

FIBER COHESION AND ITS IMPACT ON THE USE OF OXIDIZING CARBON FIBER SURFACE TREATMENTS IN COMPOSITES

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ABSTRACT

In the current paper, an oxidizing surface treatment on carbon fibers is evaluated to determine its effects on the properties of multi-fiber vinyl ester composites. Improvements in single-fiber wettability and composite strength with various resins have been shown to result from oxidizing fiber surface treatments. However, others have reported poor performance of composites formed with oxidized carbon fibers. Fiber surface oxidation levels, fiber-fiber cohesion, composite transverse strength, multi-fiber resin wettability and composite water absorption and swelling were evaluated and compared. It was found that there is a significant effect of fiber-fiber cohesion that increases with oxidation treatment time. In correlation with fiber cohesion was a reduction in fiber bundle wettability and composite transverse strength. It was also found that seawater absorption increases and swelling decreases with increased oxidation treatment time, suggesting more free volume associated with longer oxidation treatment time. It is postulated that hydrogen bonding occurs between highly oxidized fibers, which physically prohibits wetting by the high viscosity resin.

1. INTRODUCTION

Carbon fiber offers exceptional properties to composite engineers such as high strength, high stiffness and immunity to corrosion. However, employing carbon fibers into composite systems presents a major difficulty due to poor interfacial adhesion. Without good adhesion, it is not possible to fully utilize these exceptional properties and the composite performs poorly in transverse directions. To further complicate the design of carbon fiber composites, fibers are usually coated with sizing materials that are proprietary.

Surface oxidation has received considerable attention as a method for improving interfacial adhesion of carbon fibers to various resin matrices. Oxidation has been found to increase the polarity of the surface, making it more attractive to resin. It also increases the concentration of various surface functional groups that are available to bond with the resin, leading to improved interfacial strength. Jang [1] has shown that the wettability of a single carbon fiber improves with a variety of liquids after oxygen plasma treatments. He also reported increases in transverse tensile strength of compression molded carbon/bismaleimide composites with oxygen plasma treatment. This improvement is not consistent, however. Jain et al. [2] reported immediate improvements in flexural and interlaminar shear strengths in compression molded phenolic and furan composites, followed by a substantial decline with extended treatment times in nitric acid. Composite strength improvement does not directly follow with increased fiber surface oxidation as might be expected. There appear to be additional effects occurring that prevent the realization of improved interfacial bonds and wetting.

The objective of this study was to evaluate how increasing oxidizing carbon fiber surface treatments affect the performance and characteristics of multi-fiber composites. Transverse tensile strength, multi-fiber wettability, water absorption and swelling are considered.

2. MATERIALS

Two different types of carbon fibers were used: sized and unsized. The sized fiber was a high strength (T700) fiber from Toray Carbon Fibers America, Inc., with sizing "F". This represents a typical, sized fiber that is widely used, and the sizing is recommended for use with vinyl ester resin. Unsized fiber was donated by Hexcel Corp. It was AS4 type, which is comparable in strength, modulus and diameter to the sized T700. The unsized fiber was obtained to use as a baseline for experimental comparisons. It contained no sizing, but had been surface treated by a proprietary means.

Vinyl ester resin was chosen for matrix material due to its properties and popularity in marine applications. It shares some of the desirable properties of both epoxy and polyester. Like epoxy, vinyl ester is chemically resistant with high tensile strength and like polyester; it has low viscosity and can be cured quickly at room temperature. The particular resin used was Derakane Momentum 411-350 by Ashland.

Nitric acid was used as the oxidizing agent because of its ease of use and effectiveness.

3. EXPERIMENTS

To compare different surface conditions, experiments were designed to accomplish the following: (1) Fiber oxidation, (2) Quantification of the change in the fiber surface oxidation level, (3) Evaluation of fiber-fiber interaction, (4) Testing of multi-fiber transverse tensile strength, (5) Evaluation of multi-fiber wetting properties, and measurement of the water absorption and swelling behavior of multi-fiber composites.

