

Titanium Dioxide Nanoparticles-coated Aramid Fiber Showing Enhanced Interfacial Strength and UV resistance properties

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Abstract

Titanium dioxide nanoparticles (TiO₂ NP) were grown on aramid fiber (AF) by a low-temperature hydrothermal method with the aim to enhance the poor interfacial strength and the UV resistance properties of the fiber material. Prior to the growing process, AF was functionalized to increase the fiber-TiO₂ NP bonding strength. The structure, interface strength, and UV resistance properties of the resulting TiO₂ NP-modified fiber material were investigated. Anatase TiO₂ NP were uniformly grown on the fiber surface while controlling the TiO₂ particle size upon addition of polyethylene glycol (PEG). The growth of TiO₂ NP increased the interaction area and reduced the stress concentration between the fiber and the matrix material. The experimental testing results revealed a significant improvement (by 40–67%) in the interfacial shear strength (IFSS) upon development of the TiO₂ NP interphase while essentially maintaining the basic strength of the fiber material. Unlike other TiO₂-coating methodologies such as sol-gel and sizing, the herein developed process, leading to complete anatase TiO₂ NP coating, provided the fiber with effective UV-rays protection characteristics while retaining most of the tensile strength (87.1–90.5%) after long UV irradiation exposure (168 h).

1. Introduction

Aramid fiber (AF) is well-known chemical fiber that has been attracted great attention worldwide owing to its remarkable characteristics such as ultra-high strength and modulus, good thermal and chemical resistance, light weight, long life cycle, and outstanding insulation performance. AF has been used in a wide range of industrial fields such as aerospace, aviation, and bulletproof products, among others [1, 2]. However, current applications involving AF-reinforced composites are hindered by two inherent shortcomings of AF, namely, low interfacial performance and poor UV resistance. The former is produced by the lack of active groups and the smooth surface of the fiber material, both leading to weak AF-resin interfacial adhesion and, ultimately, to composites performing below the expected standards [3]. With regard to UV resistance, AF can absorb UV light ranging from 300 to 400 nm. UV absorption causes breakage of the bonds among fibers, thereby deteriorating their mechanical performance and, consequently, restricting their outdoor applications [4, 5].

Numerous efforts have been made so far to overcome two critical shortcomings of AF. However, both of these two critical shortcomings have not been desirably solved simultaneously, and thereby more efforts are needed in this sense. Herein, a low-temperature method to grow TiO₂ nanoparticles (TiO₂ NP) on AF was proposed with the aim to prepare new AF materials with enhanced interfacial performance and UV resistance characteristics. Prior to the TiO₂ NP growth, a functionalization process was employed to improve the bonding between AF and TiO₂ NP. A hydrothermal process using tetrabutyl titanate and acetic acid was conducted at low temperature (120°C) with the aim to

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preserve the tensile properties of the fiber. The morphology, structure, and properties of both AF and TiO₂ NP-modified AF were studied in detail. This characterization work was aimed at demonstrating that the nanoparticle-reinforced interphase can improve the interfacial performance of the fiber while simultaneously enhancing its UV resistance properties.

2. Experiment

Prior to its utilization, AF (Kevlar-49 fiber, DuPont Company, USA) was washed in acetone, petroleum ether, and deionized water to remove a manufacturer-applied surface adhesive. The fibers were subsequently vacuum-dried at 80 °C for 30 min. Before the TiO₂ NP growth, AF was functionalized by first soaking the fiber in a 10 wt% NaOH aqueous solution followed by an ion-exchange process (i.e., acid wash) with a 33 wt% HCl aqueous solution in a beaker for 10 s [6]. The as-obtained fiber (i.e., functionalized fiber) was dried at 100 °C for 60 min before the TiO₂ deposition process. TiO₂ NP-modified AF was synthesized by a hydrothermal method as follows. The functionalized fiber was placed in a solution (growth solution) containing 3 mL of tetrabutyl titanate (99 wt%), 10 mL of water, and 18 mL of acetic acid (99 wt%). 1 mmol of polyethylene glycol (PEG) was added to vary the morphology of the TiO₂ NP. The mixture containing the fiber and the growth solution was subsequently introduced into a sealed Teflon reactor (50 mL) and solvothermally treated at 120 °C for 5 h. After being cooled to room temperature, the resultant fiber was washed (ethanol, 3 times) and vacuum-dried at 60 °C to obtain the final TiO₂ NP-modified product.

