

Investigation of long-term water absorption behavior of carbon fabric reinforced epoxy composites containing hydrophobic nanosilica

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Abstract: The effect of water absorption on the chemical and mechanical properties of hydrophobic filler containing epoxy matrix composites was investigated by keeping them in distilled water for 9 months. Aerosil R812 (8 nm) and Aerosil R972 (12 nm) were utilized at 3% and 5% w/w filler to resin ratio and the resin/filler mixture was combined with 12-ply carbon fabric to get 15 × 15 cm samples. Samples were molded under a hot press and for each sample 50 test samples obtained by cutting them with a water jet. The obtained samples were characterized by TG, FTIR, and SEM. The effect of water absorption was evaluated by measuring percentage water absorption and flexural strength of samples over 9 months. The results revealed that filler addition lowers the damage created by distilled water a considerable amount and addition of hydrophobic fillers to epoxy matrix composites can be especially beneficial for applications where long-term water exposure is desired.

Key words: Fiber reinforced polymer, composite, water absorption, silica

1. Introduction

Fiber reinforced polymer matrix composites (FRPMCs) are well-known engineering materials with extraordinary properties that make them desirable candidates for many manufacturing applications.^{1–5} However, water uptake is a serious problem, especially for those applications where these materials are in contact with water, and it is known that a series of changes occur depending on the length and frequency of this contact. Animals and plants have certain strategies to develop hydrophobic surfaces and it is possible to create similar surfaces on manmade articles to protect them from the destructive effects of water. Filler addition is one of these strategies and it improves not only the water absorption properties but also the thermal and mechanical properties of composites. Organic and inorganic fillers used in Blackhawk coatings are good examples of this approach and the blade exchange ratio can be dropped to 0% after a 31,000-h test flight.⁶ Various hydrophobic nanofillers have already been used as additives to enhance the water absorption profile of polymer matrix composites.^{7–12}

The first studies dealing with the water damage mechanism in fiber reinforced polymer matrix composites started in the late sixties.^{13,14} Studies reveal that dimensional changes occur by water immersion. First, swelling takes place in resin with diffusion of water into the matrix and it is followed by shrinkage caused by leaching of low molecular weight materials from the resin. Second, osmotic pressure generated at the fiber/matrix interface

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is accompanied by growth of cracks into the resins and debonding between fiber/matrix interfaces is caused by resin shrinkage.

In this basic water damage mechanism, many parameters such as chemistry of the resin, type of fiber and coupling agent, and water absorption environment play an important role in outcomes of water exposure. With increasing susceptibility to water attack, dramatic changes in mechanical properties of FRPMCs are observed.^{15–19}

The parameters used in water absorption experiments also have important effects on the final properties of FRPMCs. It is possible to lower the effect of osmotic pressure by using salt solutions instead of distilled water.¹⁴ Enhanced degree of hydrolytic degradation with increasing pH is observed in the presence of alkaline salts. Especially in alkaline and leachate solutions, fiber surface degradation and pitting accompany plasticization.¹⁷

Water absorption is always accompanied by water adsorption and it is better to use water uptake terminology when addressing water damage in composite material.²⁰ The water uptake mechanism can be categorized in two classes: reversible processes (plasticization and swelling) and irreversible (hydrolysis and microcracking) processes. It is known that water plasticizes epoxy resins and makes them more compliant.¹⁶ When composites are exposed to thermal cycling between two temperatures, the amount of absorbed water may decrease due to irreversible damage in the crosslinked network.²¹ This observation is explained by Flory's two-stage theory, where two competing processes determine the water absorption behavior of polymers: water diffusion and polymer relaxation. Studies indicate that it is impossible to prevent water uptake damage unless the contact of water with the matrix and fiber is eliminated.

In order to improve the water uptake profile of composite materials, various filler systems can be used. Composite materials with improved thermal and mechanical properties can be obtained by addition of filler materials.²² However, decreasing crosslinking density can lead to higher solvent absorption and the mechanical properties of materials can decrease with filler addition in some cases.^{23,24} In the presence of hydrophobic fillers degradation starts at the interface between polymer matrix and nanofillers and this can lead to the creation of large numbers of voids and cracks in the composite.²⁵

In the present study, changes in the water uptake profile of carbon fabric reinforced epoxy composites were followed in the presence of two different hydrophobic nanofillers. Thermogravimetric analyses were performed to obtain the filler and fiber content of composite samples. The effect of filler addition on fiber/resin adhesion was assessed by following the fiber/resin fracture surface under SEM. FTIR analyses were carried out both to characterize the composite samples and to follow the changes in composite surface after 9 months in distilled water. Flexural strength of samples was measured for 9 months and the relation between filler type/amount and reduction in mechanical properties was established.

