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Synthesis, characterization and stability of chitosan and poly(methyl methacrylate) grafted carbon nanotubes

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Abstract

The single walled carbon nanotubes (CNTs) were effectively functionalized through grafting with chitosan (CTS) and poly(methyl methacrylate) (PMMA). Prior to grafting reaction, the carboxylated SWCNTs (SWCNTs-COOH) were obtained by treating pristine CNTs with a mixture of 3:1 (v/v) H₂SO₄ and HNO₃, and the successive treatment of SWCNTs-COOH with SOCl₂ yielded the acylated CNTs (CNTs-COCl). The functionalized derivatives of CNTs were characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis, atomic force microscopy, scanning electron microscopy and transmission electron microscopy. Both CTS and PMMA grafted CNTs showed better dispersability in acetic acid and tetrahydrofuran, in addition to higher stability in solution.

Keywords

Carbon nanotubes; Chitosan; Poly(methyl methacrylate); Atomic force microscopy

1. Introduction

Carbon nanotubes (CNTs) have gained an abundance of interest since its discovery in 1991 due to its excellent structural, electrical, thermal and mechanical properties [1]. CNTs have high flexibility, low mass density, large aspect ratio, and extremely high tensile moduli and strength. Significant work has been done to reveal the unique structural, mechanical, electrical, electromechanical and chemical properties of CNTs and to explore the key applications of these novel materials. The CNTs can be tailored to be conducting,

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semiconducting or non-conducting. The conducting and semiconducting carbon nanotubes can transport electrons over long lengths and through this mechanism make it more appealing than metals such as copper. In addition, the combination of mechanical and electrical properties of CNTs makes them ideal reinforcing agents in numerous applications. Since the first report of nanocomposites using CNTs in 1994 [2], many studies have been reported dealing with the polymer composites [3–6]. Recently, the nanocomposites containing polymer and CNTs are attaining significant interest owing their exceptional properties and applications [7–12].

Chitosan is a polysaccharide biopolymer obtained from the deacetylation of chitin and it has been extensively utilized in biomedical applications as it can not only be economically processed from chitin but is also nontoxic, biocompatible, and biodegradable [13–16]. Also, chitosan can be easily extracted from the exoskeletons of shrimps and crabs [17]. It has been demonstrated that chitosan can interact with CNTs forming stable dispersions [18] and a composite material with improved mechanical strength [19]. The chitosan modified CNTs were used for different applications such as the adsorption of congo red [20], the determination of copper (II) by anodic stripping voltammetry [21], removal heavy metals [22], and biosensors for different molecules such as hydrogen peroxide [23] and cholesterol [24]. In general, chitosan is a promising material to graft over CNTs and gain the needful properties [25–37]. The present study describes functionalization of CNTs with chitosan and poly(methyl methacrylate). The functionalized CNTs were characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis, atomic force microscopy, scanning electron microscopy and transmission electron microscopy.

2. Experimental

2.1. Materials

Potassium persulfate ($K_2S_2O_8$), sulfuric acid (H_2SO_4), nitric acid (HNO_3), thionyl chloride, methyl methacrylate, tetrahydrofuran (THF) and sodium hydroxide (NaOH) were purchased from Sigma Aldrich and used without further purification. High purity CNTs were purchased from Helix Material, Inc. (Richardson, Texas). The low molecular weight chitosan (CTS) received from Sigma Aldrich was purified by dissolving 10 g chitosan in 200ml of 1% acetic acid solution and filtered using glass-wool. The NaOH (2M, 200ml) was then added to the filtered sample with continuous stirring. After removal of excess NaOH, the filtrate was washed with distilled water until it reaches pH 7.0.

2.2. Synthesis of CNTs-COOH

CNTs (2g) was sonicated in a mixture of 60ml of sulfuric acid (18M) and 20ml of nitric acid (16M) at a pulse of 7 and amplitude 30% for 30min. The sonicated mixture was then washed and centrifuged until pH becomes 5–6 before being oven dried.

