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Nanocable-structured polymer/carbon nanotube composite with low dielectric loss and high impedance

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ABSTRACT

A hierarchical nanocable structure was fulfilled by grafting poly(glycidyl methacrylate) from single walled carbon nanotubes (PGMA-SWCNTs) via activators regenerated by electron transfer-atom transfer radical polymerization (ARGET-ATRP). It was found that SWCNTs were parallelly separated by the grafted PGMA brushes in the nanocables. To investigate the advantages of nanocable architecture, a composite film was prepared through filtrating the uniform solution of PGMA-SWCNTs nanocables. The dielectric properties dependent on frequency and temperature revealed that high dielectric constants, high impedance and low dielectric loss were simultaneously achieved for the PGMA-SWCNTs film. Meanwhile, thermal conductive analysis showed that the PGMA-SWCNTs film possessed a high thermal conductivity. The unique nanocable structure and the excellent interfacial interaction between PGMA and SWCNTs were believed to be the critical causes for the high performance of the nanocomposite.

1. Introduction

Carbon nanotubes (CNTs), as the ideal fillers for developing high-performance polymer nanocomposites, have received considerable attentions due to their excellent mechanical, electrical and thermal properties [1]. As previously reported, an addition of a small amount of CNTs to polymer can bring superior electrical properties [2,3]. For example, Peng et al. reported a composite foam with a conductivity as high as 3.4 S/m when CNTs loading was 10.0 wt% [3]. Owing to their high aspect ratio, a three-dimensional (3D) percolating network of CNTs can be easily formed within the composites even at a low concentration, which is known as percolation threshold [4,5]. The extremely low percolation threshold for CNTs means almost all the polymer/CNTs composites are electrically conductive. Electrical conduction will cause inferior electric insulation and high dielectric loss. The high dielectric loss results in not only wastes of energy but also overheated devices. Concerning those, polymer/CNTs composites are not suitable to such applications requiring high electrical insulation and/or good dielectric performance as capacitors, inductors and resistors in integrate circuits. To reduce the dielectric loss and/or improve the electric resistance, the connections between CNTs must be avoided in composites.

Recently, attempts have been made to hinder the conformation of electrical conductive network in polymer/CNTs composites. A strategy regarding the formation of core-shell nano-architectures is proposed to cut off the conductive network by means of physically attaching the dielectric layer onto the surface of CNTs [6–12]. Acting as an interlayer between CNTs and polymer matrix, the dielectric layer can block the charge carriers moving from one CNT to another. For instance, Nan et al. covered CNTs with a thick organic shell, which brought a relatively low $\tan\delta$ and high dielectric constant for composites [6]. Liu et al. coated CNTs with a layer of $BaTiO_3$ shells. The obtained core-shell structures endow the nanocomposites with both high dielectric constant and high thermal stability [7]. However, with the concentration increasing, especially near the percolation threshold, the CNTs approach to each other within several nanometers. In that situation, inevitable electron tunneling will occur among the CNTs and be followed with large dissipation. Moreover, the core-shell structure may be destroyed by other external forces in the process due to the weak non-covalent interaction between CNTs and the absorbed layer. Another effective approach to prevent the electrical connection and tunneling conduction between CNTs is covalently grafting polymer brushes from the surface of CNTs [13–20]. For example, Hayashida and coworkers [14,15,19] reported a low dielectric loss and high electrical resistance nanocomposite system with all the

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polymer chains being tethered on the CNTs surface prepared by atom transfer radical polymerization (ATRP). In such system, the individual CNTs was isolated at a sufficient distance by the grafting polymer, thus the tunneling conduction was suppressed effectively. But the requirement of the stringent experiment condition made the polymerization hard to control. Besides, a great amount of metal catalyst utilized in the experiment is difficult to be removed, and detrimental to the dielectric properties of nanocomposites. Therefore, a more efficient and controllable method is desired to graft polymers from the surface of CNTs. In addition, the previous researches are mainly focused on grafting polymer from multi-walled CNTs (MWCNTs). However, there are few reports on the dielectric properties of polymer grafted single walled carbon nanotubes (SWCNTs) nanocomposites system and the role of the micro-structure in determining the dielectric properties of the polymer/SWCNT composites has not been explored deeply.

In some applications, not only good dielectric performance but high thermal conductivity is essential also. However, the thermal conductivity is depressed due to the high interfacial thermal resistance in polymer/CNTs composites [21]. Significant efforts have been devoted to reduce the interfacial thermal resistance by modifying CNTs through covalent grafting, which can promote the interfacial interaction between CNTs and polymer matrix and, in turn, will improve the thermal conductivity of nanocomposites [22,23]. Furthermore, it is known that the strong interfacial interaction between CNTs and polymer matrix is important to improve the dielectric performance of nanocomposites [24–26]. Therefore, we believe that the thermal conductivity and dielectric performance of nanocomposites can be improved through appropriate interface design.

