Electrospun Hybrid Composite Poly(L-Lactide) Nanofibers Incorporating POSS-Modified Multiwalled Carbon Nanotubes


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ABSTRACT

We report the preparation of electrospun poly(L-lactide) (PLA) nanofibers incorporating polyhedral oligosilsesquioxane (POSS)-modified MWNTs. FT-IR and transmission electron microscopy (TEM) analysis confirms the existence of POSS macromers bonded to the multiwalled carbon nanotubes (MWNTs) as an extra phase. The dispersion of POSS-modified MWNTs in the PLA hybrid nanofibers is evaluated by TEM analysis. The thermal and microstructure properties of the PLA hybrid nanofibers with POSS-modified MWNTs were investigated by Thermogravimetric analysis (TGA) and Wide-angle X-ray diffraction (WAXD), respectively.

Keywords: electrospinning, hybrid nanofibers, POSS, multiwalled carbon nanotubes, nanostructures

1 INTRODUCTION

Recently, organic–inorganic hybrid composites have attracted considerable attention because of their distinctive physical and chemical properties [1]. Specifically, among them the multiwalled carbon nanotube (MWNT)-polymer composites have been widely studied. When uniform dispersion of the MWNTs in the polymer matrix is achieved without their aggregations, it is expected to have high mechanical, ultra high thermal conductivity and unusual electrical properties. Consequently, a strong MWNT/polymer matrix interaction is needed [2]. The covalent modification of MWNT is most frequently initiated by introducing carboxylic acid groups using a nitric acid oxidation method [3]. And then, the long alkyl chains and polymers can be chemically attached to the MWNTs via esterification and amidation reactions of the hydroxyl and carboxylic group moieties of the MWNTs [4]. Recently, Shimizu et al. successfully functionalized the MWNT with aminopropylisocyclohexyl-polyhedral oligosilsesquioxane (POSS) by reacting the amine group in POSS with the MWNT functionalized with –COCl groups, which was prepared by treating the purified MWNT with HNO3 followed by SOCl2, and reported that a more uniform and fine dispersion of MWNTs was achieved throughout the polymer matrix after functionalization due to the strong interfacial adhesion between the MWNTs and the polymer matrix. Moreover, POSS covers and cures any defects in the functionalized MWNTs with lowered mechanical properties due to an acid-treatment of original MWNTs, and then may strength the mechanical properties of MWNT-Polymer composites. Cage-like silsesquioxane are usually called polyhedral oligosilsesquioxanes or polyhedral oligomeric silsesquioxanes, abbreviated as POSS. This class of well-defined, highly symmetric molecules usually features a nanoscopic size, approximately 1.5 nm in diameter when the vertex (R = isobutyl, cyclohexyl, cyclopentyl, etc.) groups are included [5]. The POSS-containing materials are emerging as an interesting building block technology for the construction of nanostructured organic-inorganic hybrid structures [6,7].

In this work, the POSS-modified MWNTs are synthesized by a direct urethane linkage between the hydroxyl groups of MWNTs and the monoisocyanate groups of POSS macromers. As far as we know, there is no prior report on electrospinning studies of the poly(L-Lactide) (PLA) nanofibers incorporating POSS-modified MWNT. We attempt to electrospin from the PLA composite solution incorporating POSS-modified MWNT via electrospinning, and investigate the dispersion and thermal mechanical properties of electrospun POSS-modified MWNTs containing PLLA nanofibers depending on POSS-modified MWNT contents.

2 EXPERIMENTAL

2.1 Materials

The multiwalled carbon nanotubes (MWNTs, purity: 95%, 20-70 nm in diameter, aspect ratio > 100, [8]) was kindly supplied by Prof. Endo’s group (Department of Electrical & Electronic Engineering, Shinshu University, Japan). Poly(L-lactide) (PLA, RESOMER L210S, Mw ~ 650 kDa, intrinsic viscosity ~ 3.3 – 4.3, Tg ~ 60 – 65 °C, Tm ~ 180 – 185 °C) was purchased by Boehringer Ingelheim Pharma GmbH & Co. KG, Germany. Isocyanatopropyldimethylsilylcyclohexyl-polyhedral oligomeric silsesquioxane (POSS macromer) was purchased from Tomen Plastics Co., Japan. Dibutyl tin dilaurate (DBTDL; Aldrich, 95% purity) as a catalyst for
urethane formation was used as received. Tetrahydrofuran (THF) was dried with CaH$_2$ and then distilled prior to use. Dichloromethane (MC) and dimethylformamide (DMF) were used as received without purification.

