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Preparation and performance of long carbon fiber reinforced polyamide 6 composites injection-molded from core/shell structured pellets

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ABSTRACT

In this work, long carbon fiber reinforced polyamide 6 (LCF/PA6) composites were prepared by injection-molding a novel kind of core/shell pellets that were mass produced by a convenient and scalable process of melt impregnation assisted by a single screw extruder. The effect of fiber sizing treatment on fiber distribution, melt flowability, and mechanical properties of the LCF/PA6 composites was investigated. It was demonstrated that the melt flowability exhibited a continuous increase with the increase of sizing concentration while the mechanical properties showed peak values at a sizing concentration of 22 wt.%. In addition, the mechanical properties of the LCF/PA6 composites at the optimal sizing concentration were examined as a function of the content of carbon fibers. These findings may provide guidance for the studies aimed at developing long carbon fiber reinforced thermoplastic composites with desirable mechanical properties.

1. Introduction

Carbon fibers have been widely used as reinforcements for metallic, ceramic, and polymeric matrices in light of their excellent properties including lightweight, high strength and modulus, good electrical and thermal conductivity, stability at elevated temperatures, and decreasing cost. However, due to the lack of carbon fibers, surface modifications are mandatory in the preparation of carbon fiber reinforced polymer (CFRP) composites to improve the interfacial bonding between fiber and matrix. Various approaches have been developed for the surface treatment of carbon fibers, including oxidation, coating, grafting, and sizing treatment [1,2]. Sizing treatment is a unique approach which can not only improve handling properties of carbon fibers, protect the fibers from fuzzing and fragmenting during composite processing, but also enhance fiber wetting by the matrix and improve fiber–matrix adhesion through the reactions of functional groups on sized fibers with the matrix [2–4]. Extensive research have been carried out regarding the influence of sizing treatment of carbon fibers on the interface and properties of thermoset composites [5–8]. To the best knowledge of the authors, most sizing agents are epoxy-based which are only suitable for epoxy resin composites to produce effective bonding between treated carbon fibers and thermosetting plastics [9–12]. Unfortunately, the functional groups provided by the traditional epoxy-compatible sizing do not react chemically with thermoplastic polymers such as polyamides, polyimides, PEEK, and other thermoplastic polymers [13]. Therefore, more attention has been paid to developing the ideal sizing treatment of carbon fibers for reinforcing thermoplastic polymers [14,15].

Polyamides (PAs) are becoming more and more noticeable in the production of carbon fiber reinforced thermoplastic (CFRT) composites due to its low cost, ease of handling, and good mechanical properties [16–18]. So far extensive studies have been conducted on PA composites reinforced with short carbon fibers [16,17]. It is well known that short carbon fibers–polyamide composites are produced by screw extrusion followed by injection molding [18]. During extrusion process, matrix (fed through the main feeder) and fibers (fed through the side feeder) are mixed and pelletized to obtain composite pellets whose fibers are randomly distributed and short due to extensive fiber breakage during extrusion. Obviously, the use of short fiber reinforced thermoplastic pellets results in poor mechanical properties of CFRP composites due to the low fiber aspect ratio after injection-molding [19,20], which hinders their industrial applications. In order to improve the mechanical properties of fiber reinforced thermoplastic composites, long glass fiber reinforced thermoplastics have been developed [21]. Previous studies demonstrated that

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composites injection-molded from long glass fiber pellets could obtain better mechanical properties [19,20,22,23] but proper selection of sizing materials is crucial [23]. However, studies on long carbon fiber reinforced thermoplastic composites and the effect of fiber sizing treatment on the performance of the composites have not been reported. Furthermore, unlike long glass fiber reinforced thermoplastic composites and carbon fiber reinforced thermoset composites, sizing materials for CFRT composites are usually not commercially available. Therefore, seeking a facile and scalable process to produce high-performance carbon fiber reinforced thermoplastic composites is of paramount importance.

To this end, the present work reports a convenient and scalable process of producing a novel kind of core/shell structured pellets from which long carbon fiber reinforced PA6 (abbreviated as LCF/PA6) composites can be prepared. In this context, continuous carbon fibers were sized using a sizing solution consisting of an isocyanate modified epoxy emulsion and coupling agent. Then LCF/PA6 composite pellets with special core/shell (core was carbon fiber tow and shell was PA6) structure were fabricated by the melt impregnation process using a single screw extruder, an impregnation die, and a chopper. Finally, composite specimens were prepared by injection molding. These processes could be applied into mass production of LCF/PA6 composites. The aim of this study was to prepare sized LCF/PA6 composites, to examine their mechanical properties, and to determine the effect of fiber sizing treatment on the performance of the resultant LCF/PA6 composites.

