LONG-TERM EFFECT OF SEAWATER ON GLASS/THERMOSET COMPOSITES

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Abstract
The effects of seawater and temperature on the mechanical properties of two fiberglass/thermoset composites, namely glass/epoxy and glass/urethane materials, are presented in this paper. Test parameters included immersion time, ranging from three months to two years, and temperature including room temperature (23° C) and hot temperature (65ºC). At room temperature, the effect of seawater varies from minimum effect on glass/epoxy to moderate decrease in the properties of glass/polyurethane composites. However at 65º C, the strength of both composites decreased by nearly 40%.

1 Introduction
In addition to their ubiquitous use in watercraft such as yachts and sail boats, glass reinforced thermoset composites are increasingly used in marine infrastructure such as natural gas and desalination pipes, offshore oil rigs, and seaport structures. These applications require extended duration in seawater at varying temperatures. Extensive data is needed for designers to assess the performance of these composites in such environments. A number of researchers have investigated the durability of fiberglass/polyester and fiberglass/vinyl ester in seawater environment [1-4]. The effect of seawater and temperature environment ranging from 23°C to 65°C on glass/epoxy and glass/polyurethane composites for a duration of one year was reported in a previous study by the authors [5, 6]. The continuation of that study revealed that further deterioration in mechanical properties occurs in these composites with extended duration in seawater. The findings of this study are discussed in this paper.

2 Materials and testing methods
Samples of unidirectional glass/epoxy (52% fiber by volume) and glass/polyurethane (58% fiber by volume) composites were used in this study. Tensile specimens of 3 mm average thickness were prepared from each material according to ASTM Standard D-3039 [7] for conditioning and testing. The cut edges of the specimens were sealed by a thin layer of adhesive prior to conditioning. The specimens were conditioned by immersion in two tanks of seawater from the Arabian Gulf for duration of two years. One tank was kept at room temperature (23°C) and the other was kept at 65°C. The specimens were weighed every month to measure the moisture absorption. Three replicate specimens of each material were removed from their respective conditioning chamber every three months and tested in tension.

Results of control (unconditioned) and conditioned samples are presented and discussed in the following section.

3 Results and discussion

Tensile properties including strength, modulus, and strain to failure of control and conditioned samples of glass/epoxy and glass/polyurethane materials are shown in Tables 1 and 2, respectively. To capture the general trend, only data of six months conditioning intervals are presented in these tables. Data of the glass/epoxy composite in Table 1 show no change in strength after two years of immersion in seawater at room temperature. However after two years of immersion in seawater at 65°C the strength decreased by 37% from 794 MPa to 498 MPa. The strength of glass/polyurethane material decreased by 25% after two years in sweater at room temperature; and by 40% from an average of 853 MPa to an average of 512 MPa at 65°C, as shown in Table 2. The general trends of the strength data of both materials at room temperature and 65°C are shown in Figures 1 and 2 below.

Property	**Strength [MPa]**		**Modulus [GPa]**		**Strain to Failure [%]**	
Condition[1]	**RT**	**65°C**	**RT**	**65°C**	**RT**	**65°C**
Control Samples	794 ± 46	794 ± 46	37.1 ± 2.5	37.1 ± 2.5	2.0 ± 0.0	2.0 ± 0.0
6 Months SW	817 ± 6	761 ± 20	35.1 ± 0.8	33.6 ± 0.6	2.4 ± 0.0	2.3 ±0.2
12 Month SW	788 ± 37	749 ± 69	38.2± 2.0	35.4 ± 4.1	2.1 ± 0.23	2.2 ± 0.1
18 Months SW	787 ± 61	565 ± 48	34.2 ± 0.9	36.7 ± 1.4	2.3 ± 0.1	1.5 ± 0.18
24 Months SW	790 ± 86	498 ± 56	32.3 ± 1.7	32.7 ± 0.8	2.5 ± 0.38	1.5 ± 0.17

[1]SW: seawater; RT: room temperature

Table 1 Tensile properties of control and conditioned Glass/Epoxy material

Property	**Strength [MPa]**		**Modulus [GPa]**		**Strain to Failure [%]**	
Condition	**RT**	**65° C**	**RT**	**65°C**	**RT**	**65°C**
Control Samples	853 ± 84	853 ± 84	41.8 ± 1.4	41.8 ± 1.4	2.0 ± 0.0	2.0 ± 0.0
6 Months SW	856 ± 10	623 ± 70	40.8 ± 1.8	41 ± 2.8	2.6 ± 1.5	1.5 ± 0.3
12 Month SW	692 ± 22	592 ± 38	41.7 ± 2.5	41.5 ± 4.3	2.2 ± 0.3	1.5 ± 0.2
18 Months SW	693 ± 55	568 ± 21	41.3 ± 1.6	42.4 ± 2.6	3.1 ± 1.8	1.33 ± 0.13
24 Months SW	644 ± 22	512 ± 5.4	36.7 ± 0.0	39 ± 2.5	2.8 ± 0.68	1.62 ± 0.45