3.1 Fiber Oxidation

Fiber oxidation was carried out on the unsized AS4 fibers to measure the surface carbon/oxygen ratio and the bundle cohesion. The sized T700 fiber was available in mat form, so it was used in making the oxidized fiber composite panels. For the single-bundle transverse tensile tests and wettability evaluations, both fiber types were oxidized and produced similar results. Only the results with the T700 fibers are presented herein. It is expected that both fiber types produce similar results after a short oxidation period because the sizing, as well as a surface layer of carbon, burns off quickly. This was verified by measuring the fiber diameters at different oxidation times in a scanning electron microscope, which were found to decrease with treatment time. Oxidation of fiber tows was accomplished by wrapping the tow around a glass rod that was bent into a frame. The fiber was attached to the frame with Teflon tape and immersed in boiling acid at reflux conditions. Fiber mat was treated by securing it between a glass plate and a stainless steel screen with stainless steel wire, and then immersing the assembly into boiling acid. Before acid treatment, all fiber was washed for 2 hours in distilled water and dried for 2 hours at 120°C. For comparison, the untreated fibers were also subjected to this wash and dry

cycle. After varying acid exposure times, the treated fibers were washed in several changes of distilled water until the pH of the rinse water was equal to that of the source water. The fibers were then dried again at 120°C and either used immediately or stored under vacuum with a desiccant until use.

3.2 Fiber Surface Oxidation Level

Surface oxidation level was obtained using X-ray photoelectron spectroscopy (XPS). For purposes of comparison between treatments, the surface oxidation level was expressed as an oxygen/carbon ratio. Sized T700 and unsized AS4 fiber, as well as three different treatment times (5, 20 and 80 minutes) with AS4 fiber were analyzed. The oxygen/carbon ratios of the five samples analyzed is shown below in Figure 1.

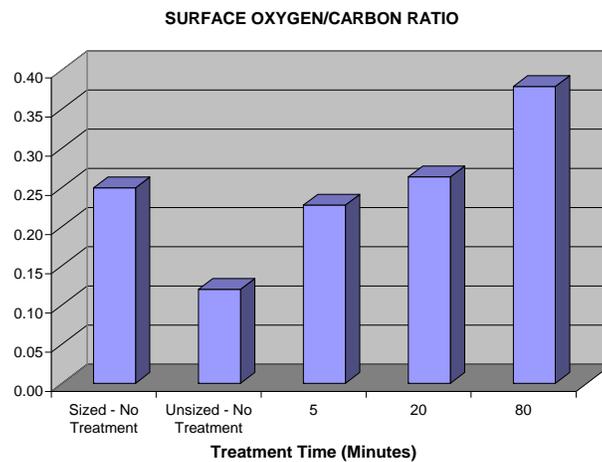


Figure 1: Fiber surface carbon/oxygen ratio at different stages of treatment.

From Figure 1, it can be seen that increased nitric acid treatment times resulted in increased levels of fiber surface oxidation. The highest level of surface oxidation occurred on the longest treated fiber and the lowest was on the unsized, untreated fiber. This was as expected, but the sized fiber also showed a significant amount of surface oxygen. It is difficult to assess the condition of the sized fiber based only on a carbon/oxygen ratio. Strictly comparing the oxygen levels does not provide an indication of the types of functional groups present. While the sized fiber is significantly oxidized, the types of functional groups may be different than those of the treated fibers.

3.3 Fiber-fiber Interaction

Fiber cohesion was evaluated by measuring the irreversible work required to separate a 25 mm long bundle of fiber along its length. This was quantified by calculating the area under the force-displacement curves. These tests were conducted by gluing a tab on the end of the bundle, separating the tab into two halves and pulling it apart, using a 2N load cell on a MTS Insight 1kN electromechanical test machine at 5 mm/min. Sized and unsized fiber bundles, as well as six different treatment times (10, 20, 40, 80, 120 and 160 minutes) of unsized fiber were analyzed. Figure 2 depicts this test.

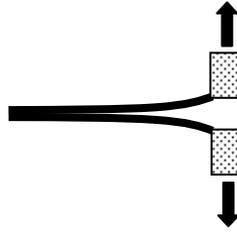


Figure 2: Fiber bundle cohesion test

The oxidizing nitric acid treatment resulted in significant fiber cohesion. Longer treatment times resulted in substantial increases in the total strain energy released in separating the fiber bundles. Figure 3 shows the work of separation for the different treatment times of AS4 fiber, as well as the as-received fiber types (sized and unsized).