2. Results and discussion

2.1. TG characterization of composite samples

Figures 1a–1d show the TG curves of resin, fabric, and fillers, respectively. Cured epoxy resin shows two-step decomposition that starts at 200 °C and ends at 625 °C. Between 200 °C and 430 °C, degradation of the epoxy network leads to a 70% weight loss and aromatic or cyclized decomposition byproducts are formed. After 430 °C, these byproducts start to decompose and a small amount of char is left after 625 °C (Figure 1a). Decomposition of the carbon fabric starts at 625 °C and ends at 800 °C (Figure 1b). Resin and fabric leave 1.5% and 0.5% residue after decomposition and there is no significant change in weight of filler in this temperature range (Figures 1c and 1d). It is possible to obtain resin and fabric percentages of the composite

samples from these curves. Weights of the sample recorded after 800 °C have contributions from resin, fabric, and filler, and filler ratios of the composite samples can be roughly obtained from the resin percentage since the filler/resin ratios used are fixed at the beginning.

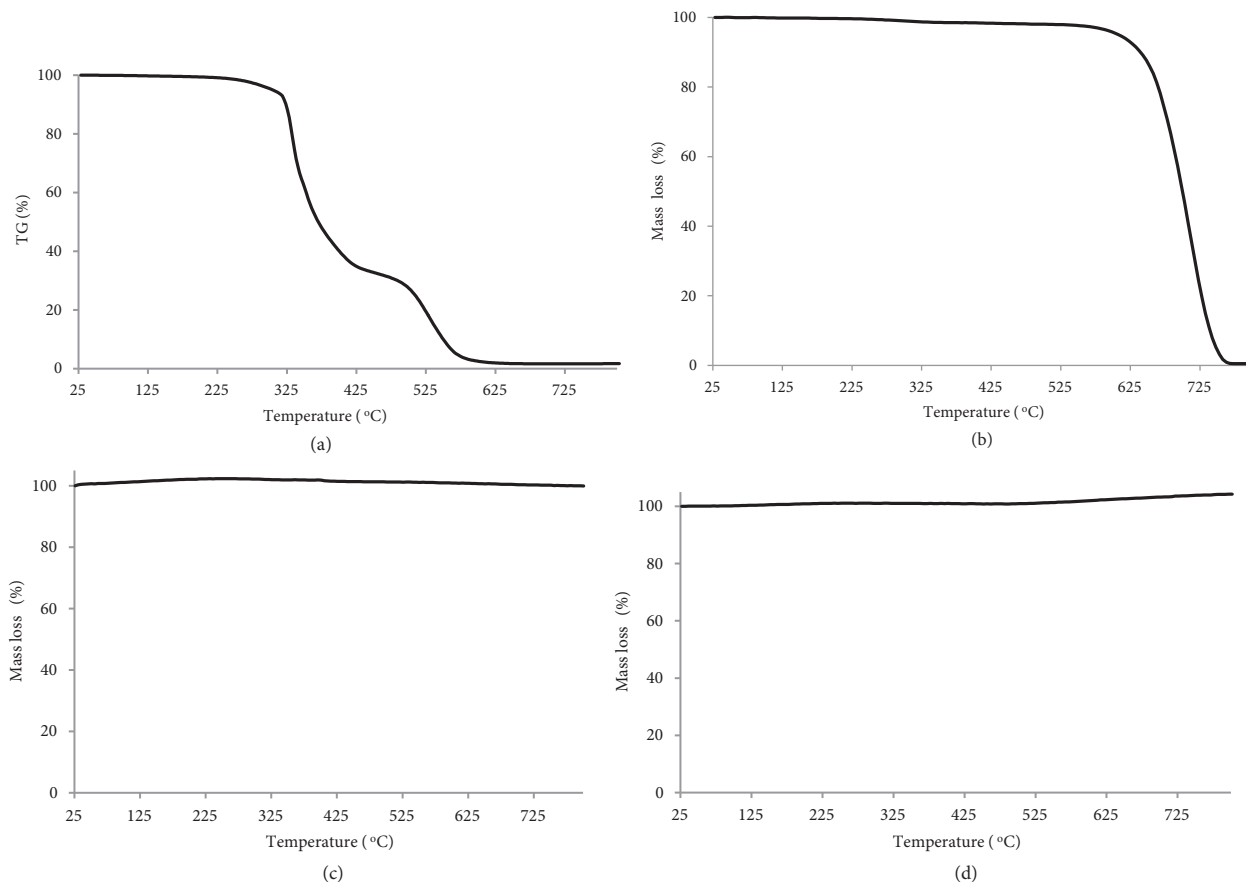


Figure 1. TG curves of a) cured epoxy resin, b) carbon fabric, c) Aerosil R 812, and d) Aerosil R 972.

There are three steps of decomposition on thermogravimetric curves between 25 °C and 800 °C and the percentages of both resin and fabric are very close to each other for all composite samples (Figure 2). FFCS, 812-3, 812-5, 972-3, and 972-5 contain ~66%, ~64%, ~66%, ~67%, and ~64% fabric, respectively. Percentages of filler calculated from resin amount are ~1.0%, ~1.7%, ~1.0%, and ~1.8% for 812-3, 812-5, 972-3, and 972-5, respectively.

2.2. SEM analysis of matrix fiber adhesion

The effect of filler addition on the fiber/resin interface was followed by analysis of SEM images of composite samples. The following pictures show the carbon fiber surface after the 3-point bending test for filler-free and filler-containing samples (Figure 3).