Table 2 Tensile properties of control and conditioned Glass/Polyurethane material

It is shown in these figures that the strength of glass/epoxy material is maintained up to one year in hot water, after which it begins to decrease significantly. The strength of the glass/polyurethane exhibits significant decrease after six months at 65°C and continues to decrease gradually to its lowest value of 512 MPa after two years of exposure. The degradation in strength is mainly due the diffusion of hot water into the matrix which in turn causes degradation at the fiber/matrix interface. It is apparent that diffusion occurs faster in the glass/polyurethane at high temperature than in the glass/epoxy material.

Seawater at both room and hot temperatures does not have a significant effect on the modulus of both materials as shown in Tables 1 and 2. Furthermore it is shown in Figures 3 and 4 that the modulus remains fairly constant over the entire conditioning period, with a maximum reduction of 12% after two years of exposure. These data indicate that in spite of the degradation at the fiber/matrix interface, the fiberglass reinforcement continues to provide more than 88% of the original longitudinal stiffness of the unidirectional composites.

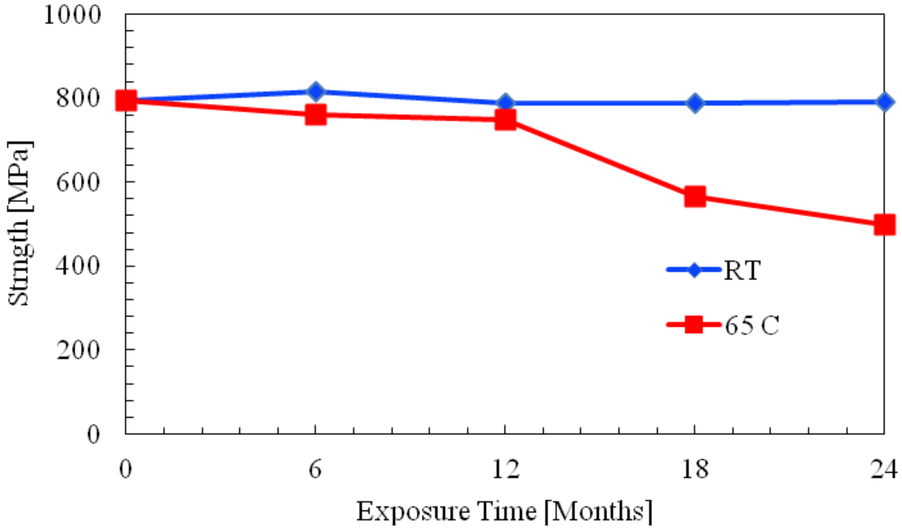

Figure 1. Variation in tensile strength of glass/epoxy material with immersion time in seawater

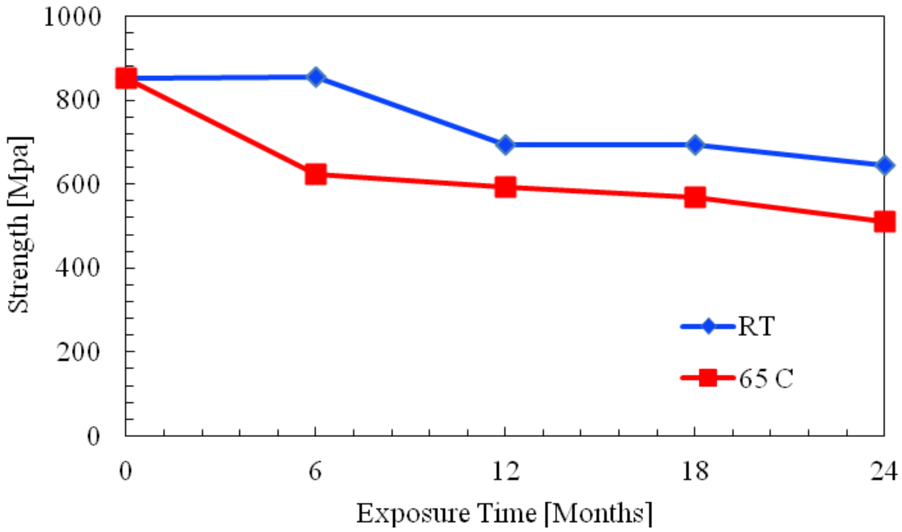

Figure 2. Variation in tensile strength of glass/polyurethane material with immersion time in seawater

