



Modification of carbon nanotubes by a novel biomimetic approach towards the enhancement of the mechanical properties of polyurethane



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ABSTRACT

Polyurethane (PU) nanocomposites incorporated with polydopamine treated carbon nanotubes (PDA-CNTs) were prepared by solution casting method *via* in-situ polymerization, achieving excellent CNTs dispersion in the PU matrix. It was observed that, with a loading of only 0.3 wt%, the tensile modulus and tensile strength were increased by 40% and 100% respectively. This reinforcement even exceeded the predicted modulus by Halpin–Tsai model. It indicates extremely enhanced interfacial interaction between the fillers and the matrix. More interestingly, it was found that the incorporation of PDA-CNTs caused a significant change in the degree of phase separation in the PU matrix leading to a unique network-like structure which is responsible for the unexpected reinforcement effect. This understanding combining with the synthetic approach should be useful for future design of PU/CNTs nanocomposites for wide range of applications.

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1. Introduction

The unique mechanical, electrical, magnetic, optical and thermal properties of carbon nanotubes (CNTs) make them ideal reinforcing agents for high performance polymer nanocomposites [1]. Since the first report of polymer nanocomposites using CNTs as a filler [2], CNTs enhanced polymer nanocomposites has become one of the most important research topics both in academic and industrial R&D [3]. Various polymer matrices such as polystyrene, poly(ethyleneimine), epoxy, polyurethane (PU), nylon 6 and polyethylene terephthalate have been used for composites with CNTs [4]. The presence of well-dispersed CNTs in polymer matrix can show remarkable enhancement of tensile strength, toughness, glass transition temperature and electrical conductivity [5].

Due to the strong Van der Waals force, CNTs tend to bundle with

each other and thus do not disperse well in the organic matrices in their pristine state. To achieve better dispersion and alignment of CNTs in organic matrix so to improve the load transfer across the CNTs-polymer matrix interface, many approaches for functionalization of CNTs including oxidation, functional groups and other covalent functionalization have been developed [6,7]. However, CNTs surface functionalization approaches showed some obvious drawbacks such as tedious chemical reactions and involvement of highly corrosive or toxic chemicals. Most importantly, the surface modifications often lead to structure defects and fragmentation of the nanotubes, which drastically decrease the mechanical and electronic properties of CNTs. Therefore, the non-covalent approaches were developed because these methods would not compromise the physical properties of CNTs but improve solubility and processability. The non-covalent approach mainly involves surfactants, biomacromolecules or polymers wrapping [8,9]. Although the non-covalent method is effective in isolation and debonding of CNTs, there remains problems that limit their wide applications. For instance, wrapping polymer with special structures required complicated chemical reactions with high cost.

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Additionally, the surfactants used for dispersion of CNTs could weaken the interfacial strength between CNTs and polymer matrix in general.

In the present work, we report the excellent dispersion of CNTs in polyurethane nanocomposites and exceptional enhancement of the tensile modulus and tensile strength by using polydopamine (PDA) coated CNTs. Motivated by mussel adhesive proteins [10], dopamine was found to form PDA layer on various types of materials including polymers, ceramic and metals through self-polymerization dopamine in aqueous solution [11,12]. PDA coatings have been widely used in numerous materials for biomedical applications due to their physicochemical properties and strong surface adhesion abilities to various surfaces [13–15]. PDA was also employed as a functionalization modifier, e.g., anti-fouling coatings [16], nanofiltration for antibiotics removal [17], CO₂-philic for gas separation [18] and superhydrophobicity for oily water treatment [19]. Besides these applications, secondary treatments can be easily achieved based on their intrinsic capacity, including inorganic Au [20], Ag [21] nanoparticles and CNTs-PDA/Co₃O₄ for Li-air batteries [22]. Moreover, PDA coating of CNTs was recently reported to improve the dispersion of CNTs in various solvents or polymer matrices [20,23,24]. Nevertheless, current PDA studies are mainly focused on surface modification for improved biocompatibility and fabrication of hybrid materials for energy or catalytic applications. In the present work, we showed that PDA coated CNTs (PDA-CNTs) could be successfully employed in PU nanocomposites. We chose PU as the polymer matrix to demonstrate the concept because PU has been widely used in our daily life, e.g., in coatings, medical devices, adhesives, foams and so on [25]. Contributed by the good dispersion of CNTs in PU matrix and enhanced interfacial interaction between fillers and matrix, 40% and 100% increments of tensile modulus and tensile strength were obtained with 0.3 wt% loading of PDA-CNTs, respectively. The influence of PDA-CNTs on the structure of PU are explored and analysed in details as well.