2. Materials and methods

2.1. Materials

The matrix material used in this work was a commercial polyamide 6 (PA6) with the trade mark of IMNC 101 (density: 1.13 g/cm^3, melting temperature: 215 °C, decomposition temperature: >300 °C), supplied by Shanghai Hersbit Chemical Co., Ltd., China. PAN-based continuous 12 k (contained 12,000 filaments) carbon fibers with a trade name of TC36S, an average diameter of 7 μm, and a density of 1.78 g/cm^3 were provided by Formosa Plastics Group, Taiwan. The sizing material used in this work was an isocyanate modified epoxy emulsion. Both the sizing material and silane coupling agent KH560 (γ-(2,3-epoxypropoxy) propytrimethoxysilane, molecular formula $(CHCH_2O)CH_2O(CH_2)_3Si(OCH_3)_3$) were purchased from Nanjing Chemical Industry Group Co., Ltd., China. Ethanol, analytical grade, was provided by Tianjin Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Sizing treatment of carbon fibers

2.2.1. Preparation of sizing agent solutions

Silane coupling agent KH560 was first hydrolyzed in an ethanol aqueous solution (deionized water to ethanol ratio = 3:1 by weight) for 20 min at room temperature and the percentage of silane agent was kept at 1.0 wt.%. The sizing material was added to the solution of KH560 at a stirring rate of 250 rpm until a homogeneous solution was formed. The concentration of sizing agent was set at 2, 6, 10, 14, 18, 22, 26, and 30 wt.% in the final aqueous sizing solutions, respectively.

2.2.2. Sizing treatment of carbon fibers

As illustrated in Fig. 1, the whole sizing treatment process was carried out through a homemade setup which could be used for large-scale production. As seen in Fig. 1, prior to sizing treatment, the commercial epoxy sized TC36S carbon fiber tow was desized by annealing in air at 500 °C for 5 min and followed by thorough washing with deionized water for 5 min and dried in air at 180 °C for 2 min. The carbon fiber tow was then passed through an ultrasonic bath containing sizing solution. Similar to that reported by Broyles et al., capillary forces provided the driving force for rapid tow wetting and the extensive use of rollers after the sizing bath spread the tow bundle and prevented the wet tow from clumping [24]. The carbon fiber tow wetted with sizing solution was automatically spooled on a drum. Finally, the carbon fiber spool was dried in an oven at 110 °C for 48 h.

2.3. Preparation of LCF/PA6 composites

The preparation process of LCF/PA6 composite samples was as follows. As shown in Fig. 2a, dried PA6 pellets were melted and forced to pass through a heated impregnation die by using a SJ-20 single screw extruder (Nanjing Giant Machinery Co., Ltd., Nanjing, China) at a screw speed of 20 Hz and a melting temperature of 230 °C. Simultaneously, carbon fiber tows in the spool were pulled through the same die where carbon fiber tows, rather than individual filaments as reported in literature [23,25], were coated with a layer of PA6, forming core–shell structured composite wire rods. The advantage of this process was that it could be used in a wider range of polymers as compared to the DRIFT process [23]. The composite wire rods were then cooled at a cooling tank, and chopped into core/shell-structured pellets (the core was carbon fiber tow and the shell was PA6, as illustrated in Fig. 2b) with an approximate length of 6 mm and a varying diameter of 2–6 mm, depending on the fiber loading in the resultant composites. As an example, Fig. 2c shows a representative photo of some pellets corresponding to a composite with a fiber content of 20 wt.%. The composite specimens with standard shapes were obtained by injection molding at 270 °C and an injection pressure of 80 MPa.

2.4. Characterizations

Tensile and flexural properties were examined by using a computer controlled CMT-4304 universal testing machine (Shenzhen Suns Technology Co., Ltd., China) according to ASTM: D638 and ASTM: D790, respectively. Notched Izod impact testing was performed with a XCD-50 impact tester (Chengde Puhui Testing Instrument Co., Ltd., Hebei, China) as per ISO 179-1:2010 [26]. All mechanical testing was performed at room temperature (25 °C) and 45% relative humidity and the reported values were collected from at least five independent tests.

Scanning electron microscopy (SEM) was performed on fiber surfaces and fractured tensile specimens using Hatchi S-4800 field scanning electron microscope. For SEM observation, samples were sputter coated with a layer of gold to reduce the incidence of surface charging.

Melt flowability of the composites was characterized by the melt flow rate (MFR). The MFR was examined by a melt flow indexer (Model MFI-1211, Chengde Jinjian Detecting Instrument Co., Ltd., China) and the procedure was the same as that reported by Yang et al. [27].

The distribution of fibers in the composites was observed by a BX41M-LED metallurgical microscope (Olympus Co., Ltd., Japan) after the specimen surfaces were polished.

3. Results and discussion

3.1. Stability of sizing agent solutions

The sizing agent solutions were prepared and left at 25 °C for 15 days to observe the separation conditions. It was found that all solutions prepared in this work was stable without separation