

Self-assembled Carbon Nanotube/Silicone Composite Films and Their Electrical Properties for Electrical Device

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Abstract: Novel composites were synthesized using AEPTES (3-(2-aminoethylamino)propyltriethoxysilane), which behaves as an excellent dispersant for MWCNTs (multiwall carbon nanotubes) in polymer film matrices. The thickness of the synthesized nanocomposite films ranged from 50 to 70 μm , having well-dispersed MWCNTs. Increasing the AEPTES concentration from 0.0196 to 0.0300 M, increased the amine content and the dispersion of MWCNTs. The film synthesized at 0.0300 M AEPTES exhibited the greatest degree of dispersion among the three samples, which is consistent with a self-assembled silane group interacting with the MWCNT surface.

Key words: Carbon nanotube, self-assembly, AEPTES, nanocomposite, electrical properties.

1. Introduction

CNTs (carbon nanotubes) are unique nanomaterials having remarkable mechanical and electrical properties, thermal stability and chemical resistance [1-5]. The development of composites that incorporate CNTs into polymers has become an attractive new subject in materials science. Investigations into high-performance functional CNT/polymer composites have been reported [6-10]. However, the percolation of CNTs due to strong van der Waals interactions prevents their practical use [3]. Therefore, development of approaches to achieve a homogeneous dispersion of CNTs is important in the field of CNT/polymer composites. Several routes have already been examined to overcome this problem using chemical and physical methods [4]. However, these methods are destructive and generate structural defects that degrade the intrinsic properties of the CNTs, which is considered to be a major disadvantage.

Therefore, the synthesis of homogeneous composites of CNTs remains a technical challenge. Furthermore, there have been few studies on the processability of CNT/polymer composites [5]. Films or fibers of CNT/polymer composites have been successfully formed from solution blending and melt blending and from in situ polymerization of CNT/polymer mixtures [6]. However, such mixtures are generally inappropriate for forming nanostructures or microstructures because of the need for solvent removal and high-temperature treatments, which can damage the CNT structure and cause aggregation. In this paper, we report that AEPTES (3-(2-aminoethylamino)propyltriethoxysilane) acts as an excellent dispersant for MWCNTs (multiwall carbon nanotubes), and we also describe the synthesis of novel composites synthesized from AEPTES and MWCNTs.

2. Materials and Methods

Self-assembled composite films with different concentrations of AEPTES (0.0196 M, 0.0250 M, and

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0.0300 M) were synthesized. MWCNTs with purity greater than 90 wt% were synthesized using chemical vapor deposition with a C₂H₂ carbon source and a Fe-Mo/MgO catalyst. MWCNTs (0.1 g) were added to AEPTEs (0.0196 M) in Wako Ind., Ltd. DMF (N,N-dimethylformamide) (100 mL), and the mixture was sonicated for 10 min. using a probe-type sonicator (Sonifier 450A, Branson). The DMF dispersion of the MWCNTs/AEPTEs composite was cast onto a Teflon sheet, dried at 150 °C for 3 h and then hot pressed at 80 °C for 1 h. The morphology and crystal structure of the obtained particles were characterized using SEM (scanning electron microscopy), TEM (transmission electron microscopy) and X-ray diffraction. The surface groups of the composite films were identified by FT-IR (Fourier-transform infrared spectroscopy) and XPS (X-ray photoelectron spectroscopy).

3. Results and Discussion

Fig. 1 shows SEM and TEM images of the as-grown MWCNTs synthesized at 700 °C. The TEM investigations of the as-grown products revealed that MWCNTs had a diameter of about 40 nm and length of 75 μ m. The morphology of the synthesized composite films was investigated by SEM and TEM.