It can be clearly seen that the surface of the carbon fiber in some samples is rougher than the others, indicating a strong adhesion of resin onto the fiber surface (Figures 3a–3c). Strength of adhesion decreases with filler addition and fiber surfaces get cleaner on the fracture surface (Figures 3d and 3e). This effect gets more severe with increasing filler content.

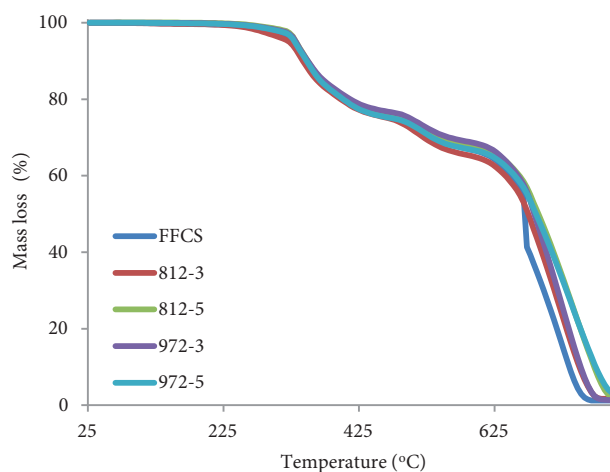


Figure 2. TG curves of composite samples.

2.3. FTIR analysis of composite structure and changes in chemical structure with exposure to distilled water

Figures 4a and 4b show the FTIR spectrums of Aerosil R 812 and Aerosil R 972, respectively. Aerosil R 812 has trimethyl silyl groups whereas Aerosil R 972 has dimethyl silyl groups chemically attached to the silica surface. There are two broad bands between 1313 cm^{-1} and 717 cm^{-1} and they correspond to $-\text{Si}(\text{CH}_3)$ and $\text{Si}-\text{O}-\text{Si}$ groups on the fillers. Figure 4c shows the filler-free composite sample (FFCS). The peak at 3386 cm^{-1} belongs to $-\text{OH}$ groups and 3 peaks centered on 2922 cm^{-1} represent $-\text{CH}_3$, $-\text{CH}_2$, and $-\text{CH}$ groups on epoxy resins. Two bands of $\text{C}-\text{C}$ groups on the aromatic phenyl ring appear at 1455 and 1607 cm^{-1} and the peaks at 1033 cm^{-1} and 1237 cm^{-1} can be assigned to ester bonds in the resin. The resin shows two peaks at 825 cm^{-1} and 928 cm^{-1} , belonging to $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{O}$ stretching frequencies. $-\text{CH}_2$ groups show a peak at 763 cm^{-1} , which is related to $-\text{CH}_2$ rocking frequency. The peaks at 1082 cm^{-1} , 1180 cm^{-1} , and 1295 cm^{-1} show the presence of $-\text{CN}$ bonds formed after the curing reaction. The band at 1508 cm^{-1} can be assigned to $\text{C}=\text{C}$ bonds on the carbon fabric, which cannot be graphitized on PAN fibers.