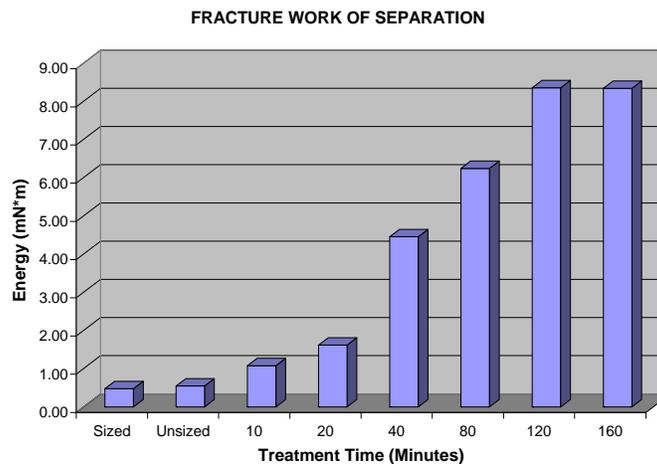


Figure 3: Fracture work to separate fiber bundles at different fiber surface conditions.

It has been reported that the functional groups imparted on oxidized fiber surfaces bond with the matrix resin, but it also appears that they are capable of bonding with each other. It is expected that surface groups, such as hydroxyls, carbonyls and carboxyls are implanted through this treatment, which are capable of hydrogen bonding. As a result, hydrogen bonding may occur between the separate fibers within a bundle. van der Waals forces may also contribute. A similar example where spontaneous fiber-fiber hydrogen bonding is believed to occur can be found in paper, where this effect is believed to contribute a significant amount of strength [3].

3.4 Multi-fiber Composite Transverse Strength

Transverse strength of a fiber bundle composite was evaluated by utilizing a test similar to that described by Ageorges et al. [4]. In this method, a fiber bundle is cast in the transverse direction across the center of a dog-bone shaped resin specimen. The specimen geometry is depicted in Figure 4. This geometry assures that the highest stress occurs in the fiber region. In addition, a specimen of this shape eliminates one of the main concerns

with the transverse tensile test. The transverse tensile test is often criticized because it is flaw-sensitive. A constant-width transverse tensile specimen will likely fail at a major flaw along its length or at the test grips, leaving this test susceptible to changes with test gage length. A dog-bone specimen with a radius of curvature along its length assures that the highest stress occurs only in the center and eliminates failure at distributed flaws. The dimensions are similar to those used by Ageorges et al. [4], with the exception that the bundle was held in place by 1mm x 1 mm channels on each side of the mold cavity, instead of placed flat between an upper and lower mold surface. Glass strips were also placed over the open mold to assure consistent thickness in the fiber and grip areas. Sized and unsized fiber bundles, as well as five treatment times (2.5, 5, 10, 20, 40 minutes) of sized fiber were analyzed. Beyond 40-minute treatments, the specimen quality was so poor that it became difficult to handle or test them. The specimens were cured for two hours at room temperature, followed by a two-hour post-cure at 120°C before testing.

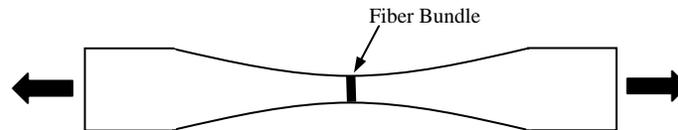


Figure 4: Single-bundle transverse tensile specimen

Figure 5 displays the transverse strength with the as-received (sized and unsized) and treated T700 bundles. It shows a significant increase with a short treatment time over both the sized and unsized fiber types. But after a very short treatment, the strength began a downward slide, until the specimens reached such poor continuity that it was difficult to handle or remove them from the mold without breaking. The strongest composite was that which was formed with the shortest treatment time. The 2.5-minute treatment resulted in a strength increase of 61.1% over the sized fiber and 24.1% over the unsized fiber. It is believed that the lower strength associated with longer treatment times resulted from a reduction in bundle wettability, as described below.

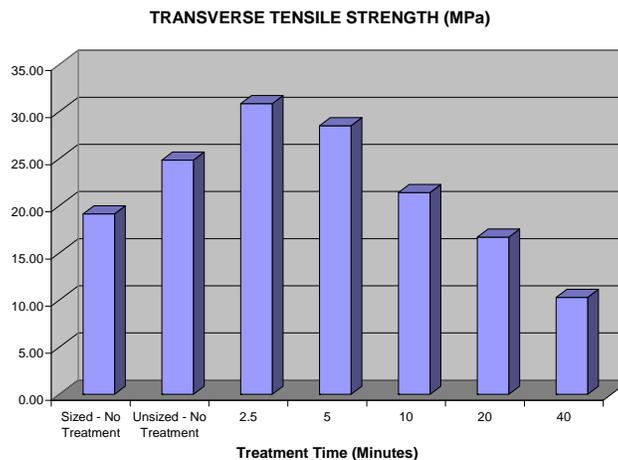


Figure 5: Transverse tensile strength of single-bundle specimens with as received (sized and unsized) and treated T700 bundles.

