Influence of aramid fiber treatment and carbon nanotubes on the interfacial strength of polypropylene hierarchical composites

P.I. Gonzalez-Chi [a], O. Rodríguez-Uicab [a], C. Martin-Barrera [a], J. Uribe-Calderon [a, *], G. Canché-Escamilla [a], M. Yazdani-Pedram [b], A. May-Pat [a], F. Avilés [a]

[a] Centro de Investigación Científica de Yucatán A.C., Unidad de Materiales, Calle 43 No.130 x 32 y 34, Col. Chuburna de Hidalgo, C.P. 97205, Mérida, Yucatán, Mexico
[b] Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, S. Livingstone 1007, Independencia, Santiago, Chile

ABSTRACT

The microbond test was used to evaluate the interfacial shear strength (IFSS) of multiscale composites based on a polypropylene (PP) matrix reinforced with aramid fibers (AFs) chemically treated by two methods and coated with multiwall carbon nanotubes (MWCNTs). AFs were treated by two types of acid solutions and coated with oxidized MWCNTs. Scanning electron and atomic force microscopies were conducted to observe the failure modes and correlate the fiber roughness to the IFSS. While both acid treatments caused a small change in fiber roughness, MWCNT deposition largely increased the fiber roughness. The microbond test results indicate that the acid treated fibers exhibited slightly higher IFSS than the untreated fibers and such IFSS is even higher for AFs containing MWCNTs. For chemically treated fibers covered with MWCNTs, a rougher surface with matrix cohesive failure at the edge of the sheared droplet suggests that the IFSS improvement is mainly due to the physicochemical interactions among AF, MWCNT and PP, in addition to mechanical interlocking.

© 2017 Published by Elsevier Ltd.

1. Introduction

Multiscale hierarchical composites are a new generation of composite materials comprising a nanometric filler, a micrometric reinforcement (typically a fiber) and a macroscopic matrix consolidating the material [1–3]. Although the nanometric filler may play a variety of roles, it typically enhances a specific property and/or adds multifunctionality to the composite [4–7]. If the filler is electrically conductive, as for the case of carbon nanotubes (CNTs), the resulting multiscale hierarchical composite may have added capabilities such as electromagnetic shielding and self-sensing of strain and damage [8–13]. Several recent works have used the approach of depositing CNTs onto the surface of engineering fibers to manufacture this kind of electro-conductive multiscale composites. Since in this architecture the CNTs are located at the fiber/matrix interface, it has been shown that the interfacial shear strength (IFSS) of the composite is increased by the presence of CNTs, mainly due to increased mechanical interlocking [14–17]. For

example, LaBarre et al. [17] deposited multiwall carbon nanotubes (MWCNTs) over Kevlar fibers assisted by N-methylpyrrolidone and found increased pull-out friction for such Kevlar fabrics. However, it is generally accepted that the interfacial strength of a composite has mechanical and chemical components, and the role of the chemical component in multiscale hierarchical composites has been scarcely investigated. Furthermore, the large majority of research works reported to date on multiscale hierarchical composites using CNTs deal with either glass or carbon fibers and a thermosetting polymer [15,18–24], and the use of aramid fibers and thermoplastic polymers have been significantly less investigated [16,25,26]. Aramid fiber (AF)/polypropylene (PP) composites are well known for their high toughness, which makes them especially suitable for impact loading scenarios [27]. However, the IFSS of AF/PP composites is frequently weak, and chemical treatments to the AF have been attempted to address this issue. Among the fiber chemical modifications reported in the literature to improve the adhesion between AFs and different polymer matrices are the treatments based on acids, chlorides, fluorinations and plasma treatments [28–31], where the selection of a specific treatment depends strongly on the polymer matrix to be used. For the most common case of epoxy matrices, amine and oxygen plasma treatments [32], as well as

* Corresponding author.
  E-mail address: jorge.uribe@cicy.mx (J. Uribe-Calderon).

treatments with phosphoric acids [33] and chlorides [29] have been reported. The use of methacryloyl chloride in wet surface treatments has been reported to improve the compatibility with polymer matrices such as epoxy [29], unsaturated polyesters [34] and polyethylene [28]. Significantly less work has been reported for the AF/PP material system, where fluorination seems to be the major surface treatment attempted to date for this material system [25]. Kevlar has been used to coat CNTs [35], but this procedure is challenging and does not benefit from the mechanical properties of aramid fibers for composites. Very few research efforts have been conducted to modify aramid fibers [25,28] to further include these CNT-modified AFs into advanced polymer composites. Advanced composites subjected to important mechanical loadings need to include a continuous fiber such as the aramid one, and the presence of carbon nanotubes at their interface may not only improve their IFSS, but also allows structural health monitoring through their electrical conductivity. Therefore, in the present research work, the microbond test was used to examine the interfacial shear strength of AF/MWCNT/PP multiscale composites prepared with AF fibers chemically treated by two methods and coated with MWCNTs. Scanning electron microscopy (SEM), and atomic force microscopy (AFM) are also conducted to correlate the fiber roughness to the measured IFSS of the composite. The fiber surface treatments and the presence of CNTs at the interface modify the interfacial properties of the composites, and the main aim of this work is to evaluate their effect and investigated the chemical and mechanical contributions.

