition region, E' dropped from glass-state level to rubber-state level. A study of E' in the rubber-state can give useful information on polymer molecular structure. High rubber-state E' values correspond to high cross-linking density and low molecular weight between crosslinks⁸. Vinylester composites exhibited no change in E' in the rubber-state after immersion in distilled water and salt solution for 17 days (408 hours). On the other hand, polyester specimens aged in distilled water and salt solution showed an increase in rubber-state E' , which could also be attributed to post-cure or monomer extraction. This outcome supports the results achieved in analyzing $\tan \delta$ behavior.

Figures 12 and 13 show that the drop in T_g was more pronounced for polyester specimens after 17-day distilled water and salt solution immersions. This drop is caused by plasticisation of matrix. Both vinylester and polyester specimens recovered their original T_g after re-drying. The distilled water and the salt solution appeared to have similar effect on both types of composites.

CONCLUSIONS

The type of environment where the FRP product is utilized has to be taken into account when selecting the resin system. Results of this study suggest that pultruded E-glass/vinylester outperforms pultruded members made of E-glass/polyester in applications that require direct contact with water or salt solution. Sorption tests

indicated that E-glass/vinylester pultruded composites had lower weight gain in both distilled water and salt solution as compared to E-glass/polyester pultruded composites. E-glass/vinylester pultruded specimens exhibited high levels of SBSS retention even after aging for 17 days (408 hours) in both 60 °C distilled water and salt solutions. In these tests, poor SBSS recovery was observed for re-dried polyester specimens, indicating permanent damage to the matrix or fiber/matrix interface. A more pronounced drop in T_g , caused by plasticisation, was observed for the E-glass/polyester specimens after the 17-day immersion test. The E-glass/polyester pultruded specimens also exhibited an increase in rubber-state storage modulus and a decrease in the width of $\tan \delta$ peak subsequent to aging, which could be attributed to extraction of low molecular weight groups from the matrix. No signs of monomer extraction were observed for the E-glass/vinylester pultruded specimens.

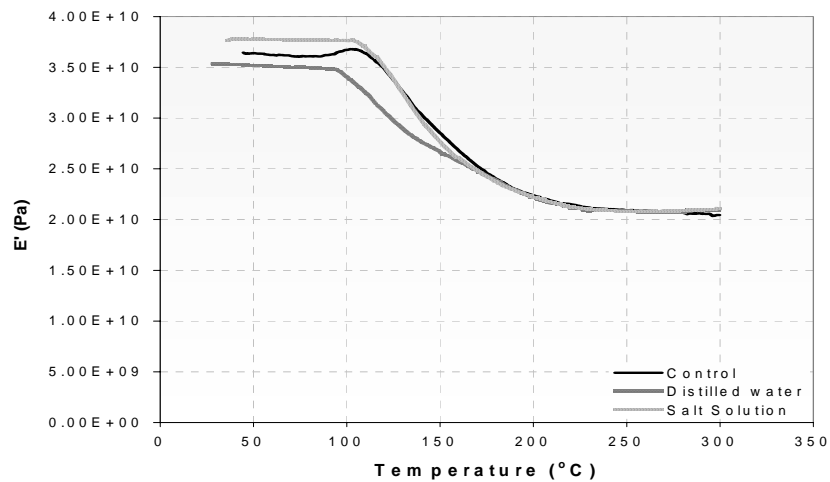


Figure 10. Storage Modulus of Vinylester Pultruded Specimens Prior to Immersion & Subsequent to Immersion for 17 Days in 60°C Distilled Water and Salt Solutions.

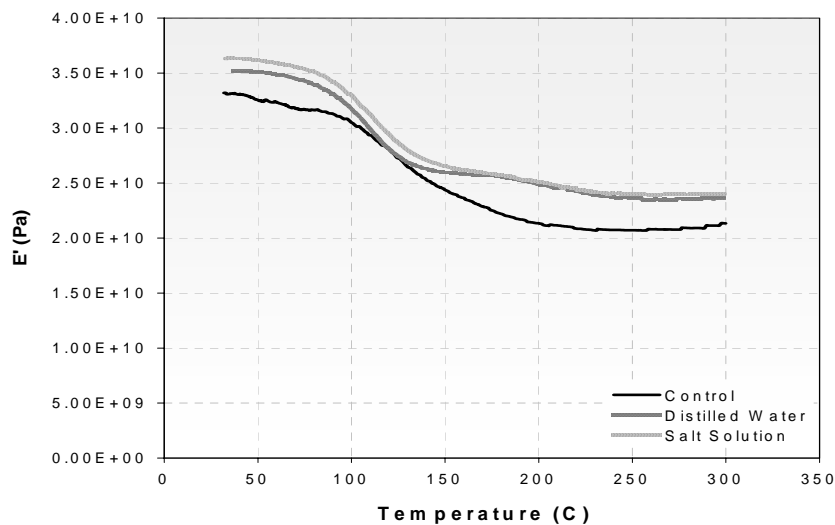


Figure 11. Glass Transition Temperatures (T_g) of E-glass/Vinylester and E-glass/Polyester Pultruded Specimens Prior to Immersion in a Wet Environment and at Re-Dried Condition.

