

Surface modification of multi-walled carbon nanotubes using 3-aminopropyltriethoxysilane

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Abstract Multi-walled carbon nanotubes (MWCNTs) were functionalized via oxidation with a mixture of concentrated sulfuric acid and nitric acid. Thus functionalized nanotubes (f-MWCNTs) were silanized using a coupling agent, 3-Aminopropyltriethoxysilane (3-APTES). The f-MWCNTs and the reaction product of f-MWCNTs and 3-APTES (APTES–MWCNTs) were characterized by Fourier Transform Infrared Spectroscopy, Energy Dispersion Spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy. The results indicate the attachment of silane molecules on the surface of the functionalized MWCNTs. This silanization method allows for the improvement of the chemical compatibility of MWCNTs with specific polymers for application in nanotube-based polymer matrix composites.

Introduction

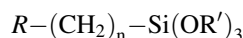
Due to their novel structures and remarkable mechanical, thermal, and electrical properties, carbon nanotubes (CNTs) have emerged as new materials with a variety of potential applications [1–4]. These CNTs have attracted much interest in the field of CNT/polymer nanocomposites [5, 6]. However, if these materials are to be utilized as reinforcements in advanced polymer composites, in addition to the homogeneous dispersion of the nanotubes, the

nanotube/polymer interface needs to be engineered for an effective transfer of mechanical loads from the matrix to the nanotubes [7].

The chemical functionalization of carbon nanotubes is one of the few methods used to enhance the interfacial adhesion between the nanotubes and the matrix. The functionalization generates functional groups at the surfaces of the CNTs. These functional groups could react with other chemicals, prepolymers, and polymers, thus enhancing the interfacial bond between the matrix and the tubes for their further application to polymer nanocomposites.

Different chemical functionalization techniques have been devised for enhancing the interfacial adhesion between the nanotubes and the matrix [8]. One of these is the oxidative process utilizing strong acids such as HNO₃ or H₂SO₄ in which carboxylic acid moieties are created on nanotubes. In this method, however, strong acids cut the CNTs into small pieces which decrease the aspect ratio of the nanotubes [9, 10].

The silanization of functionalized nanotubes is another preferred method used to enhance the interfacial adhesion between nanotubes and the matrix. The silane coupling agents most commonly used are organosilanes. The organosilanes are represented by the following formula [11]:



where $n = 0-3$, OR' is the hydrolyzable alkoxy group, and R is the functional organic group. The selection of the R group depends on the matrix being used [12, 13]; the $(\text{OR}')_3$ is generally trimethoxy $(\text{OCH}_3)_3$ or triethoxy $(\text{OC}_2\text{H}_5)_3$, which is easily hydrolyzed to form a trisilanol. This group reacts readily with the hydroxyl groups on the nanotube surface produced through oxidation and/or the reduction process. A schematic representation of the

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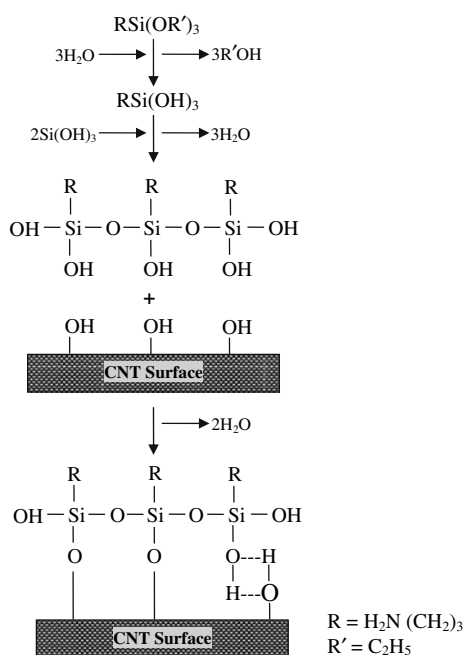


Fig. 1 Schematic representation of silanization process of multi-walled carbon nanotubes

silanization process is shown in Fig. 1 [11]. Recently, this method has been applied to functionalize the surface of CNTs by a few researchers. Ma et al. [14] and Vast et al. [15] studied the silanization of oxidized and reduced MWCNTs using 3-glycidoxypropyltrimethoxysilane and tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane, respectively. Velasco-Santos et al. [16] added a new chain to the open end cap and to the walls of the oxidized MWCNTs by silanization with 3-mercaptopropyl trimethoxysilane.

