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Material performance

Poly(sodium 4-styrenesulfonate) wrapped carbon nanotube with low percolation threshold in poly(ε-caprolactone) nanocomposites

An-Ke Du [b], Kai-Li Yang [a], Tong-Hui Zhao [a], Ming Wang [a, **], Jian-Bing Zeng [a, *]

[a] School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China
[b] Chongqing Academy of Science and Technology, Chongqing 401123, China

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were modified via a non-covalent functionalization technique with poly(sodium 4-styrenesulfonate) (PSS) as the modifier. A well dispersed and stable water dispersion of carbon nanotubes was prepared by ultrasonication of aqueous suspension of MWCNTs in the presence of PSS. Successful wrapping of MWCNTs by PSS was confirmed by High resolution transmission electron microscope (HRTEM). The dispersion was used to fabricate nanocomposites with poly(ε-caprolactone) (PCL) through solution coagulation. Scanning electron microscope (SEM) and transmission electron microscope (TEM) indicate that PSS wrapped MWCNTs dispersed uniformly in PCL matrix without obvious aggregation even with MWCNT loading increased up to 1.0 wt%. Rheological investigation confirmed that rheological network existed in the PCL/MWCNT nanocomposites with the percolation threshold of only 0.3 wt%. The electrical conductivity of the composites was investigated and the results indicate that electrical percolation threshold was also 0.3 wt%. The mechanical properties of PCL were significantly reinforced as evidenced by the improvement in yielding strength, Young's modulus, and dynamic storage modulus with incorporation of PSS wrapped MWCNTs.

1. Introduction

Carbon nanotubes (CNTs) have attracted enormous attentions from both academia and industry due to their unique mechanical, thermal, electronic, and chemical properties, as well as the high aspect ratio, one-dimensional tubular structure, and extensive potential applications [1,2]. They can be used as ideal reinforcing nanofillers for high performance polymer composites. Since Ajayan et al. [3] reported polymer nanocomposites with CNTs as nanofillers for the first time in 1994, extensive investigations have been done to incorporate CNTs into various polymer matrices and study the properties of the fabricated nanocomposites [4]. It was found that the addition of small amount of CNTs could significantly improve various properties of polymer matrices including mechanical strength and modulus [5–7], thermal stability [8,9], crystallization rate [10,11], thermal conductivity [12], electrical conductivity [13–15], electromagnetic interference shielding properties [16,17], etc. It is worth noting that the dispersion state of CNTs within polymer matrices plays a vital role in determining the final properties of the prepared nanocomposites. However, CNTs usually tend to aggregate within the polymer matrices due to the strong van der Waals intermolecular interactions caused by the high aspect ratio, which then reduce reinforcing efficiency or even deteriorate the final properties of the nanocomposites. Therefore, improvement in dispersity of CNTs in polymer matrices represents a significant challenge for preparation of polymer/CNTs nanocomposites [2].

The functionalization of CNT provides an efficient way of stopping nanotube from aggregation, which then helps to disperse and stabilize CNTs within polymer matrices. The various functionalization techniques for CNT can be classified into two categories, i.e., covalent and non-covalent functionalizations [2,18]. Although covalent functionalization is helpful to improve solubility and dispersion of CNT in solvents and polymers, this method usually disrupts the translational symmetry of CNT by changing sp^2 carbon atoms to sp^3 carbon atoms, which then weakens some excellent properties of CNT such as electronic and transport properties [19]. In contrast, non-covalent functionalization, concerning the physical adsorption and/or wrapping of modifiers to

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* Corresponding author.
** Corresponding author.
E-mail addresses: mwang@swu.edu.cn (M. Wang), jbzeng@swu.edu.cn (J.-B. Zeng).

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the surface of the CNT, is of particular interest, because it improves the dispersity and processibility of carbon nanotube but not sacrifices its physical properties. The species that are widely used to modify the surface properties and water dispersibility of CNT are the surfactants such as sodium dodecylsulfate (SDS) [20–22] and sodium dodecylbenzene sulfonate (SDBS) [23–25]. SDBS shows stronger interaction with CNT surface compared to that of SDS, since the benzene ring of SDBS can form strong π-stacking interaction towards the surface of nanotube, which can thus increase the binding and surface coverage of SDBS molecules to nanotube significantly [26].

Except for low molecular weight surfactants, polymers with suitable structures to form π-stacking interaction with CNT could also be used to wrap nanotube so as to enhance its dispersion in water or organic solvents [27–30]. Compared to low molecular weight surfactants, polymeric modifiers exhibit many advantages, such as superior thermal stability, nontoxicity and mechanical properties, which are very important for the application especially in reinforced polymer composites. Poly(sodium 4-styrenesulfonate) (PSS) is a water soluble strong polyelectrolyte with plenty of attached benzene rings, which could form very strong π-stacking interaction with the surface of graphite. Therefore, PSS is very suitable to be used as a polymeric modifier to better disperse and stabilize carbon nanomaterials in aqueous solution [31,32]. Since PSS wrapped carbon nanotubes are usually dispersible in water but not in organic solvents, they were occasionally incorporated into water soluble or dispersible polymers to form composite materials [33]. Less work has been done to incorporate PSS wrapped CNT into hydrophobic (water insoluble) polymers and evaluate effect of the nanotubes on the properties of the fabricated composites, due to the difficulty in fabrication of the composites because of the absence of mutual solvents for PSS wrapped CNT and water insoluble polymers.

