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Dispersion of aminoalkylsilyl ester or amine alkyl-phosphonic acid side wall functionalized carbon nanotubes in silica using sol–gel processing

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Abstract

Aminopropyltriethoxysilane and aminopropyl-phosphonic ester modified carbon nanotubes were prepared by reacting fluorinated carbon nanotubes (F-CNTs) with the 3-aminopropyltriethoxysilane or 3-aminopropyl-phosphonic acid reagents at 120 °C temperature, using pyridine as the base catalyst. These functionalized carbon nanotubes, APTES-CNTs, **1**, and APPA-CNTs, **2**, were characterized by transmission electron microscopy (TEM), infrared spectroscopy (IR), and thermogravimetric analysis (TGA). The homogeneous dispersion of these functionalized CNTs (0.1%) in silica were also accomplished by sol–gel processing. The TEM confirmed uniform dispersion of the functionalized CNT in silica.

Keywords

Carbon nanotube; Silica; Sol–gel preparation; Nanocomposites

1. Introduction

Carbon nanotubes have unique mechanical, electrical, thermal, optical/spectroscopic properties and chemical reactivity [1–7]. These interesting properties have attracted interest from research scientists in the field of nanocomposite materials including but not limited to application in biomedical science and engineering [8–10], as ultrahigh strength polymer composites [11–13], in nanoelectronics as electron field emitters [14–16] etc.

Mechanical properties of composites and ceramic materials have been proven to be enhanced by achieving uniform dispersal of the CNTs filler in the inorganic polymer matrix [17]. Structurally, CNTs are built generally of rolled graphene sheets which is therefore a limitation in their propensity for interfacial bonding and evidenced by their lack of uniform dispersal in both aqueous and organic media [7]. In the mechanical context, this is a drawback against the efficiency of load transfer from the matrix to the nanotubes across the

nanotube/polymer interface [18]. Consequently, there is a renewed effort to achieve covalent functionalization of CNTs in order to modify their properties [19,20], ultimately broadening the scope of their application [21–24].

Gel glasses in the CaO–SiO₂ system are generally, coated by an *apatite*-like layer when soaked in solutions mimicking blood plasma (simulated body fluid) [25]. Such glasses are said to be “bioactive” since the apatite layer was proposed as the first step in the formation of a bond between bioactive materials and the living bone tissues. However, silica glasses and ceramics are brittle thus limiting their application in orthopedics to bone fillers. Very recently, a sol–gel bioglass of composition 70% SiO₂–30%CaO has been foamed to produce macroporous 3D resorbable scaffold for tissue engineering application, with macropores in excess of 100 µm [26]. While this foamed bioglass displays excellent bone bonding ability, the mechanical properties were a disappointment and typical of porous brittle materials. As investigations of bioactive glass and ceramics progress their limited mechanical properties are becoming apparent. Incorporation of superstrong lightweight carbon nanotube structures into inorganic matrix (bioglass) is an attractive approach to the design of high performance composite materials with superior mechanical properties. Ning et al. reported that composites fabricated by direct mixing of carbon nanotubes with silica showed improvement in their mechanical properties [27].

In this letter we report the synthesis of aminoalkylsilyl and aminoalkylphosphonic acid functionalized CNTs, and the uniform dispersion in silica by sol–gel processing to form nanocomposites. This bifunctional nanocomposite should combine the excellent bone bonding ability of silica and phosphonic acid group when dispersed by sol–gel processing in silica matrix, with improved mechanical properties that will arise from the carbon nanotube. The reaction products were characterized by transmission electron microscopy (TEM), infrared spectroscopy (IR), and thermogravimetric analysis (TGA).

2. Experimental details

2.1. Materials

The fluorinated carbon nanotubes (F-CNTs) were provided by Dr. Valery Khabashesku (RICE University) and characterized by elemental analysis and thermogravimetric analysis. The following chemicals 3-aminopropyl-phosphonic acid (APPA); and 3-aminopropyltriethoxysilane (APTES) were obtained from Aldrich and were used as received. Pyridine and acetone (Aldrich) were dried with molecular sieves.

2.2. Instruments and measurements

Fourier transform infrared spectroscopy (FTIR, IR-200 Thermo-Nicolet 2.2) (KBr) in the range of 400–4000 cm^{−1} was used to confirm covalently bound amino group on CNT surface. Transmission electron microscopy (TEM) was performed at the Microscopy Laboratory at Texas A&M University on JEOL 6400 SEM at 15 kV. Thermal gravimetric analysis was performed on Universal V3.4C TA instruments. The runs consisted of a ramp at a steady rate of 40 °C/min, from 40 °C to 850 °C. All elemental analyses were recorded by Schwarzkopf Analytical Services (NY) or qualitatively from energy dispersive spectral EDS.

2.3. Preparation of 3-aminopropyltriethoxysilane and 3-aminopropyl-phosphonic acid modified single-walled carbon nanotubes

The F-CNT (80.0 mg) was charged into a round bottom flask followed by the addition of the functionalizing reagent in excess (3.0 ml), and pyridine (2.0 ml) to the reaction flask. The mixture was heated in a closed tube at 120 °C for 24 h. After cooling, the mixture was

filtered through a 0.2 μm membrane filter under vacuum. The black residue obtained was washed several times with large excess of acetone and then dried at 100 $^{\circ}\text{C}$ for 24 h, to yield APTES-CNTs, **1**, or APPA-CNTs, **2**.

The elemental analysis on the APTES-CNT (**1**) observed: C=78.65%, H=2.23%, N=4.36% suggests a mole ratio of C:H of 20.9:1, which translates to carbon nanotube to APTES functionalization ratio of approximately 11:1.