3. Results and discussions

3.1 Fiber structure

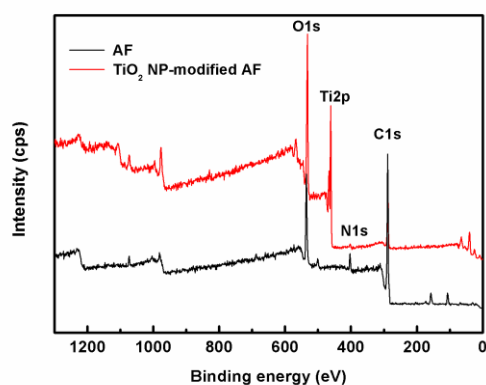


Figure 1. XPS analysis (a) and XRD patterns (b) of TiO₂ NP-modified AF

The change in the chemical structure of the fibers induced by the surface modification treatment can be observed by analyzing the XPS spectra (Figure 1a and Table 1). The result reveals that Ti atom as the emerging main component appears on the fiber surface. This reveals that the hydrothermal method herein used allows the successful growth of TiO₂ NP on the fiber surface. Moreover, the signal corresponding to the fiber carbon substrate was essentially attenuated, and no obvious signals ascribed to N element is observed in the modified fibers. Thus, it can be confirmed that TiO₂ NP fully covered the surface of the fiber after the growth process. According to Figure 1, the first two steps of the functionalization procedure are employed an ion-exchange wash to generate carboxylic acid groups on the fiber surface. These functional groups were intentionally generated to create a chemical bond between TiO₂ NP and the polymer fiber [7]. Thus, tetrabutyl titanate is hydrolyzed by the acetic acid solution during the hydrothermal growth. Once contacted with the aqueous growth solution, the carboxylic acid groups of the fibers donate a proton to the solution thereby exhibiting a negative charge (i.e., carboxylate ion). The negatively charged carboxylate ions are then coordinated with the tetrabutyl titanate hydrolysate thereby serving as seeds for TiO₂ growth [8].

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Figure 2 shows the SEM images of AF and TiO₂ NP-modified AF materials. As expected, TiO₂ NP-modified AF showed different surface morphologies as compared to AF. Thus, a layer of TiO₂ NP covered the fiber surface after the washing procedure. This result proves that TiO₂ NP can be tightly bonded on the AF surface as a result of the functionalization process [7]. The fiber diameter did not change during the coating process (Figures 5b and c), although TiO₂ NP showed different sizes. Thus, SEM images revealed that the size of TiO₂ NP decreased as result of PEG addition (from 800 to 200 nm, approximately). Although these sizes differ from those estimated by XRD because of the aggregation of TiO₂ NP in SEM images, they clearly demonstrate that TiO₂ NP growth was impeded by adding PEG in the reaction solution.

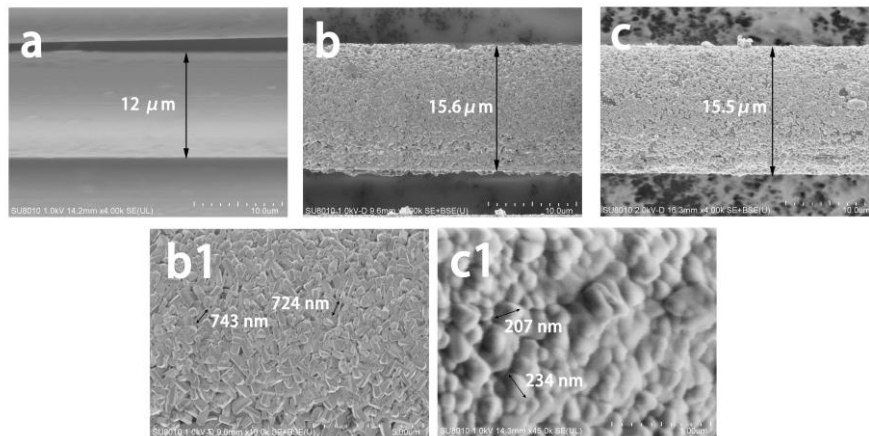


Figure 2. SEM images of (a) untreated AF and TiO₂ NP grown on AF surface without (b) and with (c) PEG solution synthesized at 120 °C for 5 h

The tensile properties of TiO₂ NP-modified fiber decreased to a low extent (4%), and this likely produced by the hydrothermal aging during the growth process. This decrease in tensile strength is lower than that produced by other surface modification treatments on the same AF material such as halogenated alkane modified (10 %) [9] and Au electrodeposited (28%) [10]. Thus, the method herein used basically maintained the properties of AF.

