



Effects of poly(oxyethylene)-block structure in polyetheramines on the modified carbon nanotube/poly(lactic acid) composites



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ABSTRACT

The hybrids of multi-walled carbon nanotube and poly(lactic acid) (MWCNT/PLA) were prepared by a melt-blending method. In order to enhance the compatibility between the PLA and MWCNTs, the surface of the MWCNTs was covalently modified by Jeffamine[®] polyetheramines by functionalizing MWCNTs with carboxylic groups. Different molecular weights and hydrophilicity of the polyetheramines were grafted onto MWCNTs with the assistance of a dehydrating agent. The results showed that low-molecular-weight Jeffamine[®] polyetheramine modified MWCNTs can effectively improve the thermal properties of PLA composites. On the other hand, high-molecular-weight and poly(oxyethylene)-segmented polyetheramine could render the modified MWCNTs of well dispersion in PLA, and consequently affecting the improvements of mechanical properties and conductivity of composite materials. With the addition of 3.0 wt% MWCNTs, the increment of E' of the composite at 40 °C was 79%. For conductivity, the surface resistivity decreased from $1.27 \times 10^{12} \Omega/\text{sq}$ for neat PLA to $8.30 \times 10^{-3} \Omega/\text{sq}$ for the composites.

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1. Introduction

Due to the problems of environmental pollution, the new development of eco-friendly plastics is an important research subject [1]. One of the biodegradable polymers, poly(lactic acid) (PLA), is produced by the ring-opening polymerization of lactide (a cyclic dimer of lactic acid). PLA is a thermoplastic, high-strength, high-modulus polymer and can be easily processed using the conventional reactors and equivalents to generate bulks, films and fibers [2,3]. However, its electrically insulating nature may cause static charge sparking or even serious incidences of fire or explosion [4]. In addition, another function of electromagnetic interference (EMI) [5,6] can also be resolved by introducing the property of electrical conductivity to the PLA derived materials.

Since the first observation of carbon nanotubes (CNT) in 1991 by Iijima [7] and the identification of their distinctive mechanical, thermal and electrical properties, the approach of using CNT/polymer composites to improve the polymers' functions has been popularly taken [8–12]. However, carbon nanotubes frequently aggregate into

bundles due to their inherent van der Waals interactions among the CNTs. Organic modification of carbon nanotubes to increase their organophilic properties is required for many industrial applications. For example, the acid-oxidation to introduce –OH and –COOH functional groups is reported for introducing the organic functionalities into the desired surface functional groups [1]. A great deal of research efforts have made on preparing soluble nanotubes [13–16]. Yoon et al. [16] described a method for modifying the surfaces of multi-walled carbon nanotubes (MWCNTs) followed by grafting with poly(l-lactide). In our previous study [17], we modified the MWCNTs by grafting with stearyl alcohol to improve the compatibility between MWCNTs and poly(butylene succinate) (PBS). As a result, the MWCNT/PBS composites exhibited not only a good dispersion of nanotubes in the PBS matrices, but an improvement in thermal and mechanical properties. Moreover, a decrease of over 10^9 fold in the electrical resistivity and an excellent anti-static capacity were obtained for the composite with 3 wt% of the modified MWCNTs. In another study [18], the MWCNTs were first pre-treated using an acid solution to obtain the functionality of carboxylic groups. In the next step, the poly(oxyalkylene)-amines, i.e., Jeffamine[®] polyetheramines, were grafted via amidation with the assistance of a dehydrating agent – N,N'-dicyclohexylcarbodiimide (DCC). According to the results of Lin et al., the DCC coupling method

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is more effective for grafting diamines onto MWCNT-COOH via amide linkages [19]. Since the poly(oxyalkylene)-amines are consisting of oxyethylene- and oxypropylene-block structures, it was expected to have a higher compatibility with PBS than stearyl alkyl group on the modified MWCNTs. Hence, the polyetheramine modified CNT actually promoted the enhancements of the mechanical properties, thermal behavior and conductivity of the composites in comparison with the counterpart modifying with stearyl alcohol.

In comparing the clay/PLA composites, only few studies were reported on the preparation of MWCNT/PLA composites [1,10]. In this study, the surfaces of MWCNTs were chemically modified by the amidation with poly(oxyalkylene)-amines which could provide a high compatibility with PLA. Through the selection of polyetheramines with different molecular weights and oxyethylene/oxypropylene composition ratios, the compatibility between MWCNTs and PLA can be optimized. The prepared MWCNT/PLA composites were examined for their mechanical properties, thermal behavior and conductivity and further correlated to the specific structure of the polyetheramines. The reinforcing effects on PLA by introducing different polarities and molecular weights of polyetheramines for grafted MWCNTs is discussed. The aim is to find the optimum polarity and organic chain length of the modifier for MWCNTs when reinforcing PLA.

2. Experimental section

2.1. Materials

PLA (NatureWorks® PLA 4032D) was supplied by NatureWorks LLC. Poly(oxyalkylene)-amines, that is, Jeffamine® polyetheramines (M600, oxyethylene/oxypropylene or EO/PO = 1/9, M.W. = 600; M1000, EO/PO = 19/3, M.W. = 1000; M2005, EO/PO = 6/29, M.W. = 1977 and M2070, EO/PO = 33/10, M.W. = 2063) were supplied by Huntsman Co. These polyetheramines are classified into hydrophilic and hydrophobic amines, oxyethylene-rich or water soluble amines such as M1000 and M2070, and oxypropylene-rich or water-insoluble amines such as M600 and M2005. Four polyetheramines were used to modify the multi-walled carbon nanotubes (purity > 95%, obtained from Sciencetech Co., Taiwan).

