Composites Part A 110 (2018) 53–61

Contents lists available at ScienceDirect

Composites Part A

journal homepage: www.elsevier.com/locate/compositesa

# Silica nanoparticle-decorated alumina rough platelets for effective reinforcement of epoxy and hierarchical carbon fiber/epoxy composites

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ARTICLE INFO

*Keywords:*
A. Carbon fibers
A. Laminates
B. Mechanical properties

ABSTRACT

Alumina platelets, ~200 nm in thickness, have been previously used as the filler of polymers, especially for bio-inspired nacre-like composites. However, to the best of our knowledge, they have not been applied to hierarchical carbon fiber/epoxy composites. Herein, the effect of smooth alumina platelets and silica nanoparticle-decorated platelets with nanoasperities on the mechanical properties of epoxy resin and hierarchical composites were investigated. The rough platelets are much more effective than the smooth ones for the reinforcement, because of the greatly improved matrix-filler interactions. The increases of mechanically properties by the submicrometer-thick rough platelets are comparative with or even better than those by carbon nanotubes, nanofibers and graphene derivatives previously reported. The increase of the total energy dissipated during flexural fracture of the hierarchical composites and Mode II interlaminar fracture toughness are also more significant than the smooth platelets. This study provides a new approach for the reinforcement of hierarchical composites.

## 1. Introduction

Carbon fiber reinforced polymer (CFRP) composites comprising epoxy as the matrices and continuous carbon fibers (CFs) as the reinforcing agent have wide range of applications in aerospace structures, ground vehicles and sports utilities [1–3]. In recent years, multi-scale or hierarchical CFRP composites containing both continuous CFs in micrometer scale as the primary reinforcement and some nanofillers or submicrometer- sized fillers as the secondary reinforcement with improved mechanical properties, especially the out-of-plane properties, have become a new generation of CFRP composites. Carbon materials, such as graphene oxide (GO) and its derivatives [4–12], carbon nanotubes (CNTs) [13–28], submicrometer vapor grown carbon fibers (VGCFs) [28,29] have been used as the secondary reinforcement of both neat epoxy resin and CF/epoxy resin (CF/EP) composites. Reduced graphene oxide (GO) is one of the most effective reinforcing agents for epoxy resins and CF/EP composites. For example, addition of only 0.2 wt% of reduced GO to epoxy remarkably improves the flexural strength of CF/EP composites by 32% [6]. CNTs [13–28] and VGCFs [28,29] can also improve the mechanical properties of CFRPs to different extent.

Alumina ($Al_2O_3$) platelets are submicrometer-thick platelets with a flexural strength as high as 5.3 ± 1.3 GPa [30], which have been used as the fillers of polymer materials to improve the rigidity, strength and toughnessand thermal conductivity [31,32]. Biological materials such as bone and nacres are platelet-reinforced materials exhibiting unique structure and mechanical properties, especially high toughness, which have motivated the development of artificial composites exhibiting new, unusual mechanical behavior. Therefore, $Al_2O_3$ platelets have been used as the building block for artificial nacres. Layer-by-layer assembly [33], filtration and combination of gel-casting and hot pressing [34] have been used to fabricate bio-inspired composites containing $Al_2O_3$ platelets. It was reported that addition of 15 vol% of $Al_2O_3$ platelets in chitosan increases the tensile strength to 315 MPa, almost 6 times higher than neat chitosan [35]. Bioinspired hierarchical $Al_2O_3$-GO-poly(vinyl alcohol) artificial nacre with optimized strength and toughness was also reported [36]. At the volume fraction of 10 vol %, $Al_2O_3$ platelets modified with a silane coupling agent increase the elastic modulus, tensile strength and fracture toughness of epoxy by 84%, 12% and 130%, respectively. [37] Libanori et al. [38] reported that combined magnetic and mechanical stimuli lead to high alignment degree of $Al_2O_3$ platelets (27 vol%,) and increase the compression yield strength of epoxy resin by 30%. The same research group also prepared rough platelets by sintering $Al_2O_3$ platelets with silica nanoparticles at 1050 °C. By combining silica nanoparticles of two different sizes in the hierarchical platelets, the stiffness and strength of the composites were improved, while the high ultimate strain and toughness were maintained. Moreover, at a volume fraction of 15%, the highly roughed and aligned platelets increase the toughness and the flexural strength of epoxy by 110% and about 57%, respectively [39]. Although $Al_2O_3$

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https://doi.org/10.1016/j.compositesa.2018.04.017
Received 6 February 2018; Received in revised form 24 March 2018; Accepted 16 April 2018
Available online 17 April 2018

platelets have been successfully used to construct bio-inspired composites with greatly improved strength and toughness, and the preparation and surface modification of $Al_2O_3$ platelets are much simpler than those of CNTs, VGCFs and GO derivatives, to the best of our knowledge, they have not been used as the secondary reinforcing agent for CF/EP hierarchical composites.

