Wettability of Nitric Acid Oxidized Carbon Fibers

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ABSTRACT: High-strength carbon fibers were oxidized by exposure to nitric acid and single-fiber wettability predictions were compared to the actual wettability of multiple fibers in resin. Single-fiber wettability was predicted through contact-angle measurements and surface-energy calculations. Multiple-fiber wettability in resin was evaluated by immersing treated fiber bundles in catalyzed vinyl ester resin, followed by cross-sectional viewing after curing. Fiber cohesion, macro-composite void content, and transverse tensile strength were also examined as a function of fiber treatment time. Fiber surface energy increased with treatment time, suggesting improved wettability. However, fiber cohesion also increased and composite wetting was found to suffer. Increasing fiber treatment times resulted in larger unwetted areas, higher void content, and declining transverse tensile strength.

KEY WORDS: wettability, surface treatments, voids.

INTRODUCTION

CARBON FIBERS OFFER exceptional properties to composite materials, such as high stiffness and high strength to weight ratio. However, their use in composites is also problematic because their surface is unreactive, leading to poor fiber/matrix interfacial adhesion. One method that is often prescribed to improve the reactivity of carbon fiber surfaces is oxidation. Surface oxidation is believed to affect both fiber/matrix bonding and wetting of the fibers by the liquid resin. A common method used to evaluate the wettability changes that result from fiber surface treatments is contact-angle measurement. The angle of contact formed when a solid, liquid, and vapor meet provides an indication of the interaction between them. Typically, a solid with high surface energy leads to a lower contact angle and the prediction of better wetting by liquids. The problem with this method is that it is a thermodynamic prediction based on the properties of only one fiber when it reacts with fluids other than matrix resin. The fluids used are varied in properties, but usually have a low viscosity. The use of a single fiber in interaction with non-viscous liquids detracts from the reality of composite materials, which contain numerous closely packed fibers combined with viscous resins.

As fibers are oxidized, their surface chemistry and energy changes and it is believed that these changes improve fiber/matrix bonding and wetting. However, the energetic and

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reactive fibers are free to interact with other fibers, in addition to the resin. This study explores the interaction between adjacent fibers after surface treatment and how this affects the wettability of composites made with multiple fibers and vinyl ester resin. Single-fiber wettability, fiber cohesion, fiber bundle wettability, composite void content, and transverse tensile strength are examined using carbon fibers oxidized with nitric acid.

MATERIALS

Two types of carbon fibers were used in this analysis. The first was T700, produced by Toray Industries, which was coated with type FOE sizing. The second was unsized AS4D by Hexcel, Co. Both types qualify as high-strength (type I) and are similar in properties. Concentrated nitric acid (70%, NF grade) was applied to oxidize the fiber surfaces. Derakane Momentum^{TM} 411-350 vinyl ester resin was used to make composites. It was catalyzed and promoted with methyl ethyl ketone peroxide (MEKP) and 6% cobalt napthenate, in the amounts of 1 phr and .05 phr respectively.

EXPERIMENTAL METHODS

Fiber Surface Oxidation

Before analysis, fibers were oxidized to differing degrees by boiling in nitric acid at reflux conditions. The degree of oxidation was controlled by changing the length of acid-exposure time, which was varied from 0 to 160 min. Individual fiber tows were treated by attaching them to glass frames and securing their ends with PTFE tape. Fiber mat was treated by positioning a section of mat between a glass plate and a 316-L stainless steel screen, and securing the assembly with 316-L stainless steel wire. Figure 1 describes the fiber mat treatment assembly.

In addition to carbon fiber, the mats are woven together with other materials, whose nature is not disclosed. There are long, continuous fibers that run transverse to the carbon fiber directions that are believed to be glass fibers. These fibers were removed prior to formation of composites. The carbon fiber bundles are also woven together with a type of soft, flexible plastic, which immediately dissolved in nitric acid. It was a small amount and
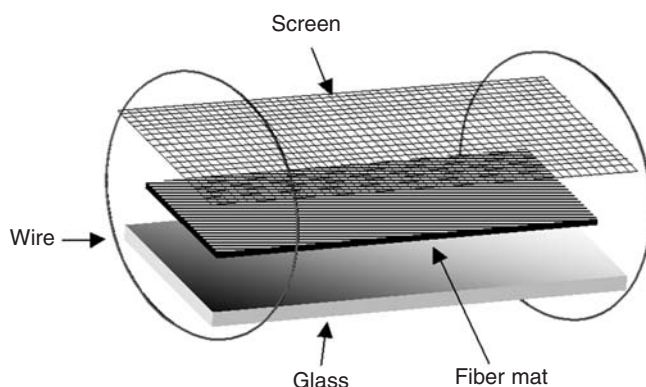

Figure 1. *Fiber mat treatment assembly.*

readily dissolved and therefore, its effects on the resultant composites were assumed to be negligible.

