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A comparison of destructive behaviors of distilled water, salty water, sulfuric acid and heat on glass/vinyl ester composites

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Abstract. In the present paper, the destructive behavior of distilled water, salty water, sulfuric acid, and heat on glass/vinyl ester composites was investigated by experimental methods. Hetron 922 vinyl ester resin and two types of mat and woven glass fibers as the reinforcements were used to fabricate composite test samples. All samples were immersed in distilled water, salty water, and sulfuric acid with three different concentrations. The tests were performed at 20°C and 70°C for the exposure duration of 1, 2, 4, and 8 weeks. Bending tests were performed after aging for all composite samples to check the degradation of the bending modulus and strength. The results show that the effect of distilled water, in comparison with salty water, on the degradation of composite samples was significant. On the other hand, almost non-sensitivity of concentrations of salty water on the weight gain of specimens has been observed. In addition, it was also observed that the degradation of samples at 70°C temperature is much more than that of at 20°C. Also, it was observed that the flexural modulus of virgin specimens exposed to salty water (2% concentration) has been recovered just after two weeks of immersion. Furthermore, in some cases, composite samples under the sulfuric acid solution have lost almost 80% of their mechanical properties.

Keywords: aging; composite materials; distilled water; environmental conditions; salty water; sulfuric acid

1. Introduction

Polymeric composite materials are sensitive to some destructive factors such as thermal aging, moisture, immersion in distilled and salty water, chemicals, etc. Recent experiences prove that the destructive effects of the environmental conditions on these materials are not deniable (Miyano *et al*. 2004, Garrido 2013). Many experimental studies have been carried out in this field (Shokrieh and Bayat 2007, Tsotsis *et al*. 2001, Davalos *et al*. 2012, Amaro *et al*. 2014, Boinard *et al*. 2000, Aktaş 2008), but there is a lack of comparison of the destructive behavior of distilled water, salty water, sulfuric acid and heat on composite materials, simultaneously (Kim *et al*. 2008, Martin 2008, Imielińska 2004, Boisseau 2012). Polymeric composites absorb water and other environmental fluids, which can have negative effects such as swelling, reduction of resin glass transition temperature, and physical and mechanial properties degradation (Amaro 2014). In previous studies, various concentrations of salty water (mainly seawater) were investigated by researchers (Abd El-Baky 2018, Heshmati *et al*. 2017). Also, the distilled water (or pure water) was considered as low-

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level importance among environmental conditions (Bal and Saha 2015). On the other hand, limited studies are demonstrating the results of the durability of polymeric composite samples exposed to sulfuric acid (or other acidic solutions). These shortcomings were the motivations of the present research.

In the present study, a wide range of experimental data was collected by performing accelerated tests on composite samples exposed to distilled water, salty water, and sulfuric acid at an exposure duration of 1, 2, 4, and 8 weeks and two temperatures of 20°C and 70°C. The change of weight, flexural strength, and bending modulus of composite specimens were studied. The novelties and unique results of the present research are:

• Conducting comprehensive experimental works on the effects of distilled water, salty water, and sulfuric acid on the degradation of mechanical properties of the same glass/vinyl ester composites.

• Observation of more destructive behavior of distilled water in comparison to salty water.

• Recovery of mechanical properties of virgin specimens exposed to salty water just after two weeks of immersion.

• Almost non-sensitivity of concentrations of salty water on the weight gain of specimens.

2. Material selection, fabrication of composite samples, and test procedures

Due to the corrosion resistance of the vinyl ester resin and its widespread use in the industry, Hetron 922 resin was used as the matrix to fabricate the composite samples. Two types of corrosion-resistant ECR glass fibers (The ECR is a modified E-glass with higher chemical resistance, including water-resistance, acid-resistance, and alkali-resistance), chopped strand glass mat with an area weight of 450 gr/m^{2,} and ECR woven fabric with an area weight of 400 gr/m^2 made by Taishan Co., China were used. Both of these fibers are shown in Fig. 1. The fiber volume fraction of composites was about 50%.

Composite sheets with 250×250 mm dimensions were fabricated by the hand lay-up method and plates were cut to 60×12 (±10% variance) mm samples. The stacking sequence of laminated composites has been shown in Fig. 2 The thickness of each ply is 0.45 mm and that of the laminate is 2.7 mm. Specimens have been cured at 40°C for 36 hours. Since in this research composite samples had immersed through an extremely corrosive environment, specifically the acidic solutions, it is imperative to select a combination of materials that could sustain the foregoing conditions, whereby this symmetric lay-up has been selected for this purpose.

