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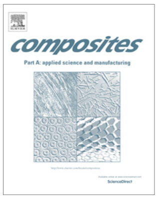

Preparation, characterization and properties of polycaprolactone diol-functionalized multi-walled carbon nanotube/thermoplastic polyurethane composite

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were chemically functionalized to prepare thermoplastic polyurethane (PU) composites with enhanced properties. In order to achieve a high compatibility of functionalized MWCNTs with the PU matrix, polycaprolactone diol (PCL), as one of PU's monomers, was selectively grafted on the surface of MWCNTs (MWCNT–PCL), while carboxylic acid groups functionalized MWCNTs (MWCNT–COOH) and raw MWCNTs served as control. Both MWCNT–COOH and MWCNT–PCL improved the dispersion of MWCNTs in the PU matrix and interfacial bonding between them at 1 wt% loading fraction. The MWCNT–PCL/PU composite showed the greatest extent of improvement, where the tensile strength and modulus were 51.2% and 33.5% higher than those of pure PU respectively, without sacrificing the elongation at break. The considerable improvement in both mechanical properties and thermal stability of MWCNT–PCL/PU composite should result from the homogeneous dispersion of MWCNT–PCL in the PU matrix and strong interfacial bonding between them.

1. Introduction

Carbon nanotubes (CNTs) have received considerable attention because of their distinctive structures and fascinating properties since first reported in 1991 [1]. Researchers show great interests in utilizing CNTs in various areas, such as electrochemical biosensors [2,3], nanowires [4], nanoprobes for high-resolution imaging [5], electromechanical actuators [6], and other applications [7,8]. Among them, polymer-based CNTs composite has been a research focus for many years. Various polymer materials have been studied as the composite matrices, such as polypyrrole [9], poly(vinyl alcohol) [10], polystyrene [11], poly(methyl methacrylate) [12] and liquid crystalline polymers [13]. The excellent mechanical, electrical, and thermal properties of carbon nanotube [14–16], combined with its high aspect ratio, make it a very promising reinforcing filler.

However, the application of CNTs to fabricating polymer-based composite with enhanced properties is strongly limited, [17,18] which is mainly due to the following two factors: first, raw CNTs tend to aggregate because of van der Waals forces, consequently making CNTs very difficult to homogeneously disperse in polymer matrices; second, lack of sufficient interfacial interaction between the two phases makes CNTs easily slide in the matrices under external forces. One effective way to improve both the dispersion and interfacial bonding is to chemically functionalize CNTs [17,19,20]. The acid-treatment method is widely adopted to modify CNTs. In general, this process consists of two steps. First, CNTs are treated with oxidants to introduce carboxylic acid groups to CNTs' surface defect sites [21,22]. Second, the attached carboxylic acid groups could change into other functional groups, like acyl chloride, amide [13,23]. The functional groups on CNTs' surface can react directly with monomers or a polymer, which opens a new route to properly functionalize CNTs based on a specific polymer matrix.

Polyurethane (PU) is one of the most versatile polymers and is widely applied as thermoplastic elastomer, adhesive, coating, foam, etc. As a block copolymer with alternating soft and hard

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segments, PU's molecular structure can be easily tailored to meet specific property requirements [24]. There are several approaches to preparation of CNT/polymer composites, such as *in situ* polymerization, melt processing and solution mixing. Among them, solution mixing may be the most common one due to its simple procedure. Another benefit of this approach is that the de-aggregation and dispersion of CNTs can be greatly promoted by agitation, which is usually provided by ultrasonication, shear mixing, magnetic stirring or reflux [25].

In this work, in order to obtain a uniform dispersion of multi-walled carbon nanotubes (MWCNTs) in the PU matrix, as well as a strong interfacial interaction between them, two kinds of chemical moieties (carboxylic acid group and polycaprolactone diol) were introduced onto the surface of MWCNTs. Because polycaprolactone diol (PCL) is one of the monomers for synthesizing PU, we expect a good compatibility between PCL–functionalized MWCNTs (MWCNT–PCL) and PU matrix when MWCNTs also contain the same molecules on their surface. The raw MWCNTs, carboxylic acid groups functionalized MWCNTs (MWCNT–COOH) and MWCNT–PCL were then incorporated into PU matrices to prepare three types of MWCNTs/PU composites via a simple solution mixing method. The functionalized MWCNTs were characterized in detail to confirm the covalent linkage. In addition, results from FESEM, TEM, tensile tests and TGA were presented and studied.

2. Experimental

2.1. Materials

The MWCNTs (purity 95 wt%) were provided by Cheap Tubes Inc (USA), with a length of 10–50 μm and outer diameter of 8–15 nm. Acetone (Aik Moh), anhydrous dimethylformamide (DMF, Tritech Scientific), tetrahydrofuran (THF, Anhydrosolv, Tritech Scientific), concentrated sulfuric acid (H_2SO_4, 95–97%, Honeywell) and nitric acid (HNO_3, 69–70%, Honeywell) were used as received. PCL (average Mn ~2000 g/mol and ~530 g/mol), 4,4′-methylenebis(phenyl isocyanate) (MDI, molecular weight 250.25 g/mol), 1,4-butanediol (BD, molecular weight 90.12 g/mol), dibutyltin dilaurate (DBTDL) and thionyl chloride ($SOCl_2$) were all obtained from Sigma–Aldrich.