[Immersion Duration: 17 Days Environment: 60 °C Distilled Water and Salt Solution]

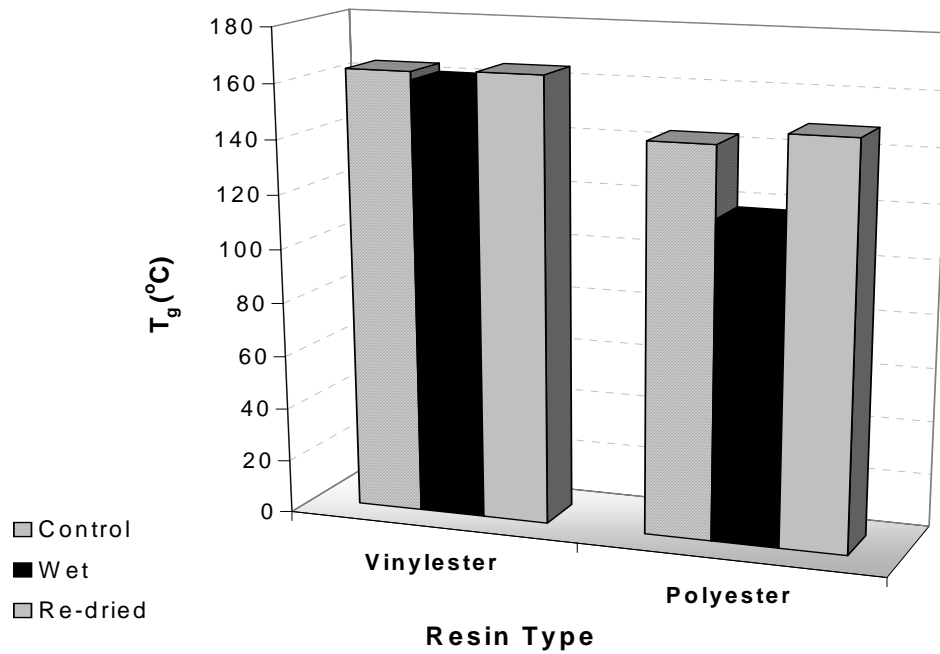


Figure 12. Glass Transition Temperatures of Vinylester and Polyester Pultruded Specimens Prior to Immersion, in e Wet Environment and at Re-Dried Condition
[Immersion Duration: 17 Days Environment: 60°C Distilled Water]

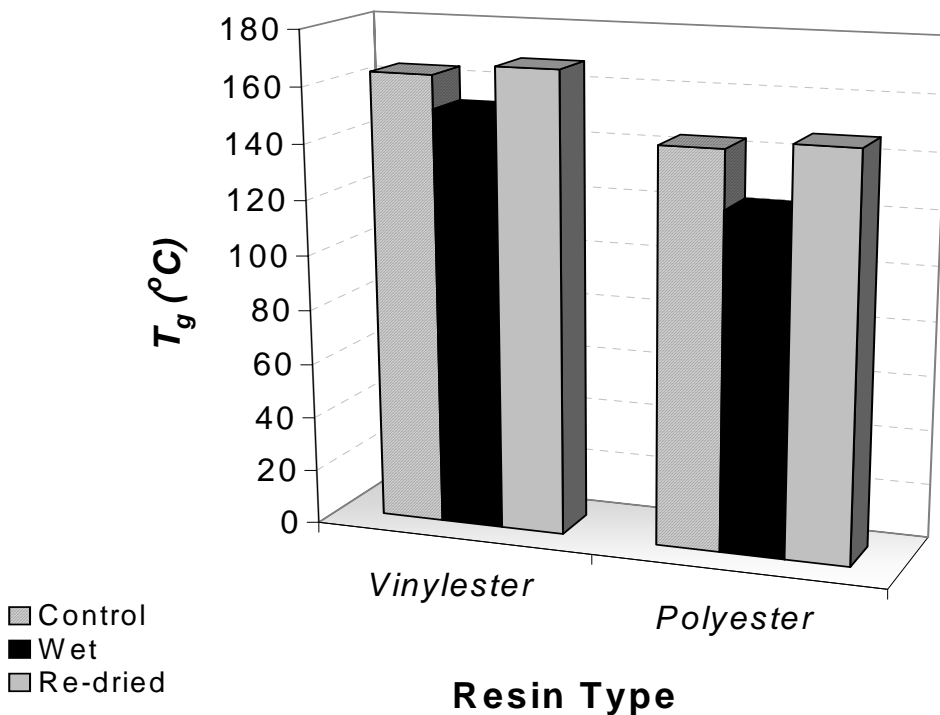


Figure 13. Glass Transition Temperatures of E-glass/Vinylester and E-glass/Polyester Pultruded Specimens Prior to Immersion, in e Wet Environment and at Re-Dried Condition.
[Immersion Duration: 17 Days Environment: 60°C Salt Solution]

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AUTHORS' BIOGRAPHIES

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