To prepare the fibers for oxidation, they were first subjected to a 2-h distilled water wash, followed by a 2-h drying period at 120°C. After acid exposure, the fibers were again washed in distilled water, which was refreshed numerous times until the pH of the wash water had stabilized and was near that of the fresh water. Following the final wash, the fibers were subjected to a final 2-h drying period at 120°C, and then stored in a vacuum with a silica gel desiccant until use.

Single-Fiber Wettability

The wettability of single fibers at various stages of treatment was determined through contact-angle measurements and surface-energy calculations. Surface energy plays an important role in determining how well a given liquid will wet out a solid. As described by Kaelble et al. [1], wetting of a liquid onto a solid is governed by the balance of forces that result at the three-phase intersection of a solid, liquid, and gas. The solid–vapor, liquid–vapor and solid–liquid interactions each contribute a force at the intersection, and the balance of these forces can be determined by measuring the angle between the intersecting phases, called the contact angle. Typically, the contact angle is directly measured by applying a liquid droplet to a solid surface, as shown in Figure 2.

However, because carbon fibers are exceedingly small in diameter ($\approx 7\,\mu m$), another method was implemented. The micro-Wilhelmy plate technique was used, which involves inserting and extracting a single fiber through a fluid surface and measuring the contact force. With this force, the contact angle can be calculated as described by Neumann and Tanner [2] and Mozzo and Chabord [3]:

$$M = \frac{C\gamma_{LV}\cos\theta}{g} \tag{1}$$

where M is the contact force, C is the fiber circumference, γ_{LV} is the liquid–vapor surface tension, $g = 980.6\,\mathrm{dyn/gm}$, and θ is the desired contact angle. The micro-Wilhelmy plate method is depicted in Figure 3.

After determining the contact angle, it can be used along with the known liquid–vapor surface tension to determine the solid–vapor surface energy. The Young–Dupre equation
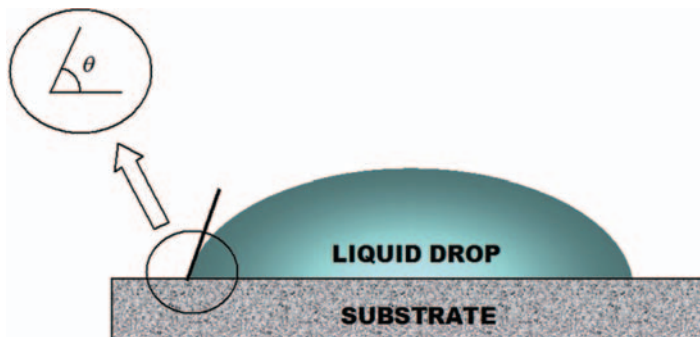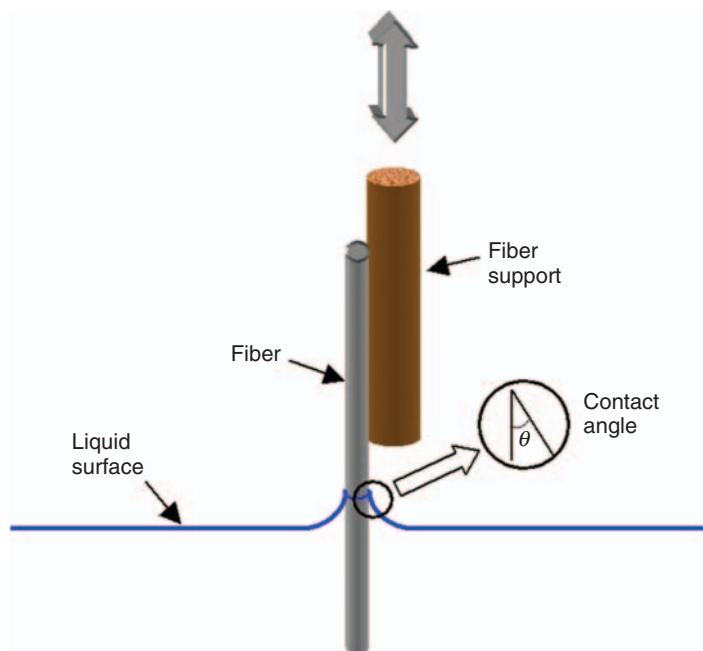

Figure 2. Contact angle of droplet on solid surface.