2.2 Acid Treatment of MWNT

The carboxylated or hydroxylated MWNTs were prepared by the treatment of MWNTs in mixture of H$_2$SO$_4$ and HNO$_3$ (3:1, v/v) under sonication at 55°C for 9 hours [9]. Then the acid-treated MWNTs were washed with distilled water 4 times until pH reaches to neutrality. The resulting acid-treated MWNTs were vacuum-dried.

2.3 Synthesis of Hybrid POSS-Modified MWNT

The acid-treated MWNTs dispersed in THF were sonicated for 10 minutes and added to a three-neck reactor. Afterward, the mixture containing DBTDL and POSS macromers was injected to the reactor drop by drop using a syringe. The reaction mixture was kept at 80°C for 5 hours with stirring and then further at 90°C for 1 hr in order to achieve complete reaction. Then the reaction mixture was precipitated in an excess of THF and washed with fresh THF several times to remove the unreacted POSS macromer and catalyst. The synthesized POSS-modified MWNTs (Scheme 1) were vacuum-dried.

2.4 Preparation of Electrospun PLA Fibers Incorporating POSS-Modified MWNT

The PLA was dissolved in MC/DMF mixed solvent with a weight ratio of 7 to 3. The concentration of PLA solution was 3 wt%. The PLA solution was mixed with various MWNTs contents of 0.1, 0.3, and 0.5 wt%. The pure PLA and PLA/MWNTs blend solutions for electrospinning were supplied through a plastic syringe attached to a capillary tip. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution, and a negative electrode (cathode) was attached to a metallic collector. A high-voltage power supply (CPS-60 K022V1, Chunpa EMT Co., Republic of Korea) capable of generating voltages up to 60 kV, was used as a source of electric filed. The voltage was fixed at 12 kV. The distance between the capillary tip and the collector was fixed to be 15 cm, and the plastic syringe was placed at an angle of 10° from the horizontal direction.

2.5 Characterization

Raman spectra were recorded with a Raman spectrometer (Hololab 5000, Kaiser Optical Systems Inc., USA), and argon laser at 532 nm, with a Kaiser holographic edge filter. Fourier Transform infrared spectroscopy (FT-IR, THERMO NICOLET AVATAR 370, Thermo Fisher Scientific Inc., USA) was carried out, and the spectra were recorded from 600 to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. The morphology of electrospin fibers was observed with scanning electron microscopy (SEM, VE-8800, Keyence Co., Japan). Wide-angle X-ray diffraction (WAXD) experiments were performed at room temperature with nanofiber samples using a Rotaflex RTP300 (Rigaku Co., Japan) X-ray diffractometer operating at 50 kV and 200 mA. Nickel-filtered Cu K$_\alpha$ radiation was used for the measurements, along with an angular range of 5 < 2$\theta$ < 50°. Thermogravimetric analysis (TGA) of the synthesized POSS-modified MWNTs was carried out with Rigaku Thermo Plus 2 TG-8120, Japan by heating from 50°C to 800°C under a continuous N$_2$ purge of 20 mL/min. The heating rate was 20°C/min. HRTEM observations were carried out in a JEOL JEM-2010F instrument operated at 200 kV (equipped with an omega filter, a Gatan multi-scan camera and an energy dispersive X-ray-EDX-Oxford Instruments Detector).

3 RESULTS AND DISCUSSION

3.1 Characterization of POSS-Modified MWNTs

To identify the chemical structures of the resulting POSS-modified MWNTs, FT-IR analysis was done using a THERMO NICOLET AVATAR 370 (Thermo Fisher Scientific Inc., USA). The weak carbonyl (-C=O) and amine (-NH) bands appeared at 1700 cm$^{-1}$ and 1570 cm$^{-1}$, respectively. The broad and slightly less intense band at 1570 cm$^{-1}$ is assigned to the combination of the bending vibration of the N-H bond and the stretching vibration of the C-N bond of the amide group [10], and verify the existence of POSS macromers bonded to the MWNT through the urethane reaction (data not shown). The effect of POSS treatment on the MWNTs was investigated by TEM, and the results are shown in Fig. 1. After POSS treatment, the microstructure significantly changed. That is, the wall of pristine MWNTs (Fig. 1a) is relatively smooth and clean and does not appear covered with any extra phase, whereas the POSS-modified MWNTs (Fig. 1c and 1d)
exhibit stained surface with an extra phase, probably due to the grafted POSS materials.