Figures 4d and 4e show the composite with 5% Aerosil R 812 and 5% Aerosil R 972 filler content. An increase in intensities of peaks caused by $-\text{Si}(\text{CH}_3)$ and $\text{Si}-\text{O}-\text{Si}$ groups between 1313 cm^{-1} and 717 cm^{-1} can be observed for filler-containing samples.

Except for the sample with 5% Aerosil 972 content (Figure 5a), there is a decrease in intensities of the peaks from the fillers in the samples held in distilled water for 9 months (Figures 5b–5d). This indicates a weak interaction between filler and epoxy resin, which leads to erosion of nanofillers from the composite surface by leaching distilled water.

2.4. Water absorption of composite samples

Figure 6 shows the changes in percentage water absorption values with time for the composite samples stored in distilled water for 9 months. The results reveal that type and particle size of the filler have no significant effect on the water absorption percentage of epoxy matrix composites. Percentage water absorption values fluctuate and the averages of these values obtained between 1440 and 6480 h are 0.83%, 0.93%, 0.85%, 0.87%, and 0.85% for FFCS, 812-3, 812-5, 972-3, and 972-5, respectively. Percentage water absorption values of polymer matrix composites reach a saturation limit depending on the voids present in the composites and interfacial adhesion

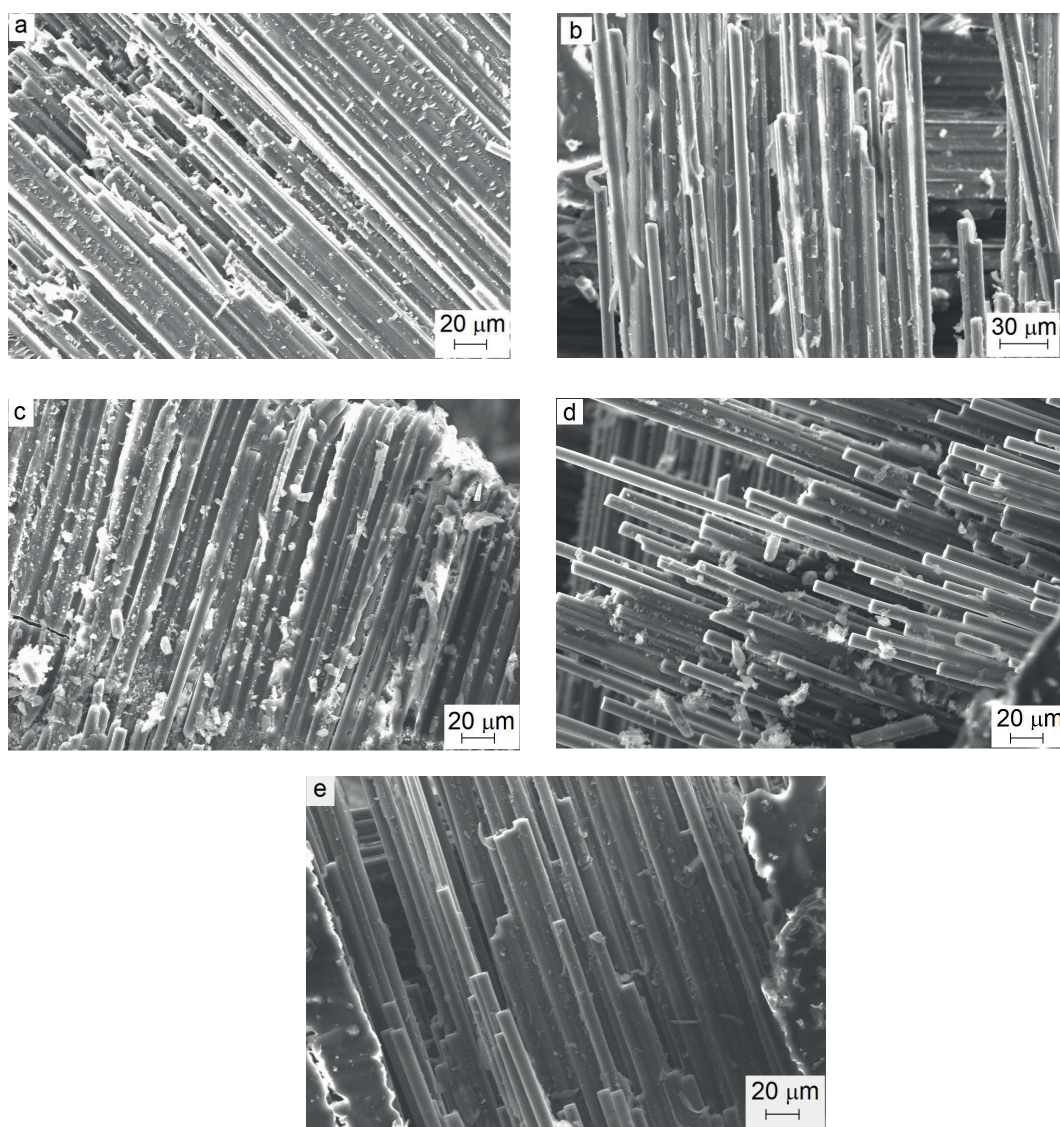


Figure 3. SEM images of carbon fiber surface after 3-point bending test. a) FFCS, b) 8123-3, c) 973-3, d) 812-5, and e) 972-5.

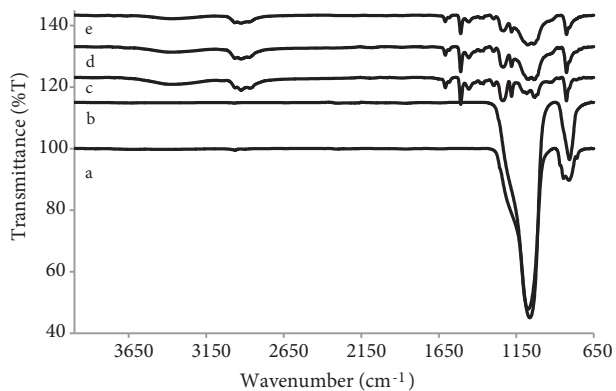


Figure 4. FTIR spectrums of a) Aerosil R812, b) Aerosil R 972, c) FFCS, d) 812-5, and e) 972-5.

between the fiber and matrix. The saturation limit is reached after 1000 h for all samples and no remarkable difference is observed until 4000 h. However, an increase in % water absorption is observed after 4000 h and additional voids created by erosion of filler from the polymer matrix may be responsible for this increase after the saturation limit.