Figure 3. *Micro Wilhelmy plate method of measuring contact angle.*

defines the reversible work of adhesion that occurs when an interface is formed between two surfaces:

$$W_a = \gamma_{LV}(1 + \cos\theta) \tag{2}$$

where W_a identifies the reversible work of adhesion. Furthermore, the surface energies of solids and liquids can be divided into polar (Keesom-p) and dispersive (London-d) components:

$$\gamma_{LV} = \gamma^d_{LV} + \gamma^p_{LV} = a_L^2 + b_L^2 \tag{3}$$

$$\gamma_{SV} = \gamma^d_{SV} + \gamma^p_{SV} = a_S^2 + b_S^2 \tag{4}$$

where a_L and b_L are the square roots of the respective dispersive and polar constituents of the liquid–vapor surface energy, and a_S and b_S are the square roots of the respective dispersive and polar constituents of the solid–vapor surface energy. Using Equation (3) and Equation (4), the work of adhesion can also be expressed as [1]:

$$W_a = 2(a_L a_S + b_L b_S) \tag{5}$$

which can be rearranged to give:

$$\frac{W_a}{2a_L} = a_S + b_S\left(\frac{b_L}{a_L}\right) \tag{6}$$

By using at least two different liquids, a plot of $(W_a/2a_L)$ vs. (b_L/a_L) will yield a straight line, with its slope and intercept defining the values of b_S and a_S, respectively, for the solid of interest [1]. Therefore, the dispersive and polar components of surface energy, γ_{SV}^d and γ_{SV}^p, can be determined by squaring a_S and b_S, respectively.

In the current study, the fiber/liquid contact force was measured using a CAHN DCA-322 Dynamic Contact Angle Analyzer with WinDCA32 software. Five to ten separate fibers were analyzed for each fiber type tested and each fluid used. The CAHN DCA-322 electrobalance has a sensitivity of ± 0.1 mgm. The fiber circumference was determined by measuring the diameter of each fiber before analysis, using a Mitutoyo LSM-6200 Laser Scan Micrometer and averaging two–three measurements along the immersion length of each fiber.

Two fluids were used in the analysis: water and diiodomethane. These two particular fluids were chosen because they represent a broad range in polarity, which leads to a comfortable separation between the types of reactions each of the fluids had with the solid surfaces. Both types of untreated fiber were analyzed, as well as the nitric acid-treated unsized fiber after 40, 80, 120, and 160 min of treatment.

Fiber Interaction

It was previously shown that treating high-strength carbon fibers with nitric acid causes a substantial increase in the amount of carbonyl and carboxylic acid groups on fiber surfaces [4]. Those surface chemistry changes undoubtedly affect the fiber/matrix interaction, but interaction between adjacent fibers themselves should also be considered. The surface functional groups on one fiber may react with those on another fiber, as well as with the matrix resin. In order to evaluate this effect, fiber cohesion was measured by recording the irreversible work required to separate 25-mm (1-in.) long bundles of fiber along their length. This effect was quantified by calculating the area under the force–displacement curve. To determine this value, tabs were attached to the bundle ends, and they were slowly pulled apart, using a 2N-load cell on an MTS Insight 1-kN electromechanical test machine at 5 mm/min. Sized (T700) and unsized (AS4) fiber bundles, as well as six different nitric acid treatment times (10, 20, 40, 80, 120, and 160 min) of unsized fiber were analyzed. At least five samples of each were tested. Figure 4 describes this test.

To arrive at a final value for the work of separation, the test was continued for at least 5 mm after complete bundle separation and the load level recorded during that time was used as the baseline. It was necessary to subtract the baseline because the weight of the upper half of the bundle produced a significant non-zero bias into the force–extension curves.

Fiber Bundle Wettability

Single-fiber analysis with non-resin fluids may indicate increased wettability for oxidizing surface treatments, but it does not necessarily follow that a bundle of fibers will show the same increased wettability in resin. Single-fiber wettability analysis is usually the method of choice when predicting how a given fiber surface treatment will improve or decrease fiber wetting in a composite [5], but there are additional variables that affect a composite material that may drastically affect the true wettability. Fiber–fiber interaction is ignored, as well as the significant viscosity of most resins. Resin viscosity may hinder its infiltration into small inter-fiber spaces, especially if there is significant attraction between
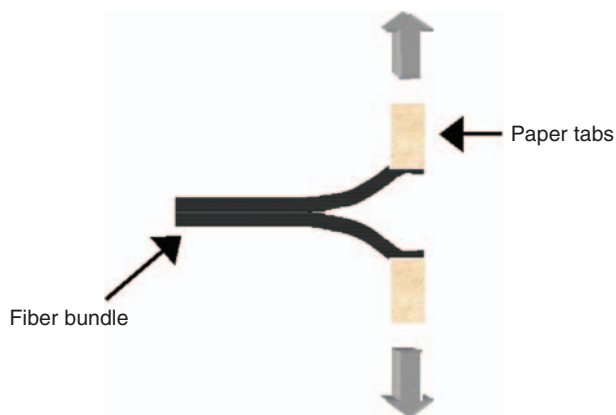
Figure 4. *Fiber cohesion test.*
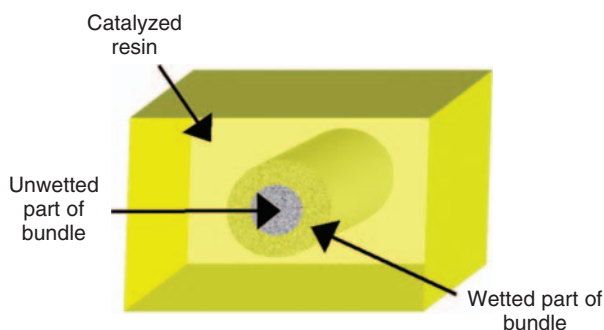
Figure 5. *Bundle wettability test.*