In the present study, 3-aminopropyltriethoxysilane (3-APTES) was used as the silane agent to treat MWCNTs. 3-APTES is an important aminosilane that finds wide applications in nylon, phenolic, epoxy, and melamine resin based composites. Multi-walled carbon nanotubes (MWCNTs) were functionalized by oxidation with a mixture of concentrated nitric acid and sulfuric acid. The functionalized MWCNTs were chemically modified by covalent bonding of the 3-aminopropyltriethoxysilane molecule with oxidized carbon nanotubes, in an aim to improve their compatibility with other polymers for application in nanotube-based polymer matrix composites.

Experimental

Materials

Multi-walled carbon nanotubes (MWCNTs) used in this study were synthesized by catalytic chemical vapor deposition (supplied by Iljin Nanotech Co. Ltd., Korea). The

diameter range of the MWCNTs was 10–15 nm and the purity is above 95%. 3-aminopropyltriethoxysilane with purity of 99% (Aldrich) was used as the silane functionalization agent. The following reagents were used without further purification: nitric acid (70%, MS, Osaka, Japan), sulfuric acid (95%, Dae Jung Chemicals, Korea), acetone (99.5%, Dae Jung Chemicals, Korea), tetrahydrofuran (99.5%, Aldrich) and ethanol (99.5+%, Sigma Aldrich).

Functionalization of multi-walled carbon nanotubes

Three grams of MWCNTs was dispersed in 300 mL of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:2 v/v) solution at 50 °C and stirred for 20 h. The solution was filtered, washed with water and acetone. The resulting functionalized MWCNTs (f-MWCNTs) were then dried under vacuum at 100 °C for 24 h.

Silanization of f-MWCNTs with 3-aminopropyltriethoxysilane

About 0.050 g of f-MWCNTs was dispersed in 50 mL of ethanol via ultrasonication for 30 min. Then the reaction was conducted with 3-aminopropyltriethoxysilane while stirring at 70 °C for 4 h. After completion of the reaction, the product was purified by repeated washing with water followed by acetone. The resulting silanized nanotubes (APTES–MWCNTs) were separated by filtration and dried under vacuum at 80 °C for 12 h.

Characterization

Fourier Transform Infrared (FT-IR) spectra of raw-, oxidized-, and silanized-multi-walled carbon nanotubes were recorded using a JASCO FT-IR spectrometer with KBr pellets. The silane-functionalized MWCNTs were characterized by Energy Dispersion Spectroscopy (EDS) in the EDAX-equipped SEM (Leica Cambridge, England). A Field Emission Scanning Electron Microscope (FE-SEM) (LEO SUPRA 55, Carl Zeiss, Germany) and a Transmission Electron Microscope (TEM) (FEI Company, USA) were used to study the surface morphology of functionalized MWCNTs. The samples for FE-SEM analysis were prepared by taking one drop of acetone containing the dispersed MWCNTs on a silicon wafer and allowing it to dry in a vacuum oven for 30 min. For TEM, the samples of MWCNTs were ultrasonically dispersed in tetrahydrofuran and a drop of sample was placed onto a 400 mesh carbon coated copper grid. The samples were dried in a vacuum oven for 24 h at room temperature before measurement.

Results and discussion

The FT-IR spectrum of raw MWCNTs is shown in Fig. 2. The incidence of $3,440\text{ cm}^{-1}$ and $1,048\text{ cm}^{-1}$ width bands are attributed to the presence of hydroxyl groups ($-\text{OH}$) on the surface of the MWCNTs, which resulted from either ambient atmospheric moisture or oxidation during purification of the raw material [17]. The IR spectrum of the oxidized nanotubes (f-MWCNTs) is presented in Fig. 3. Two new bands appeared at $1,716\text{ cm}^{-1}$ and $1,162\text{ cm}^{-1}$ corresponding to the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations of the carboxylic groups ($-\text{COOH}$), respectively [18]. An absorption peak at $3,440\text{ cm}^{-1}$ is observed for the OH functionality and a peak at $1,384\text{ cm}^{-1}$ is due to the OH bending deformation in $-\text{COOH}$. All these observations indicate that the surface of the MWCNTs has been functionalized by oxidation and hence the formation of $-\text{OH}$ and $-\text{COOH}$ groups on MWCNTs.

The FT-IR spectrum of the reaction product of f-MWCNTs and 3-APTES (APTES-MWCNTs) is presented in Fig. 4. From the figure, a characteristic absorption peak is observed at $1,070\text{ cm}^{-1}$, attributed to a $\text{Si}-\text{O}$ vibration. Another peak appears at 803 cm^{-1} , attributed to $\text{Si}-\text{OH}$ [19]. Thus the above spectrum indicates the reaction of 3-APTES with f-MWCNTs.