Aliphatic polyesters with good biodegradability have drawn many interests since the widespread use of conventional nondegradable polymers has caused serious environmental problems [34–37]. Poly(ε-caprolactone) (PCL) is such an aliphatic polyester that is not only biodegradable but also biocompatible with many potential applications such as scaffold for tissue engineering, controlled drug release, bone regeneration, and shape memory biomaterial [38–42]. However, the insufficient mechanical performance would limit its application such as in load-bearing orthopedic areas [43], and some specific applications such as nerve regeneration or in spinal cord repair require PCL to have high electrical conductivity [44]. Those properties can be realized by the addition of carbon nanotubes. Although a lot of works have been reported to incorporate CNT into PCL to reinforce the properties, less effort has been paid to incorporate non-covalently functionalized CNTs into PCL matrix to fabricate reinforced nanocomposites. In this study, we modified multi-walled carbon nanotubes (MWCNTs) by wrapping with PSS in aqueous solution and then incorporated the modified MWCNTs into PCL to fabricate PCL/MWCNT nanocomposites through a solution coagulation method. The morphology, rheological behavior and electrical conductivity of the fabricated PCL/MWCNT nanocomposites were systematically investigated.

2. Experimental

2.1. Materials

Poly(ε-caprolactone) (PCL, trade mark Esun500C) with molecular weight of 5.0×10^4 g/mol and melt index of 9–11 g/10 min was purchased from Guanghua Weiye industrial co., LTD (Shenzhen, China). Multi-walled carbon nanotubes (NC 7000) were procured from Nanocyl Corporation (Belgium). Poly(sodium 4-styrenesulfonate) (PSS) with 21 wt % aqueous solution was obtained from Micxy Chemical Co., LTD (Chengdu, China). The molecular weight of PSS is 7.0×10^4 g/mol as provided by the manufacturer. Tetrahydrofuran (THF) and other chemicals with analytical grades were bought from Kelong Chemical Co., LTD (Chengdu, China). All the materials and chemicals were used as received.

2.2. Preparation of PSS wrapped MWCNT

PSS wrapped MWCNT was prepared by dispersing nanotubes in water solution of PSS with the aid of ultrasoniction. The weight ratio of PSS to MWCNTs was 5:1 and the concentration of MWCNTs in water was 2.0 g L^{-1}. The detailed process is as follow: 0.4 g MWCNTs, 9.52 g 21 wt% PSS solution, and 190.18 g deionized water were added into a 500 mL beaker to prepared the mixtures, which were then sonicated using a probe sonicator (SCIENTZ-IID, Ningbo China) for 30 min to generate a uniform dispersion. For comparison, MWCNTs water dispersion in the absence of PSS was also prepared by the similar processing.

2.3. Fabrication of PCL/MWCNT composites

PCL nanocomposites containing different contents of MWCNTs varying from 0.1 to 1.5 wt% were fabricated by a solution coagulation technique. Taking the composite containing 0.1 wt% MWCNTs as an example, the detailed fabrication procedures were as follows: 9.99 g PCL was completely dissolved in 200 mL THF with the aid of mild stirring at 50 °C for 2 h; after cooling to room temperature, 5 g of the above prepared MWCNT water dispersions were dropwise added into the strongly stirred PCL solution, then additional excessive deionized water was dropped into the solution to precipitate the coagulated composites. The composites were collected via filtration, washed with ethanol, dried in a 50 °C air blast oven to evaporate solvents, and finally dried in a 50 °C vacuum oven for 48 h to remove any residual solvent. For brevity, the nanocomposite was abbreviated as PCL/MWCNT-n, where n is a number that indicates the weight content of MWCNT. For example, PCL/MWCNT-0.1 represents the nanocomposite containing 0.1 wt% PSS wrapped MWCNTs. For comparison, neat PCL was also treated with the same procedures. The sample sheets with thickness of 1 mm were prepared by hot pressing for further characterization.

2.4. Characterization

High resolution transmission electron microscope (HRTEM) for pristine MWCNTs and PSS functionalized MWCNTs were carried out on a JEM-2100F TEM at an accelerating voltage of 200 kV. The morphologies for the cryo-fractured surfaces of PCL/MWCNT nanocomposites with different nanotube loadings were observed by a XL-30s FEG (Philips, Holland) scanning electron microscope (SEM). The dispersion of PSS wrapped MWCNTs was observed by transmission electron microscope (TEM) measurement. Ultrathin section of ca. 70–80 nm in thickness sliced by a Leica EM FC6 cryo-ultramicrotome was used for observation. The measurement was carried out on a FEI Tecnai G2F20 S-TWIN TEM (Holland) with an accelerating voltage of 200 kV. The mechanical properties including tensile strength, elongation at break, and Young's modulus of neat PCL and PCL/MWCNT nanocomposites were measured on a Sansi Universal Testing Machine (CMT6503) at a crosshead speed of 50 mm/min at room temperature. An international standard (ISO 527-3-1995) has been referenced during tensile testing. The width and thickness of dumbbell-shaped