2.4. Dispersion of **1** and **2** in silica

To a suspension of APTES-CNTs, **1**, (10.0 mg) or APPA-CNTs, **2**, (10 mg) dispersed in 5 ml ethanol was added a solution of 5 g of tetra-ethoxy-*ortho* silane in 5 ml ethanol, followed by 0.1 ml of 28% ammonium hydroxide solution. The mixture was stirred at room temperature for 2 h and allowed to gel (about 2 days), forming black gel monolith. The monolith was dried in the oven at 100 $^{\circ}\text{C}$ and characterized by TEM, EDS, FTIR and thermal analysis.

3. Results and discussion

The aminoalkylsilyl and phosphonic acid functionalized CNTs were prepared as shown in Scheme 1 by the reaction of side wall functionalized fluorinated carbon nanotube with amine group as reported in the literature [28].

3.1. Thermal analysis

The TGA of received carbon nanotube (CNT) (Fig. 1) showed a significant weight loss at 600 $^{\circ}\text{C}$ associated with the loss of carbon nanotubes leaving a residual weight of less than 4% (iron oxide impurities from catalysts used in CNTs preparation). The fluoro carbon nanotubes (F-CNT) shows two distinct weight losses. The first weight loss between 300 and 450 $^{\circ}\text{C}$, with approximately 23%, is due to the loss of the fluoro group on F-CNT, and supports the C_5F formulation. The second weight loss from 500 to 600 $^{\circ}\text{C}$ is due to the loss of carbon nanotubes, leaving a residual weight of less than 2% (iron oxide impurities). The thermal behavior of the APTES-CNT, **1**, labeled CNT-SiO₂, in Fig. 1, shows two distinct weight losses. The first weight loss at 300–450 $^{\circ}\text{C}$ (approximately 12%) is the loss of the amino-propyl group on the CNT. The second weight loss occurred between 500 and 700 $^{\circ}\text{C}$ is associated with CNT. The residual weight of approximately 13% is mostly silica.

3.2. FTIR

The infrared spectrum (IR) for the F-CNT (not shown) is characterized by a vibrational mode at 1220 cm^{-1} indicative of the C–F vibration with no other so obvious vibration [24]. The FTIR of **1** and **2** respectively are shown in Fig. 2. The FTIR of **1** shows the CH_2 stretching vibrations between 2847 and 2990 cm^{-1} , the stretching vibration of the vicinal silanol group overlaps the NH asymmetric stretching vibration centered around 3377 cm^{-1} . In addition, the O–H deformation vibration appears at 1635 cm^{-1} , the 1609 cm^{-1} corresponding to N–H in plane, and the Si–O stretching vibration appears around 1034 cm^{-1} [29]. In the FTIR of **2**, the CH_2 vibration shows peak at 2984 cm^{-1} .

The broad peak centered around 3458 cm^{-1} is diagnostic of the asymmetric stretching vibrations of the secondary amine N–H. The P–OH stretches vibrations appeared at 1176, 1096, 970, 830 and 565 cm^{-1} are supportive of the functional group presence in the nanocomposite.

3.3. Transmission electron micrograph

The TEM and EDS analyses on **1** and **2** confirm the functionalization of the side wall of the carbon nanotubes. Fig. 3 shows the TEM images of **1** and **2** respectively labeled 2a and 2b with kinks on the side walls of CNT confirming functionalization. In addition, dark spots of amorphous silica or phosphonic acid groups are very clear. The EDS of **1** and **2** (Appendix A: Fig. S1) confirmed the elements present in the group.

The dispersion of **1** and **2** in tetraethoxysilane by sol–gel hydrolysis and condensation yielded the respective nanocomposites where the functionalized CNTs are well integrated into silica matrix. The TEM of the nanocomposites is also shown in Fig. 3, where images labeled 3a and 3b represents the dispersion of compounds **1** and **2** in silica respectively. The TEM images clearly showed the spherical silica nanoparticles and the carbon nanotubes, mostly functionalized single walls. The dispersion of aminopropyltriethoxysilane in TEOS was also carried out, and its TEM picture (as Supplementary material Fig. S2) shows the spherical silica nanoparticles with no carbon nanotubes.

4. Conclusions

Aminoalkyl trialkoxysilane and aminoalkylphosphonic acids functionalized CNTs are synthesized via reaction of F-CNTs with the amino alkyl functionalizing reagents. The uniform dispersion of these functionalized CNTs in ceramics to form monolith has also been accomplished. These nanocomposite materials that incorporate superstrong lightweight carbon nanotube structures into inorganic matrix (bioglass) are an attractive approach to the design of high performance composite materials with superior mechanical properties. The bone bonding ability in simulated body fluid and their mechanical properties are being investigated, especially as suitable material in bone tissue engineering.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Thermogravimetric analysis of the carbon nanotubes (CNT), fluorinate carbon nanotube (F-CNT) and aminopropyltriethoxysilane functionalized carbon nanotubes CNTs, APTES-CNTs, **1** (SiO₂-CNT).

Fig. 2. Fourier transform infrared spectra of APTES-CNT, **1** (green) and APPA-CNT, **2** (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. TEM image of APTES-CNT, **1** (labeled 2a), APPA-CNT, **2** (labeled 2b), nanocomposite of **1** in silica at 0.1 wt.% (3a) and nanocomposite of **2** in silica at 0.1 wt. % (3b.).

Scheme 1.

Synthetic scheme for **1**, **2** and corresponding nanocomposites.