2. Experimental

2.1. Materials

The Twaron Aramid fibers (TF) used were provided by Teijin Aramid Inc. (Emmen, The Netherlands). According to the manufacturer, the fiber elastic modulus ranges from 130 to 180 GPa, the density is 1.45 g/cm^3 and the diameter of a single filament is ~12 μm. The Twaron yarn is composed of approximately 1000 individual filaments. Commercial MWCNTs (Cheaptubes Inc., Vermont, USA) with a length ranging from 1 to 6 μm, internal diameter 5—15 nm and the external diameter 30—50 nm were used.

2.2. Surface treatments

2.2.1. MWCNT oxidation

MWCNTs were chemically oxidized with a 3.0 M solution of an equimolar mixture of nitric and sulfuric acids following the procedure reported in the literature [36]. Briefly, 0.3 g of MWCNTs were mechanically stirred with 70 mL acid solution in a hot plate for 15 min at ~60 °C. The dispersion was sonicated in an ultrasonic bath (70 W, 42 kHz) for 2 h, and then filtered and thoroughly washed with distilled water. Finally, the slurry was dried in a convection oven at 100 °C during 24 h.

2.2.2. Fiber surface treatments

Prior to TF surface modifications, the commercial fiber surface coating (sizing) was removed by a sequential Soxhlet extraction with chloroform, ethanol, acetone, and methanol, as reported elsewhere [37]. The extraction time was 6 h for each solvent followed by overnight drying at 70 °C in a convection oven. Two chemical treatments were carried out on the TF after sizing removal, one (aggressive) based on a mixture of nitric and sulfuric acids, and a (milder) second one based on a solution of chlorosulfonic acid in dichloromethane, as described elsewhere [38]. The first treatment was performed by immersing the TF yarn free of sizing in 490 mL of a 3.0 M mixture of HNO_3 and H_2SO_4 for 1 h. Then, the

fibers were washed with 1.5 L of distilled water. For the second treatment, the TFs (free of sizing) were treated with 500 mL of a solution of chlorosulfonic acid in dichloromethane (0.2% w/w) at room temperature for 2 min; then, the TFs were soaked in distilled water for 2 min and finally dried for 1 h at 70 °C. This treatment is expected to generate sulfonic groups (SO_3H) at the fiber surface [38]. The nomenclature used to identify the fibers and their chemical treatments are listed in Table 1.

2.2.3. Surface coating of aramid fibers with carbon nanotubes

As-received and chemically treated aramid fibers were covered with MWCNTs by a immersion coating method assisted by ultrasound, as described elsewhere [38]. Briefly, 4 mg of previously oxidized MWCNTs were deposited onto ~550 mg aramid fibers rolled on a cylindrical frame and immersed into 100 mL of chloroform. The MWCNT deposition onto aramid fibers was conducted by using an ultrasonic horn for 1 h at 165 W and 20 kHz, drying the fibers in a convection oven.

2.3. Fiber roughness and microscopy analysis

The surface topography of the fibers was observed by tapping-mode AFM. Tapping mode, oscillating the tip near its resonance frequency, was preferred for keeping the probe tip close enough to the sample while preventing it from sticking to the surface. The AFM images were recorded with a Bruker SPM8 AFM scanning probe microscope in air at room temperature at a resonant frequency of 320 kHz. Commercially available silicon cantilevers were used (TESP-SS nanoprobe, Bruker) with a cantilever spring constant of 42 N/m, a tip cone angle of 10° and tip radius of about 2 nm, using a scanning frequency of 1 Hz. AFM analysis was conducted over 3 μm by 3 μm sampled areas on the fiber surface. A statistical analysis of 2.5 μm by 2.5 μm central sections of the AFM sampled areas was then carried out. To this aim, the 2.5 μm × 2.5 μm area was divided into 25 sub-areas of 500 nm × 500 nm and the root mean square (RMS) roughness of each sub-area was measured with the Bruker "NanoScope" analysis software. The average and coefficient of variation (CV) of the 40 data were calculated using the RMS roughness of each sub-area as a central metric. For SEM analysis, the AFs were gold-coated and observed using a JEOL JSM-630-LV SEM operated at 20—25 kV.

2.4. Microbond test

Specimens for microbond test consisted of six groups of individual Twaron fibers (as listed in Table 1) containing a PP microdroplet. To this aim, PP powder was previously sieved by using a Tyler # 100 mesh and sprinkled onto the fibers, held by a 15 cm × 8 cm metallic frame. The frame was then heated to 190 °C for 1 h in a vacuum oven (Precision Scientific) to melt the PP powder. Then, the frame was taken off the oven to cool it down to room temperature. Each microdroplet was observed in an optical microscope (Leica DMLM) using transmitted light, 20× objective lens. A picture was captured for each microdroplet, and the

Table 1
Nomenclature of the Twaron fibers and their treatments.

Fiber	Treatment
TF	As-received (untreated) TF.
TFAC	TF modified with 3.0 M mixture of HNO_3 and H_2SO_4.
TFCL	TF modified with chlorosulfonic acid.
TF-MWCNT	As-received TF coated with oxidized MWCNTs.
TFAC-MWCNT	TFAC coated with oxidized MWCNTs.
TFCL-MWCNT	TFCL coated with oxidized MWCNTs.