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A novel surface modification of carbon fiber for high-performance thermoplastic polyurethane composites

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ABSTRACT

Properties of carbon fiber (CF) reinforced composites depend largely on the interfacial bonding strength between fiber and the matrix. In the present work, CF was grafted by 4,4′-diphenylmethane diisocyanate (MDI) molecules after electrochemical oxidation treatment. The existence of functional groups introduced to the fiber surface and the changes of surface roughness were confirmed by FTIR, AFM, XPS, SEM and Raman spectroscopy. To evaluate the possible applications of this surface modification of carbon fiber, we examined the mechanical properties as well as the friction and wear performance of pristine CF and MDI-CF reinforced thermoplastic polyurethane (TPU) composites with 5–30 wt.% fiber contents, and found that the mechanical properties of TPU composites were all significantly improved. It is remarkable that when fiber content was 30 wt.%, the tensile strength of TPU/MDI-CF was increased by 99.3%, which was greater than TPU/CF (53.2%), and the friction loss of TPU/MDI-CF was decreased by 49.09%. The results of DMA and SEM analysis indicated the positive effects of MDI modification on the interfacial bonding between fibers and matrix. We believed that this simple and effective method could be used to the development of surface modified carbon fiber for high-performance TPU.

1. Introduction

Carbon fibers (CF) present exceptional properties, such as high stiffness, high specific strength, and outstanding wear resistance, which have attracted considerable research interest in exploiting them as excellent reinforcements for thermoplastic resin composites [1–3]. The polymer usually acts as the continuous phase (the matrix) while the carbon fiber is the discontinuous phase, improving both the strength and toughness of the composites [4].

Thermoplastic polyurethane (TPU), a kind of thermoplastics with the mechanical performance characteristics of rubber, is described as “bridging the gap between rubber and plastics”. TPU is widely applied for daily use ranging from ski boots and footwear to gaskets, hoses, and seals because of its high elasticity combined with high abrasion resistance [5]. However, the strength and abrasion resistance of TPU yet to be further improved to deal with more demanding conditions. Short carbon fiber can be used to reinforce the abrasion resistance of TPU as well as other mechanical properties [4]. However, short carbon fiber reinforced TPU shows less effective in properties such as stress-strength, tear resistance, hardness compared to other reinforcing materials such as aromatic polyamide due to the less intensive matrix-fiber interaction [4,6,7]. Thus, researchers devote to modify the surface of CF to improve adhesion to the resin since the inadequate interphase between fibers and matrix would be a drawback [8,9].

Compared with some traditional modification methods, such as acid oxidation treatment [10], plasma treatment [11,12], gas phase oxidation [13], heat treatment [14,15], and so on, polymerization treatment of carbon fiber demonstrates many advantages. Graft polymerization treatment is to graft macromolecules on the carbon fiber surface, so as to rough the fiber-matrix interaction area and introduce functional groups. For different resin matrix, the suitable surface functional groups are needed [16] according to compatibility, cost, production conditions, and so on. Before grafting process, people usually need to do an oxidation process so that reactive functional groups could form on the surface of fiber. Electrochemical oxidation is the most prevalent surface treatment of the carbon fiber, by which the surface chemistry of fiber would be improved, so as to improve its application potential on materials such as carbon fiber reinforced composites [17]. A previous study [18] used toluene-2,4-diisocyanate (TDI) to bind isocyanate functional groups on carbon nanotudes, which produced polyurethane (PU) composite coatings and improved its wear properties. However, TDI molecules have small molecular weight compared to

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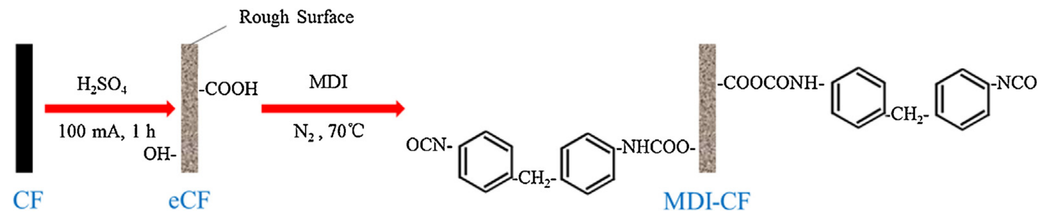

Fig. 1. Modificateion procedure of MDI-CF.