In this work, $Al_2O_3$ platelets were prepared by the molten-salt growth method with an aspect ratio (diameter against thickness) above 30. The $Al_2O_3$ platelets were modified with a silane coupling agent 3-aminopropyltriethoxysilane (APTES) and then used as the reinforcing agent of epoxy resin and hierarchical CF/EP composites. The $Al_2O_3$ platelets were also decorated with $SiO_2$ nanoparticles by simple sol–gel process under room temperature to prepare rough $SiO_2$-decorated $Al_2O_3$ ($SiO_2$-$Al_2O_3$) platelets, which were further modified with APTES to obtain silanized $SiO_2$-$Al_2O_3$ (s$SiO_2$-$Al_2O_3$) and then used as the reinforcing agent of epoxy resin and hierarchical CF/EP composites. The purpose of decorating $Al_2O_3$ platelets with $SiO_2$ nanoparticles and silanization is to create rough interfaces and improve the interfacial interaction between the platelets and epoxy matrices. The thermodynamic properties, mechanically properties of s$SiO_2$-$Al_2O_3$/epoxy composites and hierarchical s$SiO_2$-$Al_2O_3$/CF/EP composites were investigated. Significant improvement of the storage modulus and flexural properties were observed for the s$SiO_2$-$Al_2O_3$/epoxy composites. For the s$SiO_2$-$Al_2O_3$/CF/EP hierarchical composites, flexural properties and ILSS were significantly improved. In contrast, the smooth silanized $Al_2O_3$ platelets (s$Al_2O_3$) without $SiO_2$ decoration are less effective for the improvement of mechanical properties of epoxy resin and the s$Al_2O_3$/CF/EP hierarchical composites.

## 2. Experimental

### 2.1. Materials

Epoxy resin triglycidyl para-aminophenol (TGPAP) was purchased from Shanghai Research Institute of Synthetic Resins (China). 3,5-dimethylthio-2,4-toluenediamine (DMTDA), used as a curing agent, was supplied by Tianjin Zhongxin Chemtech Co., Ltd. (China). Silane coupling agent APTES was supplied by Sinopharm Chemical Reagent Co., Ltd. $Al_2(SO_4)_3$, $Na_2SO_4$, $K_2SO_4$, $Na_2CO_3$, tetraethyl orthosilicate (TEOS) and other chemicals were of reagent grade and purchased from Shanghai Chemical Reagents Company, China. Unidirectionally aligned CF fabrics (T700-12K) were purchased from Toray (Japan).

### 2.2. Preparation of $Al_2O_3$ platelets

$Al_2O_3$ platelets were prepared by previously reported molten salt method with certain modifications [40]. $Al_2(SO_4)_3$ (Al source), $Na_2SO_4$ and $K_2SO_4$ (molten salt), at the mole ratio 1:1.6:2.4, were dissolved in deionized water. $TiCl_3$ and TEOS were used as the additives to control the size of $Al_2O_3$ platelets. $Na_2CO_3$ solution was then added drop by drop until a gel is obtained. After drying and grinding, the gel was heat-treated at 1200 °C for 5 h. The product was washed with water, HCl solution and NaOH solution, and then dried to obtain the $Al_2O_3$ platelets. The final weight ratio for $Al_2(SO4)_3$, $Na_2SO_4$, $K_2SO_4$, $TiCl_3$ and TEOS was 79.9:40.9:33.4:1.6:0.4.

### 2.3. Preparation of $SiO_2$-$Al_2O_3$ and s$SiO_2$-$Al_2O_3$ platelets

The rough $SiO_2$-$Al_2O_3$ platelets were prepared by the well-known Stöber method with some modifications [41–43] in the existence of $Al_2O_3$ platelets. 3 g of the $Al_2O_3$ platelets were dispersed in a mixture of 300 mL of alcohol and 90 mL of water, and sonicated for 10 min. 75 mL of $NH_3{\cdot}H_2O$ and 6 g of TEOS were then added. After mechanical stirring of 12 h and washing with alcohol, $SiO_2$-$Al_2O_3$ platelets were obtained. The $SiO_2$-$Al_2O_3$ platelets were further modified with APTES to obtain the s$SiO_2$-$Al_2O_3$ platelets. After 3 g of $SiO_2$-$Al_2O_3$ and 250 mL of ethanol were sonicated for 30 min in a three-necked flask, the mixture of APTES (3g), ethanol (13.5 mL) and $H_2O$ (1.2 mL) was added. The silanization was conducted under 80 °C for 6 h. The rough s$SiO_2$-$Al_2O_3$ platelets were used to fabricate the s$SiO_2$-$Al_2O_3$/EP composites and hierarchical s$SiO_2$-$Al_2O_3$/CF/EP composites. The $Al_2O_3$ platelets without $SiO_2$ decoration were also silanized with APTES to prepare the s$Al_2O_3$/EP composites and hierarchical s$Al_2O_3$/CF/EP composites for comparison.

