PREPARATION, MORPHOLOGY AND PROPERTIES OF FREE RADICAL MODIFIED MWCNT/POLYIMIDE NANOCOMPOSITE

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Abstract

Mutilwall carbon nanotube(MWCNT) was modified by free radical reaction with vinyltriethoxysilane(VTES). Silane functional groups were grafted on the MWCNT(VTES-MWCNT). Precursor of polyimide, polyamic acid has been prepared by reacting 4,4'-Oxydianiline(ODA) with 3,3',4,4'- Benzophenone tetracarboxylic dianhydride (BTDA). The silane modified MWCNTs (VTES-MWCNT) were well dispersed in the polyamic acid before imidation at 300℃. Polyimide does not connect with MWCNT but interpenetrate into the VTES-MWCNT network. The electrical resistivity decreased due to the VTES-MWCNT network which provides an effective electrical pathway. Furthermore, the percolation threshold appeared in the lower MWCNT content. Percolation threshold appeared at 5.0phr when unmodified MWCNT was used and at 2.5 phr when VTES-MWCNT was used. The volume resistivity of the MWCNT/PI composites decreased from 1.53 x 10^{17}Ω-cm(neat polyimide) to 4.09 x 10^{5}Ω-cm(7.5 phr unmodified MWCNT) and 6.25 X 10^{2}Ω-cm(7.5 phr VTES-MWCNT).

1 Introduction

Carbon nanotubes (CNTs) generated many interesting research topics since S. Ijima identified their structures [1] in 1991. They possess excellent mechanical properties, low density, high strength, high toughness, high surface area, flexible, high chemical stability and excellent electrical and thermal conductivity[2]. CNT/polymer composites are one of the interesting topics since CNT can improve the mechanical properties and bestow electrical conductivity of the composites [3]. CNT/polyimide composites are one of the interesting materials and have been extensively studied [4-8]. In our previous investigation,[8] unmodified-, acid modified- and amine modified- MWCNT/polyimide nanocomposites were prepared and their morphology and electrical, thermal and mechanical properties were examined . In this study, Multi-walled carbon nanotube (MWCNT) was modified by free radical reaction with vinyltriethoxysilane (VTES). Precursor of polyimide, polyamic acid has been prepared by reacting 4, 4' - Oxydianiline with 3, 3', 4, 4' - Benzophenone tetracarboxylic dianhydride. Free radical modified MWCNT (VTES-MWCNT) was then mixed with polyamic acid and heated to 300℃ to form carbon nanotube/ polyimide composite. During the imidization processes, the silanes on CNT surface reacted with each other and may be connected together with covalent bonding (Si-O-Si). The free radical modified MWCNTs were analyzed by FT-IR specta. Morphology of the free radical modified MWCNT/polyimide composites was investigated by TEM. Electrical resistivity decreased signifycantly comparing to the unmodified MWCNT/polyimide composites.

2 Preparation of MWCNT/PI composite

2.1 Free radical modified of MWCNT

Unmodified MWCNT was functionalized by refluxing with mixture of Benzoyl peroxide and Vinyltriethoxysilane (VTES) at 80℃ for 8 hours. [9].

2.2 Preparation of MWCNT/Polyimide compositres

Polyamic acid has been prepared by reacting 4,4'-Oxydianiline(ODA) with 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA). VTES-MWCNT was added to the polyamic acid and heat to 300℃ to prepare VTES-MWCNT/polyimide composites.

3. Properties Measurement

3.1 Fourier transfer infrared spectroscopy

Fourier transform infrared (FT-IR) spectra of MWCNT were recorded between 400 and 4000 cm^{-1} on a Nicolet Avatar 320 FT-IR spectrometer, Nicolet Instrument Corporation, Madison, WI, USA. The sample was coated on a CaF_2 plate. A minimum of 32 scans was averaged with a signal resolution of 2 cm^{-1} within the 400–4000 cm^{-1} range.

3.2 Characterization of MWCNTs by Raman spectrum

Raman spectroscopy (Spectra one Raman image system of Dilor with a CCD multi-channel detector) was used to investigate the change of structure of VTES-treated carbon nanotubes. A 632.8 nm (1.96 eV) He—Ne laser was used as the light source and optical filters were used to adjust the power of the laser. The illuminated spot on the sample surface was focused to about 2 mm in diameter. The resolution of the Raman spectra was better than 1cm. Raman signal was collected by CCD that cooled by the liquid nitrogen.

