Effects of Surface Treatment on the Properties of Carbon Fibers and Their Composites (Postprint)

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Abstract

Carbon fiber surface treatments including deionized water ultrasonication, concentrated nitric acid immersion, and concentrated nitric acid ultrasonication were performed, and the effects of surface treatment on the microstructure, surface chemical composition, phase structure, multifilament tensile strength of carbon fibers, as well as the structure and mechanical properties of modified carbon fiber reinforced epoxy resin composites were investigated. The results show that nitric acid oxidation and ultrasonic treatment effectively modified the carbon fiber surface, wherein nitric acid treatment significantly increased the surface roughness and the number of oxygen-containing functional groups of carbon fibers, while ultrasonic treatment imparted good dispersibility to carbon fibers and increased the specific surface area and oxygen-containing functional groups. The combination of nitric acid oxidation and ultrasonic cavitation enhanced the oxidation and etching effects on the carbon fiber surface, thereby strengthening the "mechanical anchoring" and chemical bonding at the interface between carbon fibers and the resin matrix, effectively improving the interfacial bonding strength between carbon fibers and resin, and thus significantly enhancing the mechanical properties of the composites.

Full Text

Preamble

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Effect of Surface Treatment on Properties of Carbon Fiber and Reinforced Composites

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Abstract

Carbon fibers were surface-treated via ultrasonic irradiation in deionized water, immersion in concentrated nitric acid, and nitric acid treatment combined with ultrasonication. The effects of these surface treatments on the microstructure, surface chemical composition, phase structure, multifilament tensile strength of carbon fibers, and the structure and mechanical properties of modified carbon fiber-reinforced epoxy composites were investigated. Results demonstrate that nitric acid oxidation and ultrasonic treatment effectively modify carbon fiber surfaces. Nitric acid treatment significantly increases surface roughness and the quantity of oxygen-containing functional groups, while ultrasonic treatment improves fiber dispersibility and increases both the specific surface area and oxygen-containing functional groups. The combination of nitric acid oxidation and ultrasonic cavitation intensifies surface oxidation and etching, thereby enhancing both "mechanical anchoring" and chemical bonding at the carbon fiber-resin matrix interface. This effectively improves interfacial bonding strength and significantly enhances the mechanical performance of the resulting composites.

Keywords: composites, carbon fiber, nitric acid, ultrasonic, surface modification

Introduction

Carbon fiber-reinforced epoxy composites exhibit high specific strength, specific modulus, fatigue resistance, and ablation performance, making them widely applicable in both military and civilian sectors. However, the graphite-like structure of carbon fibers renders their surfaces chemically inert, preventing effective wetting and chemical reaction with resin matrices. This chemical inertness results in poor adhesion between carbon fibers and matrix resins, which is detrimental to fabricating high-performance carbon fiber-reinforced polymer composites. Surface modification of carbon fibers can increase polar functional groups and surface roughness, thereby improving fiber-resin wettability and reactivity and enhancing interfacial bonding strength. Common surface modification methods include oxidation, plasma treatment, surface coating, and chemical grafting.

Ultrasonic irradiation represents a unique energy input method that surpasses conventional optical, electrical, and thermal approaches. The high temperatures and pressures generated by collapsing cavitation bubbles significantly promote chemical reactions on solid surfaces, enhancing reactivity and reaction rates. Additionally, high-frequency ultrasonic vibration facilitates better dispersion of carbon fibers in liquids, while high-speed microjets and shock waves produced during bubble collapse create surface pitting. This study investigates the effects of ultrasonic treatment in deionized water, concentrated nitric acid immersion, and nitric acid combined with ultrasonication on carbon fiber surfaces and their composite performance.

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1. Experimental Methods

1.1 Carbon Fiber Surface Treatment

T300 PAN-based carbon fibers (linear density: 360 g/km, bulk density: 1.74–1.79 g/cm^3) were first refluxed in a 1:1 ethanol/acetone solution for 48 h to remove the sizing agent. The desized fibers were then subjected to three surface treatment protocols: (1) ultrasonication in deionized water at 60°C for 2 h using a KS-250E ultrasonic cleaner (250 W, 40 kHz); (2) immersion in concentrated nitric acid at 60°C for 2 h; and (3) ultrasonication in 65% concentrated nitric acid (chemical grade) at 60°C for 2 h. After treatment, the carbon fibers were washed to neutral pH and dried to constant mass under vacuum at 80°C.

1.2 Composite Preparation

Carbon fiber-reinforced epoxy composites were prepared at a fiber-to-resin mass ratio of 6:4. E-51 epoxy resin (industrial grade) was diluted with acetone to 36% concentration, then mixed with molten m-phenylenediamine (analytical grade) at 14 wt% of the epoxy resin. The resin solution was brushed onto both sides of carbon fiber fabric using orthogonal brushing. The impregnated fabric was placed between flat mold plates and cured following a specific schedule: room temperature soaking, then 85°C/2 h, 130°C/2 h, and 180°C/2 h. The mold was pressurized every 2 h during curing, with final compression to achieve a composite thickness of 2 mm.