2.3. Synthesis of CNTs-COCl

CNTs-COOH (1g) was reacted with 10 mL thionyl chloride for 24 hr at temperature 70°C with stirring in a round bottom flask. The reaction was terminated with 10ml THF washed and centrifuged 5 times before being oven dried.

2.4. Synthesis of CNTs -CTS

CNTs-COCl (0.75g) was added to 1g of chitosan and 100ml of 1% acetic acid and allowed to react for 24hrs at 70°C in a round bottom flask with continuous stirring. Similarly to the synthesis of functionalized CNTs-COCl, 10ml of tetrahydrofuran (THF) was used to terminate the reaction. Then the sample was centrifuged 5 times and oven dried at 150°C to obtain the sample in a powdered form.

2.5. Synthesis of CNTs-CTS- poly(methyl methacrylate) (PMMA)

Methyl methacrylate (2g) along with 0.5g of the sample produced from the functionalized CNTs-CTS and 0.05g $K_2S_2O_8$ were weighed then reacted for 24hrs at 70°C and the reaction terminated with 10ml THF before oven drying. The overall functionalization of CNTs is schematically depicted in scheme I.

2.6. Synthesis of CNTs-phenylene diamine (PDA)

CNTs-COCl (0.75g) was added to 1g of PDA and 100ml of 1% acetic acid and allowed to react for 24hrs at 70°C in a round bottom flask with continuous stirring. Similarly to the synthesis of functionalized CNTs-COCl, 10ml of tetrahydrofuran (THF) was used to terminate the reaction. Then the sample was centrifuged 5 times and oven dried at 150°C to obtain the sample in a powdered form.

2.7 Synthesis of CNTs- -PDA-PMMA

Methyl methacrylate (2g) along with 0.5g of the sample produced from the functionalized CNTs-PDA and 0.05g $K_2S_2O_8$ were weighed then reacted for 24hrs at 70°C and the reaction terminated with 10ml THF before oven drying. Then the sample was centrifuged 5 times and oven dried at 150°C to obtain the sample in a powdered form.

2.8. Characterization

Fourier Transform Infrared (FTIR) spectra were obtained using IR-200 thermo-Nicolet 2.2 in the range of 400–4000 cm^{-1} . Thermogravimetric analyzer (TGA) Q500 was used to analyze the thermal stability of the various derivatives produced, in conjunction with Universal V3.4C TA program which aided in the interpretation of the resulting scan from the Thermogravimetric analyzer. Scanning Electron Microscopy (SEM) was conducted using FEI Quanta 600 FE-SEM and JEOL JSM at 10kv. The specimens were coated with 4nm Pt/Pd layers using Cressington 208HR in order to produce high resolution imaging. Atomic force microscopy (AFM) was used to assess the dispersion state for each sample. Atomic Force Microscopy (AFM) was performed using MultiModeTM SPM (Digital Instrument, model MMAFM-2), Nanoscope IIIa controller (model NS3A), scanner type “E”. Images were scanned in tapping mode. For AFM, samples were sonicated by tip sonication with 30% amplitude for 30mins in acetic acid or tetrahydrofuran and deposited on mica by micropipette. The Transmission Electron Microscopy (TEM) measurement was performed using a FEI Tecnai G2 F20 FEG-TEM at 200 kV, which was equipped with an Oxford INCA X-ray energy dispersive spectroscopy (EDS) system.

3. Results and Discussion

3.1. FTIR Spectroscopy

FTIR spectroscopy (Figure 1) was used to confirm the presence of desired functional groups in functionalized CNTs. The peak hydrocarbon stretching peak H-C-H bonds and is seen at 2810 cm^{-1} , and the peak at 1423 cm^{-1} was attributed to H-C-H bending. The presence of –COOH was confirmed by the peak displayed at 1638 cm^{-1} which indicated C=O stretching. The reaction with thionyl chloride yields the attachment of COCl functional group to the CNTs yielding peaks at 606 cm^{-1} . The addition of phenylene diamine was confirmed by the presence of peaks at 3000 cm^{-1} aromatic C-H and 1500 cm^{-1} indicating the incorporation aromatic ring. The broad and strong peak that is seen at near 3450 cm^{-1} in all spectra indicate -OH in functionalized CNTs and could include -NH stretching in CNTs-PDA. The phenylene derivative was then reacted with methyl methacrylate to afford CNTs -PDA-PMMA in which the presence of peaks at 1650 cm^{-1} and a doublet between 1200 and 1300 cm^{-1} indicated presence of the C=O stretching of the amide bond and C-N stretching and N-

H bending of the amide. The spectrum of CNTs -chitosan (not shown) indicated that PMMA was grafted onto CNTs-chitosan derivative as indicated by peaks around 1100 cm^{-1} and 1400 cm^{-1} associated with the presence of PMMA and chitosan, respectively.