The synthesized films were flexible (inset Fig. 2a) and the thickness ranged from 50 to 70 μ m depending on the AEPTEs concentration. As the AEPTEs concentration increased from 0.0196 to 0.0300 M, MWCNTs tended to disperse more uniformly on the nanocomposite films. The highest degree of dispersion of MWCNTs was observed with 0.0300 M AEPTEs. This was confirmed from a fracture-surface image of the composite films (inset Fig. 2c), showing well-dispersed MWCNTs in the SiO_x matrix. We assume that the amino groups in AEPTEs (i.e., -NH₂, -NH) formed cross-linking hydrogen or ionic bonds with silane groups (Si-O-R) or its hydrolyzed Si-OH groups in nearby aminosilane molecules. In other words, a two-dimensional network of the oligomer aggregates forms and diffuses around the MWCNT

surface, directly interacting with the functional groups of the MWCNT. These aggregates may also interact with AEPTEs molecules that have already formed in monolayers. These structures form across multiple AEPTEs molecules, and may be considered a multilayer structure (Scheme).

The surface group of the composite films was studied by FT-IR in diffuse reflection configuration, operating at a resolution of 4 cm⁻¹ (Fig. 3). The peaks between 900 and 1,100 cm⁻¹ are characteristic of the siloxane group [7]. The peaks at 1,027 and 1,107 cm⁻¹ are signatures of the antisymmetric stretching mode of siloxane (Si-O-Si) [8], which increased with AEPTEs concentration (Fig. 3b-d). As described earlier,

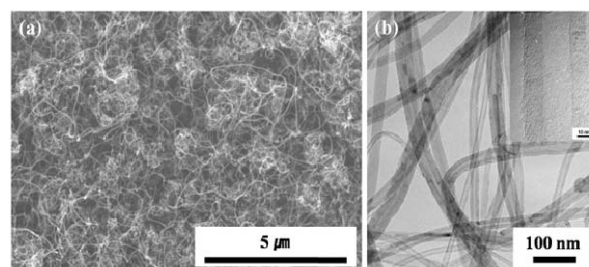


Fig. 1 SEM and TEM images of as-synthesized MWCNT.

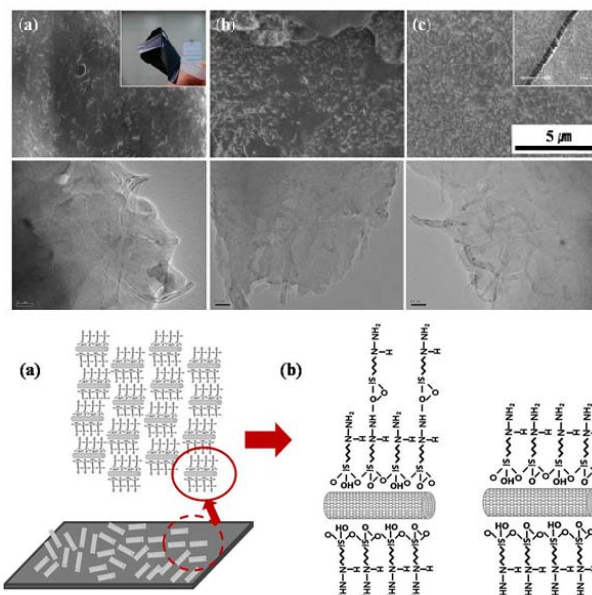


Fig. 2 SEM and TEM images of composite films with different concentrations of AEPTEs: (a) 0.0196 M (inset: Optical images of synthesized nanocomposite film), (b) 0.0250 M, and (c) 0.0300 M (Scheme. Self-assembled nanocomposite film).

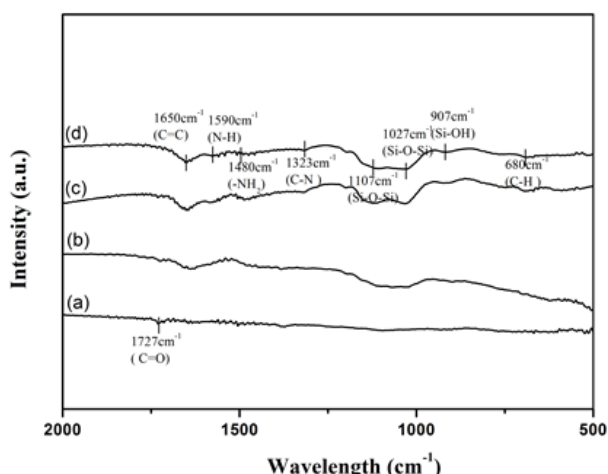


Fig. 3 Fourier-transform infrared spectroscopy spectra of the nanocomposite films with different concentrations of AEPTEs: (a) pristine MWCNTs, (b) 0.0196 M, (c) 0.0250 M, (d) 0.0300 M.

