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Enhanced interfacial adhesion between polypropylene and carbon fiber by graphene oxide/polyethyleneimine coating

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ABSTRACT

In order to improve the interfacial properties in polypropylene/carbon fiber (PP/CF) composites, graphene oxide and brached polyethyleneimine were coated onto the surface of carbon fiber by layer-by-layer assembly in this work. Compared with the origin PP/CF composite, the composites reinforced by PP/CF–GO showed significant enhancement not only in tensile strength but also in elongation at break. The improved fiber–matrix adhesion was proved by fracture morphology observation of scanning electron microscopy and almost unaffected mechanical properties of the fiber itself during the coating process. The optimal assembly time was found to be 10 for enhancing the overall composite mechanical performance.

Introduction

Owing to its excellent thermo-physical properties, high specific strength and modulus, good resistance to corrosive environment, low density and easy modeling, carbon fiber reinforced polymers (CFRPs) have been widely used as desired reinforcement in aerospace, civil engineering, sports and automobile industries [1–3].

However, for the mechanical properties of CFRPs, no matter the thermosets or thermoplastics, are influenced by many factors such as the interfacial adhesion between fiber and matrix, the amount of fiber, the aspect ratio of fiber, the orientation of fiber refer to specified forming process, etc [4,49].

It is well-known that effective reinforcement requires not only a reasonable selection of fiber and matrix but also good bonding between them. This is why the interaction between carbon fiber (CF) and the polymer matrix is a critical concern in the design process of CFRPs [5]. However, the chemical inert and smooth surface of CF resulted from carbonization and graphitization process will cause poor compatibility and weak adhesion between the fiber and surrounding polymer matrix, thus limit the reinforcing performance of CF [6]. Therefore, the modification of the surface of CF plays an indispensable role in determining the wetting property and bonding strength between the fiber and matrix, which is closely related to its macroscopic mechanical properties. Numerous techniques have been proposed to modify CF in order to improve the fiber–polymer matrix interfacial interaction and interlocking in the past decades, including oxidation treatment [7], chemical grafting [2], sizing or coating [8,9], discharge plasma treatment [10] etc.

Since the successful growing of carbon nanotube on CF by professor T. W. Chou in 2002 [11], this new kind of multi-scale reinforcements has attracted significant attention because the smaller scaled nanoparticles can realize good attachment on the fiber instead of agglomeration in the matrix, so the fiber–matrix interfacial adhesion will see an improvement. Actually, various kinds of submicrometer or nanometer scale materials can be assembled or grafted on the surface of CF to enhance the quality of CF/matrix interfacial adhesion, such as carbon nanotube (CNT) [11–14], graphene oxide (GO) [15–17], graphene (G) [18], aramid nanofiber (ANF) [19], inorganic whiskers [20] etc. Meanwhile, different methods can be used to prepare CF-based hierarchical composites, including CVD deposition [21–23], electrophoresis deposition [24–26], chemical grafting [27,28], sizing [9,29] etc. While most of the above methods also have certain limitations. Due to the catalyst contamination, degraded mechanical properties of CF at high temperature and low deposition density during CVD and electrophoresis depositions will result in the limited reinforcing effect of the multi-scale reinforcements in CFRPs [22,25]. Although the assembly of nano-level particles by

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chemical grafting will obtain better bonding between CF and the nanoparticles, most processes of chemical modification are step-tedious and some reaction conditions are strict and drastic [27,30].

Serving as an easy and effective way, sizing or coating has attracted considerable attention in fiber surface treatment. Li et al. [6] prepared the CF–GO multi-scale reinforcement by a simple physical absorption method. The results showed that the GO coating at a proper content of 0.5 wt% for treating SCFs can simultaneously enhance the tensile strength, Young's modulus, flexural strength and flexural modulus of the polyethersulphone (PES) composites. Ashori et al. [9] also investigated the effect of exfoliated graphene nanoplatelet (xGnP)-coated short carbon fiber (SCF) on the mechanical and the thermo-mechanical properties of composites. However, due to poor bonding between the physically-adsorbed nanoparticles and CF, the interface enhancement between fiber and matrix was not significant.

Layer-by-layer assembly, a prevalent method for building functional thin coating or films, has obtained considerable attention in the past 20 years. By absorbing oppositely charged materials alternatively onto a substrate, this repeated process will obtain a multilayer film with a specific structure. Owing to the flexible designability and high level of controllability in a nanoscale single bilayer, as well as the broad adaptability of different substrates such as porous membranes, particles, and biological matter, LBL technologies have seen rapid development and been applied in photoelectric devices, separation or catalysis components, biomedical materials and other new frontiers [31]. However, most research about LBL assembly aimed at the designation and preparation of functional membranes or films, research on the application of LBL in fiber reinforced polymer composites, especially for CFRPs, were rarely reported.

Q4 As a general thermoplastic polymer, polypropylene (PP) and its nanocomposites have been investigated intensively [52,55]. But the non-polar chain structure of PP makes it hard to bond with the reinforcements and fillers, and few researchers pay attention to the micro interfacial properties of CF/PP composites.

