



Multiscale graphene oxide–carbon fiber reinforcements for advanced polyurethane composites



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ABSTRACT

Multiscale graphene oxide/carbon fiber (GO/CF) reinforcements were developed for polyurethane (PU) elastomer composites. GO was first coated on CF surface by electrophoretic deposition (EPD), aiming to improve the CF/PU interfacial adhesion. The EPD process improved the mechanical anchoring and chemical interaction between CFs and PU through increased surface roughness and oxygen content of CFs, thereby improved the CF/PU interfacial shear strength. The fibers were then mechanically mixed with GO to achieve a multiscale reinforcement. The strengthening of the matrix, especially the local stiffening of fiber/matrix interphase, is beneficial for the interfacial mechanical anchoring. The multiscale reinforcement resulted in an improvement of 46.4% in the tensile strength of PU elastomer. Compared with untreated-CF/PU, individual process of EPD treatment and mechanical mixing of GO resulted in an improvement of 16.9% and 13.9% of the strength, respectively. The enhanced reinforcing performance of GO-deposited CFs was attributed to the improved fiber–matrix interfacial adhesion.

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1. Introduction

Carbon fiber reinforced polymer (CFRP) composites attracted both academic and industrial interest due to their unique attributes: light-weight and high-strength. CFRP materials are displacing traditional metallic materials in a wide range of high-performance structural applications, such as aerospace and automotive industries [1,2]. CF/epoxy resin as a common CFRP composite system appeared in most studies [3]. Rare attention was paid to polyurethane (PU), which represents one of the most rapidly developing branches in polymer industry [4]. PU elastomers, with distinguished elasticity, toughness and wear resistance, play an increasingly important role in the fields of structure and wear-resistant materials [4,5]. However, pure PU elastomers possess a low stiffness and poor heat-resistance, which severely limit their advanced applications [6]. CFs were proved to be effective fillers for improving the thermal and mechanical properties of PU materials [5–7].

It is generally accepted that mechanical properties of CFRP composites depend directly on the properties of their individual constituents as well as the interaction degree between the reinforcements and polymer matrix [8,9]. In structural or

functional composites based on a polymer matrix, mechanical damage in the polymer matrix or debonding at the matrix–filler interface is usually responsible for the decrease in intended properties [10]. A good fiber–matrix interface offers effective load transfer from the polymer to the reinforcement, which is essential to reduce the stress concentrations and improve the bulk mechanical performance [2]. However, the poor interfacial adhesion between CFs and PU, caused intrinsically by the chemically inert surface of CFs, limits the mechanical and thermal performance of PU composites.

Therefore, we present here the design of multiscale reinforcements for PU composites, which aims to improve simultaneously (i) the mechanical strength of PU matrix by dispersing nanofillers throughout the matrix and (ii) the fiber–matrix interfacial adhesion by modifying nanofillers onto primary reinforcing fibers.

Graphene oxide (GO) was selected as the nanofiller here due to its unique properties. Graphene, one-atom-thick two-dimensional planar sheet of sp^2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice, is regarded as “the thinnest material in the universe” and predicted to have a variety of unique properties, such as high thermal conductivity, extraordinary electronic transport property and superior mechanical properties [11,12]. These intrinsic properties make graphene promising for a wide range of frontier applications including thermally and electrically conducting nanocomposites, electronic circuits, sensors as well as

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transparent and flexible electrodes for displays and solar cells [12–15]. However, pristine graphene is usually incompatible with polymer matrix due to its chemical inertness. GO sheets are heavily oxygenated graphene which bears hydroxyl, epoxide, diols, ketones and carboxyl groups, thereby exhibiting better compatibility with polymer matrix [12]. Incorporation of nanofillers that are compatible with the polymer matrix could effectively improve the mechanical properties of CFRP composites [16–18].

Chemical grafting [19], electrophoretic deposition (EPD) [20–22] and nanocomposite sizing [23] have been reported to be effective techniques for attaching GO sheets onto CFs to obtain a hierarchical fibrous reinforcement. EPD represents an effective and versatile approach for the deposition of nanomaterials on CF surface. Moreover, online EPD process allows a continuous deposition which is compatible with CF production process. A subsequent thermal annealing process could afford a stable binding of GO on CF surface [20]. Recently, Huang et al. reported the deposition of GO thin film on CF surface by ultrasonically assisted EPD process. Such GO-deposited CFs exhibited a significant increase in surface roughness in comparison with the bare CFs, which leads to an improvement in the interfacial shear strength (IFSS) between CFs and resin matrix through enhanced mechanical interlocking [20]. Similarly, grafting CNTs onto fiber surface was also found to enhance the interfacial strength via increased chemical bonding, mechanical interlocking and/or local stiffening of the polymer chains at the fiber/matrix interface, all of which are beneficial to improve the stress transfer efficiency [24].