Further evidence for the covalent modification of oxidized MWCNTs (f-MWCNTs) was provided by energy dispersion spectroscopic (EDS) analysis. The spectrum of APTES-MWCNTs is shown in Fig. 5. The elemental composition of the APTES-MWCNTs is given in Table 1. The data confirms the attachment of silane molecules on the surface of the functionalized MWCNTs. The resulted atomic percentage ratio of $\text{Si}:\text{C}$ (0.0272) was found to be slightly better than that reported by Ma et al. (0.0189) via

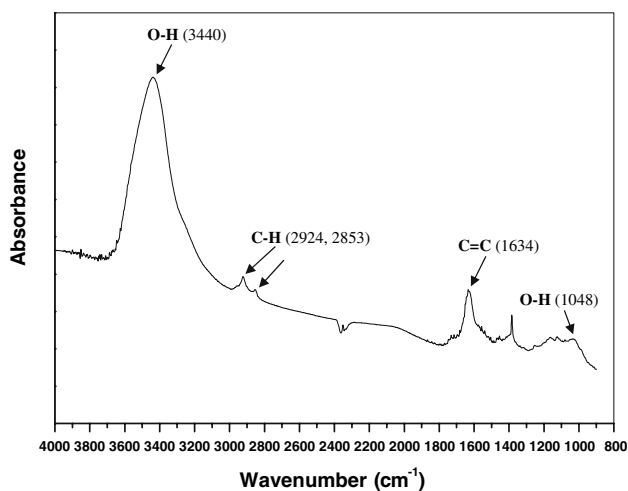


Fig. 2 FT-IR spectrum of raw multi-walled carbon nanotubes

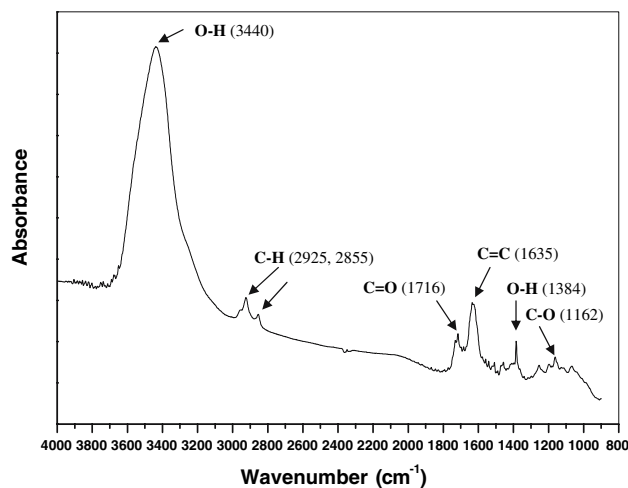


Fig. 3 FT-IR spectrum of oxidized multi-walled carbon nanotubes

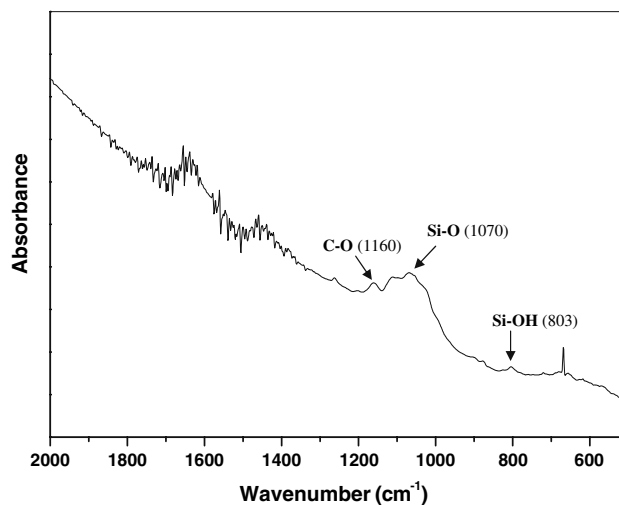


Fig. 4 FT-IR spectrum of silanized multi-walled carbon nanotubes

XPS analysis in which case 3-glycidoxypropyltrimethoxysilane was used [14].

The surface morphology of MWCNTs after functionalization was observed using FE-SEM and TEM. The FE-SEM images of raw MWCNTs, f-MWCNTs, and APTES-MWCNTs are shown in Fig. 6. A clear distribution of MWCNTs is observed after oxidation and silanization. In addition to this, the morphology of MWCNTs after functionalization is observed to have remained intact. No destruction of MWCNTs is observed which indicates that the MWCNTs are strong enough to withstand the functionalization process.