In this work, we aimed to enhance the interfacial characteristics by applying novel LBL assembly of graphene oxide and polyethyleneimine (PEI) on the surface of carbon fiber. The morphology, surface element composition, and mechanical properties of the CF–GO hybrid reinforcement were systematically characterized by SEM, XPS, and SFTT. In addition, the mechanical properties of PP/CF and PP/CF–GO composites with various assembled GO layers and compatibilizer were also investigated. The investigation showed a very significant improvement of interfacial interlocking between PP and CF–GO hybrid reinforcement as proved by the remarkable increasing in mechanical properties and the morphology of fractured surfaces.

Experimental section

Materials

PP pellets (T30s, MFR = 3.1 g/10 min, Du Shan Zi Petro-Chemical, China) and CF (T800 12 K, Shanxi Gangke Carbon Material Co., Ltd., China) were used as the polymer matrix and the reinforcing material. The low-temperature expandable graphite (EG), with an initially expanded temperature of 150 °C and a particle size of nearly 300 μm (Supporting Information), was obtained from Shijiazhuang ADT Trading Co., Ltd (China). Polyethyleneimine (PEI) with Mw of 600 was purchased from Aladdin Co., Ltd., Shanghai, China. Maleic anhydride grafted PP (MAPP, Eastman Chemical Products, Co.) with a MAH content of 4.0 wt% was used as a compatibilizer.

Preparation of GO aqueous solution

GO was synthesized by Improved Hummers' method, which was reported by Marcano in 2010 [32]. Specifically, expanded graphite was prepared by expanding EG in an ordinary microwave oven under 1000 W and 30 s. After that, 400 ml concentrated H_2SO_4 and H_3PO_4 mixture with a volume ratio of 9:1 was slowly added to a mixture of expanded graphite (3.0 g, 1 wt equiv) and $KMnO_4$ (18.0 g, 6 wt equiv) in a 2000 ml beaker. After simple stirring for a few minutes, the reaction was then heated to 50 °C and stirred for 12 h. Then the mixture was cooled to room temperature and poured into ~1000 ml ice, after that, 4–5 ml 30% H_2O_2 aqueous was dropped into the mixture with stirring until no more air bubbles generated. After centrifugation and rinsing by 10% HCl for 5–6 times until no more SO_4^{2-} was detected by 0.1 M $BaCl_2$ solution. Then the precipitate was redispersed in 300 ml deionized water to form a GO aqueous with a high concentration near 20 mg/ml. Finally, the high concentrated GO solution was poured into a PTFE tray and dried overnight at 50 °C, obtaining 6 g of product. GO aqueous with certain concentration was prepared by sonicating 300 ml solution in an ultrasonic bath under 40 kHz for 30 min.

Preparation of CF–GO hybrid reinforcement by LBL assembly

Before LBL assembly, pristine CF bundle (~3 g) was refluxed in acetone for 72 h to eliminate surface sizing and then washed with acetone for 3 times again. After drying under vacuum overnight, the desized CF was applied in a 320 ml mixture of concentrated nitric acid and sulfuric acid with volume ration of 3:1 and then treated at 80 °C for 3 h. The acidulated CF was then washed by a large amount of water until the water on fiber surface was neutral and then dried under vacuum at 60 °C overnight.

For the process of LBL assembly, a bundle of acidulated CF was first immersed into PEI aqueous solution with a concentration of 1 mg/ml for 15 min leading to a nanoscale deposition of PEI on CF (Step 1). After that, the CF bundle was rinsed with deionized water to remove excess material and followed by drying with clean air (Step 2). The cationic CF bundle was then immersed in 1 mg/ml GO aqueous solution for 15 min (Step 3) before similar washing and drying procedures (Step 4) were carried out. Each deposition cycle, consisting of steps 1–4, resulted in the deposition of a nanoscale bilayer. By repeating the process, CF–GO hybrid reinforcement with the desired number of bilayers can be obtained (see Fig. 1). Accordingly, a L_x CF–GO hybrid reinforcement was prepared by accomplishing x deposition cycles. In this article, the number of bilayers was set as 5, 10 and 15.

Preparation of CF/PP micro droplet

Q5 The CF/PP micro droplet samples were prepared according a simple knotting-melting method reported by Liu et al. [50]. The PP resin was melted and then pulled into fibres, then the fibres were knotted carefully with the carbon fibres together. After heating at 200 °C until the PP knotting was fully melted and form regular droplet for testing, the sample was then put away from the hot plate and cooled down to ambient temperature. Then the samples were placed in a petri dish and annealed under 110 °C for 2 h to release the internal stress.

Preparation of PP composites

The composites were fabricated by melt blending through the HAAKE MiniLab micro compounder. The rotor speed and temperature were set at 30 rpm and 190 °C, the mixing time was set for 10 min. The samples name and relative composition are listed in

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