neighboring fibers. Fluids are typically chosen for their polarity in single-fiber wettability tests and usually, they are of low viscosity. Water is commonly used.

Thus, to extend the single-fiber wettability results to a composite material, multiple fibers and resin were used. Fiber bundles (treated or untreated) were immersed in catalyzed vinyl ester resin and allowed to cure for 24 h. The resultant single-bundle composite blocks were then post-cured for 2 h at 120°C and then cross-sectioned, polished, and viewed in a SEM to evaluate the degree of wetting that occurred before matrix hardening. A Quanta 200 model ESEM by FEI was used, without employing environmental mode. If complete wetting did not occur, an area of unwetted fiber was found in the interior of the bundle. Figure 5 depicts this test.

This test was conducted for sized (T700) fiber, unsized (AS4) fiber, and six different nitric acid treatment times (2.5, 5, 10, 20, 40, and 80 min) on unsized fiber.

Composite Void Content

To evaluate the impact that nitric acid fiber treatment has on macro-composite wetting, carbon fiber composites were formed with vinyl ester resin and the void content was determined in accordance with ASTM D 3171 (Standard Test Methods for Constituent Content of Composite Materials). It was necessary to treat sized fiber to

make macro-composites, because it was the only type available in woven mat form. It has been shown previously that both the sized and unsized fiber types used herein exhibit similar properties after nitric acid exposure [4].

The composites were produced by saturating four plies of fiber mat (treated or untreated) in promoted and catalyzed resin, placing them between two 15.24 cm × 15.24 cm (6 in. × 6 in.) steel plates, taping the transverse edges with cellophane tape to prevent fiber extrusion, and compressing the resin-soaked mats with an MTS Insight 50 electromechanical testing machine. The steel plates had been polished to a mirror-like finish and coated with a silicone-based mold release agent. It was necessary to make at least one composite from the unsized fiber, which was not available in the woven mat form, so a single tow was wrapped around a frame several times to simulate a mat before introduction into the composite. It was wrapped so that there was the same number of bundles per width as the pre-woven sized fiber mat. Compression was necessary to form the composites because there was a significant difference in wettability between some of the different fiber treatments. All composite panels were made with the fiber layers oriented in a unidirectional direction. They were first compressed to 344 kPa (50 psi) and then to 688 kPa (100 psi), and left under pressure for 24 h to cure. The panels were then post-cured for 2 h at 120°C. They were made with sized and unsized fiber, as well as three acid treatment times (2.5, 5, and 10 min) of sized fiber.

After determining the composites' densities in accordance with ASTM D 792, the composite samples were immersed in 40 mL of 70% nitric acid for 6 h at 100°C to digest the matrix material, and then the contents were passed through sintered glass filters so that only the fiber remained. The fiber was then rinsed, dried, and weighed in accordance with ASTM D 3171 to determine how much it contributed to the total composite weight.

Vinyl ester is a chemically resistant resin, which led to the requirements of a long exposure time and a high nitric acid temperature for matrix digestion. This long rigorous exposure can also result in fiber volume loss. It was shown previously [4] that high-strength carbon fiber diameters decrease with extended nitric acid exposure time. To account for fiber mass change, a blank of fiber that was equivalent to the amount of fiber in the composite specimens was subjected to the same acid exposure. One gram of unsized fiber was used. It was expected that the mass loss of the unsized fiber would also be representative of the mass loss of the sized fiber, because it has been previously shown that the diameter loss of both types in nitric acid is similar [4]. The digested composite fiber weights were then compensated to account for the amount of fiber mass loss found in the blank fiber test, in accordance with ASTM D 3171.