The TEM images of raw MWCNTs, f-MWCNTs, and APTES-MWCNTs are shown in Fig. 7. It can be seen from the Fig. 7a that the tips of the raw MWCNTs were closed (pointed by white arrows), which is a feature of unmodified MWCNTs. After acid-oxidation, however, the end tips of

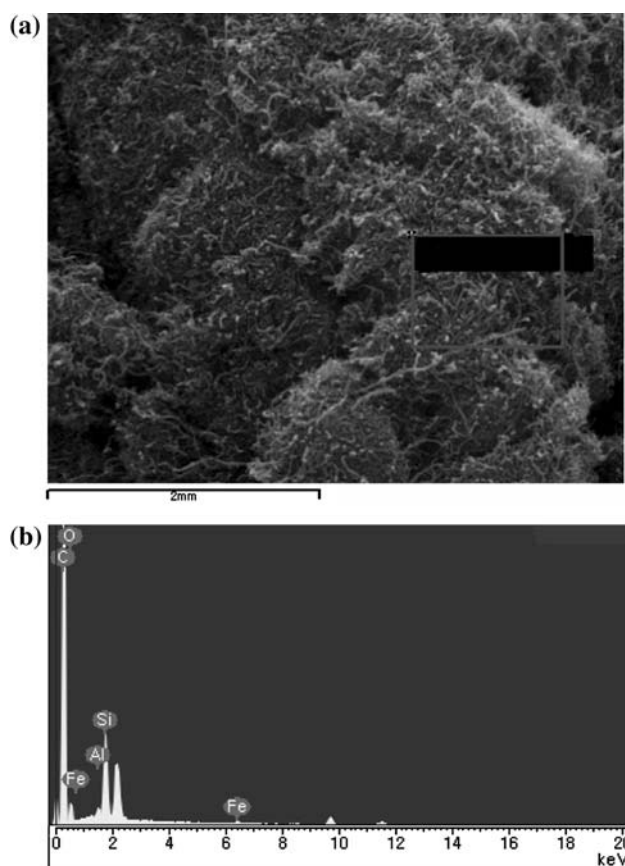


Fig. 5 EDS spectrum of APTES-MWCNTs (b) in the selected region of SEM image of APTES-MWCNTs (a)

Table 1 Elemental composition of APTES-MWCNTs by EDS analysis

Element	Wt%	At%
C	79.76	85.94
Si	5.08	2.34
O	13.98	11.31
Al	0.56	0.27
Fe	0.62	0.14

many MWCNTs were opened (Fig. 7b, pointed by black arrows), indicating the breaking of the C–C bond along the graphene layers of the co-axial tubes [20] and thus allowing for the generation of functional groups at the open ends. Figure 7c shows the surface morphology of the silane-functionalized MWCNTs. Some amorphous materials are observed to be attached to the surface of the silanized MWCNTs which were supposed to be derived from the silane molecules of 3-APTES. The presence of these silane molecules was also confirmed by the EDS analysis (Figure 5). The layered structure of the MWCNTs remained largely intact, which indicates that there was no real damage to the MWCNTs during the silanization