3.2. Thermogravimetric Analysis (TGA)

TGA indicated that pure CNTs shows significant thermal stability up to 600°C (Figure 2). The attachment of functional groups to CNTs shows a significant decrease in the thermal stability of CNTs derivatives as indicated by the weight loss displayed in thermograms. In the thermogram for CNTs-COCl and CNTs-COOH, there occurs small weight loss below 100°C , which is attributed to the evaporation of moisture absorbed on the surface of CNTs. The thermogram for CNTs-PDA showed an onset of degradation near 450°C which is in agreement with the onset of degradation of phenylene diamine. The thermogram for CNTs-PDA-PMMA indicates that the degradation near $165\text{--}220^{\circ}\text{C}$ may be attributed to the degradation of head to head structure of PMMA which is well documented when radical polymerization conditions are employed [38]. This thermogram also further shows that PMMA backbone may be degrading near 400°C , however, much of the integrity is maintained due to the presence of the CNTs.

Also shown in Figure 2 is thermograms for CNTs-CTS and CNTs-CTS-PMMA. In this case, when the source of amine functionality is changed from phenylene diamine to chitosan, the thermal behavior of the CNTs-CTS and CNTs-PDA derivatives seem similar. The degradation for chitosan usually occurs between $200\text{--}540^{\circ}\text{C}$ which is seen in the thermograms which include chitosan. Specifically, between $200\text{--}300^{\circ}\text{C}$, the degradation of the amine and N-acetyl of chitosan occurs [39–41]. Both the CNTs-PMMA derivatives indicate that degradation of PMMA occurs near 400°C . One important note is that CNTs-PDA-PMMA derivative has a weight loss of 55% at 1000°C while that of CNTs-CTS-PMMA reflects a weight loss of 20% at 1000°C . This indicates that chitosan has greater thermal stability than phenylene diamine and is confirmed by the difference in weight loss of CNTs-PDA (70%) versus CNTs-CTS (50%).

3.3. Dispersion studies

The dispersion state of CNTs derivative were observed after tip sonication in either acetic acid solution or tetrahydrofuran for 30 minutes and maintained in each solvent for 7 months (Figure 3). During the 7 month period, the CNT-COOH derivative may have been converted to CNT-CO₂C(O)CH₃ when in the presence of acetic acid and CNT-COCl derivative may have converted to CNT-COOH when in the presence of acetic acid. Based on the appearances of CNTs-COCl, CNTs-PDA, CNTs-CTS and CNTs-CTS-PMMA derivatives, we decided to explore AFM to investigate the dispersion of functionalized CNTs in THF and acetic acid.

3.4. Atomic Force Microscopy

AFM images of CNTs-COCl did not show much dispersion but rather shows that there were some small particles, which could be CNTs, in the solution that did not precipitate. This results were similar to CNTs-CTS and CNTs-CTS-PMMA as shown in Figure 4a and b, respectively. AFM image of CNTs-CTS-PMMA on bundled CNTs (Figure 4c and d) shows particles attached to CNTs. When the same samples were dispersed in acetic acid solution and preserved for 7 months, the solutions appeared as shown in Figure 5. AFM of CNTs-COOH shows in Figure 5(a) that small tiny round particles were dispersed on the surface of mica. These maybe ordered but shortened CNTs. AFM indicated that there were no particles on mica surface for CNTs-CTS, but AFM scans for CNTs-PDA shows many particles on the mica surface with the majority of the particles being small and spherical. These may have also been shorten CNTs. Further AFM images for CNTs-PDA-PMMA shows the presence