Transverse Tensile Strength

Changes in composite wetting can be expected to impact strength. Fully wetted composites will exhibit better strength than similar composites that were not completely wetted by the matrix resin. Poor wetting leads to higher void content and less fiber/matrix interfacial bonding. To extend wetting behavior observed in nitric acid-treated carbon fiber composites to strength measurements, a single-bundle transverse tensile test was used, similar to that presented by Ageorges et al. [6]. This test was chosen because it requires only one bundle, instead of a woven mat, and the unsized fiber used herein was only available in the single-bundle form. In this method, a fiber bundle is cast in the transverse direction across the center of a dog-bone-shaped resin specimen. The single bundle transverse tensile test is depicted in Figure 6.
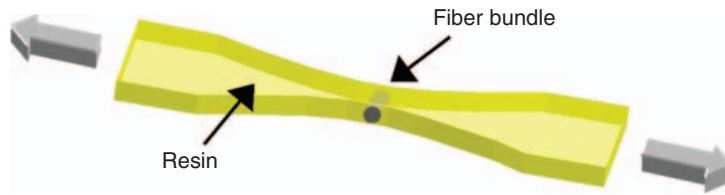
Figure 6. *Single-bundle transverse tensile test.*

This geometry assures that the highest stress occurs in the narrow region where the fibers are located. In addition, a specimen of this shape eliminates one of the main concerns expressed 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, leading to a low-strength prediction. This also makes 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 used are similar to those used by Ageorges et al. [6], with the exception that the bundle was held in place by 1 mm × 1 mm channels on each side of the mold cavity, instead of placed flat between an upper and lower mold surface.

Sized and unsized fiber bundles, as well as five nitric acid treatment times (2.5, 5, 10, 20, 40 min) of unsized fiber were analyzed. Beyond 40-min treatments, the specimen quality was so poor that it became difficult to handle or test them. A set of at least ten samples was tested for each treatment type. All specimens were cured for 24 h at room temperature, followed by a 2-h post-cure at 120°C before testing, in accordance with the resin producer's recommendations. They were tested on an MTS Insight 1-kN test machine at 0.2 mm/min.

RESULTS

Single Fiber Wettability

Nitric acid treatment of carbon fibers alters their surface energy significantly, leading to predictions of improved wettability. Both polar and dispersive components are affected. Figure 7 describes the changes in polar, dispersive, and total surface energy.

From Figure 7, it can be seen that the polar component of fiber surface energy, γ_{SV}^{p}, increases linearly with nitric acid treatment time. However, the dispersive energy, γ_{SV}^{d}, showed the opposite trend, decreasing with treatment time. The total fiber surface energy is the summation of the polar and dispersive energies and in this case is largely dominated by the polar component. Like the polar component, it increased with nitric acid treatment. The increase in solid–vapor surface energy seen with nitric acid treatment of carbon fibers indicates that they are likely to be more easily wetted by liquids, such as resin.

Fiber Interaction

Treating high-strength carbon fibers with nitric acid significantly affects their surface chemistry [4], which is likely the source of the surface energy changes that are described above. Surface chemistry changes, such as oxidation, are also known to affect fiber
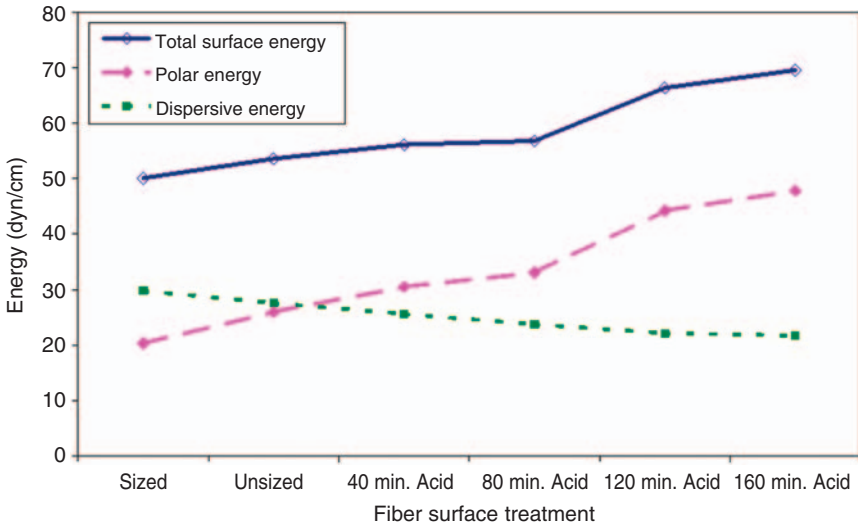
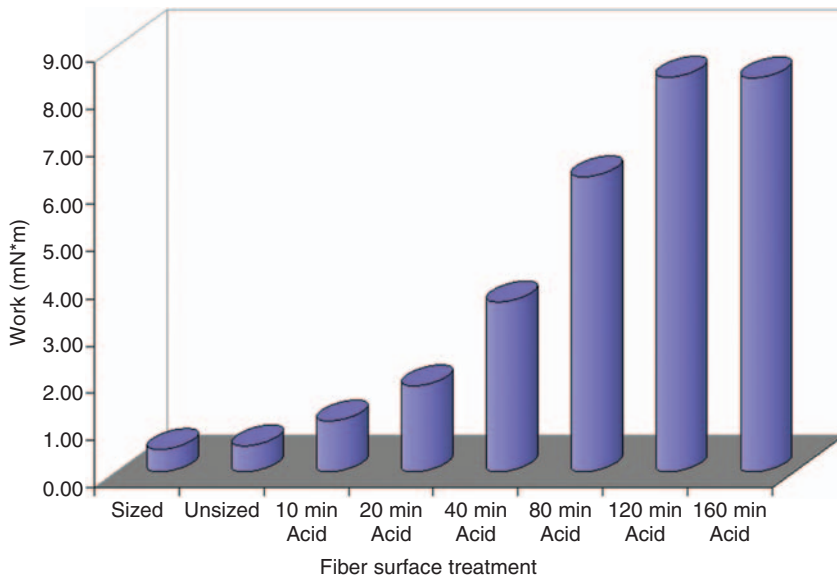**Figure 7.** *Total, polar and dispersive fiber surface energies.*