It was previously argued by the authors [5] that the degradation in the matrix and interface in an extreme hot seawater environment is caused by a number of factors. These include hydrolysis, leaching out of materials at the interface, plasticization in some matrixes and anti-plasticization in others, and break-down of molecular weight of the matrix. It is shown in this study that these factors are exacerbated with time and high temperature. Evidence of this observation is given in Figures 5 and 6 below. In these figures, the stress-strain behavior of control specimens and specimens immersed in seawater for 24 months at room temperature and at 65°C are presented. The reduction in longitudinal tensile strength and modulus is shown by the decreased slope of the conditioned samples. Furthermore, samples conditioned in hot seawater exhibit further reduction in strain to failure of the glass/epoxy and glass/polyurethane composites as shown in Figures 5 and 6 and Tables 1 and 2, respectively. This shows that the severe hot seawater environment causes both matrixes to become brittle and lowers the strength and ductility of the composites. It is remarkable however to see in Figures 3 through 6 that there is no substantial decrease in modulus. It is postulated that some regions at the interface have maintained adequate connections between the fibers and matrix allowing a composite action and preserving more than 88% of the modulus in both materials. These regions can be described as "spot welding" at the interface. It would be interesting to investigate whether these regions will endure the test of time in hot seawater environments.

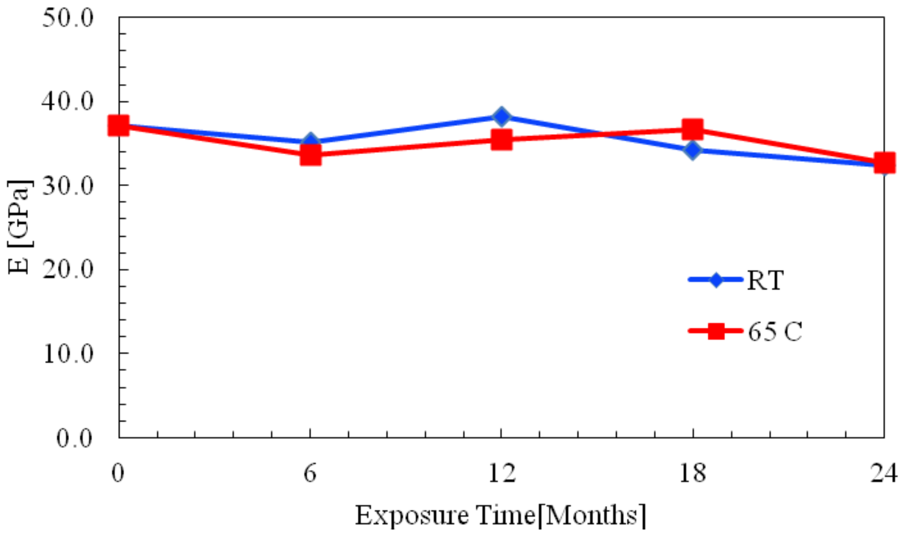

Figure 3. Variation of Modulus of glass/epoxy with immersion time in seawater

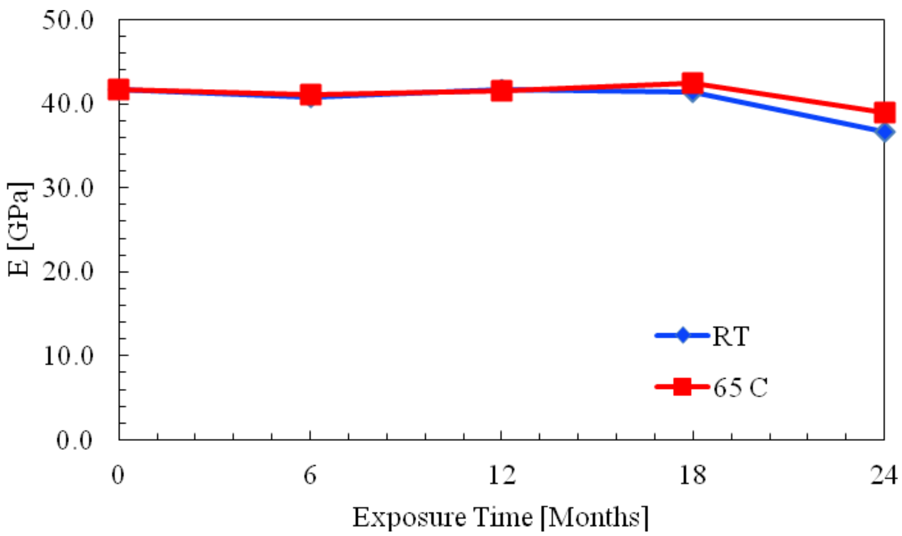

Figure 4. Variation of Modulus of glass/polyurethane with immersion time in seawater