The effects of distilled water and salty water on glass/vinyl ester laminated composites, under different thermal and exposure duration conditions, were investigated. The exposure durations of 1,

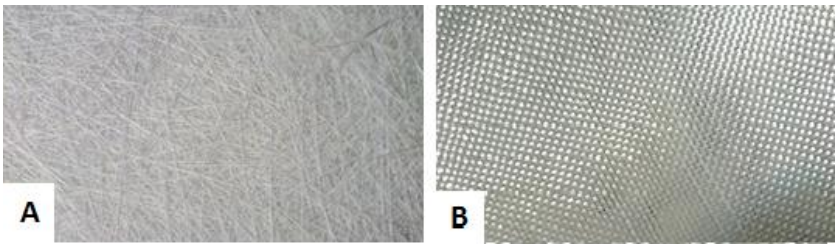


Fig. 1 The ECR glass fibers used for the fabrication of composite specimens A) chopped strand mat and B) woven fabric

Mat
Woven
Mat
Mat
Woven
Mat

Fig. 2 The stacking sequence of composite samples

Table 1 The test matrix of the present study

Environmental conditions	Distilled water	Salty water	Sulfuric acid solution
Concentration	-	2%, 2.5%, and 3%	10%, 20%, and 30%
Temperature (°C)	20 and 70	20 and 70	20 and 70
Exposure time (days)	7, 14, 28, and 56	7, 14, 28, and 56	7, 14, 28, and 56
Number of performed tests for each case (Total Tests)	3 (24)	3 (72)	3 (72)

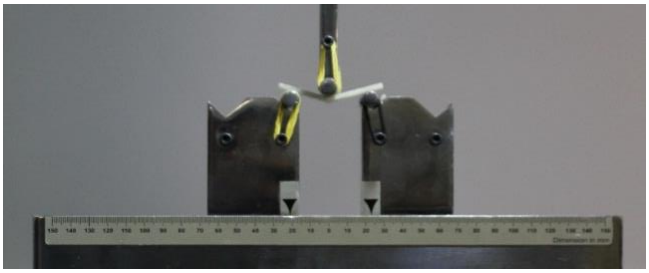


Fig. 3 The three-point bending test fixture

2, 4, and 8 weeks were considered. The salty water solutions with concentrations as 2, 2.5, and 3% were prepared.

Table 1 summarizes the test conditions. According to this table, three composite samples were placed in each environmental condition and tested. These samples were tested after 7, 14, 28, and 56 days. Therefore, by testing six more virgin samples a total of 174 samples were tested. The three-point bending test according to ASTM D 790-03 was used to test the samples. The length, width, and thickness of the samples are 60, 12.7, and 2.7 mm, respectively.

To maintain the test conditions and keep them stable, a durable and thick glass container was used. Also, all containers and the samples inside were coded.

To create a constant temperature environment of 20°C for 56 days, an insulating chamber was used. A furnace was also used to create an environment with a temperature of 70°C. Both of these devices are equipped with a digital thermometer, to continuously control the environmental conditions.

After removing the samples from the accelerated aging test conditions, they were tested by the three-point bending method. By comparing the properties of the aged samples with the virgin ones, the effects of environmental conditions were studied. A view of the bending test device is depicted in Fig. 3.

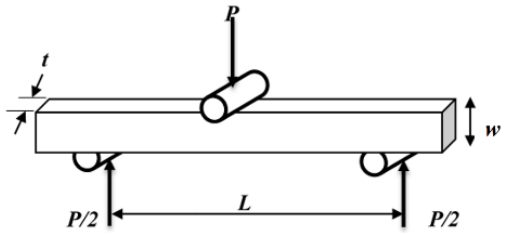


Fig. 4 A schematic of the three-point bending test

3. Data analysis

For analysis of the three-point bending test data, it is necessary to convert the force-displacement diagram, recorded by the test machine, into the stress-strain diagram. To this end, the following equation was used (which is the result of the elastic analysis):

$$\sigma_{fb} = \frac{3LP_f}{2tw^2} \tag{1}$$

where σ_{fb} is the ultimate stress and P_f is the ultimate force. Also, L, t, and w are the length, thickness, and width of the beam, respectively (Fig. 4).