Figure 8. *Work of separation required for acid-treated fiber bundles.*

interaction with the matrix resin [5,7,8]. However, the modified surfaces are not limited to reacting only with the resin, and it should not be overlooked that the reactive and energetic fiber surfaces are likely to affect each other. Figure 8 shows the results of the fiber cohesion tests.

Figure 8 illustrates a significant effect of fiber cohesion that increases with treatment time. When the abscissa (*x*-axis) is made to be linear, it can be found that the increase in separation work is a linear function of acid treatment time, until 120 min of treatment is reached, at which time it appears to plateau. This plateau may indicate a maximum level of
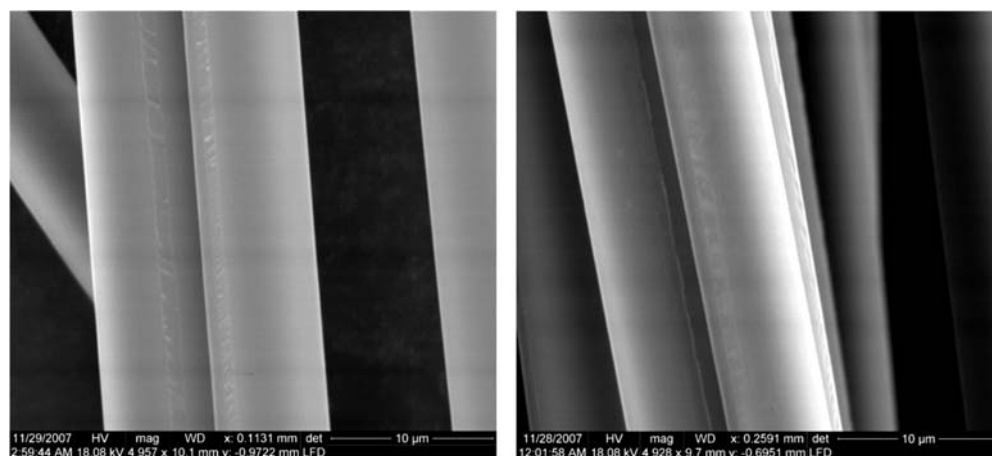
Figure 9. *Fiber cohesion markings on acid-treated fibers: (a) 120-min treated unsized fiber, and (b) 160-min treated sized fiber.*

oxidation that can be achieved with this type of surface oxidation. The levels of carbonyl and carboxylic acid groups on the fiber surfaces were also observed to reach stable values after extended treatment [4]. It is postulated that the fiber–fiber cohesion is a result of hydrogen bonding between functional groups on adjacent fibers, and as the functional group concentration is increased (carboxyl and carbonyl), the cohesion also increases. 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 [9,10].

Further evidence of the fiber cohesion phenomenon was found by viewing nitric acid-treated fibers with a SEM at 5000 times magnification. Both examples in Figure 9 show fibers with longitudinal markings that match similar markings on the adjacent fibers. These markings appear to have been caused by the separation of the cohering fibers.

Fiber Bundle Wettability

Wettability of multiple fibers in resin was evaluated to serve as a comparison to the predictions arrived at by single-fiber contact angle and surface-energy measurements. Although the single-fiber results led to predictions of improved wettability, the opposite was found to be true with fiber bundles in vinyl ester resin. The results are shown in Figure 10.

Based on the total surface energy from the contact angle tests, an increase in wettability would be expected with increasing nitric acid treatment time. But as nitric acid treatment time increased, there were increasingly larger areas of unwetted fiber or voids within the bundles.