1.3 Characterization

Surface and fracture morphologies were examined using a JSM-5600LV cold field-emission scanning electron microscope (SEM) equipped with EDS for elemental analysis. Phase structure was analyzed via X-ray diffraction (XRD) using a Shimadzu XRD-7000 diffractometer. Multifilament tensile strength was measured according to GB/T3362-2005 on a Shimadzu AG-10 universal testing machine. Composite tensile and flexural strengths were tested per GB/T1447-2005 and GB/T1449-2005 standards, respectively, using a Shimadzu AG-50 universal test-

ing machine. Tensile specimens measured 250 mm × 25 mm × 2 mm with a loading rate of 5 mm/min, while flexural specimens were 40 mm × 15 mm × 2 mm tested at 1 mm/min.

2. Results and Discussion

2.1 Effect of Surface Treatment on Carbon Fiber Morphology

Figure 1 [Figure 1: see original paper] shows SEM images of carbon fibers after different treatments. Desized fibers exhibit relatively smooth surfaces (Figures 1a and 1e). After ultrasonication in deionized water at 60°C for 2 h (Figures 1b and 1f), groove structures appear and surface roughness increases, indicating "cavitation etching" from ultrasonic effects. Nitric acid immersion at 60°C for 2 h creates uniformly dense grooves with narrow ridges (Figures 1c and 1g) through oxidative etching. The combined nitric acid-ultrasonic treatment (Figures 1d and 1h) produces deep grooves along with numerous blocky, spherical, or linear protrusions and marks, yielding the roughest surface. This results from simultaneous oxidative etching and ultrasonic cavitation, which generates high-speed microjets and shock waves at the solid-liquid interface, effectively modifying the fiber surface. These results indicate that water ultrasonication alone has limited effect on morphology, nitric acid oxidation is more significant than cavitation alone, and the synergistic effect produces the most pronounced surface roughening.

2.2 Effect of Surface Treatment on Surface Elemental Composition

EDS spectra and elemental data for differently treated fibers are presented in Figure 2 [Figure 2: see original paper] and Table 1 . Desized fibers show high carbon content and low oxygen content. After water ultrasonication, nitric acid immersion, and nitric acid-ultrasonic treatment, carbon content decreases progressively while oxygen content increases, raising the O/C ratio. This occurs because desized fibers initially contain few oxygen functional groups. During water ultrasonication, cavitation generates ·OH radicals that partially oxidize the surface. Nitric acid immersion increases hydroxyl, carbonyl, carboxyl, and lactone groups, raising oxygen content to 11.29%. The nitric acid-ultrasonic combination further enhances oxidation, increasing oxygen content to 12.96%—double that of desized fibers. These results demonstrate that nitric acid oxidation substantially increases surface oxygen, while ultrasonic cavitation promotes additional oxidative etching, and their synergy significantly elevates the O/C ratio and surface active groups.

2.3 Effect of Surface Treatment on Carbon Fiber Tensile Strength

Figure 3 [Figure 3: see original paper] shows the tensile strength variation of treated carbon fiber multifilaments. All treatments reduce tensile strength to

varying degrees due to surface etching that weakens the fibers. More pronounced etching correlates with greater strength reduction. Nitric acid-treated fibers show lower strength than water-ultrasonicated fibers, indicating that nitric acid oxidation causes more severe etching than ultrasonic cavitation under identical temperature and duration. The combined nitric acid-ultrasonic treatment produces the most extensive etching, reducing tensile strength by approximately 5.8%. Despite this modest reduction, the increased surface roughness and activity enhance interfacial bonding, ultimately benefiting composite performance.

2.4 Effect of Surface Treatment on Carbon Fiber Phase Structure

XRD patterns of treated carbon fibers appear in Figure 4 [Figure 4: see original paper]. All samples show a prominent diffraction peak near 2 = 25°, corresponding to the graphite (002) crystal plane. The (002) peak intensity remains stable for desized, water-ultrasonicated, and nitric acid-treated fibers but becomes broader and weaker for nitric acid-ultrasonic treated fibers. A weaker peak near 2 = 43° appears in all samples, representing the graphite (100) plane. While this peak is similar for the first three treatments, it becomes sharper and slightly more intense for the nitric acid-ultrasonic treatment.

Using the (002) and (100) peaks, the interlayer spacing d_{002}, crystallite stacking thickness Lc, and crystallite width La along the fiber axis were calculated according to standard XRD formulas (with $\lambda = 0.1542$ nm, K = 0.94 for Lc, and K = 1.84 for La). The results are summarized in Table 2 . Nitric acid-ultrasonic treatment reduces d_{002} from 0.362 nm to 0.358 nm, indicating improved crystallinity and more compact crystal arrangement. Lc remains approximately 2.1 nm across all treatments, suggesting minimal effect on stacking dimension. However, La decreases from 13.80 nm to 13.60 nm, revealing a crystallite refinement effect. Under ultrasonic cavitation, concentrated acid reacts with sp-hybridized carbon atoms at defect sites, partially converting them to sp^2 hybridization and healing defects, thereby densifying and ordering the graphitic layered structure. Smaller graphite crystallites increase the number of unsaturated carbon atoms at edges and corners, enhancing surface activity and promoting stronger bonding with the resin matrix.

