Composites Science and Technology 98 (2014) 15–21

Contents lists available at ScienceDirect

Composites Science and Technology

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

Synergistic effect of exfoliated graphite nanoplatelets and short glass fiber on the mechanical and interfacial properties of epoxy composites

Diego Pedrazzoli [a,b], Alessandro Pegoretti [a], Kyriaki Kalaitzidou [b,c,*]

[a] Department of Industrial Engineering and INSTM Research Unit, University of Trento, Trento 38123, Italy
[b] G.W. Woodruff School of Mechanical Engineering – Georgia Institute of Technology, Atlanta, GA 30336, USA
[c] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30322, USA

ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form 26 March 2014
Accepted 22 April 2014
Available online 2 May 2014

Keywords:
A. Short-fiber composites
B. Interfacial strength
B. Debonding
D. Dynamic mechanical thermal analysis (DMA)
D. Rheology

ABSTRACT

In this study, the properties of hybrid composites made by epoxy reinforced with short glass fibers (GF) and exfoliated graphite nanoplatelets (GNP) were determined as a function of the GF loading. The addition of GNP, either within the matrix or at the GF surface (GFc), promoted the formation of a stronger GF–epoxy interface, as evaluated by the single-fiber microdebonding test, resulting in an increase of the interfacial shear strength by ~60% exhibited by the hybrid epoxy composite reinforced with 5 wt% GNP. Quasi-static tensile tests and impact tests were performed in order to explore how the combined effect of the nano- and micro- size reinforcements affected the macroscopic mechanical properties under low and high strain rates. The improved tensile modulus, ultimate tensile strength and impact resistance exhibited by the hybrid composites revealed that it is possible to introduce the nano-materials at the fiber/matrix interface and significantly improve the interfacial properties, leading to lighter and stronger composites. Furthermore, the storage modulus and the viscoelastic behavior of GF/epoxy composites were remarkably enhanced upon addition of GNP, indicating strong GNP–polymer interactions and immobilization of the polymer chains. In conclusion, the combined effect of nano-materials and micro-size reinforcements can be exploited to produce light-weight hybrid composites with enhanced mechanical properties.

1. Introduction

Due to their low density and good adhesive and mechanical properties, epoxy resins are the most commonly used polymers for structural composites. As reported, the introduction of small amounts of nanomaterials (<10 wt%) in epoxy resins can remarkably increase their mechanical properties and thermal stability [1], dramatically enhance the electrical [2,3] and thermal [4,5] conductivity of the resulting composites and play a beneficial role on the interfacial properties of structural composites [6]. Addition of more than 10 wt% nanomaterials in polymers frequently leads to poor dispersion, difficult processability [7], and increased cost and density of the composite.

Short glass fiber reinforced polymers with 30–50 wt% fiber loading are commonly used as light-weight structural components due to their higher specific mechanical properties, superior corrosion resistance and improved fatigue resistance with respect to conventional engineering materials. Because short-fiber reinforced composites are less resistant to mechanical load and fatigue damage than the corresponding continuous-fiber-reinforced composites, it is of great interest to explore whether combining two fillers of rather different size scales (i.e. micro- and nano-scale) would give the desired performance at low to intermediate filler loadings [8–10].

Therefore, the aim of this study is to investigate how the morphology and the mechanical properties of short glass fiber reinforced epoxy composites are affected by the presence of a carbonaceous nanofiller namely, graphite nanoplatelets (GNP). There are only very few studies reporting the effect of nanomaterials on the interfacial adhesion of fiber reinforced epoxy composites [6,11,12]. In this research, the mechanical behavior of hybrid epoxy composites was studied in order to determine the role of the fiber–matrix adhesion on the quasi-static, viscoelastic and impact properties of the resulting materials. The investigation of the interfacial strength, in order to characterize the adhesion between matrix and fibers, was carried out by microdebonding tests.

* Corresponding author at: G.W. Woodruff School of Mechanical Engineering – Georgia Institute of Technology, Atlanta, GA 30336, USA. Tel.: +1 404 385 3446; fax: +1 404 894 9342.
E-mail address: kyriaki.kalaitzidou@me.gatech.edu (K. Kalaitzidou).

http://dx.doi.org/10.1016/j.compscitech.2014.04.019
0266-3538/

2. Experimental section

2.1. Materials and fabrication of composites

A bicomponent epoxy resin, supplied by US Composites (West Palm Beach, FL), was used as matrix. The epoxy resin consisted of a mixture of 635 thin epoxy and a 556 slow aminic hardener at a weight ratio of 2:1. This specific epoxy resin is typically used in engineering applications for the large-scale production of composites components by sheet molding compound (SMC) used in the automotive industry. Exfoliated graphite nanoplatelets, xGnP®-M5 purchased by XG Sciences Inc., with an average diameter of ~5 μm and thickness in the range of 10–20 nm were used. E-glass fibers, with the trade name RO99 P319 supplied by Saint-GobainVetrotex were used as-received. These GF are indicated as treated with a silane based coupling agent. Chopped strand glass fibers (single fiber diameter = 15.3 ± 1.5 μm, average length = 6.50 ± 0.44 mm) were obtained by chopping long glass fibers using a chopper gun CDA-08 provided by GlasCraft.