of many tiny particles on mica surfaces; some which were rope-like and may be attributed to the presence of CNTs. AFM image of CNTs-CTS-PMMA (Figure 5c) shows some particles crystallized in spiral shape. At the top part of phase image (Figure 5d indicated by red arrow), it was noticed that the middle section was different from the outer part. This seems to indicate that CNTs may have another functional group attached to it. AFM was performed only on the supernatant part of the dispersion systems for CNTs-CTS-PMMA in both acetic acid solution and tetrahydrofuran which seem to show that CNTs may be surrounded by other functional groups. There was no solution that gave long CNTs dispersion even though some of them appeared grey while most of the noticeable dispersed CNTs on mica were very small and shortened.

3.5. Scanning Electron Microscopy

The amine derivatives, phenylene diamine and chitosan, was attached to CNTs before grafting PMMA onto the CNTs. It was believed that these amine containing compounds would assist in the alignment of CNTs. Thus, SEM and TEM was employed to assess the morphology and structure of newly synthesized CNTs derivatives. SEM displayed the long white strings in each micrograph which indicate there was attachment of the CNTs as seen before where there is uniform interspersions of CNTs in the chitosan (Figure 6).

3.6. Transmission Electron Microscopy

TEM observations were performed on CNTs derivatives synthesized using free radical polymerization conditions in order to determine the structure CNTs. Figure 7 a and b show the TEM image of CNTs-PDA and CNTs-PDA-PMMA, respectively and reveal that the tubes are bundled and coated. In some areas in each sample, some CNTs appeared debundled and coated. In the debundled areas, CNTs-PDA-PMMA derivative seems to have more coating than CNTs-PDA and this was attributed to the presence of PMMA. The CNTs displayed in figure 7 a and b TEMs are quite different for CNTs-CTS and CNTs-CTS-PMMA (Figure 7c and d) in that the dark spots which were attributed to chitosan are present. The CNTs were bundled but in some cases the bundled CNTs surrounded the chitosan and chitosan-PMMA matrix.

4. Conclusions

In conclusion, the CNTs were successfully functionalized through grafting of CTS and PMMA. The FTIR and TGA studies demonstrated that CTS and PMMA are perfectly grafted onto CNTs. Both, CNTs-COCl-CTS, CNTs-COCl-CTS-PMMA are well dispersible in acetic acid and tetrahydrofuran and have good stability in solution. The shortening and chemical functionalization technique may afford a simple way of aligning carbon nanotubes, however, more studies need to be done in finding the most suitable functional group and reaction conditions that will improve dispersion.

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Highlights

- Effective functionalization of CNTs through grafting of CTS and PMMA.
- CTS and PMMA grafted CNTs are well dispersible.
- Partial alignment of functionalized CNTs was achieved through reported method.
- Effective functionalization was revealed using atomic force microscopy.

Fig. 1.
FTIR spectra of pristine CNTs, CNTs-COOH, CNTs-COCl, CNTs-PDA and CNTs-PDA-PMMA.

Fig. 2. TGA profiles of pristine CNTs, CNTs-COOH, CNTs-COCl, CNTs-PDA, CNTs-PDA-PMMA, CNTs-CTS and CNTs-CTS-PMMA.

Fig. 3. Dispersibility of functionalized CNTs in (a) tetrahydrofuran and (b) acetic acid.

Fig. 4. AFM images of (a) CNTs-COCl (b) CNTs-CTS and, (c and d) CNTs-CTS-PMMA in tetrahydrofuran.

Fig. 5. AFM images of (a) CNTs-COOH, (b) CNTs-PDA, (c) CNTs-PDA-PMMA and (d) phase image of CNTs-PDA-PMMA in acetic acid.

Fig. 6.
SEM images of (a) CNTs-CTS, (b) CNTs-PDA-PMMA and (c) CNTs-CTS-PMMA.

Fig. 7. TEM images of (a) CNTs-PDA, (b) CNTs-PDA-PMMA, (c) CNTs-CTS, (d) CNTs-CTS-PMMA and (e) Pristine CNTs.

Scheme I.
Functionalization of CNTs.