### 2.4. Preparation of s$SiO_2$-$Al_2O_3$/EP composites

The s$SiO_2$-$Al_2O_3$ platelets were dispersed in TGPAP at the mass ratio of 1:10 by three roll milling. In order to prepare the s$SiO_2$-$Al_2O_3$/EP composites with various s$SiO_2$-$Al_2O_3$ contents, the s$SiO_2$-$Al_2O_3$/TGPAP mixture was further diluted with various amounts of TGPAP and the curing agent DMTDA. The mass ratio of TGPAP versus DMTDA in the final mixtures was set at 2:1. The s$SiO_2$-$Al_2O_3$ contents in the epoxy resin varied between 1 and 6 wt%. After being sufficiently degassed in a vacuum oven at 120 °C and at 10 kPa for 15 min, the mixtures were then poured into a steel mold preheated to 110 °C. The mixtures were pre-cured at 120 °C for 0.5 h, 150 °C for 0.5 h, cured at 170 °C for 2.5 h and then post-cured at 200 °C for 0.5 h. The s$Al_2O_3$/EP composites were fabricated under the same conditions.

### 2.5. Preparation of the hierarchical CF/EP composites

The hierarchical s$SiO_2$-$Al_2O_3$/CF/EP composites were fabricated by hot pressing. Unidirectional carbon fiber fabrics (10 cm × 15 cm) were dried in a vacuum oven at 80 °C for 2 h. Subsequently, the TGPAP/DMTDA mixture and those containing various amounts of s$SiO_2$-$Al_2O_3$ platelets (2, 4, and 6 wt%) were coated onto the both sides of the CF fabrics to obtain CF prepregs. Ten layers of the prepreg sheets were then stacked with the same orientation and degassed sufficiently in a vacuum oven at 120 °C and 10 kPa for 15 min before being laminated by hot pressing and cured under the same curing conditions for the preparation of the s$SiO_2$-$Al_2O_3$/EP composites. The pressure for the hot pressing was 2 MPa and maintained throughout the curing reaction. The s$Al_2O_3$/CF/EP hierarchical composites were also fabricated under the same conditions. The volume fraction of carbon fibers is measured to be about 67.5% for all the hierarchical composites.

### 2.6. Characterization

Thermogravimetric (TG) analysis was performed on a SDT Q600 TG analyzer (TA instrument, USA) under nitrogen atmosphere. A Hitachi S-4800 (Hitachi, Japan) scanning electron microscope (SEM) was employed to observe the size and morphology of the platelets, and the morphologies of the fracture surfaces of the s$SiO_2$-$Al_2O_3$/EP composites and hierarchical s$SiO_2$-$Al_2O_3$/CF/EP composites. Dynamic mechanical analyzer (DMA Q800, TA Instruments, U.S.A.) was used to analyze the thermo-mechanical properties in a three-point-bending mode from 30 to 250 °C at a frequency of 1 Hz and a constant heating rate of 3 °C/min. The size of specimens for the DMA measurements was 35 × 10 × 2 $mm^3$. The flexural properties and ILSS were measured at room temperature using an electrical universal material testing machine (RG-3010, Shenzhen Reger Instrument Co. Ltd., China) following ASTM D790 and ASTM D2344, respectively. In the flexural tests, rectangular specimens were loaded with a span of 32 mm at a crosshead speed of 2.0 mm/min for the s$SiO_2$-$Al_2O_3$/EP composites and a span of 64 mm at a crosshead speed of 2.0 mm/min for the hierarchical CF/EP composites. The size of the specimens used in the flexural test was 50 × 10 × 2 $mm^3$ for the s$SiO_2$-$Al_2O_3$/EP composites and 80 × 15 × 2 $mm^3$ for the hierarchical CF/EP composites. In the ILSS short-beam shear tests of the hierarchical CF/EP composites, the span length was 8 mm and the crosshead velocity was 1.0 mm/min. Rectangular specimens with dimensions of 80 × 20 × 2 $mm^3$ were used for the ILSS tests and at least six specimens were used for all the mechanical property