In this work, a hierarchical polymer-CNTs nanocable was fabricated by grafting poly(glycidyl methacrylate) from SWCNTs (PGMA-SWCNTs) via activators regenerated by electron transfer-atom transfer radical polymerization (ARGET-ATRP), since less metal catalysts were required and the polymerization could be carried out without strict deoxygenation condition [27]. It shows that SWCNTs are individually isolated by the grafted PGMA brushes within the nanocable. In order to explore the advantages of the nanocable structure, a composite film was obtained by filtrating the uniform solution of PGMA-SWCNTs nanocables. The dielectric properties of the film were systematically characterized over a broad frequency range of 10^2–10^7 Hz at temperature from 20 to 160 °C, and compared with that of PGMA film. Thermal Stimulated Depolarization Current (TSDC) measurements were utilized to give information on electron trapping and dipolar orientation of PGMA-SWCNTs composite. Furthermore, a multi-layer model was proposed to explore the molecular relaxation and electron transport in the PGMA-SWCNTs composite. Finally, thermal conductivity of PGMA-SWCNTs was also detected from 25 to 125 °C. It exemplifies that the nanocable is a favorable structure for suppressing the tunneling conduction and improving the interfacial interaction of CNTs nanocomposites.

2. Experimental section

2.1. Materials

SWCNTs were purchased from Carbon Solutions, Inc. 3,4-dihydroxybenzaldhyde, N-methylglycine, 2,2-Bipyridine (bpy), Cupric bromide ($CuBr_2$) and Ascorbic acid were purchased from Shanghai Darui Fine chemical Co., Ltd (China). Glycidyl methacrylate (GMA) (97%) and 2-bromoisobutyryl bromide (98%) were purchased from Aladdin. Acetone (Tianjin Kemiou Chemical Reagent Co. Ltd) were previously distilled and kept in the presence of 4 Å molecular sieve to eliminate any traces of water from it. All of the solvents (AR grade) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd (China) and used as received.

2.2. Attachment of initiator onto SWCNTs

The procedure for immobilization of initiator on the SWCNTs surface was divided into two steps. Steps 1; Prior to the attachment of initiator, SWCNTs (10 mg) were functionalized with phenolic hydroxyl groups via 1,3-dipolar cycloaddition (SWCNTs-*f*-OH). SWNTs (10 mg), 3,4-dihydroxybenzaldehyde (100 mg, 0.72 mmol), and N-methylglycine (100 mg, 1.12 mmol) were suspended in 50 mL of N,N-Dimethylformamide (DMF). The dispersion was sonicated and heated gradually until 130 °C for 120 h. After the reaction, the product was collected and purified by filtration through a Teflon membrane (200 nm pore) and then redispersion in DMF, Tetrahydrofuran (THF), and methanol (MeOH) separately. The purified SWCNTs-*f*-OH was dried at 25 °C for 48 h under vacuum. Step 2; the available phenolic hydroxyl groups on the surface of SWCNTs were converted into ATRP initiators by reacting with 2-bromoisobutyryl bromide in the anhydrous acetone. A 100 mL flask was charged with anhydrous acetone (20 mL), SWCNTs-*f*-OH (20 mg) and triethylamine (1 mL, 0.73 g, 7 mmol). Then 2-bromoisobutyryl bromide (1 mL, 1.86 g, 8 mmol) dissolved in 10 mL of anhydrous acetone was added dropwise at 0 °C in 60 min. The reaction was allowed to proceed for 2 h at 0 °C and 24 h at room temperature. Thereafter, the resulting mixture was isolated by filtration through a Teflon membrane (200 nm pore) and thoroughly washed with THF and ethanol to remove the reactants and byproducts. Then the obtained SWNTs-*f*-Br were finally dried under vacuum at room temperature for 48 h.

2.3. Grafting of glycidyl methacrylate from initiator-functionalized SWCNTs

First, a sealed 100 mL Schlenk flask containing Ascorbic acid (15 mg, 0.085 mmol) was degassed and refilled with N_2 five times. Then, the SWNTs-*f*-Br (10 mg) was mixed with 24 mL mixture of DMF/water (3:1 v/v) and followed by ultrasonic treatment for 3 min. The solution was bubbled with N_2 for 3 min to remove the air and then added into Schlenk flask. After that, GMA (1 mL, 1.08 g, 7.6 mmol) and 2 mL $CuBr_2$-bpy stock solution (containing $CuBr_2$, 0.0045 mmol, 1.0 mg and bpy 0.096 mmol, 15 mg in 2 mL methanol) were added into the Schlenk flask (via a syringe) respectively under magnetic stirring. The reaction mixture was stirred at 25 °C for 24 h, and then terminated by opening the flask in the air. The PGMA grafted SWNTs (PGMA-SWCNTs) were isolated by filtration through a Teflon membrane (200 nm pore) and purified by four addition cycles of filtration and redispersion in DMF, THF, chloroform ($CHCl_3$) and methanol separately. The purified PGMA-SWCNTs was dried at 25 °C for 48 h under vacuum.

In order to obtain the grafted PGMA brushes, the phenolic ester bonds of PGMA-SWNTs was cleaved according to reported procedure [28]. Typically, 20 mg of PGMA-SWCNTs was mixed with 7 mL of $CHCl_3$ in a 25 mL flask. After the addition of 2 mL of a saturated solution of $NaHCO_3$ in MeOH, and an extra 100 mg of $NaHCO_3$, the mixture was stirred overnight at room temperature. After cleavage, the polymer was isolated by diluting the reaction mixture with $CHCl_3$ and then passing the solution through a silica gel column with $CHCl_3$ as the eluent to remove the SWCNTs. The majority of the solvents were removed by rotary evaporation, and the polymer was dissolved in a minimum amount of $CHCl_3$, was poured into a large excess of MeOH. The precipitated products were filtered and dried in a vacuum oven at room temperature.

To prepare the PGMA-SWCNTs composites film, the obtained PGMA-SWCNTs were dispersed in THF. And then the uniform