GNP-coated glass fibers were prepared by sonication of xGnP-M5 in isopropanol with a filler concentration of 5 mg/ml. Sonication was carried out using a Misonix S-4000-010 for 1 h (30% amplitude, 8 W power) equipped with a probe of 12.5 mm diameter. After adding the GF to the solution, the sonication was continued for ½ h. Coated glass fibers were finally rinsed in isopropanol and dried at ambient temperature overnight. The GNP content added onto the GF surfaces, as measured by weighting the GF before and after the sonication and assuming homogeneous distribution of the graphite nanoplatelets on the fiber surfaces, was ~0.10–0.15 wt% with respect to the composite's weight. Specifically, the GF were weighted after complete solvent evaporation occurred under hood overnight. Glass fiber surfaces appear partially coated by graphite platelets, as observed by optical microscopy in Fig. 1 (Leica DMRM, Buffalo Grove, IL, USA). In particular, GNP are supposed to deposit onto the surfaces of GF by establishing weak interactions during sonication. The authors believe that no chemical bond is formed between graphite and GF, while physical adsorption and mechanical interlocking might occur.

The composites were made as follows: first the GNP were dispersed in isopropanol by sonication using the same conditions as mentioned above. Once the isopropanol was filtered away the GNP powder was mixed with the epoxy at 800 rpm and $T = 60$ °C for 40 min using a magnetic stirring plate. The GF were then added to the solution and stirring was continued for 20 min followed by addition of the curing agent and subsequent stirring at 800 rpm for 30 min. The mixture was degassed in a vacuum oven and cured in a mold at $T = 80$ °C for 1 h, followed by post-curing at $T = 100$ °C for 4 h. Post-curing as an accelerated thermal treatment was carried out according to the protocol provided by the epoxy supplier. Composites are designated by the amount and type of the filler, for example the composite containing 5 wt% of xGnP-M5 and 10 wt% GF is indicated as 5GNP/10GF/epoxy. Coated GF were indicated as GFc.

2.2. Experimental techniques

The effect of the GNP on the fiber–matrix adhesion, was investigated through microdebonding tests on specimens consisting of an epoxy microdrop deposited onto a single fiber filament supported on a paper tab. Epoxy microdrops were distributed symmetrically around the filament while observing under an optical microscope. The drops were cured for 1 h at 80 °C followed by 4 h at 100 °C. Prior to testing, the samples were examined using an optical microscope (Leica DMRM, Buffalo Grove, IL, USA) in order to determine the fiber diameter (d), embedded fiber length (L), and the maximum droplet diameter (D), as indicated in Fig. 2a. Microdebonding tests were conducted at a crosshead speed of 1 mm/min by an Instron 33R 4466 tensile tester equipped with a 500 N load cell. During testing the paper tab attached to one end of the glass fiber was slowly pulled up, while the droplet was constrained by a shearing plate, fixed on a stationary support as shown in Fig. 2(b). The interfacial shear strength (ISS) was computed by Eq. (1):

$$\mathrm{ISS} = \frac{F_c}{\pi d L} \tag{1}$$

where F_c is the critical applied load, recorded during the test, at which the fiber–matrix interface fails. Each value of interfacial shear strength is an average of at least ten measurements. The single fiber specimens were observed by SEM before and after the test.

The fracture surface of the composites was studied using a Phenom G2 Pro (Phenom-World BV) scanning electron microscope (SEM), at an acceleration voltage of 5 kV. A thin gold coating was applied onto the surface by plasma sputtering to minimize the charging effects. The rheological behavior of the composites was analyzed by an ARES-G2 rheometer (TA Instruments) under controlled strain conditions using parallel plate geometry. The test specimens were disks with a diameter of 25 mm and 1.5 mm thickness. Isothermal frequency sweep tests, in the 0.1–200 rad/s range, were carried out below and above the glass transition temperature of the epoxy (T_g), at 25 and 100 °C, respectively (measured $T_g = 64.8$ °C). During the measurement, a small amplitude (10%) oscillatory shear strain, which was within the linear viscoelastic range, was applied to the samples. Each data point is an average of three measurements.

Tensile tests were performed according to ASTM D638 with an Instron model 33R 4466 tensile tester equipped with a 10 kN load cell at a crosshead speed of 5 mm/min. Each data point is an average of at least five measurements. Axial strain was recorded by using a resistance extensometer Instron® model 2630-101 with a gauge length of 10 mm. The elastic modulus was measured as a secant value between longitudinal deformations of 0.05% and 0.25%. Dynamic mechanical thermal analyses (DMTA) in tensile mode were carried out using a DMA Q800 (TA Instruments) over a temperature range of 20–160 °C, at a heating rate of 5 °C/min and a frequency of 1 Hz. A prestress of 0.2 MPa and a maximum strain of 0.05% were imposed on rectangular samples 25 mm long, 3.30 mm wide and 3.27 mm thick. Impact tests (Izod type) were

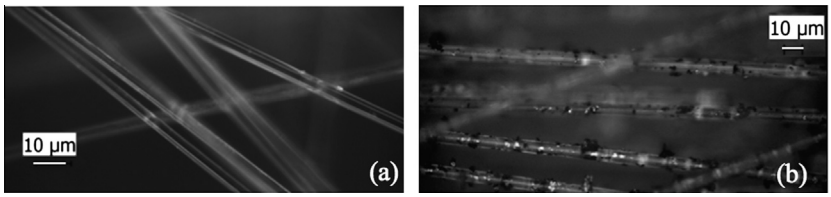

Fig. 1. Optical micrograph of (a) as-received GF and (b) GNP-coated GF.