The bending strain ε_f was calculated using Eq. (2). The flexural deflection v of the beam is the displacement of the loaded point of the beam.

$$\varepsilon_f = \frac{6wv}{L^2} \tag{2}$$

Using Eqs. (1) and (2), the slope of the linear portion of the stress-strain diagram can be obtained from the force-displacement graph. The flexural elastic modulus, which is the slope of the stress-strain curve in the linear region, is calculated by the following equation:

$$E_f = \frac{L^3 m}{4tw^3} \tag{3}$$

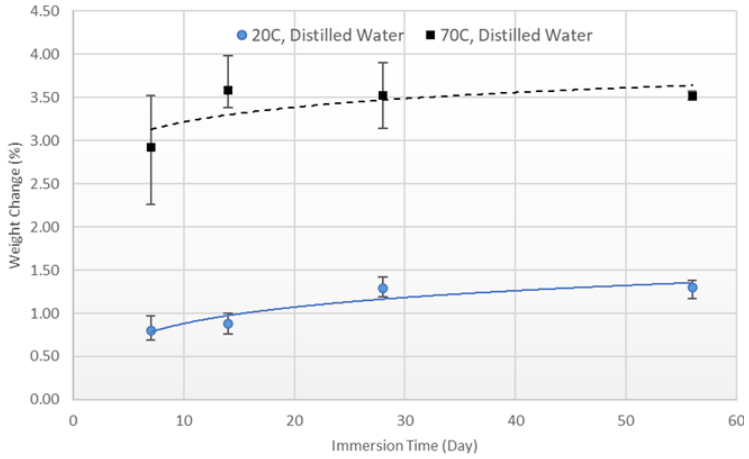
where m is the slope of the linear part of the load-displacement curve. Also, to find the weight change percentages of the submerged samples, Eq. 4 was used as follows:

$$W(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{4}$$

where W_{dry} and W_{wet} are the weight of the sample before and after immersion. Using Eq. (1) to (4), the stress-strain curves of samples under three-point bending load were obtained and then the flexural strength and stiffness degradation of composite specimens were investigated.

4. Experimental results

In this section, the change of the weight, flexural strength and bending modulus of specimens immersed in various environmental conditions (distilled water, salty water, and sulfuric acid) have been presented.



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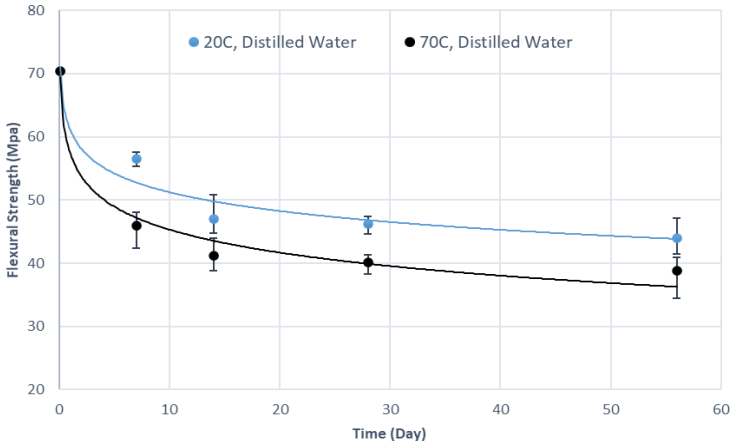

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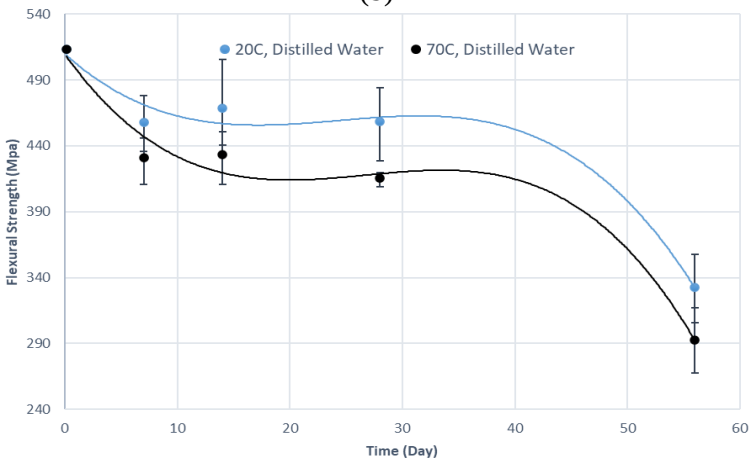


(c)

Fig. 5 The experimental results of samples immersed in distilled water; a) weight change, b) flexural strength, c) flexural modulus

4.1 Effects of distilled water on the composite specimens

In this subsection, the effects of distilled water on the behavior of composite samples are presented.