While a single fiber may be more wettable with an oxidizing nitric acid treatment, a group of fibers behaves differently. It is likely that the fiber cohesion discussed and measured herein plays an important role, as well as the resin viscosity. Fiber cohesion draws the fibers together, making areas of the fiber bundle difficult for the high-viscosity resin to pervade. Contact-angle measurements are conducted on one fiber at a time with non-viscous fluids. Thus, the oxidizing treatment makes the fiber groups less wettable, instead of more wettable as commonly believed.
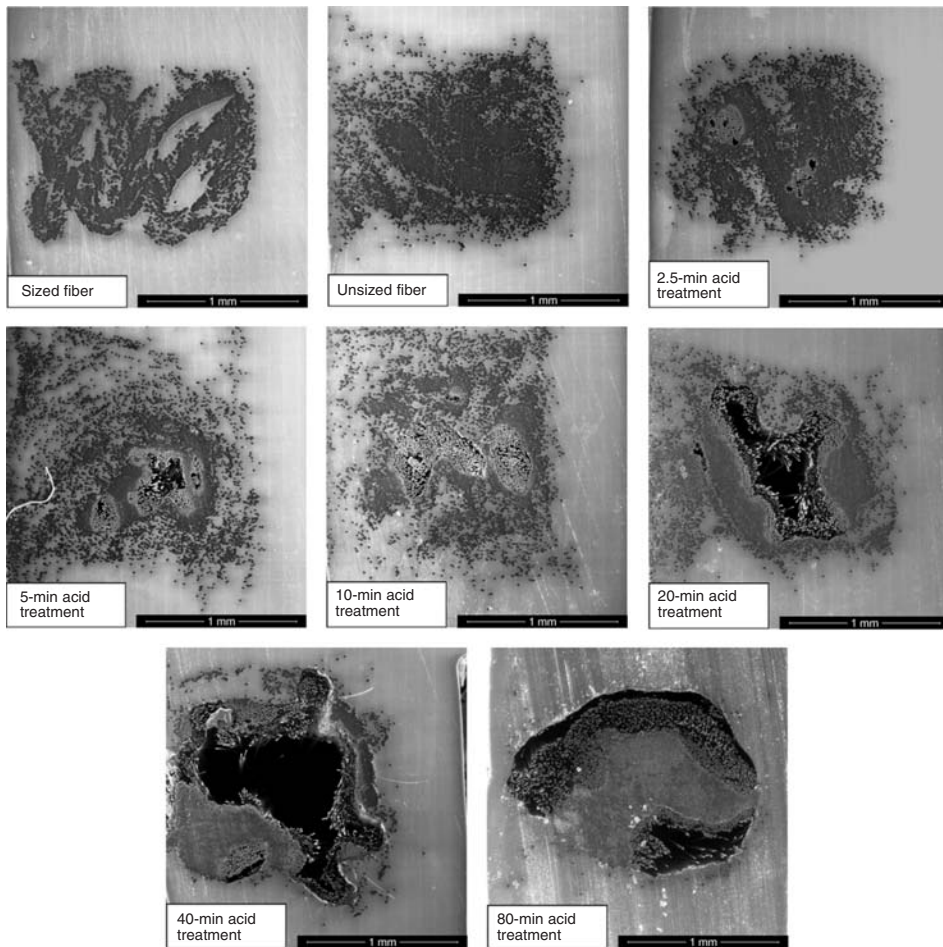
Figure 10. SEM views of fiber bundles in vinyl ester resin at different stages of surface treatment.

Composite Void Content

The fiber bundle wettability tests were done without the aid of pressure or vacuum, so that differences in wetting could easily be observed. This begs the question of whether the observed wettability changes would matter when macro-composites were formed with the aid of pressure or vacuum. To answer this question vacuum-assisted resin transfer molding (VARTM) was initially attempted. Two treatment lengths were used (5 and 20 min) and four plies of fiber mat were used for each. Both types wetted too poorly to be useful, indicating that the wetting problem observed in the single-bundle tests extends to the VARTM case. Based on the failure to form composites with VARTM, the compression method described herein was used. The void content found for the untreated and treated fiber type composites is shown in Figure 11.

Review of Figure 11 immediately yields that the void content of the nitric acid-treated fiber composites increased in correlation with increasing acid-treatment time. Increasing void content is a result of nitric acid-fiber treatment with or without the aid of vacuum or compression in composite formation.

