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Synthesis and characterization of polyvinyl alcohol based multiwalled carbon nanotube nanocomposites



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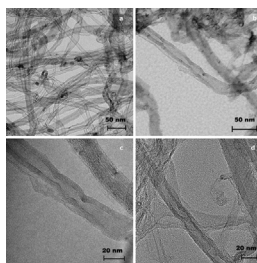
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HIGHLIGHTS

- “Grafting to” approach was carried out to synthesize PVA based CNT nanocomposites.
- Simple and mild conditions were used for oxidation of CNTs.
- No intermediate treatments were required for grafting the PVA to the oxidized CNTs.
- TGA results show high level of functionalization for CNTs.
- Obtained thermal durability of the PVA-grafted MWCNT nanocomposite is rather high.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 January 2014

Received in revised form

17 March 2014

Accepted 26 March 2014

Available online 3 April 2014

Keywords:

Carbon nanotube

Nanocomposite

Polymer-matrix composite

Grafting to

Scanning/Transmission Electron Microscopy

Thermogravimetric analysis

ABSTRACT

Multiwalled carbon nanotubes were synthesized by chemical vapor deposition over an Fe–Co/alumina catalyst. Nanotubes were then oxidized and grafted with polyvinyl alcohol (PVA). The obtained nanostructure was characterized by Raman spectroscopy, XRD, FTIR, EDX, SEM, TEM and TGA methods. FTIR confirmed the presence of the characteristic peaks of the anticipated ester group. The formation of polymer nanocomposites based on polyvinyl alcohol and multiwalled carbon nanotubes was confirmed by SEM and TEM. High resolution electron micrographs revealed that the primary binding sites for PVA grafting are the sidewall defects of the nanotubes. The novelty of this work is the use of the Fischer esterification reaction for creating the permanent link between the nanotubes and the PVA matrix.

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1. Introduction

Multiwalled carbon nanotubes (MWCNTs) can be considered as a set of single walled carbon nanotubes, i.e. thin graphene stripes

rolled into seamless cylinders, arranged coaxially with regularly increasing diameter [1]. Carbon nanotubes (CNTs) have received considerable attention recently owing to their unique electronic and mechanical properties that are expected to lead to a breakthrough in industrial applications. CNTs can be synthesized by chemical vapor deposition (CVD) [2–4], laser ablation [2,5–7] and d.c. arc discharge [2,6–8]. Among these techniques, CVD has inherent advantages such as better control over process parameters and good scalability [9].

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In CVD a supported transition metal catalyst is heated to a high temperature (500–1000 °C) in a tube furnace and hydrocarbon–inert gas mixture is fed into the reactor over a period of time. The steps of the basic mechanism of CVD carbon nanotube growth are (1) the in situ reduction of the transition metal precursor by the hydrocarbon feed and the simultaneous formation of metallic nanoparticles on the support, (2) the dissociation of hydrocarbon molecules catalyzed by the transition metal and the saturation of the metal nanoparticles with carbon, and (3) the subsequent precipitation of carbon from the metal particle which leads to the formation of tubular carbon solids in a sp^2 structure which are called carbon nanotubes [2].

Carbon nanotubes exhibit a well-known tendency to form agglomerates due to van der Waals forces, which makes them extremely difficult to disperse and align in a polymer matrix. Thus, a significant challenge in developing high performance polymer/CNTs composites is to introduce the individual CNTs into a polymer matrix in order to achieve better dispersion and alignment, promote strong interfacial interactions and improve load transfer across the CNT–polymer matrix interface. The functionalization of CNTs is an effective way to prevent nanotube aggregation, which helps in dispersing and stabilizing carbon nanotubes within a polymer matrix. There are several approaches towards CNT functionalization including defect functionalization, covalent functionalization and non-covalent functionalization [10,11].

CNTs are purified after synthesis by oxidative methods to remove metal particles or amorphous carbon from the raw product mixture [11,12]. The process involves the generation of sp^3 defect sites appearing preferentially at the open nanotube ends and to some extent, on the cylindrical walls as well. Nanotube fragmentation can also occur during oxidation. The generated defects are generally converted into –COOH groups in the reaction [13,14]. The defect density after a typical purification process is not high enough to promote a good dispersion in polymer/CNT composites. However, the –COOH groups can be used as bridgeheads for the covalent attachment of other organic functional groups by converting them into acid chlorides and subsequently reacting these with e.g. amines to give amides [15,16]. The functionalized CNTs are more soluble in organic solvents than the raw CNTs [17].