2.2. Surface modification of MWCNTs

Surface modification of MWCNTs was achieved by the followings. First, 5 g of original MWCNTs (P-MWCNT) were dispersed in 500 mL of HNO₃ and kept at 120 °C for 60 min in the reflux system to introduce carboxyl groups at their open ends and defect locations on their walls. Then this product was filtered and washed with distilled water until the pH of the filtered water reached about 7. 3 g of the obtained MWCNT-COOH after dried at 70 °C in vacuum was dispersed in dry DMF, mixed with 9 g of Jeffamine® polyetheramines (M600, M1000, M2005 and M2070) and 9 g of N,N'-dicyclohexyl-carbodiimide (DCC), and reacted at room temperature for 48 h to graft the Jeffamine® polyetheramines onto the MWCNTs, respectively. Then these products were filtered and washed with DMF several times to remove the unreacted Jeffamine® polyetheramines and DCC. As a result, organically modified MWCNTs (MWCNT-M600, MWCNT-M1000, MWCNT-M2005 and MWCNT-M2070) were obtained (Fig. 1).

2.3. Preparation of MWCNT/PLA composites

MWCNT/PLA composites were prepared through melt-blending at 180 °C with a rotor speed of 50 rpm for 5 min. The mixed samples were then compressed under a pressure of about 100 kgf/cm² at 180 °C for 3 min using a hot press. The MWCNT/PLA composites,

with 3% P-MWCNT, MWCNT-M600, MWCNT-M1000, MWCNT-M2005 and MWCNT-M2070, are named as PM, PM-M600, PM-M1000, PM-M2005 and PM-M2070, respectively.

2.4. Characterizations

Thermal stabilities were performed using a thermogravimetric analyzer (TGA; TA Instruments Q50). Samples were heated from room temperature to 900 °C at a heating rate of 20 °C/min under a nitrogen purge. Thermal transition behavior was analyzed using a Differential Scanning Calorimeter (DSC; TA Instruments Q20). Samples were heated from room temperature to 180 °C at a heating rate of 10 °C/min. A Raman Spectrum (TRIAx 550 Jobin-Yvon) was used to analyze the structure of the MWCNTs after modification. Gel Permeation Chromatography (GPC) was used to determine the changes in the average molecular weight of PLA after compounding. The test specimens were dissolved in tetrahydrofuran, THF (HPLC grade, Sigma), to give a final concentration of PLA of 0.1% (w/v). The solutions were filtered using a 0.2 mm Teflon filter to remove the insoluble species before injecting the solute into the columns. The GPC was conducted on a Waters GPC (Waters 515 HPLC pump & Waters 717 Plus Autoinjector) at 1.0 mL/min and 35 °C calibrated with polystyrene standards. Weight-average and number-average molecular weight as well as polydispersity index were determined using the Millennium analysis software. Melt flow index (MFI) according to ASTM D-1238 has been checked with Dynisco D4004 melt flow indexer. Dynamic mechanical behaviors of the composites were measured by TA Instruments Q800. The dimensions of the samples were 35.0 mm × 13.5 mm × 1.5 mm, and the tests were performed in a three-point bending mode at a frequency of 1 Hz. Surface resistivities of the composites were measured using a Hioki SM-8220 Ultra Megohmmeter and GWInstek GOM-802 DC Milli-OHM Meter. The dimensions of the samples were 20.0 mm × 10.0 mm × 0.1 mm. All of the results were taken as the average value of five samples. Scanning electron microscopy (SEM)(HITACHI S-4800) was used to observe the fractured surface of the MWCNT/PLA composites. Transmission electron microscopy (TEM) observation of the morphology was carried out on a JEOL JEM-2010.

3. Results and discussion

3.1. Characterization of Jeffamine® polyetheramine grafted MWCNTs

For comparison, the pristine carbon nanotubes (P-MWCNT) was first shown their insolubility or dispersibility in water and chloroform in Figs. 2(a) and 3(a). The dispersibility was remarkably changed after the modification. For example, the oxidation to MWCNT-COOH became hydrophilic and well dispersed in water (Fig. 2(b)). Further amidation with polyetheramines consisting of oxyethylene-rich block, both of MWCNT-M1000 and MWCNT-M2070 were well dispersed in water (Figs. 2(d and f)). By comparison, the use of hydrophobic or oxypropylene-rich block polyetheramines rendered the modified CNT such as MWCNT-M600 and MWCNT-M2005 to be well dispersed in chloroform (Fig. 3(c) and (e)). The trend of dispersibility in water and chloroform was consistent with the nature of polyetheramine backbones with the differences in oxyethylene and oxypropylene block.

In Fig. 4, it is shown that the TGA thermograms of the pristine MWCNTs, MWCNT-COOH and polyether-backbone modified MWCNTs. For the pristine MWCNTs, no weight loss was observed in the temperature range of 50–500 °C. Similarly, MWCNT-COOH was low in organic decomposition due to the high thermal stability of carbon tubes or a residue of 98.08 wt% remained at 500 °C. On

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