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Greatly enhanced cryogenic mechanical properties of short carbon fiber/polyethersulfone composites by graphene oxide coating

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ABSTRACT

In order to employ polyethersulfone (PES) in cryogenic engineering field, its cryogenic mechanical performance should be examined and should also be improved to meet the high requirement for cryogenic engineering application. In this work, pure PES, graphene oxide (GO)/PES, short carbon fiber (SCF)/PES, GO/SCF/PES and GO-coated SCF/PES composites are prepared using the extrusion compounding and injection molding techniques. The tensile and flexural properties of these composites are systematically investigated at a typical cryogenic temperature (77 K). It is shown that the cryogenic mechanical properties are enhanced by the addition of GO, SCFs and coated-SCFs. In particular, the GO-coated SCF/PES composites display the greatly enhanced cryogenic mechanical properties with the highest values compared to other PES composites. In addition, it is exhibited that the cryogenic mechanical properties at 77 K of PES and its composites are far higher than those at room temperature (RT).

1. Introduction

Polyethersulfone (PES) is an important transparent amorphous high performance special engineering thermoplastic consisting of repeated phenyl, ether and sulfone groups with very high thermal oxidation resistance and broad chemical resistance [1]. It possesses relatively high modulus, mechanical strength and glass transition temperature (around 225 °C) among polymers. PES has a heat deflection temperature of ca. 200 °C, which is significantly higher than that of high performance semicrystalline polymers, such as polyetheretherketone and polyphenylenesulfide [1]. In addition, it has low creep, excellent insulation property, high dielectric strength, good impact strength and high resistance to hydrolysis. Therefore, PES has been widely used in medical instruments, aviation, microelectronics, automobile, membrane separation, etc. [2–4]. However, its relatively low mechanical properties compared to metal materials have limited its applications in automobile, aerospace, sporting, etc. which have high requirements and thus its mechanical properties need to be improved for these high-requirement engineering applications [5]. Carbon fibers, glass fibers and graphene oxide, etc. can be introduced into PES to enhance its mechanical properties and also reduce linear coefficient of thermal expansion [2,6]. Especially, carbon fiber reinforced PES composites have displayed great potential for applications in automobile, aerospace, sporting, off-shore technology, and chemical engineering areas, etc. [7,8].

Carbon fiber is a widely used reinforcement in polymer–matrix composites owing to its excellent mechanical properties, high thermal and electrical conductivity, excellent corrosion resistance, low linear thermal expansion coefficient and low density [9,10]. In particular, short carbon fiber (SCF) reinforced polymer composites are very attractive because of their manufacturing ease, low cost and superior mechanical properties. They can fill the mechanical property gap between the continuous-fiber laminates used as primary structures by the aircraft and aerospace industry and the unreinforced polymers used in partial-load-bearing applications [11,12]. In addition, SCF reinforced polymer composites can be readily manufactured using highly efficient conventional techniques of extrusion compounding and injection molding, etc. for polymers [13,14]. For a given reinforcement and matrix system, the resulting properties of the composites mainly depend on interfacial adhesion because the interface plays a critical role in stress transfer between the fiber and surrounding resin matrix. However, the chemically inert surface of carbon fibers seriously affects the interfacial adhesion in carbon fiber/PES composites. In recent years, a range of special surface modification methods have been applied to increase the interfacial adhesion between carbon fibers and

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thermoplastic resins, such as electrochemical treatment, plasma etching, high energy irradiation, grafting and sizing treatment [6,15–17]. As for the sizing treatment, it can also protect carbon fibers from mechanical damage during the processing and improve the wetting of carbon fibers by polymer matrices. Thus, the sizing treatment is an appropriate approach for tailoring fiber–matrix interface.

Graphene oxide (GO) as graphene derivative and a potential multifunctional sizing agent can be uniformly dispersed and firmly adsorbed on surfaces of carbon fibers to synthesize a new hierarchical reinforcement due to its unique two-dimensional structure, large specific surface area, good mechanical properties, etc. Moreover, GO contains various oxygen functional groups such as epoxide, hydroxyl and carbonyl groups. GO coating on SCFs can enhance the SCF–PES interfacial adhesion [18] and thus the applied load can be more effectively transferred from PES to SCFs to enhance the composite mechanical properties [19–21]. In addition, GO can be introduced as a nanofiller into PES to make PES nanocomposites with the purposes of improving both mechanical properties and dimensional stability because the large specific surface area of GO can increase the available contact area of reinforcing phase and polymer matrix to form strong interactions between the polymer and GO [20,21]. Both PES and its composites can be compression molded, extruded, or injection molded using conventional equipments. Extrusion compounding and injection molding processes are conventional techniques for fast manufacturing of thermoplastics and are most often used to manufacture short fiber and nanofiller/thermoplastic composites [22]. In addition, the injection molding process also allows intricately shaped parts to be easily manufactured. It is well known that some processing steps in the two techniques of extrusion compounding and injection molding may reduce fiber length of fiber reinforced composites because of high shear force and high processing temperature [22]. As a result, the performance of PES composites depends on filler type, filler amount, filler–matrix interface quality and processing technology, etc. [23].