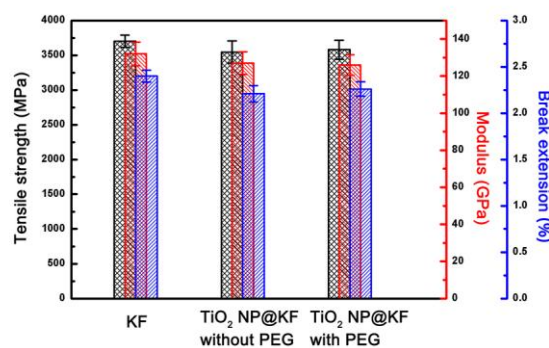


Figure 3. Tensile properties of AF and TiO₂ NP-modified AF after UV irradiation

3.2 Interfacial performance

It is widely accepted that the interfacial region between the reinforcing fiber and the resin matrix plays a significant role in determining the load transfer mechanisms and, ultimately, the mechanical performance of the advanced fiber-reinforced composites [11]. Figure 4 shows the IFSS values of TiO₂ NP-modified AF composites. The maximum IFSS for TiO₂ NP-modified fiber after adding 1 mmol PEG reached 59.3 MPa (67% increased as compared to AF). However, the IFSS of TiO₂ NP-

modified fiber prepared without PEG decreased to 49.3 MPa, thereby revealing that the size of TiO₂ NP has an effect on the interfacial properties. When the TiO₂ NP covered on the fiber surface, the TiO₂ NP act as anchors to locally reinforce the material at the interfacial region. The interfacial area increases with decreasing TiO₂ NP size. This leads to a stronger interaction between the fiber and the matrix and, ultimately, to a stronger mechanical interlocking [12].