4,4′-diphenylmethane diisocyanate (MDI) molecules, which makes them more volatile with high vapor-pressure. Besides, TDI has certain toxicity, which may even be carcinogenic. On the other side, the two –NCO groups of MDI have similar activities, while that of TDI are different: the activity of the *o*-methyl –NCO group is 25 times smaller than *p*-methyl –NCO group. So in this study, MDI was used as a replacement of TDI due to its better properties. MDI is commonly used as a raw material to produce polyurethane, and it can be used to modify the surface of pristine carbon fibers to improve the interfacial characteristics between CF and TPU matrix. Furthermore, the electrochemical method we use is quick and easy, which is more suitable for industrialized continuous production compared to the former method, needing CF to be immersed into mixed acid solution for 2 h.

In this paper, the effects of MDI surface treatment on CF, which was electrochemically oxidized in advance, were investigated by fourier-transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, atomic force microscope and scanning electron microscope. We revealed the potential of MDI grafting polymerization to be developed as an effective surface modification of carbon fibers. To evaluate the possible applications of this surface modification carbon fiber, we compounded the MDI modified CF with TPU matrix and presented a series comparison between CF and MDI-CF reinforced TPU composites, using methods of tensile properties test, dynamic mechanical performance test, tribological test, and hardness test. It is proved that MDI grafting polymerization is an effective CF surface treatment to raise the interfacial adhesion between fiber and matrix, which gives TPU composites outstanding mechanical properties and excellent wear resistance for applications.

2. Experimental

2.1. Materials

The carbon fibers used in this study were T700SC PAN-based 12 K tow fibers purchased from Toray Industries, Inc. Granular TPU (Polyester Type, AVALON® 85 AE) and MDI with purity of 99% 4,4′-isomer were provided by Huntsman Polyurethanes Shanghai Ltd. and used as received. Sulfuric acid (AR grade, 98%), acetone were supplied by Sinopharm Chemical Reagent Co., Ltd.

2.2. Surface modification of carbon fiber

The detailed scheme for the MDI modified CF is illustrated in Fig. 1. Carbon fibers, which took positive power supply, were bundled by groups and immersed in 1000 mL 0.5 mol/L dilute sulphuric acid, and the nickel foam connected with the cathode. Switch on the power to form into a circuit and treated fibers via electrolysis (the current intensity was 100 mA) for 1 h. Then CF were washed with distilled water until the pH turned into 7.0 and were dried in an air-circulating oven at 60 °C for 12 h. Then those electrochemical treated carbon fibers (eCF) were chopped into an average length of 10 mm in preparation. MDI of 100 mL was firstly dissolved in 200 mL acetone in a three-necked flask and then heated up to 70 °C. 5 drops of stannous octoate were added into this solution after it being stirred for 15 min under a nitrogen atmosphere. 15 g short eCFs were then soaked in the solution and stirred for 4 h under N_2. After the reaction, the MDI modified CF (MDI-CF) were washed repetitively with acetone and then dried in a vacuum oven at 50 °C for 12 h.

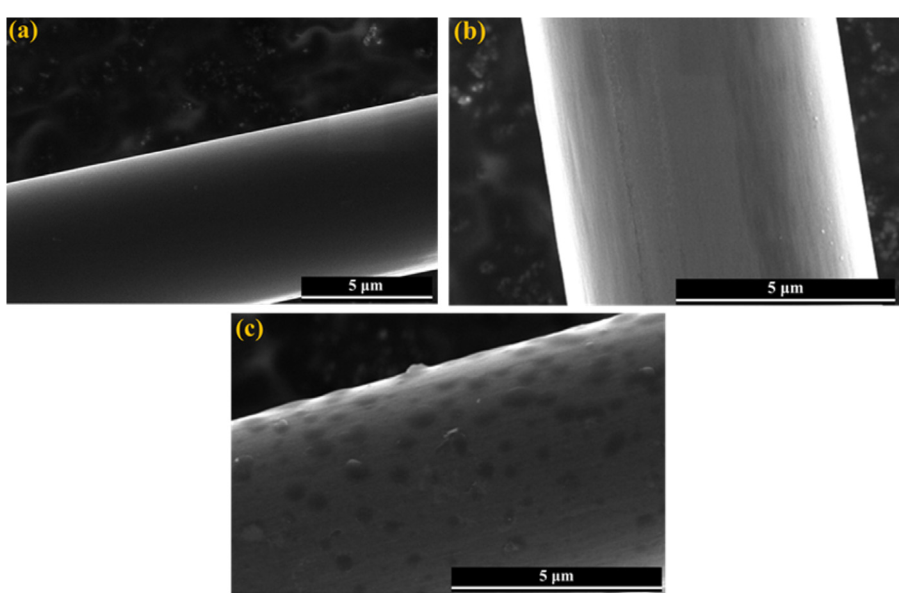

Fig. 2. SEM images of (a) CF (b) eCF (c) MDI-CF.