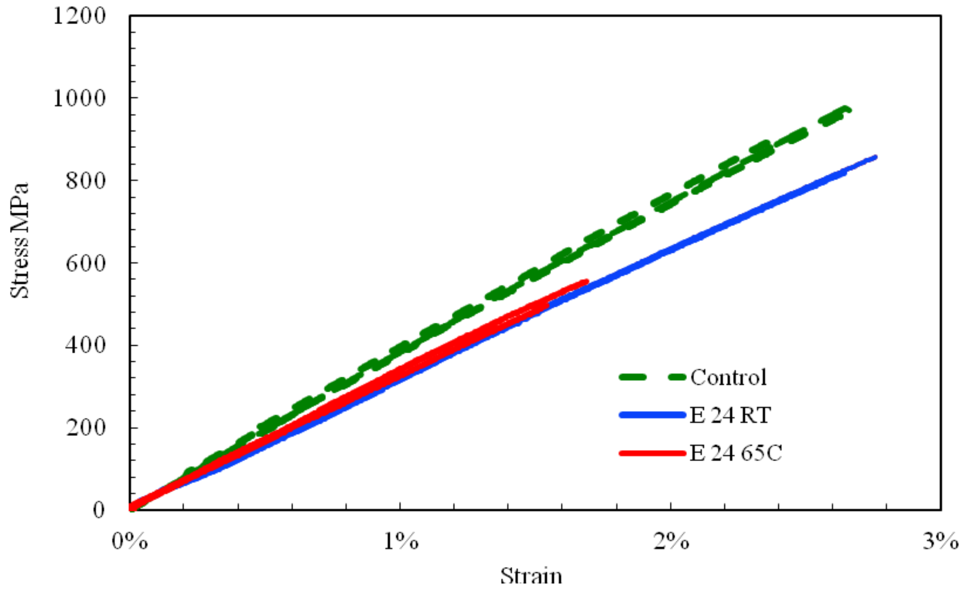

Figure 5. Glass/epoxy: Stress-strain behavior of control and specimens conditioned for 24 months in seawater

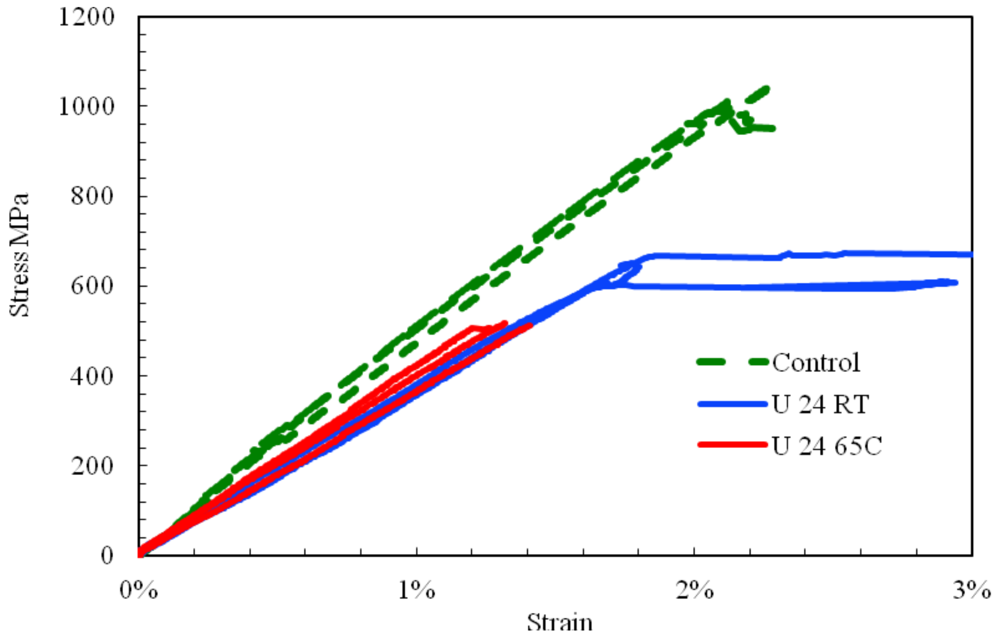

Figure 6. Glass/Polyurethane: Stress-strain behavior of control and specimens conditioned for 24 months in seawater

Conclusions

Glass/epoxy and glass/polyurethane thermoset composites were immersed in seawater from the Arabian Gulf for two years at 23°C and 65°C. Samples were tested in tension at intervals of three months up to two years. No significant change in tensile strength was observed in the glass/epoxy material after two years of exposure to seawater at room temperature; however a

37% decrease in strength was observed at 65°C. The glass/polyurethane composite exhibited 25% and 40% decrease in strength at room temperature and 65°C; respectively, after two years of immersion in seawater. The effect on the modulus was less substantial in both materials in both temperature environments with a maximum of 12% reduction in the longitudinal modulus of the materials. It is concluded that the degradation occurs at the fiber matrix interface and is accelerated at the higher temperature of 65°C. This degradation at the interface lowers the strength and leads to matrix brittleness and a 25% reduction in failure strain at high temperature in both materials.

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