3.5 Multi-fiber Wetting

Multi-fiber wetting was evaluated by taking advantage of the same dog-bone specimen discussed above (Fig. 4). Fiber bundles were placed in the mold and resin was poured. No vacuum or pressure was used. After curing for 24 hours and post-cure for two hours at 120°C, the specimen was then cross-sectioned perpendicular to the bundle direction, polished and overall bundle wetting was evaluated using Scanning Electron Microscopy (SEM) in a FEI Quanta 200 environmental scanning electron microscope. Environmental mode was not employed. Sized and unsized fiber bundles, as well as five treatment times (2.5, 5, 10, 20, 40 minutes) were examined. The results are presented in Figure 6.

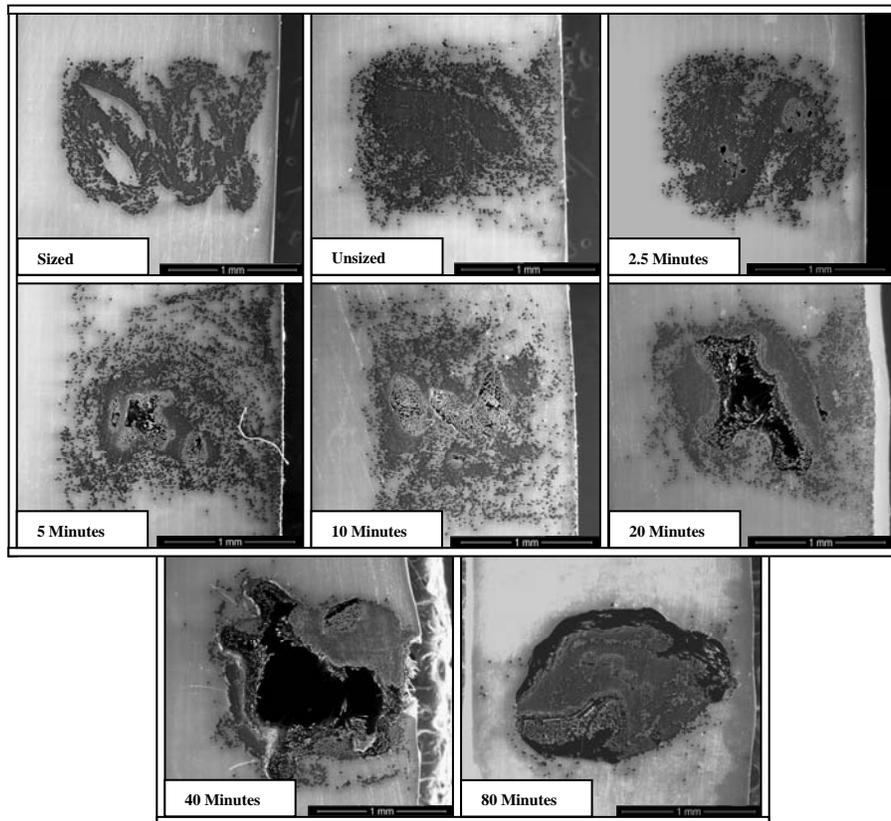


Figure 6: SEM views of the cross-sections of single fiber T700 bundles in vinyl ester resin at different fiber surface conditions.