2.5 Composite Mechanical Properties

2.5.1 Tensile and Flexural Strength Figure 5 [Figure 5: see original paper] compares the tensile and flexural strengths of composites reinforced with differently treated carbon fibers. Both strength values increase progressively for composites using desized, water-ultrasonicated, nitric acid-treated, and nitric acid-ultrasonic treated fibers. The nitric acid-treated composite shows significantly higher strengths than the water-ultrasonicated version, while the combined treatment yields the most substantial improvement. This enhancement stems from two factors: (1) nitric acid treatment dramatically increases surface roughness and oxygen functional group content, and (2) ultrasonic treatment improves fiber dispersion and intensifies oxidative etching. These effects

strengthen mechanical anchoring and chemical bonding at the interface, leading to superior composite mechanical properties.

2.5.2 Flexural Load-Displacement Behavior Load-displacement curves for flexural testing reveal distinct characteristics for each composite (Figure 6 [Figure 6: see original paper]). Maximum bending loads occur within 0.5–1.5 mm displacement and increase sequentially with treatment severity, with particularly notable improvements for nitric acid-treated and nitric acid-ultrasonic treated composites. After reaching peak load, the load-displacement behavior diverges. Composites treated with nitric acid (Figures 6c and 6d) exhibit abrupt load drops shortly after maximum load, with the nitric acid-ultrasonic sample showing the most pronounced decrease. This indicates stronger interfacial bonding, where extensive fiber fracture occurs at maximum load, causing sudden load reduction. Higher interfacial strength promotes brittle fracture behavior. In contrast, ultrasonicated composites (Figures 6b and 6d) show slight load recovery when displacement increases from 2 mm to 3.5 mm, suggesting improved fiber dispersion enables more uniform load transfer from matrix to fibers. Thus, the combined nitric acid-ultrasonic treatment enhances both maximum load capacity and load distribution efficiency.

2.6 Effect of Surface Treatment on Composite Fracture Morphology

SEM images of flexural fracture surfaces are presented in Figure 7 [Figure 7: see original paper]. The desized fiber composite (Figures 7a and 7e) shows severe fiber-matrix debonding, scattered matrix debris, disordered fracture surfaces, and delamination, indicating poor fiber dispersion and weak interfacial bonding. The water-ultrasonicated composite (Figures 7b and 7f) exhibits stepped fracture surfaces with relatively uniform fiber distribution and deep holes where fibers pulled out, suggesting moderate interfacial strength and sequential fiber failure. The nitric acid-treated composite (Figures 7c and 7g) shows clean, non-delaminated fracture surfaces with sparse matrix protrusions and minimal fiber pull-out, indicating improved interfacial strength but poor dispersion and brittle fracture characteristics. The nitric acid-ultrasonic treated composite (Figures 7d and 7h) displays the most uniform fiber distribution, shallow holes, and predominantly fiber fracture rather than pull-out, demonstrating that the synergistic treatment optimizes both dispersion and interfacial strength, resulting in enhanced brittle fracture behavior.

2.7 Mechanism of Nitric Acid-Ultrasonic Synergistic Treatment

Figure 8 [Figure 8: see original paper] schematically illustrates the proposed modification mechanism. Nitric acid oxidation etching (Figure 8a) increases surface roughness and generates oxygen-containing polar functional groups (hydroxyl, carbonyl, carboxyl) whose concentration grows with etching time. Ultrasonic cavitation (Figure 8b) and radical oxidation (Figure 8c) produce $\cdot$OH radicals and hydrogen peroxide through shockwave-induced pyrolysis, creating

impact etching and additional surface oxidation that increase specific surface area and oxygen functional groups, thereby enhancing interlaminar bonding. The nitric acid-ultrasonic synergy intensifies both oxidation and etching, further increasing surface roughness and polar functional group density. The abundant oxygen functional groups form numerous strong chemical bonds with the epoxy resin and amine curing agent, while the roughened surface enables mechanical interlocking as resin flows into grooves and pits, creating an "anchor effect" that tightly binds the fibers and matrix. This combination of strong mechanical anchoring and chemical bonding produces a robust interface and yields composites with superior mechanical performance.

Conclusions

1. Surface treatments including water ultrasonication, nitric acid immersion, and nitric acid-ultrasonic treatment effectively modify desized carbon fiber surfaces, with the nitric acid-ultrasonic synergy producing the most significant modification.
2. The combined nitric acid-ultrasonic treatment integrates oxidative etching and cavitation effects, improving fiber dispersion, increasing surface roughness and oxygen functional group content, reducing crystallite size, and enhancing crystallinity.
3. This synergistic surface modification strengthens mechanical anchoring between carbon fibers and the resin matrix, improves wettability and reactivity, promotes chemical bonding at the interface, and thereby significantly enhances the tensile and flexural strengths of carbon fiber-reinforced epoxy composites.

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Note: Figure translations are in progress. See original paper for figures.