4.1.1 Experimental data

Fig. 5 shows the weight change, the flexural strength, and the flexural modulus of composite samples submerged in distilled water. The weight of the specimens was measured before immersion. For each environmental condition, three samples have been tested and the points shown in Fig. 5 are calculated from the average of the three experimental data. To fit a curve on the weight change (in all conditions) data resulted from the accelerated aging tests, the following equation was used:

$$K = a\log(t) + b \tag{5}$$

Also, the following equation was used to curve fit the recorded data for both flexural strength and flexural modulus (in all conditions):

$$K = at^b \tag{6}$$

where K represents the flexural strength and modulus, t is the exposure time, a and b are the material constants.

In Fig. 5, all curves obtained by experiments represent the percentage of the weight change, flexural strength, and flexural modulus of samples within 56 days.

As shown in Fig. 5, the flexural properties of samples exposed to distilled water at both 20°C and 70°C temperatures, degraded sharply until the second week of the test. It was also observed that the degradation of samples at 70°C temperature is much more than that of at 20°C. It should be noted that the strength and modulus of virgin samples were 70.43 MPa and 513.44 MPa, respectively. In these environmental conditions, the strength of the samples at 20°C, up to the end of the 56^{th} day, which is the last day of the accelerated test, degraded from 70 MPa to 44 MPa. In other words, it can be concluded that the rate of loss of flexural strength decreases with time. There are the same conditions for distilled water at 70°C.

Moreover, concerning the flexural modulus of the specimens immersed in distilled water, it is clear that the trend of degradation between 10 to 30 days after immersion follows a polynomial curve whereby, the degradation of specimens with a gentle fluctuation remains in an analogous state. Thereafter, with a sharp decline in the mechanical property, for both temperature conditions, the modulus of the laminated composites has been sharply dropped to about 340 and 290 MPa for 20°C and 70°C, respectively.

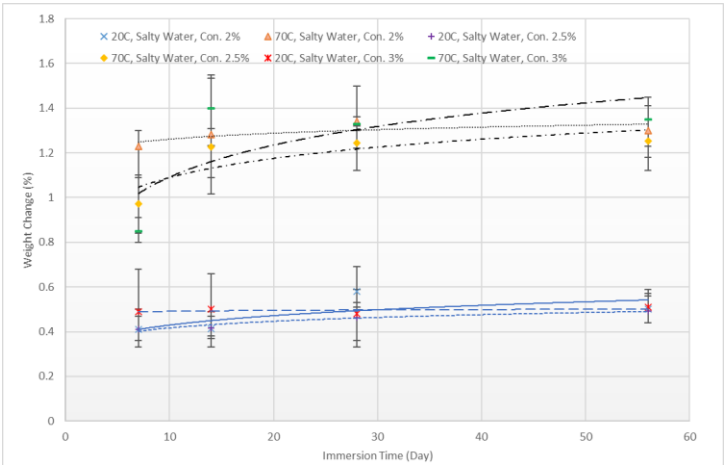
4.2 Effects of salty water

In this subsection, the effects of salty water on the behavior of composite samples are presented.

4.2.1 Experimental data

In Fig. 7, the effect of salty water solutions with different concentrations on the weight gain, the flexural strength, and the flexural modulus of composite samples have been shown.

The trend of all graphs related to weight change is ascending, and most of them show a significant weight gain of composite specimens at the beginning of the immersion. In the second month of the test, the rate of the weight gain decreased and the samples have been saturated with the ambient