Figure 1: TEM micrographs of (a) pristine MWNT, (b) acid-treated MWNT, (c) POSS-modified MWNT, and (d) higher magnification image in image (c). The indicate shows the POSS macromers bonded to the multiwalled carbon nanotubes (MWNTs) as an extra phase.

Fig. 2 shows the behavior of weight loss of pure MWNT, acid-treated MWNT, and POSS-modified MWNT under N$_2$ atmosphere. The acid-treated MWNT started to decompose earlier than pure MWNTs, which can be attributed to the presence of carboxyl groups on the tubes [11]. The POSS-modified MWNT exhibited a weight loss of about 14 wt% when the temperature is up to 800 °C due to the degradation of the alkyl of grafted POSS on the MWNT, and the residues above 800 °C are compliant with MWNT.

Raman analysis of pure PLA nanofibers and PLA nanofibers incorporating acid-treated MWNTs and POSS-modified MWNTs was also carried out to investigate the presence of MWNTs in the PLA nanofibers. In general, Raman spectrum of the pure MWNT exhibited G band at 1334 cm$^{-1}$ due to the graphite structure, and D band at 1561 cm$^{-1}$ due to the defect of graphite and amorphous. The G/D intensity ratio of pure MWNT was about 6.4, while POSS-modified MWNTs was found to be about 1.9, suggesting that the POSS-modified MWNT was lower purity than that of the pristine MWNT and therefore the highly ordered graphitic tubular structures were essentially disrupted by acid-treatment. Moreover, Raman spectra of PLA nanofibers incorporating acid-treated MWNT and POSS-modified MWNT exhibited both peaks corresponding to the PLA and MWNT, respectively, which is an evidence for the well-inclusion of both acid-treated MWNT and POSS-modified MWNT in the PLA nanofibers.

Figure 2: Thermogravimetric analysis of (a) pure MWNT, (b) acid-treated MWNT, and (c) POSS-modified MWNT.

Fig. 3 shows the WAXD patterns of pure PLA nanofibers and hybrid PLA nanofibers incorporating acid-treated MWNTs and POSS-modified MWNTs. As seen in Fig. 3, the characteristic peaks of PLA were gradually decreased as increasing the amounts of POSS-modified MWNTs, indicating that POSS-modified MWNTs disturbed the crystal structure of PLA. Moreover, typical (002) peaks of graphite (Fig. 3b) was also observed at 2θ = 26° [12]. It was found that the POSS-modified MWNTs could exist as crystal in the hybrid PLA nanofibers when the concentration of POSS-modified MWNTs increased to 0.3 wt%.
3.2 Hybrid PLA Nanofibers Incorporating POSS-Modified MWNTs

Fig. 4 (top) shows SEM images of PLA nanofibers electrospun from the solutions with different amounts of POSS-modified MWNTs. As the content of POSS-modified MWNTs increased, the fiber diameter slightly decreased (Fig. 4, bottom) due to higher conductivity of the incorporated POSS-modified MWNTs. The inset in Fig. 4 demonstrates that POSS-modified MWNTs are well incorporated into PLA nanofibers, as confirmed by TEM analysis.

We have successfully prepared electrospun PLA nanofibers incorporating POSS-modified MWNTs. FT-IR and TEM analysis confirmed the existence of POSS macromers bonded to the MWNTs as an extra phase. Because of higher thermal stability of POSS, it might be expected that uniform electrospun fibers (average diameter of 650 – 750 nm) with POSS-modified MWNTs enhanced thermal/mechanical properties. Furthermore, the crystalline peaks of PLA were gradually decreased as increasing the amounts of POSS-modified MWNTs, indicating that POSS-modified MWNTs disturbed the crystal structure of PLA. The PLA hybrid nanofibers were successfully prepared from the PLA blend solution with POSS-modified MWNTs via electrospinning. As the content of POSS-modified MWNTs increased, the fiber diameter slightly decreased due to higher conductivity of the incorporated POSS-modified MWNTs. The well-incorporation of POSS-modified MWNTs was confirmed by TEM analysis.

5 ACKNOWLEDGEMENTS

This work was supported by project for “Innovation Creative Center for Advanced Interdisciplinary Research Area” in Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors acknowledge the support of Shinshu University Global COE Program “International Center of Excellence on Fiber Engineering”.

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