2.2. Functionalization of MWCNTs

MWCNT–COOH was obtained via the following process: raw MWCNTs (1 g) were dispersed in 100 ml mixture of H_2SO_4/ HNO_3 (volumetric ratio 3:1) using an ultrasonicator. Then the mixture was heated gradually to 90 °C and kept for 30 min with vigorous magnetic stirring under reflux. Afterward, the reaction system was diluted and filtered via a filter with 0.22 μm Millipore membrane. The filtered powders were then washed, filtered till the filtrate became neutral. Finally, the acid-treated MWCNTs were collected and desiccated to a constant weight.

To prepare MWCNT–PCL, $SOCl_2$ was used for further functionalization. The as-prepared MWCNT–COOH was dispersed in $SOCl_2$ with the aid of an ultrasonic bath. Then the mixture was kept in a 65 °C oil bath under reflux for 1 day. After that, the mixture was filtered via a 0.22 μm polytetrafluoroethylene (PTFE) membrane filter. Dry acetone was used to wash the filter cake to get the acyl chloride intermediate MWCNT–COCl solid. The solid was immediately transferred into a solution of PCL (average Mn ~530 g/mol) in dry THF and stirred at 60 °C for another 24 h. Afterward, the reaction mixture was filtered, washed and dried to give MWCNT–PCL. The schematic for the preparation of MWCNT–COOH and MWCNT–PCL is shown in Fig. 1.

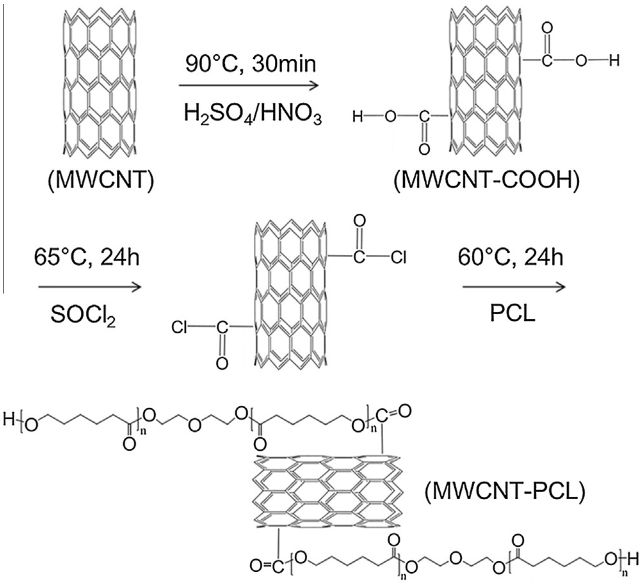

Fig. 1. Schematic for preparation of MWCNT–COOH and MWCNT–PCL.

2.3. Fabrication of MWCNTs/PU composites

PU was synthesized from two monomers (MDI and PCL) via a prepolymerization method [26], using BD and DBTDL as the chain extender and catalyst, respectively. A molar ratio of 1:6:5 of PCL: MDI: BD was adopted, giving 50.6 wt% of soft segment. The MWCNTs/PU composite films were fabricated through a solution mixing method. For the MWCNT–PCL/PU composite film, the procedure was as follows: MWCNT–PCL was firstly dispersed in DMF solution at a concentration of 0.6 g/L and ultrasonicated at room temperature for 1.5 h. A certain amount of as-prepared pure PU was added into the solution and dissolved with assistance of magnetic stirring. After PU was completely dissolved, the mixture was stirred continuously at room temperature for 48 h [27]. Then the mixture was put into an ultrasonic bath for another 1.5 h. At last, the MWCNT–PCL/PU composite film was prepared by solution casting. The other two composite films (raw MWCNT/PU and MWCNT–COOH/PU) were prepared using the same procedure, while pure PU film was obtained without incorporating any MWCNTs. In this study, the fractions of MWCNTs for all types of MWCNTs/PU composites were fixed at 1 wt%. The weight percent of functionalized MWCNTs in the composite was calculated based on the weight of MWCNTs before functionalization, which did not include the amount of grafted functional groups or PCL which was determined by TGA tests as shown later.

2.4. Characterization

FTIR spectroscopic tests were conducted on FTIR Frontier (from Perkin Elmer) with Attenuated Total Reflection (ATR). The filler samples were prepared by mixing MWCNTs with potassium bromide and pressing into transparent pellets in a pellet-forming die. The FTIR spectra of film samples were obtained using ATR. Confocal Raman spectroscopy (Witec alpha300 SR) was applied to characterize the structural changes of MWCNTs, using a 633 nm laser as the light source. Thermo-gravimetric analysis (TGA) measurements were used to determine the functionalization degrees of MWCNT–COOH and MWCNT–PCL, conducted on TGA Q500. The powder samples were heated from 25 °C to 900 °C at a speed of 10 °C/min in the presence of nitrogen. The same TGA