Morphological properties

Morphological properties were investigated by a Scanning Electron Microscope Hitachi, FE-SEM (S-4200) and by a Transmission Electron Microscope (TEM) JEOL-2000EX.

Measurements of Electrical properties.

Surface and volume electrical resistivity were measured by a ULTRA Mesohmeter SM-8220, DKK TOA Corporation. The Surface and volume electrical resistivity of the MWCNT/polyimide composites were measured after the addition of variors contents of MWCNT. The charge time was 30s, and the current stress of the measurements was 100V. An average value was obtained from six measurements of each sample.

Measurements of tensile properties

Tensile strength test was carried out by using an Instron machine Model 4488 at room temperature. Test procedure was followed the ASTM-D882. Dimensions of test specimen were 50mm x 5mm x 0.1mm; the crosshead speed was 5mm/min.

4. Results and Discussion

4.1 Fourier transfer infrared spectroscopy

The VTES-MWNTs were characterized by FTIR spectroscopy in Figure 1. Figure 1 displayed the peaks of C=C double-bond stretching in the range of 1600–1475 cm^{-1}. Moreover,the functionalized MWNTs posses peaks of Si-O-C groups at 1175, 1100, 1075, and 970–940 cm^{-1}. In the range of 1610–1590 cm^{-1} no peaks were observed, this indicates that no C=C bond of VTES remained. FTIR spectra confirm that the C=C bonds of VTES attached to the MWNTs or underwent the selfaddition reaction of the C=C group.

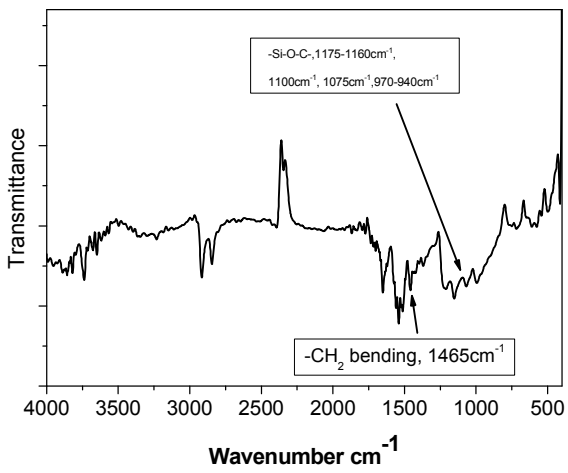

Figure 1 FT-IR spectrum of free radical modified MWCNT

4.2 Raman spectrum

Usually, CNTs possess two bands: the disorder band (D-band) at about 1350 cm^{-1}, and the graphitic

band (G-band) at about 1580 cm^{-1}. [10] The Raman spectra of unmodified and modified MWNTs are shown in Figure 2. The area ratio of the D-band to the G-band of unmodified MWCNT, VTES-MWCNT is 1:1.32 and 1:0.82, respectively. The D-band was enhanced; VTES was attached to the side walls of the MWNTs.