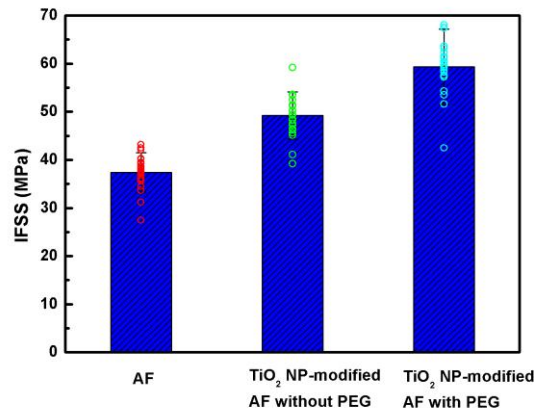


Figure 4. Tensile properties of AF and TiO₂ NP-modified AF

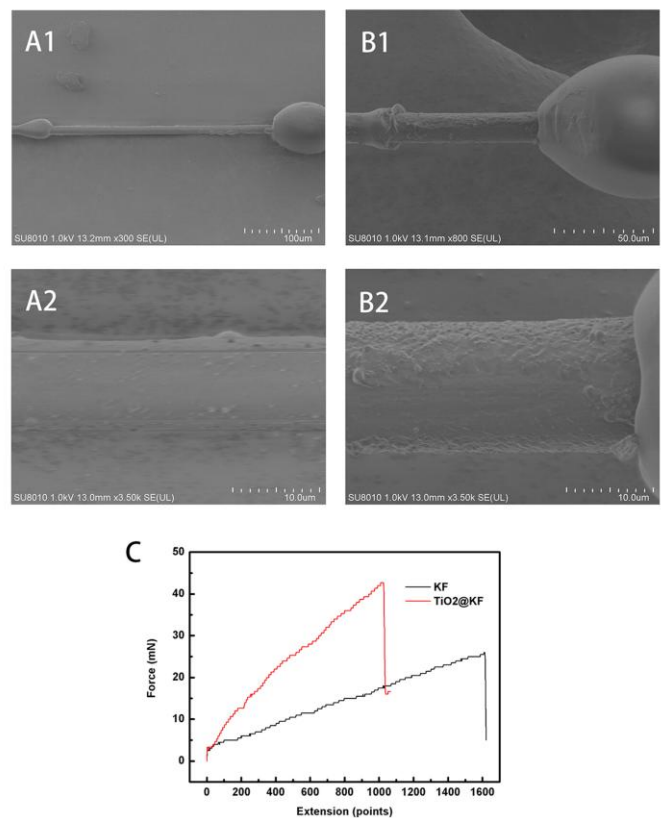


Figure 5. SEM images of AF (A) and TiO₂ NP-modified AF(B) micro-droplet after de-bonding, (c) Plots of force vs. extension curves for AF and TiO₂ NP-modified AF micro-droplet

Figure 5 depicts the surface morphology of fiber de-bonded from the resin matrix. For AF, the de-bonded fiber surface was almost clean (only several epoxy fragments were found, Figure 5A). Thus, the interface can be easily de-bonded because of the weak van der Waals forces between the fiber and the resin matrix. However, in the case of TiO₂ NP-modified fiber, a large number of epoxy fragments

were found (Figure 5B). Moreover, some TiO₂ NP attached with epoxy fragments can be traced on the fiber surface, and some of them were embedded in the resin matrix thereby indicating a stronger mechanical interlocking. The shear stress versus the displacement curves, recorded in a single-fiber micro-droplet shear tests, are illustrated in Figure 5C. The shear stress increased monotonically until reaching a peak after which a sudden load drop occurs (i.e., the matrix droplet breaks away from the fiber) [13]. In the case of TiO₂ NP-modified AF, a higher load was required to break the matrix droplet thereby indicating that the de-bonding process is effectively hindered by TiO₂ NP, with the resulting improvement of the interfacial strength properties.

3.3 UV-resistance

According to the characteristics of AF, the fiber structure will inevitably suffer molecular chain scission reactions under UV irradiation and thus deterioration of the fiber mechanical performance. However, this phenomenon was greatly altered by the presence of the TiO₂ NP coating on the surface of AF. Thus, AF preserved a 75.4, 72.1, and 83.7% of its original tensile strength, modulus, and break extension values, respectively, after 168 h of UV irradiation exposure (Figure 6), and these values increased to 87.1 (90.5), 89.8 (93.6), and 93.8% (94.1%) (values in brackets indicate samples without PEG) for TiO₂ NP-modified AF, which represents a 10–15% increase versus the original AF material. These attractive data clearly demonstrate that the TiO₂ NP coating can effectively protect fiber from long term UV irradiation damage. Additionally, the synthesis method herein developed results in better UV resistance values as compared to most of the TiO₂ modification methodologies for AF. Specifically, the tensile strength for a sol–gel sample was only 37% of the original value after 168 h of UV exposure, and this was produced by the low crystallinity of TiO₂ [14]. This value increased to 95% for an acrylic sizing sample containing 5 wt% of TiO₂, but the thick TiO₂ coating developed (20 μm) limited further applications [15].

