European Polymer Journal 45 (2009) 1002–1008

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Covalent functionalization of multiwalled carbon nanotubes with poly(styrene-*co*-acrylonitrile) by reactive melt blending

Jia-Hua Shi, Bing-Xing Yang, Suat Hong Goh *

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

A R T I C L E   I N F O

Article history:
Received 4 August 2008
Received in revised form 17 December 2008
Accepted 17 December 2008
Available online 4 January 2009

Keywords:
Functionalization
Multiwalled carbon nanotubes
Poly(styrene-*co*-acrylonitrile)
Reactive blending

A B S T R A C T

A small amount of cyano groups in poly(styrene-*co*-acrylonitrile) (SAN) was converted to oxazoline groups through reaction with 2-aminoethanol. Reactive melt blending of oxazoline-containing SAN and acidified multiwalled carbon nanotubes (MWCNTs) leads to the grafting of polymer chains onto MWCNTs arising from reactions between oxazoline and carboxylic acid groups. Spectroscopic, thermal and microscopic techniques confirmed the successful grafting of SAN onto MWCNTs. This method is comparatively simpler and greener than a previously reported method, and can be adopted to graft other acrylonitrile-containing polymers onto MWCNTs.

1. Introduction

Carbon nanotubes (CNTs) are noted for their outstanding electrical, mechanical and thermal properties. However, the practical uses of pristine CNTs are impeded by their tendency to agglomerate and their insolubilities in organic solvents or water. In order to impart solubility and to reduce the tendency of agglomeration, singlewalled and multiwalled carbon nanotubes (SWCNTs and MWCNTs, respectively) are often functionalized with organic moieties and polymers [1–5]. Polymer-grafted CNTs are highly effective reinforcing fillers for polymers [6–16]. When the polymer grafted onto CNTs is the same as or miscible with the matrix polymer, stress can be effectively transferred from the matrix to CNTs which results in significant improvements in the mechanical properties of the matrix polymer.

CNTs can be functionalized covalently or non-covalently with various polymers. Non-covalent interactions such as π−π interaction, π−cation interaction and ionic interaction between CNTs and polymers enable the absorption of polymers onto the CNT surfaces [17–21]. CNTs are functionalized covalently with polymers usually by "grafting-to" and "grafting-from" methods. For the "grafting-from" method, polymers are grown from CNTs commonly using surface-initiated polymerization processes such as atom transfer radical polymerization (ATRP) [22–28], and reversible addition–fragmentation chain transfer polymerization [29,30]. For the "grafting-to" method, preformed polymers are grafted to CNTs through reactions between suitable functional groups of CNTs and polymers [31–34]. The functionalization of CNTs with acrylonitrile-containing polymers has received scant attention. Petrov et al. [35] reported the functionalization of MWNTs with polyacrylonitrile (PAN) by electropolymerization of acrylonitrile in the presence of MWNTs. Shanmugharaj et al. [22] recently reported the grafting of poly(styrene-*co*-acrylonitrile) (SAN) onto MWCNTs using ATRP. The grafting process is rather time-consuming which required a total reaction time exceeding 69 h. From a practical point of view, it is highly desirable to develop simple grafting methodologies. We have recently used a reactive melt blending method to graft polyethylene (PE), polypropylene (PP), and poly(hydroxyether of bisphenol-A) (phenoxy) onto MWCNTs [12–14]. PE and PP containing reactive

---

* Corresponding author. Tel.: +65 65162844; fax: +65 67791691.
E-mail address: chmgohsh@nus.edu.sg (S.H. Goh).

0014-3057/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.12.040

maleic anhydride groups, and phenoxy containing reactive epoxy rings were allowed to react with suitably functionalized MWCNTs in the melt to achieve grafting. We now report the grafting of SAN onto MWCNTs using the reactive blending method via oxazoline groups. To our knowledge, there have been no reports on the grafting of acrylonitrile-containing polymers onto CNTs by this method. This approach can be used to graft other acrylonitrile-containing polymers such as PAN and poly(butadiene-*co*-acrylonitrile) onto CNTs. Other polymers can also be grafted onto CNTs using this approach by first incorporating a small amount of acrylonitrile units through copolymerization. Therefore a large variety of polymers can be grafted onto CNTs using this approach. The present methodology is comparatively simpler and greener than the previously reported method by Shanmugharaj et al. [22].