Despite the increased wettability reported for individual fibers with increased oxidation, bundle wettability showed the opposite trend. Referring to Figure 6, it can be seen that bundle wettability decreased as the treatment time increased. This is likely interrelated with the increasing fiber cohesion described above. All treated specimens showed an obvious, visual decrease in wetting over the untreated sized and unsized fibers. Increasingly large areas of unwetted fibers can be seen with increasing treatment time. Matrix shrinkage also seems to make this trend more apparent. The dog-bone molds used for these evaluations kept the ends of the specimens constrained during the first 24 hours of room temperature cure, causing a tensile shrinkage force at the mid-section of the

specimen where the fiber bundle was. Up to a 40-minute treatment, it appears that the matrix adheres to the outer region of the bundle and during cure shrinkage, the matrix pulls the center of the bundle apart. At the 80-minute treatment time, it can be seen that the matrix separates at the edges of the fiber bundle, suggesting that the fiber-fiber cohesion is stronger than the bonding between the resin and outer boundaries of the fiber bundle during cure. There is some wetting in areas of the 80-minute treated bundle, but the fibers remain very close together. This poor wetting explains the declining transverse tensile strength found with increased treatment time. It should be noted that both the sized and unsized fiber bundles were better wetted than any treated bundle, but some treated bundles performed better in transverse tensile strength. This indicates that the oxidizing treatment introduces significant improvements in fiber-matrix adhesion, but it is countered by the flaws introduced by decreases in wetting. Eventually, the poor wetting dominates the transverse strength. The poor wetting of treated fiber bundles was also verified when the VARTM process was attempted with four layers of fiber mat that had been treated for 5 and 20 minutes. The 5-minute treatment wetted slightly better than the 20-minute treatment with VARTM, but the wetting of both were extremely poor.

3.6 Water Absorption and Swelling of Multi-fiber Composites

To evaluate water absorption and swelling, it was necessary to fabricate macro-composites. This was accomplished by placing 4 plies of fiber mat (treated or untreated) in between two 15cm x 15cm steel plates with catalyzed and promoted resin, taping the transverse edges with cellophane (packing) tape, and compressing the soaked mats with a MTS Insight 50 Electromechanical testing machine. The unsized fiber was only available in tow form, so it was necessary to wrap it around a frame to simulate a fiber mat. The tow was wrapped so that there was the same number of bundles per width as the mat. Compression was necessary because there was a significant difference in wettability between some of the different treatments. All composite panels were made with the fibers oriented in a unidirectional direction. It should be noted that the Vacuum Assisted Resin Transfer Molding (VARTM) process was initially tried, but no composites could be made with treated fiber, due to extremely poor wetting. The composites were prepared using a hand lay-up method and then compressed, first to 344 kPa (50 psi) and then to 688 kPa (100 psi), and left under pressure overnight to cure. After removal and post-cure (24 hours at room temperature followed by 2 hours at 120°C), the composite panels were then cut into 63.5 mm x 12.7 mm specimens with the fiber ends exposed along the long direction of the specimen. The panels were approximately 1 mm thick. Panels were made with sized and unsized fiber, as well as three treatment times (2.5, 5 and 10 minutes).

The composite specimens were immersed in 40°C seawater, and periodically removed, wiped dry, weighed and measured. Only the longitudinal direction was measured. The thickness was too small to accurately measure small dimensional changes and little swelling was expected in the fiber direction, due to fiber resistance to elongation.

Figures 7 and 8 show the weight gain and swelling data, respectively. Comparing the weight gain data with the geometric swelling of the seawater-immersed composites provides interesting information. The composite specimens with more extensively treated

fibers gained more weight. The order of weight gain was as follows: (1) 10-minute treatment, (2) 5-minute treatment, (3) 2.5-minute treatment, (4) sized-untreated and (5) unsized-untreated. However the order of increasing swelling was the opposite. Less swelling occurred with longer treatment time, with the exception of the 2.5 and 5-minute treatments, which were approximately equal.

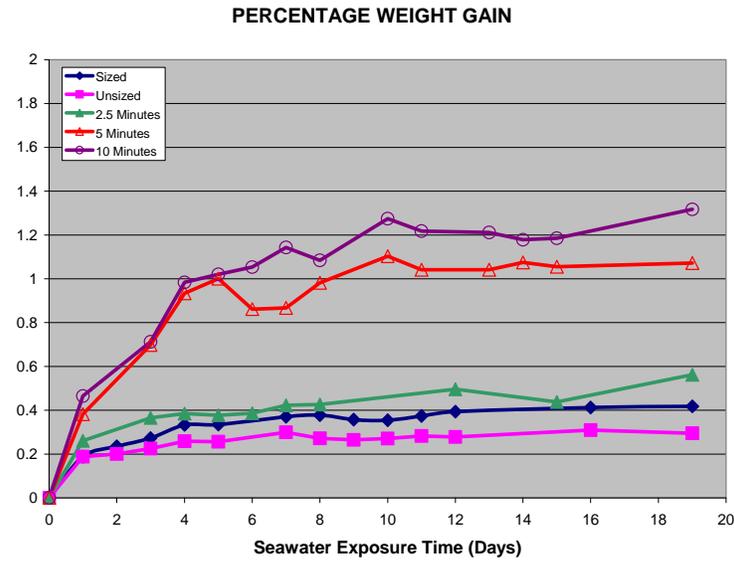


Figure 7: Percentage weight gain of composite specimens made with fibers at different surface conditions.