Non-covalent functionalization of nanotubes does not compromise their physical properties but improves solubility and processability. This type of functionalization mainly involves the attachment of surfactants, biomacromolecules or wrapping nanotubes with polymers. CNTs can be dispersed well in water using anionic, cationic and non-ionic surfactants. The interaction between the surfactants and the CNTs depends on the chemistry of the surfactants such as their alkyl chain length, headgroup size and charge. If the surfactant includes benzene rings in the structure then it usually exhibits an improved affinity towards CNTs due to the possibility of π -stacking interaction. The dispersion of CNTs in both water and organic solvents can be enhanced by the physical association of polymers with CNTs; polymers can wrap around CNTs to form supramolecular complexes [11].

Carbon nanotubes are more reactive than flat graphene sheets because of two curvature-induced factors: (i) the distortion of the sp^2 hybrid orbitals due to curvature induced strain, and (ii) the π orbital misalignment between adjacent carbon atom pairs. Therefore, they have a higher affinity towards covalently bonding chemical species than graphene [11,18]. In the case of covalent functionalization, the translational symmetry of CNTs is disrupted by changing sp^2 carbon atoms to sp^3 carbon atoms and the electronic and transport properties of CNT are affected [19]. The functionalization of carbon nanotubes can improve their solubility as well as dispersion properties in solvents and in polymers. Covalent functionalization can be carried out either by the modification of surface-bound carboxylic acid groups or by directly attacking the sidewalls of nanotubes. Usually, functional groups such as –COOH or –OH are formed on the CNTs during oxidation by oxygen, air, concentrated sulfuric acid, nitric acid or

aqueous hydrogen peroxide [20,21]. Acid treated MWCNTs have defects in the carbon–carbon bonds. The number of functional groups on the nanotube surface depends on acid treatment temperature and time, increasing with increasing temperature [22]. Nanotube end caps can be opened as the result of oxidation process [11]. The presence of carboxylic groups on the CNT surface is advantageous from the synthetic chemistry point of view because a variety of chemical reactions can be conducted with this group. The –COOH and –OH groups on the nanotube surface help the attachment of organic or inorganic materials, which is important for solubilizing nanotubes [18,23]. Functionalization of CNTs with polymer molecules (polymer grafting) is particularly important for obtaining polymer/CNT nanocomposites [24,25].

The two main pathways suggested for the covalent grafting of polymers to CNTs are the “grafting to” and the “grafting from” approaches. The former is based on the attachment of as-prepared or commercially available polymer molecules to the CNT surface by chemical reactions, such as amidation, esterification, radical coupling, etc. The polymer macromolecule must possess adequate reactive functional groups for this approach to work [11,26,27]. Polymer grafted CNTs were formed by covalently attaching nanotubes to highly soluble linear polymers, such as poly(propionylethylenimine-co-ethylenimine) via amide linkages or poly(vinyl acetate-co-vinyl alcohol) via ester linkages [28,29]. The resulting grafted CNTs were soluble in PVA solution and the nanocomposite films showed very high optical quality without any observable phase separation [11].

Abuilaoui et al. [30] reported the functionalization of MWCNTs via the Fischer esterification method. Four functional groups: phenol, dodecylamine, 1-octadecanol and polyethylene glycol were covalently attached to MWCNTs via amidation or esterification. A similar reaction was reported by Sobkowicz et al. [31]. Fischer esterification of surface hydroxyl groups on multiwalled carbon nanotubes, carbon nanospheres, and cellulosic nanowhiskers using acetic and butyric acid is presented as a green approach to decorate the surfaces of nanoparticles.

In the “grafting from” approach, the polymer is bound to the CNT surface by in-situ polymerization of monomers in the presence of reactive nanotubes or CNT-supported initiators. In this process the polymer–CNT nanocomposites can be prepared with high grafting density [11].

In this paper the “grafting to” approach was used to graft polyvinyl alcohol (PVA) to MWCNTs. The process was carried out using concentrated sulfuric acid through the Fischer esterification route, i.e. by connecting the MWCNTs to the PVA via ester groups. The solubility of the MWCNTs was improved by the functionalization. Grafting MWCNTs with PVA helps in reducing the nanotube–nanotube adhesion and the tendency to form entangled stacks, which generally make MWCNTs unusable for manufacturing advanced plastic materials. Moreover, the obtained grafted structures can be oriented by exploiting the conformational changes of PVA macromolecules. Therefore, the obtained material can be a precursor for the manufacturing the advanced plastic composite materials or an additive to construction materials for strengthening purposes.

The novelty of this work is that PVA macromolecules are attached to MWCNT–COOH via Fischer esterification route for the first time without any other intermediate treatment. The long PVA chains in the resulting material are able to screen and protect the nanotubes from entanglement during dispersion.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical reagent grades. Transmission Electron Microscopy images were taken with a FEI TECNAI G2 20

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