2. Experimental

2.1. Materials

MWCNTs (purity > 95%, diameter within 20–30 nm) produced by chemical vapor deposition was obtained from Shenzhen Nanotech Port Co. Ltd, China. SAN with 30 wt% of acrylonitrile (M_w = 185,000), 2-aminoethanol (AE) and zinc acetate [$Zn(Ac)_2$] were purchased from Aldrich. Chloroform, acetone, tetrahydrofuran (THF) and methanol were used as received.

2.2. Modification of SAN

SAN (1.0 g) was first fed into a Laboratory Mixing Molder (ATLAS, USA) at 150 °C, and a mixture of 0.1 g of AE and 1.2 mg of $Zn(Ac)_2$ was then quickly added to the SAN powder. The mixture was allowed to mix at 150 °C for 10 min using a rotation speed of 80 rpm. The temperature of the mold was then raised to 200 °C and the blending was continued for another 20 min. The oxazoline-modified SAN (SANm) was then extruded from the mold. SANm was dissolved in 100 mL chloroform, and then precipitated in 1000 mL methanol. This procedure was repeated to ensure the complete removal of $Zn(Ac)_2$ residue and AE. The resulting SANm was dried in a vacuum oven at 70 °C for 48 h.

2.3. Preparation of SAN-grafted MWCNTs

Carboxylic acid-functionalized MWNTs (MWCNT-COOH) were prepared by oxidation of pristine MWCNTs via sonication in nitric-sulfuric acid (1/3, v/v) at ca. 50 °C for 6 h. SANm and MWCNT-COOH (weight ratio of 10:1) were melt blended using the Laboratory Mixing Molder at a speed of 80 rpm at 200 °C for 30 min. The resulting material was dissolved in THF and filtered through a 0.2-μm poly(tetrafluoroethylene) membrane and washed with THF for several times to remove un-grafted SANm. MWCNTs grafted with SAN were too big to pass through the membrane. The SAN-g-MWCNTs were removed and re-dissolved in THF, and filtered through the membrane and washed with THF. The process was repeated several times to ensure the complete removal of un-grafted SANm. SAN-g-MWCNTs were then characterized by Raman spectroscopy, thermogravimetric analysis (TGA), Fourier-transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HR-TEM). For comparison purposes, SAN/MWCNT-COOH and SANm/pristine MWCNTs were also prepared by melt blending.

2.4. Characterization

FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000 IR spectrometer, with 32 scans averaged at a resolution of 4 cm^{-1}. ^{1}H NMR spectrum was acquired using a 500-MHz Bruker Avance DRX500. Raman spectra were acquired using a micro-Raman system (ISA JOBIN YVON-SPEX T64000) at an excitation laser wavelength of 514.5 nm over the range 1100–1800 cm^{-1}. Curve fitting of Raman spectrum was performed using PeakFit v4.11. XPS measurements were carried out with a VG ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV) and a hemispherical analyzer. At least two separate locations were analyzed for each sample. In curve fitting, the widths of Gaussian peaks were kept constant in a particular spectrum. TGA measurements were performed using a TA Instruments 2050 thermogravimetric analyzer. The samples were heated from 30 to 1000 °C under nitrogen at a heating rate of 20 °C min^{-1}. The morphology of SAN-g-MWCNTs was examined using a JEOL JSM-6701F scanning electron microscope. For SEM observation, samples were coated with platinum via sputtering for 30 s. HR-TEM images were recorded on a JEOL JEM-3010F electron microscope operating at 300 kV. The samples for TEM measurements were prepared by placing one drop of sample onto lacey copper grid, followed by solvent evaporation in air at room temperature.

3. Results and discussion

Cyano groups attached to polymer chains are converted to oxazoline groups by reaction with AE in solution or in melt [36,37]. Oxazoline group is reactive toward other functionalities bearing labile hydrogen atoms such as carboxyl, amine, hydroxyl, phenol and mercaptan [38,39]. Since oxazoline group can directly react with carboxylic acid to form ester [38,39], the reaction between SANm and MWCNT-COOH is expected to lead to the grafting of polymer chains onto MWCNTs.

In this study, some of the cyano groups of SAN were first converted to oxazoline groups through reaction with AE in the presence of $Zn(Ac)_2$. The oxazoline-modified SAN (SANm) was then melt blended with MWCNT-COOH to achieve grafting (Fig. 1).

FT-IR spectroscopy was used to verify the conversion of cyano group to oxazoline group. As shown in Fig. 2, both SAN and SANm exhibit the C=C vibration band of styrene units at 1601 cm^{-1} and the C≡N vibration band at 2237 cm^{-1}. For SANm, a new band at 1664 cm^{-1} corre-