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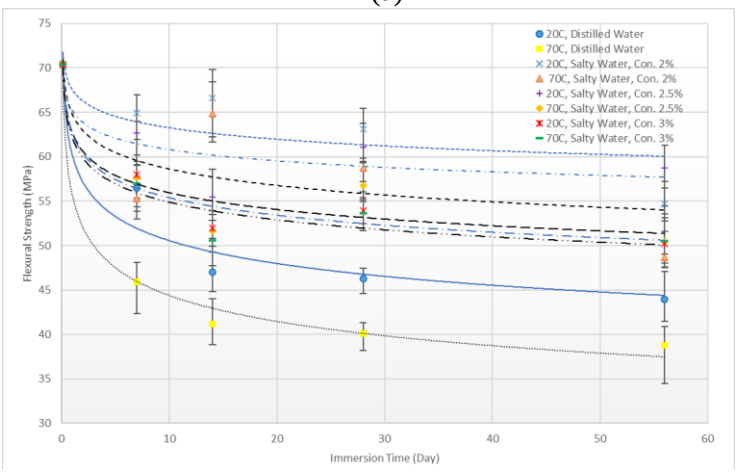

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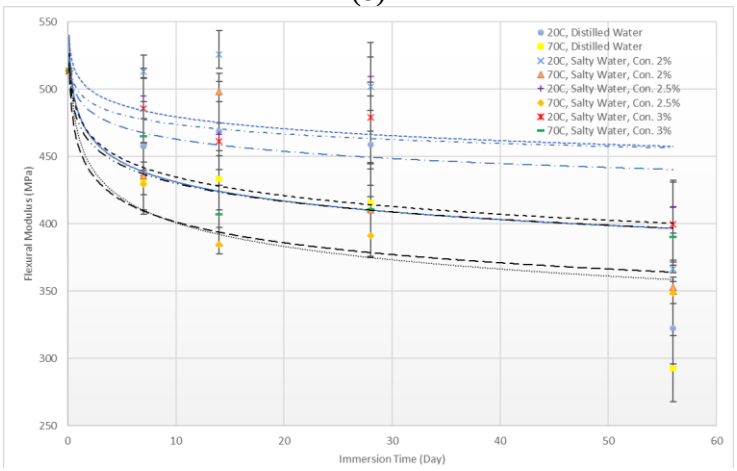

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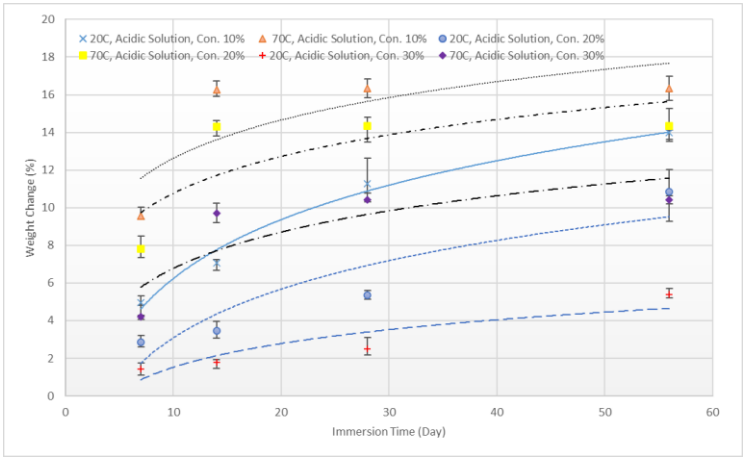
Fig. 6 The experimental results of samples immersed in salty water; a) weight change b) flexural strength c) flexural modulus



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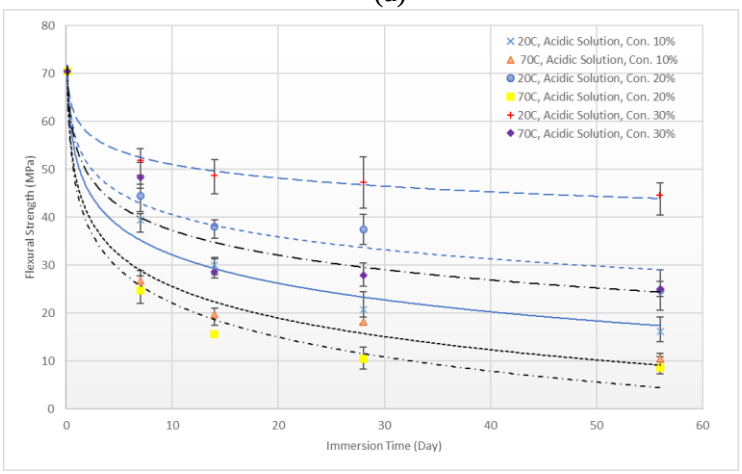