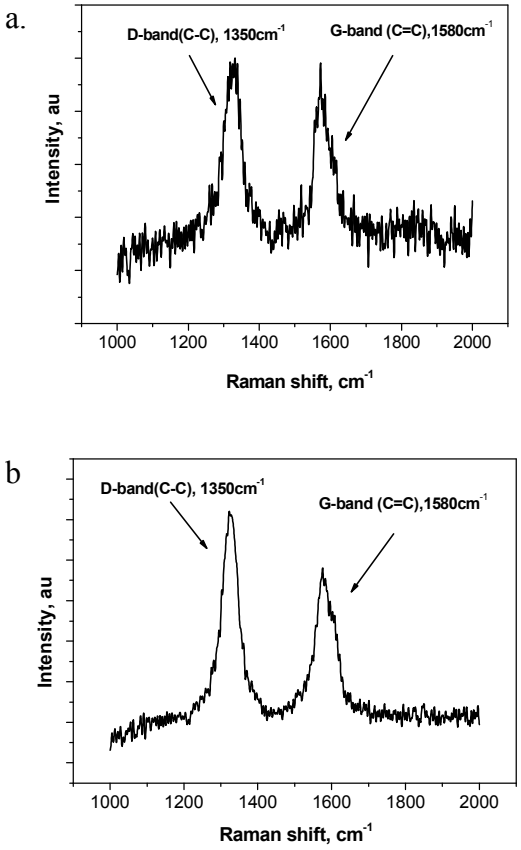

Figure 2 Raman spectra of the (a) unmodified and (b)free radical modified MWCNT

4.3 Morphology of the MWCNT/PI composites

Figure 3 illustrates SEM microphotographs of the VTES-MWCNT/polyimide composites. All SEM microphotographs of the VTES-MWCNT /polyimide composites show the MWCNTs were dispersed in the polyimide matrix.

Figure 4 shows TEM microphotograph of the VTES-MWCNT/polyimide composites. VTES was grafted on the MWCNT and exhibit "feather" shape. Some of the "feather" shape species connect each other.

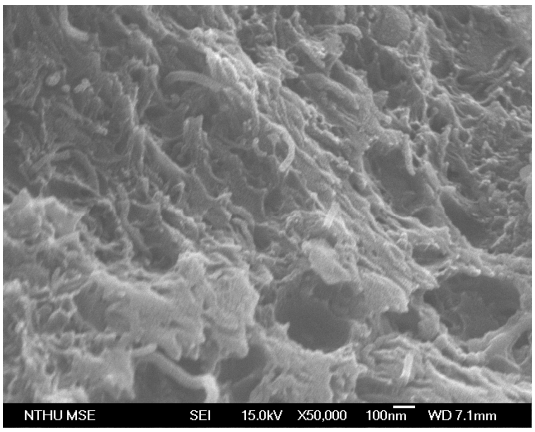

Figure 3 SEM microphotograph of VTES-MWCNT/Polyimide composites

Figure 4 TEM microphotograph of VTES-MWCNT/Polyimide composites

3.4 Electrical properties

CNTs have high aspect ratios and posses many π-bonds. The electrons will be transferred through the π-bond of CNTs. Adding a small quantity of CNT will significantly decrease the electrical resistivity of the nanocomposites. When MWCNT was modified by VTES via free radical reaction, the silane functional group can be connected with each other. Polyimide molecule does not react with the MWCNT but interpenetrates into the connected VTES-MWCNT network. It causes electrical conducting pathway more effective, consequently, the electrical conductivity will be increased. Figure 5 illustrates the volume electrical resistivity of the

VTES-MWCNT/polyimide composites. Volume resistivity of the nanocomposites decreased from 1.53 x 10^{17}Ω-cm (neat polyimide) to 7.08 x 10^{14}Ω-cm (2.5phr VTES-MWCNT/polyimide composites) and to 8.17 x 10^{3}Ω-cm (2.5phr VTES-MWCNT/polyimide composites).

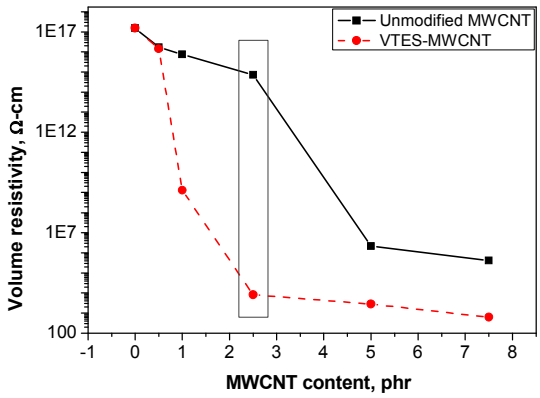

Figure 5 Effect of MWCNT content on the volume resistivity of the VTES- MWCNT/polyimide composites