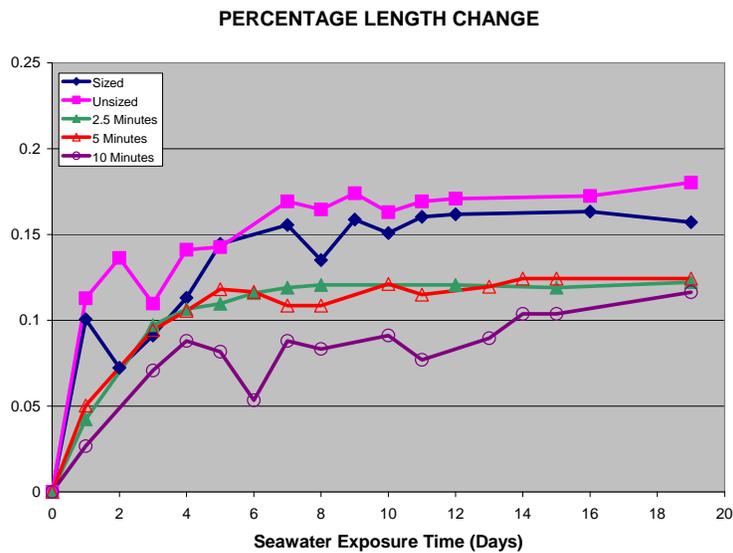


Figure 8: Percentage length increase of composite specimens made with fibers at different surface conditions.

The increasing water absorption with treatment time could indicate that the increased polarity at the interface attracts more water and/or there are more voids to contain water in

the more highly treated specimens. It is likely a combination of both, but the inverse weight gain and swelling behavior strongly suggests the presence of more voids associated with longer treatments. The composite doesn't have to swell as much because as water enters, it already has space for it. This is in accordance with the bundle wetting information discussed above, and upon SEM examination, it was found that voids were more easily identified in the specimens with treated fibers.

4. CONCLUSIONS

While oxidizing surface treatments on carbon fibers improve both fiber-matrix interfacial bonding and single-fiber wettability with various fluids, these effects are difficult to extend to macro composites due to interactions among treated fibers. Increased oxidation on carbon fiber surfaces increases the oxygen/carbon ratio, translating into more surface polarity and functional groups available for bonding. However, these surface features are available for interaction with other fiber surfaces, as well as the matrix. A large component of fiber-fiber cohesion was found that corresponded to oxidizing treatment time. And in addition, wetting of a multi-fiber bundle by resin was found to decrease in correlation with increasing fiber cohesion. Hydrogen bonding likely occurs between surface groups of adjacent fibers (hydroxyl, carboxyl and carbonyl), holding them together and effectively prohibiting the influx of the resin. van der Waals forces may also contribute, and resin viscosity may play an important role, as less viscous fluids would likely wet the bundles. The ability of the fluid to form hydrogen bonds may also contribute. A strong hydrogen-bonding, less-viscous fluid, such as water would be expected to easily replace the solid-solid bonds with solid-liquid bonds and wet the bundle. Despite this effect, low oxidation treatment times resulted in much stronger composites in the transverse direction, suggesting that the improved fiber-matrix bonding is significant, even with the presence of flaws created due to poor wetting. This effect was eventually lost with longer treatment times as the lack of wetting became more severe and the composite degraded to strengths less than those obtained with untreated fibers. The seawater absorption and swelling of composites made with treated and untreated fibers with the aid of compression indicated an inverse relationship. Longer treatments resulted in more weight gain and less swelling. This also supports the idea that longer treatments resulted in more voids within the composite.

In order to take advantage of the improved bonding achieved from oxidizing carbon fiber surfaces, it may be necessary to keep the treatment time, and oxidation level, low or to separate the fibers prior to incorporation into a composite so that wetting may occur. It may also be possible to achieve acceptable wetting with enough compression to force the resin between the fibers.

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