2. Experimental section

2.1. Materials

The multi-walled carbon nanotubes (CNTs, Nanocyl™ NC 7000 with an average diameter of 9.5 nm and length of 1.5 μm) synthesized by chemical vapour deposition were purchased from Nanocyl S.A. Polyisocyanate (N3390 with the isocyanate content 19.6%, from Bayer Company), defoamer (BYK A535), anhydrous N, N-Dimethylformamide (DMF, 99.8% Sigma–Aldrich) and dibutyltin dilaurate (95% provided by Sigma–Aldrich) were used as received. Polyol (Capa 7203, hydroxyl value is 54 mg KOH/g) was dehydrated in vacuum oven at 110 °C overnight before use. Cyclohexanone (ACS reagent, ≥99.0%) was dried at least 48 h by 4 Å molecular sieves before use. Dopamine hydrochloride (99%) and tris (hydroxymethyl)-aminomethane hydrochloride were purchased from Regent Chemicals Pte Ltd.

2.2. Preparation of PDA-CNTs

The PDA-CNTs preparation was done as described in the literature [26,27]. The slightly modified procedure was briefly described as below. 0.2 g CNTs was dispersed into DMF containing Tris buffer solution (pH 8.5) in ultrasonic bath. After formation of a homogeneous suspension, 2 mg/ml dopamine was added into CNTs/DMF suspension and the mixture of dopamine and CNTs was mildly magnetically stirred for 6 h at room temperature. The PDA-CNTs were obtained by repeated centrifugation and washed by deionized water for 3–4 times in order to remove unreacted dopamine monomers and free PDA. After that, the modified CNTs were dried

by freeze dryer for 48 h. The pure PDA was also synthesized following the same procedure.

2.3. Fabrication of PU/CNTs nanocomposites

PU/PDA-CNTs nanocomposites were prepared *via* in-situ polymerization. Firstly, PDA-CNTs were ultrasonically dispersed into large amount of DMF for 2 h, followed by the addition of certain amount of polyisocyanate. Then, the mixture of polyisocyanate and PDA-CNTs was continuously stirred at 80 °C for 2 h in nitrogen atmosphere. The obtained mixture concentrated by rotary evaporation was further added into a three-neck flask containing stoichiometric polyol and catalyst. Finally, PU/PDA-CNTs films were obtained by casting the solution onto a glass plate and subsequently removing the solvent at 60 °C in vacuum for 24 h. The solid samples were kept for one week in dry box before the characterization. In this paper, the samples were defined as PU/PDA-CNTs X. For example, PU/PDA-CNTs 0.1 means PU nanocomposite containing 0.1 wt% PDA-CNTs. To compare the effects of pristine CNTs and PDA-CNTs, the same weight percentage of CNTs was used. For example, the weight percentage of pristine CNTs in PU/Pristine CNTs 0.3 is 0.24 wt%, which corresponds to the practical CNTs loading in PU/PDA-CNTs 0.3. The isocyanate index (molar ratio of –NCO groups to –OH groups) used in this paper was fixed at 1.1:1 for neat PU, while the isocyanate indexes for PU/PDA-CNTs nanocomposites were slightly adjusted in order to optimize the properties of PU/PDA-CNTs nanocomposites [28]. The procedure of preparing PDA-CNTs and PU/PDA-CNTs nanocomposites is shown in Scheme 1 and Scheme 2, respectively.

2.4. Characterizations

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the modification of CNTs by PDA and attenuated mode was employed to study hydrogen bonding within the hard domains and the degree of order of the hard segments in nanocomposites. The tests were carried out using Frontier FTIR/NIR spectrometer (PerkinElmer). A total of 32 scans were done on each specimen with a resolution of 2 cm^{−1} within 650 and 4000 cm^{−1}. The carbonyl regions within 1800 and 1600 cm^{−1} were used to study hydrogen bonding in the hard domains. Thermogravimetric analysis (TGA) by Q500 (TA Instruments) was used to estimate the percentage of PDA on CNTs. A typical specimen weight of 10 mg was placed in a platinum sample pan. Specimens were studied at a heating rate of 10 °C/min under an air atmosphere (balance gas: nitrogen 60 ml/min and sample gas: air 40 ml/min). Transmission electron microscopy (TEM) was employed to investigate the morphological structure of pristine CNTs and PDA-CNTs. Specimens were prepared by placing one droplet of diluted ethanol suspension on carbon-coated copper grid and dried at 60 °C. The TEM images were recorded on a JEOL 2010 TEM at 200 kV. The fracture surfaces of nanocomposites were investigated by using a field emission-scanning electron microscope (Jeol FESEM 7600F) at 5 kV. The cryo-fracture surfaces of specimens were prepared by immersing them in liquid nitrogen before fracturing, and a layer of platinum coating with a thickness of 20 nm was sputtered on the fracture surfaces in order to obtain clear images. Mechanical properties of the nanocomposites were evaluated by tensile test (Instron 5567). For tensile tests, the specimens were punched using ASTM D638-V dog bone die. The testing film had a gauge of length of 9.53 mm and width 3.52 mm. The crosshead speed was kept at 20 mm/min to measure the stress vs strain behaviour of neat PU, PU/Pristine CNTs and PU/PDA-CNTs nanocomposites. Each nanocomposite with varied formulations was tested using at least five specimens in order to obtain an average.

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