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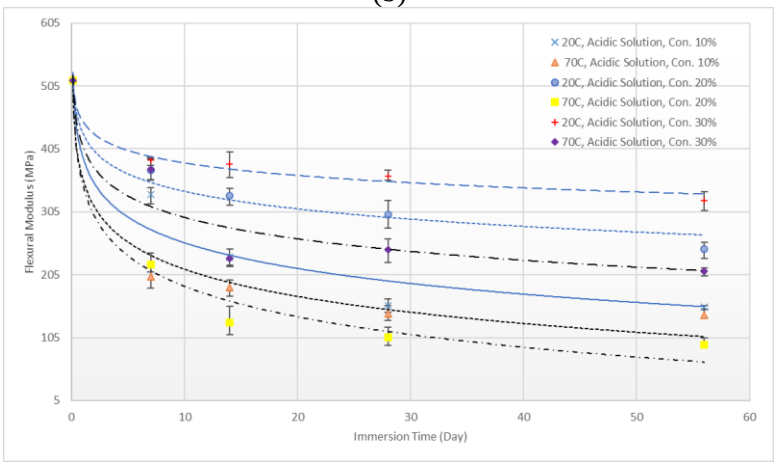


(c)

Fig. 7 The experimental results of samples immersed in the acidic solution, a) weight change, b) flexural strength, c) flexural modulus

fluid. Lower water absorption for specimens in the salty water solution with different concentrations at the temperatures of 70°C and 20°C was observed in comparison with the distilled water case.

As shown in Fig. 6, increasing the temperature from 20°C to 70°C does not have a significant effect on the flexural strength and flexural modulus at these two conditions.

The recorded values for the flexural strength of samples exposed to salty water with a concentration of 3% are close to each other at the two temperatures. According to Fig. 6, the salty water absorption rate at 70°C is 3 times that at 20°C. The reason could be the saturation of samples exposed to salty water at 20°C with the salt. Therefore, increasing the presence of salt in the specimen and the higher temperature will increase its destructive effects.

4.3 Effects of sulfuric acid

In this subsection, the effects of the sulfuric acid solution on the behavior of composite samples are presented. By depicting experimental data, Arrhenius diagrams and master curves have been illustrated.

4.3.1 Experimental data

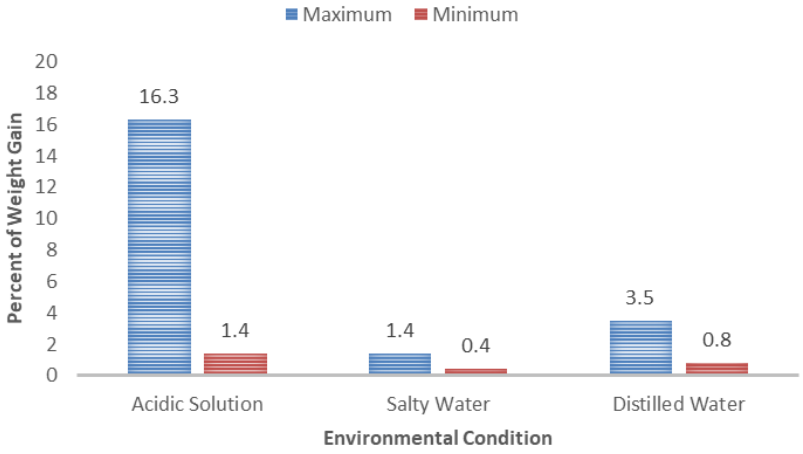
In Fig. 7, the effect of sulfuric acid solutions with different concentrations on the weight gain, the flexural strength, and the flexural modulus of composite samples is shown. There is a considerable difference in solution absorption or properties degradation in different temperatures so that the intensity of absorbing in the 70°C is remarkably more than that of the 20°C.

According to Fig. 7, there is a sharp degradation in the flexural strength and flexural modulus of composite samples exposed to the sulfuric acid solution at both 20°C and 70°C, in the second week of the test. Then, after the second week, it was observed that the rate of degradation was decreased. It can be seen that the samples absorption in sulfuric acid with a 30% concentration at 70°C is more than that of the 10% concentration at 20°C. This observation shows that the heat accelerates the rate of specimen absorption. Also, at a constant temperature, increasing the concentration of acidic solution decelerates the rate of the specimen absorption. As an example, the weight gain of the specimen in the acidic concentration of 30% at 70°C is less than in 10% concentration at 70°C conditions.