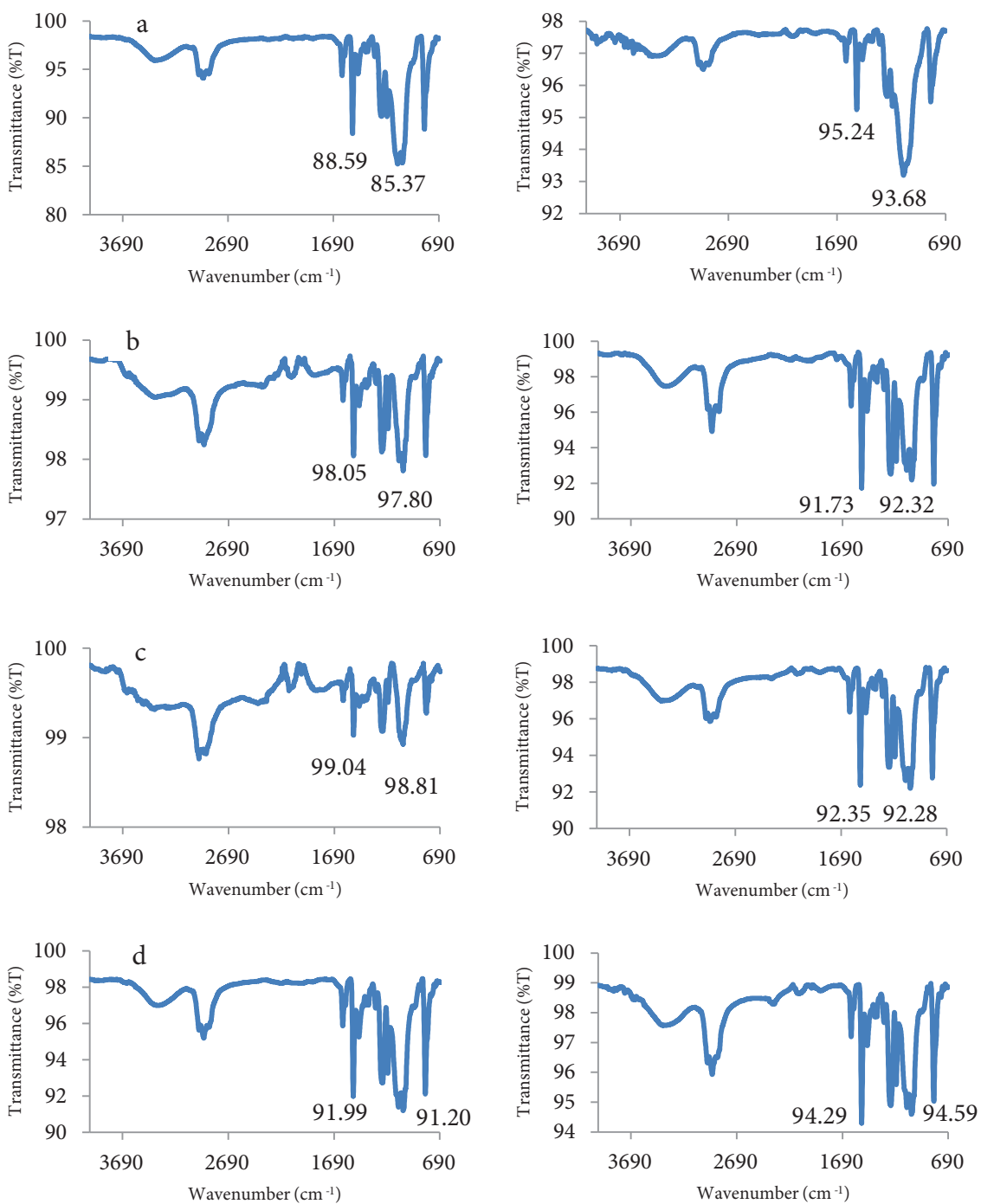


Figure 5. FTIR spectra of samples before water absorption (left) and after 9 months (right) in distilled water a) 972-5, b) 812-3, c) 812-5, and d) 972-3.

The following equation is generally used to describe the water uptake profile of composite samples:²⁶

$$\frac{M_t}{M_\infty} = K t^n,$$

where n is called the diffusional exponent and k is a constant that depends on the diffusion coefficient and thickness of the film. n values of samples can be obtained by performing nonlinear regression of $\frac{M_t}{M_\infty} \propto t$ data and mechanisms of diffusion can be categorized based on the value of n . Figure 7 shows the diffusional exponent values obtained by regression analysis and all values are lower than 0.5 for all of our samples. This situation corresponds to pseudo-Fickian behavior and absorption-desorption curves of pseudo-Fickian behavior resemble the Fickian model. In this type of behavior, equilibrium is reached more slowly than predicted by Fickian diffusion and it is observed at high temperature and humidity conditions.

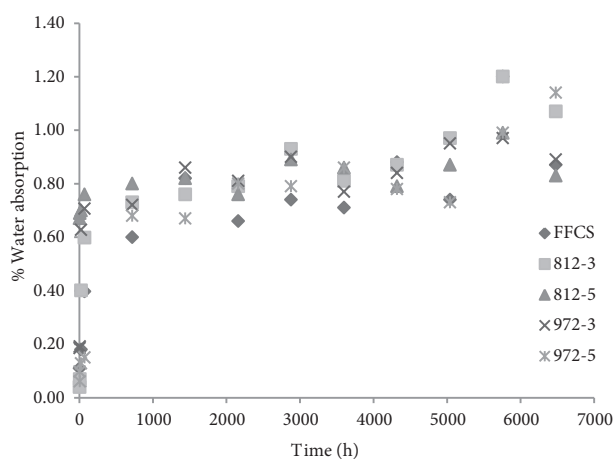


Figure 6. Water absorption of the samples over 9 months.

