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Titanium dioxide nanoparticles-coated aramid fiber showing enhanced interfacial strength and UV resistance properties

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ABSTRACT

Titanium dioxide nanoparticles (TiO_2 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-TiO_2 NP bonding strength. The structure, interface strength, and UV resistance properties of the resulting TiO_2 NP-modified fiber material were investigated. Anatase TiO_2 NP were uniformly grown on the fiber surface while controlling the TiO_2 particle size upon addition of polyethylene glycol (PEG). The growth of TiO_2 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 TiO_2 NP interphase while essentially maintaining the basic strength of the fiber material. Unlike other TiO_2-coating methodologies such as sol-gel and sizing, the herein developed process, leading to complete anatase TiO_2 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 these two critical shortcomings of AF. In this sense, a large number of strategies such as chemical etching [6], chemical grafting [7], and physical irradiation [8] have been developed with the aim to improve the interfacial characteristics of the composite materials. However, chemical etching and physical irradiation typically involve either high energy/temperature or high corrosive treatments. These harsh treatments significantly degrade the mechanical properties of the fiber material thereby resulting in a composite with reduced in-plane properties [9]. Chemical grafting is considered as a time-consuming and expensive technique. Additionally, grafting specific chemical groups on the surface of the fiber material is not feasible for all the types of matrixes employed [10]. Alternatively, the growth of a nanostructured material on the fiber surface is a promising method that fulfills the applicability requirements of the matrix. In this sense, carbon nanotubes were directly deposited onto carbon fibers through chemical vapor deposition to increase the fiber surface area [11], although the high temperatures required for the deposition process hinder the application of this methodology in organic fibers.

The utilization of an UV-absorber protective component is a common approach for improving the UV resistance of a material. In this sense, cost-effective TiO_2, with its 3.2 eV electronic band gap, is sensitive to the UV radiation (wavelengths below ca. 380 nm), and has been previously used as a photo-stabilizer for polymers being exposed to UV lights [12]. However, the current approaches used to directly deposit a protective coating of TiO_2 on the AF surface have not been successful, and the resulting AF materials showed poor properties (e.g., usage temperature limited to 180 °C and low corrosion resistance against hydrochloric acid). Two kinds of methodologies have been employed so far to protect fiber from UV irradiation via TiO_2 deposition. First, a sol-gel method has been employed to deposit the TiO_2 material, but the low temperatures used led to TiO_2 particles showing low cristallinity and thereby poor UV resistance (i.e., 37% of the original tensile strength after 168 h of UV irradiation exposure) [13]. The second approach

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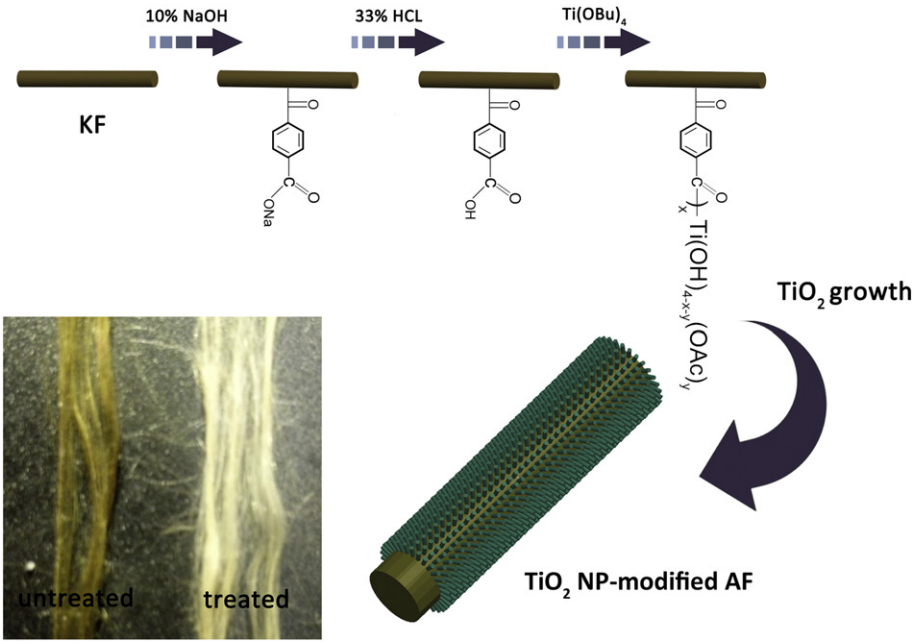

Fig. 1. The preparation procedure of TiO_2 NP-modified AF.

involves a protective sizing of nanoparticle-containing UV absorber material such as TiO_2 [14], ZnO [15], and $Ce_{0.8}Ca_{0.2}O_{1.8}$ [16]. This methodology was effective in retarding UV aging as the corresponding fibers showed good retention values. However, this preparation methodology involves multiple steps and leads to fibers maintaining smooth morphologies and lack of covalent bonds, both of them indicatives of a poor interfacial adhesion [17].

According to previous reports, these two critical shortcomings of AF have not been desirably solved and thereby more efforts are needed in this sense. Herein, a low-temperature method to grow TiO_2 nanoparticles (TiO_2 NP) on AF was proposed with the aim to prepare new AF materials with enhanced interfacial performance and UV resistance characteristics. Prior to the TiO_2 NP growth, a functionalization process was employed to improve the bonding between AF and TiO_2 NP. A hydrothermal process using tetrabutyl titanate and acetic acid was conducted at low temperature (120 °C) with the aim to preserve the tensile properties of the fiber. The morphology, structure, and properties of both AF and TiO_2 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.

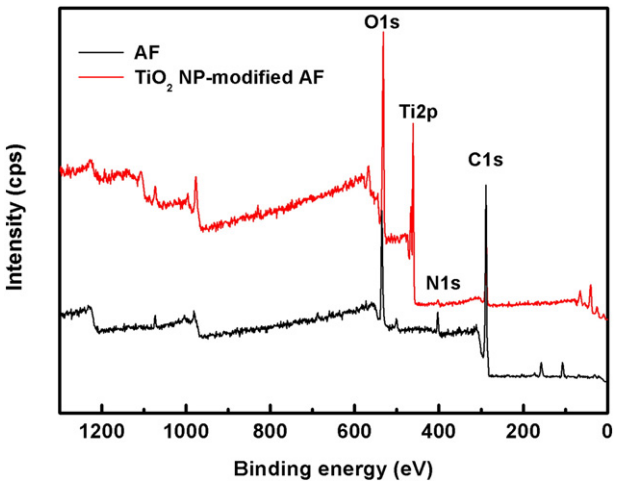

Fig. 2. Wide XPS spectra of AF and TiO_2 NP-modified AF.

2. Experiment

2.1. Preparation

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. The preparation procedure is shown in Fig. 1. Before the TiO_2 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 [18]. The *as*-obtained fiber (i.e., functionalized fiber) was dried at 100 °C for 60 min before the TiO_2 deposition process. TiO_2 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 TiO_2 NP. The mixture containing the fiber and the growth solution was subsequently introduced into a sealed Teflon reactor (50 mL) and

Table 1
Chemical compositions on the surface of fibers.

Sample	Chemical composition (%)			
	C1s	O1s	N1s	Ti2p
AF	70.3	17.52	5.64	–
TiO_2 NP-modified AF	36.63	43.74	–	19.63