3.5 Mechanical properties

CNTs possess excellent mechanical properties. A small quantity of CNTs can significantly increase the tensile properties of the polymer matrix. Figure 8 illustrates the tensile properties of the VTES-MWCNT/PI composites. Figure 6 illustrates the tensile properties of the VTES-MWCNT/PI composites. When unmodified MWCNT was used, the tensile strength of the MWCNT/polyimide composite was increased from 102MPa (neat polyimide) to 121MPa (6.98wt% unmodified MWCNT/PI composites). When VTES-MWCNTs were used, tensile strength increases dramatically when the VTES-MWCNT content lower than 0.5wt%. The tensile strength of the neat polyimide was 101.71MPa and it increased to 165.22MPa(0.5wt% VTES-MWCNT-2). However, when the VTES-MWCNT content was higher, the tensile strength of the VTES-MWCNT/polyimide composites decreased. The tensile strength of the VTES-MWCNT/polyimide composites decreased to 130.78MPa(6.98wt% VTES-MWCNT-2).Young's Modulus also increased significantly with the VTES-MWCNT. The Young's Modulus of the neat polyimide was 2.34 GPa and was increased to 3.19 GPa (6.98wt% unmodified MWCNT/polyimide composites) and to 5.05GPa(6.98wt% VTES-MWCNT-2/polyimide composites). When the VTES-MWCNT content was higher, the tensile strength of the VTES-MWCNT/polyimide composites was decreased but Young's Modulus still increased. When the VTES-MWCNT was added to the polyimide matrix, the composites may become brittle hence possess higher Young's Modulus.

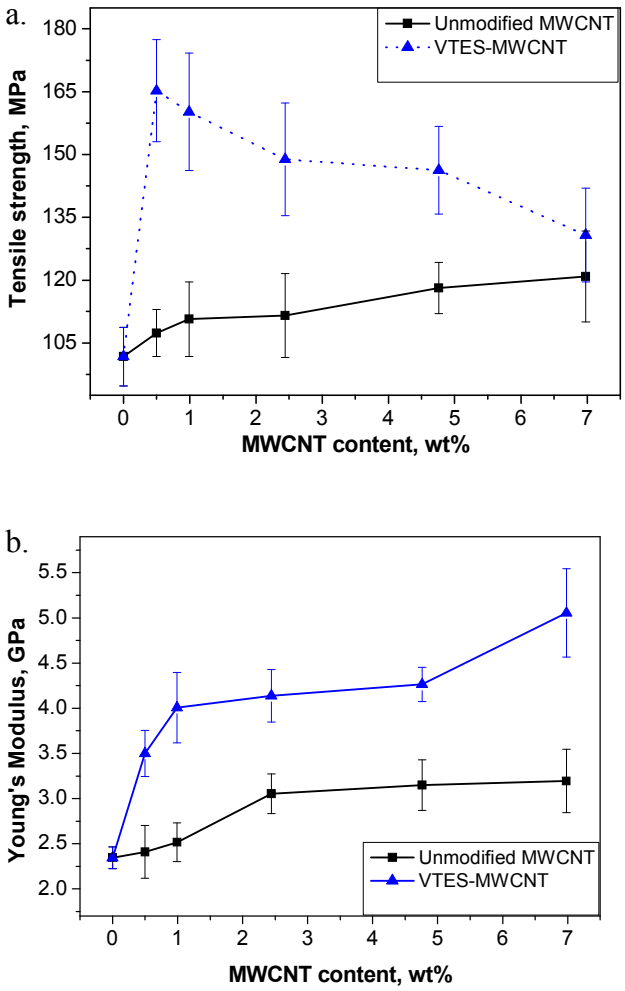

Figure 8 Effect of MWCNT content on the tensile properties in the VTES-MWCNT/ polyimide composite (a)tensile strength (b)Young's Modulus.

Conclusions

Unmodified MWCNT was successfully modified with with vinyltriethoxysilane(VTES) via free radical reaction. Which was added to the polyamic acid and reacted at 300 ℃ to form VTES-MWCNT/polyimide composites. TEM microphotograph shows that MWCNT network was formed and polyimide molecule may interpenetrate

to the crosslinked CNT network. The volume electrical resistivity of the MWCNT/polyimide composites was decreased more significantly when VTES-MWCNTs were used. The percolation threshold of the VTES-MWCNT/polyimide composites (2.44wt%) was lower than that of the unmodified MWCNT/polyimide composites (2.44wt%). The tensile strength of MWCNT/polyimide composites increased significantly when VTES-MWCNTs content was low, but it was decreased when VTES-MWCNTs content was higher. Young's Modulus of the VTES-MWCNTs/polyimide composites increased with high VTES-MWCNTs content. However, the nanocomposites may become brittle when VTES-MWCNTs content was high.

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