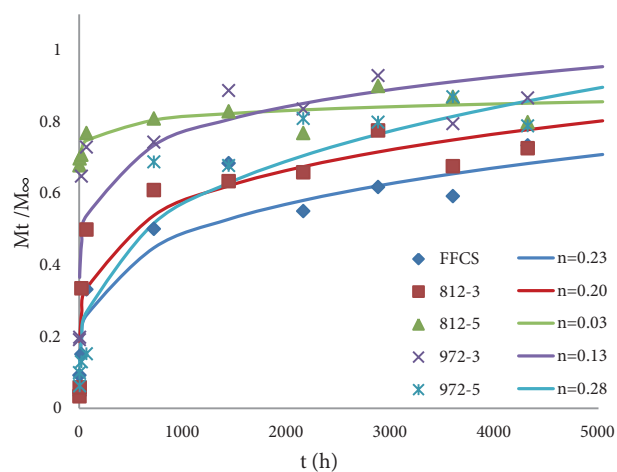


Figure 7. $M(t)/M(\infty)$ vs. t graphs used for nonlinear regression to obtain n values from experimental data.

Fickian type diffusion occurs when a polymer behaves in a rubbery fashion such that the chain molecules are able to adjust quickly during absorption. Pseudo-Fickian type behavior indicates swelling and plasticization of the polymer matrix during water exposure and the results indicate that hydrophobic fillers do not change the diffusion character of our samples since all n values are lower than 0.5.

2.5. Change in flexural strength with exposure to distilled water

Figure 8 shows the changes in flexural strength with time for the composite samples stored in distilled water for 9 months. Slopes of the lines obtained for each sample represent the change in flexural strength with time. A positive contribution of hydrophobic filler on decrease in flexural strength caused by distilled water is evident. There is a significant difference in the slope of the lines corresponding to filler-free and filler-containing samples. While flexural strength decreases 123.18 MPa per month for the filler-free sample in distilled water, this number drops to 5.32 MPa per month for the sample containing 3% Aerosil R 972.

In the present study, Aerosil R812 and R 972 were utilized to evaluate the contribution of hydrophobic nanofillers to water absorption of epoxy matrix composites. The results show that it is possible to decrease the effect of distilled water on FRPMC damage by adding hydrophobic nanofillers. Various fiber, filler, and resin systems have already been employed to improve the water absorption behavior of polymer matrix composites

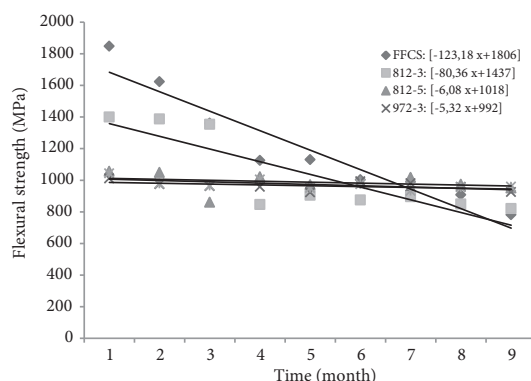


Figure 8. Change in flexural strength with time and obtained linear equations for each sample.

in the literature. Depending on the type of components in the composites, minor or major changes have been observed in both water absorption and mechanical properties of final products. In a study conducted by Chow, water absorption percentages of glass fiber/epoxy composites were evaluated and a change from 2.3% to 1.2% was observed by addition of 3 wt% organically modified montmorillonite nanoparticles.²⁷ Chang et al. studied the effect of 0~2 wt% SiO₂ additions on both water absorption and mechanical properties of glass fiber reinforced epoxy composites and it was observed that addition of nanofiller reduces water absorption values from 0.0704% to 0.0573%.²⁸ There was a 13.82% increase in storage modulus upon addition of nanofiller. However, filler addition decreases the adhesion between the matrix and fiber in our samples and there is a considerable decrease in flexural strength upon addition of hydrophobic nanofiller. A negative effect of nanofiller on mechanical properties can be observed in different composite systems and our findings are consistent with the various studies in the literature.^{29–31} As long as further penetration of water is prevented by using hydrophobic fillers without applying any force, decrease in mechanical strength does not contribute to water absorption of composite samples. It is necessary to perform water absorption experiments under continuous load to assess the effect of adhesion strength between fiber and matrix on the water absorption of composites. However, it is possible to use hydrophobic filler-containing composite in applications where long-term water contact is needed if the mechanical properties of these materials satisfy the desired criteria.