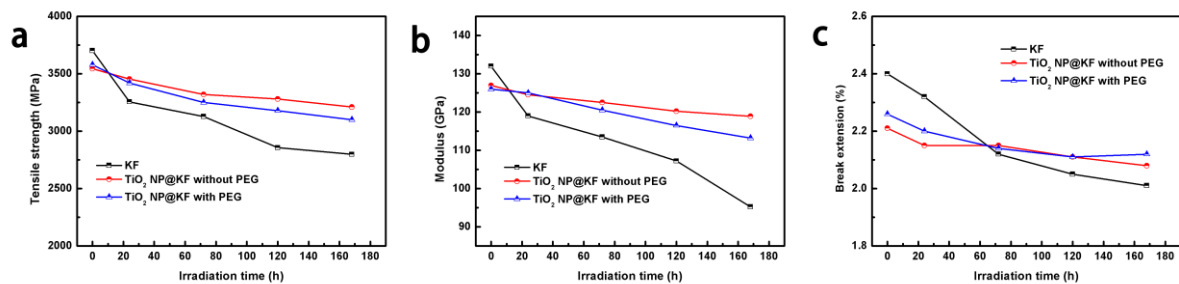


Figure 6. Tensile properties of AF and TiO₂ NP-modified AF after UV irradiation

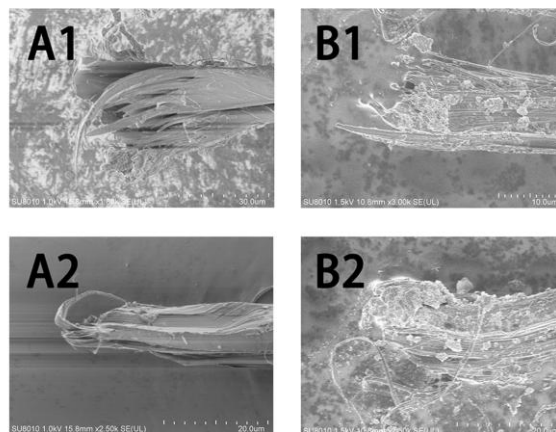


Figure 7. SEM images of tensile broken ends of AF (A) and TiO₂ NP-modified AF (B) before (1) and after (2) 168 h irradiation

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Figure 7 shows the fiber surface morphology before and after UV irradiation after the tensile tests. Before irradiation, both AF and TiO₂ NP-modified AF showed the typical break appearance of fibril splitting, although the fractured end of TiO₂ NP-modified AF still exhibited splitting after irradiation as compared to AF which turned brittle. This change in the breaking mode proves that the TiO₂ NP protection can maintain the inherent fracture behavior of AF, thereby reducing the damage from UV irradiation.

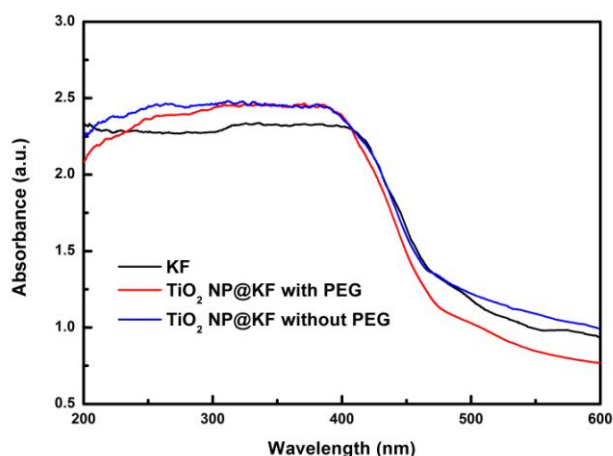


Figure 8. UV-Vis absorption spectra of AF and TiO₂ NP-modified AF

The UV-Vis absorption spectra (Figure 8) can help explain the reasons behind this protective behavior. TiO₂ NP-modified AF showed more intense absorption below 400 nm as compared to AF. This is produced by TiO₂ which can absorb UV light and convert it into harmless heat energy, thereby protecting the fibers from irradiation [16]. Additionally, the size of TiO₂ NP also affected the absorbance behavior (Figure 8), in agreement with previous studies stating that large TiO₂ NP promote light scattering phenomena [17]. According to the SEM analysis, the size of TiO₂ NP decreased after adding PEG this leading to increased light absorption. Hence, fibers containing larger size TiO₂ NP (i.e., TiO₂ NP-modified AF prepared without PEG) preserved their mechanical properties to a larger extent as a result of UV light scattering.

4. Conclusions

In summary, a developed low-temperature hydrothermal method was employed to grow TiO₂ NP on the AF surface. The prepared fibers simultaneously improved interfacial strength and UV resistance, both being considered as the two biggest shortcomings of AF. The IFSS was greatly improved (40–67%) after the TiO₂ NP growth. The increased interaction area and the reduced stress concentration were the main contributors for such an enhancement. In addition, a complete TiO₂ NP coating protected fibers from UV irradiation damage. Thus, TiO₂ NP-modified AF showed excellent mechanical properties (87.1–90.5% of the original tensile strength values) after 168 h of UV exposure. The TiO₂ NP size was controlled by adding PEG during the growth process. The TiO₂ NP size simultaneously affected the interfacial strength and the UV resistance properties, thereby suggesting that the practical application of the fiber materials can be improved by controlling the growth of TiO₂ NP.

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