5. Conclusions

By considering Figs. 5-7 (for the salty water), contrary to distilled water and sulfuric acid solution, which strength degradation of composites are continuously descending, in some cases the degradation is not descending. For example, for the salty water with a concentration of 2% at 70°C, some properties were recovered in the second week of the test, and an increase in the properties of samples was observed.

For a physical explanation of mechanical property degradation, various reasons should be taken into account. The results of the experiments show that the major failure mechanism in the degraded samples is delamination. A comparison between the virgin and degraded samples shows that the failure area of the degraded sample is affected by delamination. It means that the environmental conditions weaken the adhesion between the layers. Also, checking the surface of failure does not give any sign of intensified fiber-matrix debonding or fiber breakage. The other mechanism of failure which may affect the degradation of the sample is matrix cracking. To show this type of



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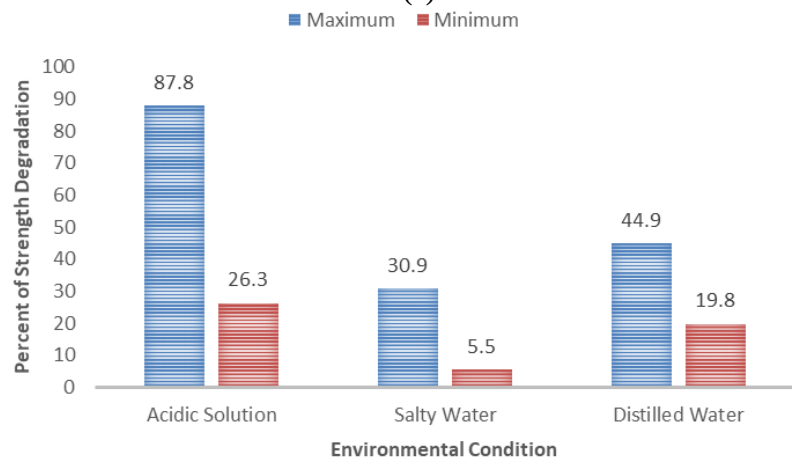

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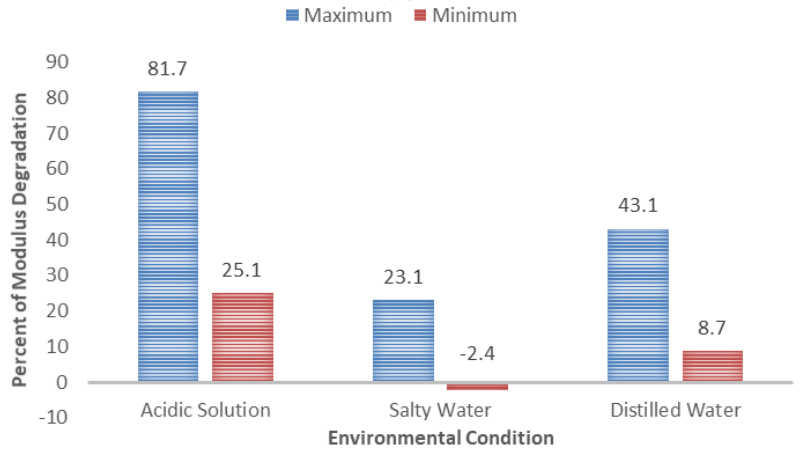

(c)

Fig. 8 The minimum and maximum values of aged samples immersed in three environmental conditions a) weight change, b) flexural strength, c) flexural modulus

failure, some pure resin samples (dog-bone samples) were fabricated. A part of them degraded under environmental conditions and the rest of them were kept intact. The results of tensile tests of the pure resin show the strength of the sample exposed to the environmental condition is degraded, therefore, another reason for the degradation of mechanical properties of composite samples is the matrix cracking failure mode.

By comparing the amount of fluid absorption of samples submerged in the distilled water, salty water, and acidic solution (Fig. 8), it can be concluded that the absorption of samples submerged in the salty water is less than that of those submerged in the distilled water. Likewise, the absorption of the samples submerged in the distilled water is less than that of those submerged in the acidic solution. In other words, the higher penetration of the fluid in composites means that the depth of the composite specimen is subjected to degradation by environmental conditions. However, it does not mean that the destruction of the composite sample exposed to distilled water is faster than that in a salty water solution. In other words, although the salty water solution was penetrated slightly less than the distilled water at the depth of the composite sample, this solution transfers the salt particles to the internal regions of the sample and causes more degradation.

Acknowledgments

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