The results show that water exposure swells the polymer matrix and plasticization of matrix structure occurs in both filler-free and filler-containing samples. However, this effect is more dominant in filler-free composite samples. The amount and type of hydrophobic filler do not have a significant effect on the decrease in flexural strength upon water absorption. Other than 812-3, use of the filler content lowers the decrease in flexural strength/time ratio to 6.08 MPa/month, 5.32 MPa/month and 8.32 MPa/month for 812-5, 972-3 and 972-5, respectively. Amounts of hydrophobic fillers decrease with time on the composite surface and they are separated from the matrix by distilled water exposure. However, fillers below the surface repel water and prevent plasticization further in the matrix. This creates significant improvements in the mechanical properties of composites after water absorption by changing the swelling behavior of the polymer matrix.

3. Experimental

3.1. Materials

Duratek 1000 type epoxy resin and DTS1100 type hardener were generously provided by Duratek, Turkey. Aerosil R 812 and Aerosil R 912 were supplied by Evonik, Germany, and they were utilized as hydrophobic filler in various ratios. Carbon fabric of 200 g/m² and plain structure was purchased from Spinteks, Turkey.

3.2. Sample preparation

Resin and hardener were combined in 74 to 26 mass ratio and mixed with a spatula to get a homogeneous mixture. In order to prepare filler containing resin, 3% and 5% w/w hydrophobic silica were added to the resin/hardener mixture and this mixture was mixed thoroughly with a spatula to get a homogeneous distribution of nanoparticles inside the resin/hardener system. Both filler-free and filler-containing epoxy resins were employed to prepare two identical pieces of composite to obtain test samples.

Carbon fabric reinforced composite samples were prepared by using two stainless steel plates in 20 × 20 cm dimensions. One of these plates had a 0.5 cm wide and 0.2 cm deep o-ring groove enclosing an area of 15 × 15 cm at the center of the mold. A silicone o-ring with 0.5 cm diameter was placed into the groove and 15 × 15 cm release film was placed on the bottom and top of the mold walls to provide easy removal of samples upon curing. Twelve plies of carbon fabric were used to prepare composite samples and filler-containing or virgin resin was applied to each ply using a roller. To set the final thickness of the samples, 0.3 cm thick spacers were placed between two plates before molding and the samples were cured in a heated press at 80 °C under 5 t for 1 h.

Two similar plates were prepared for each sample and 50 test samples were obtained for each composite by cutting molded samples in 1 × 7 cm pieces using a water jet. The Table shows the codes of the test samples with different filler content.

Table. Codes of the samples.

Filler free	3% Aerosil 812	5% Aerosil 812	3% Aerosil 972	5% Aerosil 972
FFCS	812-3	812-5	972-3	972-5

3.3. Characterization

Thermogravimetric analyses of composite samples were performed by NETZSCH STA 449 F3 Jupiter instrument at 10 °C/min heating rate under atmospheric air. Chemical analysis of the samples before and after water absorption studies was carried out by PerkinElmer Spectrum One FTIR instrument between 650 and 4000 cm⁻¹ interval using an ATR apparatus.

Fifty test samples were labeled from 1A–E to 10 A–E and water absorption experiments carried out on 45 samples, leaving 5 samples dry for comparison. Forty-five samples were placed in distilled water and 5 of these samples were removed at the end of each month. The water used in the immersion experiments was replaced with fresh distilled water every month. Consequently, 10 sample groups with 0 to 9 months' water interaction time were obtained at the end of the study. Percentage water absorption of each sample was calculated over 9 months by taking the excess water on samples using a damp paper towel and recording their weight on a balance with 4 decimal places. Final percentage water absorption values are an average of 5 values obtained for the samples with the same water contact history.

Three-point bending tests of each sample were performed using a SHIMADZU AG-IS 100 kN universal test instrument. The tests were conducted at 2 mm/min displacement rate and a span distance of 6 cm was employed during measurements. For each case, 5 test samples were used for flexural strength measurement and the final results were given as the average of these 5 values.

SEM analysis was performed on the fractured surface of the composite samples after the three-point bending test by using a LEO 1430 VP model SEM instrument. Dried samples were placed on a pin mount stand using carbon conductive tape and coated with carbon film prior to the analysis.

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