Transverse Tensile Strength

The reduced wetting observed with fiber bundles also became evident when examining transverse tensile strength, which was examined for both fiber types at various lengths of treatment. The two fiber types (sized and unsized) produced different results before acid treatment, but behaved similarly afterward. A very interesting feature that is clearly visible in Figure 12 is that although the acid treatment initially increases the transverse tensile strength, it is followed by a steady decline for both fiber types. The initial strength increase
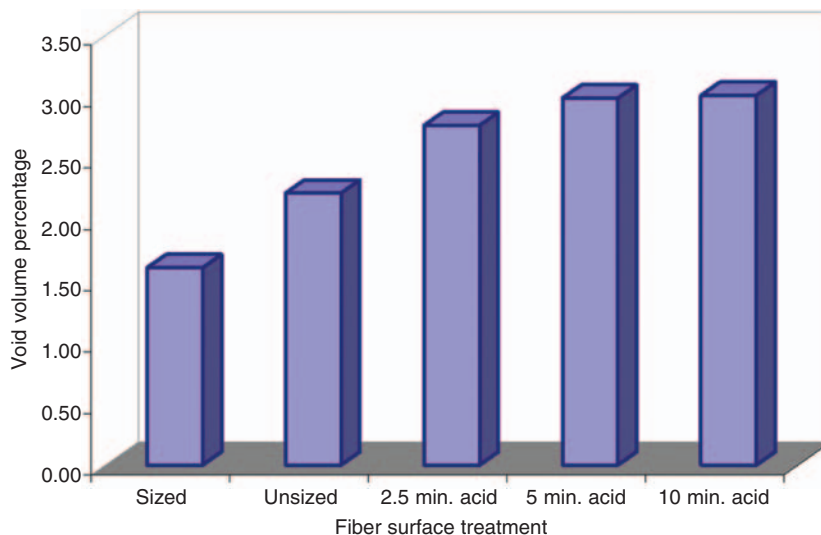

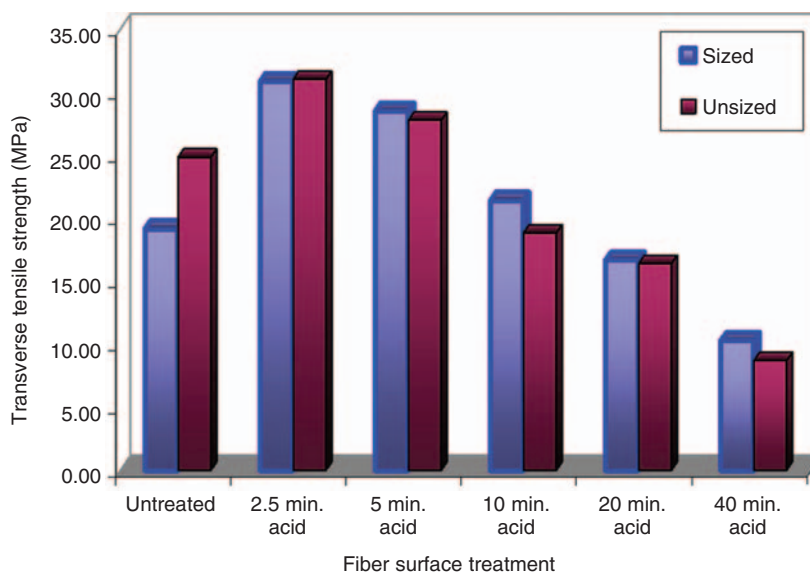**Figure 11.** *Composite void content.*

Figure 12. *Transverse trensile strength at different stages of fiber surface treatment.*

is probably due to improvements in fiber/matrix adhesion. The fact that the two fiber types become equal after acid exposure, even though they start out different, indicates that the acid has removed the sizing and it is no longer acting as a factor in the transverse tensile strength. The strength decline that occurs with increasing acid treatment time is a result of the declining wettability of the fibers. The nitric acid treatment appears to lend increased fiber/matrix adhesion (2.5 and 5 min) to improve strength, but it comes at the price of reduced wettability that dominates at longer treatment times.

DISCUSSION

While single-fiber contact-angle measurements lead to predictions of improved wettability of carbon fibers that have been oxidized with nitric acid, tests conducted with multiple fibers in vinyl ester resin argue otherwise. Fiber bundles exhibited unwetted areas when submerged in promoted and catalyzed resin that grew larger with increased fiber oxidation time. This wetting problem was also observed when macro-composites were produced using vacuum and compression. Using the VARTM method, composites could be formed with fibers that had not been oxidized, but no acceptable composites were achieved with treated fibers, due to extremely poor wetting. Composites were successfully formed when applying compression, but their internal void content increased in correlation with the nitric acid treatment time of their fibers. The contradiction in wetting found when switching from single fibers to multiple fibers is likely due to the interaction between adjacent fibers. After the fibers were oxidized, their surfaces became reactive and energetic and they became more difficult to separate. Fiber cohesion appeared to prevent successful wetting on all composite types, whether they were made with vacuum, pressure, or without any aid. Furthermore, the degraded wetting of the fibers by the resin presented itself in transverse tensile-strength measurements, where the composites became weaker with extended nitric acid treatment of their fibers.

ACKNOWLEDGMENTS

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