Polymers and their composites have been considered for applications as structural and functional parts to replace metals because of their unique and highly tailorable properties, such as high voltage insulators, cryogenic dewars, cryogenic seals and bearings in liquid nitrogen environment [24–26]. In order to develop high performance polymer composites for cryogenic engineering applications, it is necessary to understand how polymer composites behave at cryogenic temperatures and how their cryogenic properties are affected by factors such as filler content and filler type. Takeda et al. [27] investigated the through-thickness tensile behavior of woven glass fiber reinforced polymer (GFRP) composite laminates at cryogenic temperatures. It is found that the through-thickness Young's modulus of the woven GFRP composite laminates is dominated by the properties of the matrix polymer in a given temperature while the tensile strength is determined by both the fiber to matrix interface energy and the cohesion energy of the matrix polymer. Our previous work [28] employed multi-walled carbon nanotubes to reinforce diglycidyl ether of bisphenol F/diethyl toluene diamine epoxy system modified by PES for enhancing the cryogenic mechanical properties. The results implied that the simultaneous usage of PES and MWCNTs in a brittle epoxy resin was a promising approach for efficiently modifying epoxy resins for cryogenic engineering applications. Lau et al. [29] addressed the viability of using coiled carbon nanotubes (CCNTs) and randomly-oriented nanoclay-supported nanotubes (NSCNTs) to enhance the cryogenic mechanical properties of epoxy resin at 77 K. In our another work [30], the cryogenic interlaminar shear strength (ILSS) at 77 K of glass fabric (GF)/epoxy composites was investigated as a function of graphene oxide (GO) weight fraction from 0.05 to 0.50 wt% relative to epoxy. The results showed that the cryogenic ILSS was greatly improved by about 32.1% and the RT ILSS was enhanced by about 32.7% by the GO addition at an appropriate content of 0.3 wt% relative to epoxy.

There have been many reports on the mechanical properties at room temperature (RT) of SCF reinforced polymer composites [31–34]. However, the cryogenic mechanical properties of SCF reinforced composites have been rarely reported and especially those of SCF/PES composites have not been investigated yet. Moreover, GO has never been employed as a sizing agent to treat SCFs for enhancing cryogenic mechanical properties of PES. In this work, the pure PES and PES composites are prepared via the extrusion compounding and injection molding techniques. The PES composites are obtained by introducing graphene oxide (GO), short carbon fibers (SCFs), both GO and SCFs simultaneously, GO and SCFs separately, and GO-coated SCFs. In our recent work [18], the mechanical properties at RT of the GO-coated SCF/PES composites were studied taking into consideration the effects of GO coating content. In the present work, in order to explore their possible applications in cryogenic engineering field, the tensile and flexural properties at a typical cryogenic temperature (77 K) of these composites are systematically investigated and compared with those obtained at RT. And greatly enhanced cryogenic mechanical properties of PES composites are observed by GO coating.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES, granules, E3010) and short carbon fibers (SCFs, 6 mm length, C30 S003/6 APS) were respectively obtained from BASF and SIGRAFIL, Germany. Graphite powders (1000 mesh) were offered by a commercial supplier (Qingdao AoKe ShiMo Co., Ltd., China). Ethanol, concentrated sulfuric acid, potassium permanganate, sodium nitrate and hydrochloric acid were all purchased from Beijing Chemical Works, China. All of the raw materials were used without any further treatment.

2.2. Preparation of GO, GO coated SCF and PES composites

2.2.1. Preparation of GO

Graphite powders were oxidized through the acid oxide consisting of concentrated sulfuric acid, potassium permanganate and sodium nitrate via a way similar to the Hummers method [35] and graphite oxide was thus obtained. The oxidation product was purified by rinsing with a 10% HCl solution, repeatedly washing with copious amounts of deionized water. Then, the obtained graphite oxide was subsequently dispersed in deionized water to form a suspension of 0.2 mg/ml. The resulted suspension was treated by ultrasonic technique (1000 W) for 3 h to exfoliate the graphite oxide to layered GO and form a homogeneous GO aqueous solution.

2.2.2. Preparation of GO-coated SCFs

An appropriate amount of SCFs was added to the GO aqueous solution and the formulation was given in Table 1. The as-obtained mixtures were stirred for 24 h. After that, the resultant mixtures were dried at 100 °C to remove water and then cooled naturally to room temperature. Finally, the GO-coated SCFs were obtained. The details for GO sizing onto SCFs were given in our previous work [18].

2.2.3. Preparation of PES composites

The formulation of PES composites was given in Table 1. The 12.5 wt% of SCFs is a typical fiber content for effectively improving the mechanical properties of polymer composites [36]. The pure