In this study, multiscale GO/CF reinforcements were developed for a simultaneous strengthening of the PU matrix as well as the CF/PU interface. GO sheets were first modified on CF surface by EPD. The fibers were then mixed with GO sheets in PU matrix. In the designed system, CFs serve as a structure reinforcement and GO sheets distribute uniformly to reinforce the PU matrix, thereby achieving a multiscale reinforcement. The effect of EPD treatment on the surface morphology and chemical composition of CFs, as well as the CF/PU interfacial shear strength were investigated. The performance of GO/CF multiscale reinforcements on the mechanical properties of PU elastomer was studied. To further investigate the respective contribution of EPD and mechanical mixing of GO to the final reinforcing performance of multiscale reinforcements, composites adopting individual EPD or mechanical mixing were prepared and their mechanical properties were compared. The reinforcing mechanism was explored based on the surface morphology, roughness, and chemical composition of CFs, the CF/PU interfacial shear strength, the mechanical properties of CF/PU composites, and the surface morphology of the fractured CF/PU specimens for mechanical test.

2. Experimental section

2.1. Materials

CFs used in this study were PAN-based epoxy resin-sized T300 (3000 single filaments per tow, nominal diameter is 7 μm , tensile strength is 3.53 GPa) supplied by Toray Industries, Inc. 3 mm short CFs were obtained by cutting continuous T300 CFs technically supported by Zhonglibangye Co. Ltd. China. Graphene oxide, prepared according to Ref. [25], was kindly supplied by Chengmeng Chen's group, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, China. 4,4'-diphenylmethane diisocyanate (WANNATE[®]-MDI-100, purity $\geq 99.6\%$, chromaticity (Pt-Co) ≤ 30 , hydrolyzed chlorine percent (%) ≤ 0.005 , cyclohexane insoluble (%) ≤ 0.3) was supplied by Wanhua Chemical Group Co. Ltd. China. Polyethylene propylene glycol adipate (ODX-218, $M_w = 2000$, hydroxyl value: 53.50–58.50, acid value ≤ 0.5 , melting point: 35–45 °C,

moisture (%) < 0.03 , chromatic number ≤ 50) was supplied by Huada Chemical Group Co. Ltd. China. 1, 4-Butylene glycol (BDO, $\geq 99.9\%$) was purchased from BASF Co. Germany. All the other chemicals (analytical grade) were purchased from Tianli Chemical Reagent Co. Ltd. China and used as received.

2.2. Desizing of CFs

As-received epoxy resin-sized T300 CFs were desized by acetone in a Soxhlet extractor at 75 °C for 24 h, followed by vacuum drying at 60 °C for 8 h, obtaining desized CFs. All the CFs used afterwards in this study are desized CFs if not specified.

2.3. Electrophoretic deposition of GO on the surface of CFs

An online EPD setup was established based on a CF bundle as the positive electrode, a graphite cathode plate as well as a pH 10.0 aqueous solution as the media prepared by adding 0.1 M sodium hydroxide solution to pH 7.0 phosphate buffer solution. Typical concentration of GO aqueous dispersion was 0.25 g/L. The voltage used here was 0 V (control sample) and 3 V. The resulting samples of GO-deposited CFs were then denoted as CFGO-0 and CFGO-3, respectively. During the EPD process, bubbling was observed at both the working and counter electrodes due to the electrolysis of water. Therefore sonication was used to immediately remove the newly-formed bubbles in order to avoid the trapped gas pockets that may impede the deposition [20]. Afterwards, GO-deposited CFs were annealed at 150 °C for 1 h to improve the weak interaction between GO and CFs [20]. The online EPD and annealing system is inspired by Ref. [16] and schematically illustrated in Fig. 1.

2.4. Preparation of CF/PU composites

In this study, CF/PU composites were prepared through a pre-polymerization method. MDI and ODX-218 were used as hard segments and soft segments, respectively. First, 160.0 g of ODX-218 was vacuum dehydrated at 120 °C for 3 h to remove the traces of moisture. Then, calculated amount of carbonaceous fillers (1 wt% CFs and/or 0.1, 0.2 or 0.3 wt% GO) were added to ODX-218 with stirring in a three-neck round-bottom flask. In the case of mechanical mixing GO and CFs in PU matrix, GO sheets were first added into ODX-218 under stirring at 500 rpm to achieve a uniform distribution followed by adding chopped CFs. Afterwards, excessive MDI (76.3 g) was added in GO/ODX-218 dispersion and the content of free -NCO groups after pre-polymerization was set at 8%. Reaction was maintained at 80 °C for 120 min. Afterwards, air bubbles were removed from pre-polymers with a vacuum pump for 30 min. The chain extension reaction was carried out by fast stirring for 2 min after adding 19.2 g of chain extender BDO into pre-polymers. Then, 100.0 g of chain-extended pre-polymer was press vulcanized in a steel picture-frame mold at 120 °C for 1 h at a pressure of 10 MPa, followed by oven curing at 120 °C for 24 h and further curing at room temperature for 24 h. The dimension of the resulting CF/PU composites is 18 cm * 18 cm * 2 mm. The schematic illustration of the distribution of carbonaceous fillers in PU composites was shown in Fig. 2.

2.5. Analysis and characterization techniques

X-ray photoelectron spectroscopy analysis (XPS, AXIS ULTRA DLD, Japan) was used to characterize the chemical composition and elemental distribution of CF surface. A monochromatic Al K α X-ray source which provides photons with energy of 1486.6 eV was used. Scanning electron microscopy (SEM, JSM-7001F) was used to characterize the morphology of CFs and GO sheets. For

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