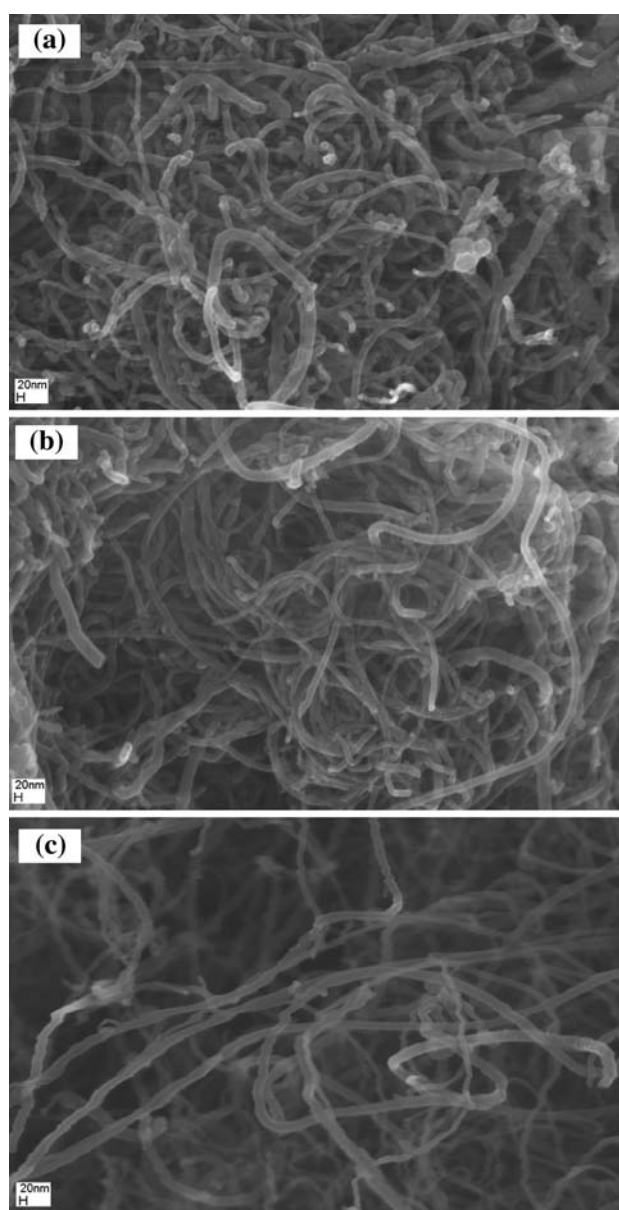


Fig. 6 FE-SEM images of multi-walled nanotubes (a) as received (b) oxidized, and (c) silanized with 3-aminopropyltriethoxysilane

process. It is also observed from these figures that MWCNTs retained their external average diameter of 10–15 nm even after their oxidation and silanization.

Conclusions

Multi-walled carbon nanotubes were functionalized via an oxidative process using a mixture of concentrated sulfuric acid and nitric acid. These oxidized MWCNTs were silanized with 3-aminopropyltriethoxysilane. The reaction of MWCNTs and 3-APTES was confirmed by FT-IR, EDS, SEM, and TEM analysis and the results indicated the

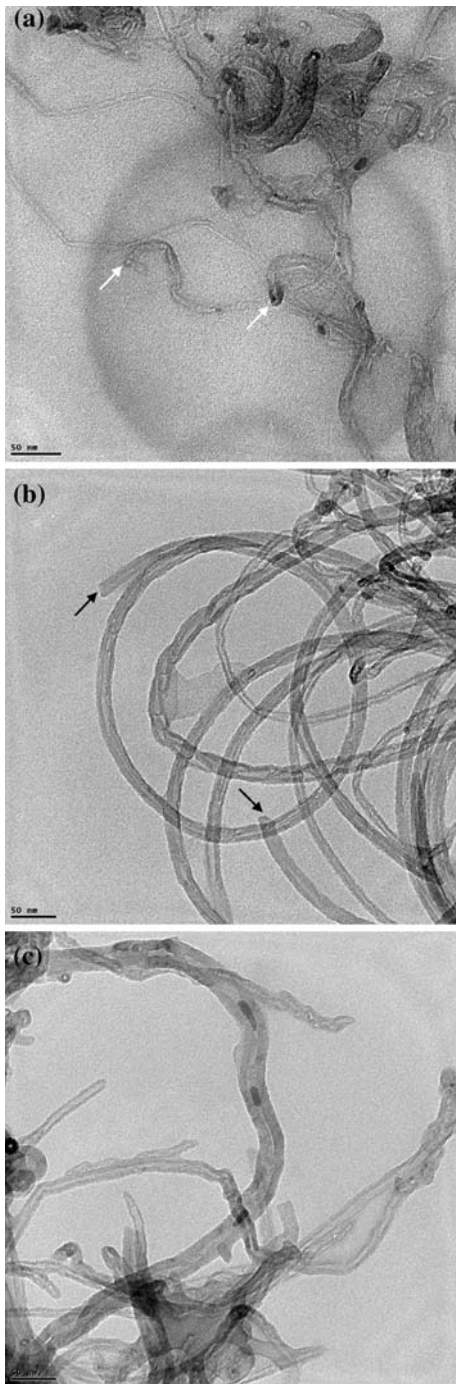


Fig. 7 TEM images of multi-walled nanotubes (a) as received (b) oxidized, and (c) silanized with 3-aminopropyltriethoxysilane

attachment of silane molecules onto the surface of the MWCNT. This silanization method allows for the enhancement of the chemical compatibility of MWCNTs with specific polymers for application in nanotube-based polymer matrix composites, which will be the focus of our future work.

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