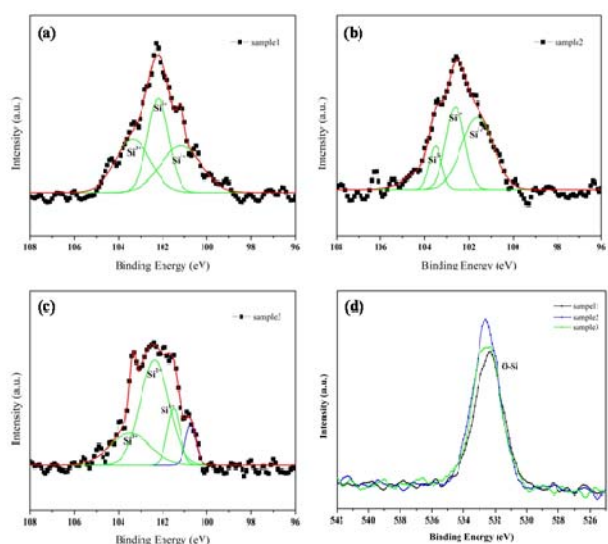


Fig. 4 Si 2p XPS spectra for the composite films with different concentrations of AEPTEs: (a) 0.0196 M, (b) 0.0250 M, (c) 0.0300 M, (d) O1s XPS spectra for the composite films.

the AEPTEs molecules become cross-linked with the neighboring molecules via intermolecular condensation of Si-OH groups to form Si-O-Si bonds. Consequently, increasing AEPTEs concentration increases the number of Si-O-Si bonds, which facilitates the formation of MWCNT network films. The singlet at 907 cm^{-1} is assigned to the Si-OH stretching mode. Increasing the concentration of AEPTEs also increased the intensity of the peak at

907 cm^{-1} [9], suggesting that incompletely cross-linked siloxane molecules remained in the self-assembled film. However, the peak at 1,727 cm^{-1} (-COOH) in pristine MWCNTs was not found in the composite films, indicating that the MWCNT surface was covered by the siloxane compound. The surface properties of the composites were determined by XPS using a vacuum generator XPS system operating with Al K α ($h\nu = 1,486.6$ eV) radiation (Fig. 4). To extract detailed chemical structural information from the Si 2p peaks, it is necessary to establish a suitable peak-fitting procedure.

As shown in Fig. 4, our procedure was based on five Gaussian functions [$\text{Si}^n + (n = 0, 1, 2, 3, \text{ and } 4)$] to simulate the five silicon oxidation states corresponding to Si, Si₂O, SiO, Si₂O₃, and SiO₂, respectively. It has been reported that all five oxidation states exist in non-stoichiometric SiO_x ($0 < x < 2$) films [10]. In our samples, the Si 2p spectra showed three peaks at 101.2, 102.5, and 103.3 eV, which can be assigned to Si¹⁺, Si²⁺, and Si³⁺, respectively. In addition, the effect of concentration on the chemical structures can be clearly demonstrated by comparing differences in the Si 2p peak, as shown in Fig. 4.

In the films with 0.196 M AEPTEs, the contribution of Si²⁺ (Si₂O) is larger than that of Si¹⁺ (SiO) and Si³⁺ (Si₂O₃). This confirms the suggestion that the AEPTEs molecules were not completely cross-linked, explaining the low intensity of the Si-O-Si peak (Si₂O). However, the Si¹⁺ and Si³⁺ peaks increased with increasing AEPTEs concentration. Consequently, the Si-O-Si peak increased, which indicated that the AEPTEs molecules were cross-linked by Si-O-Si bonds. These results were confirmed by the presence of FT-IR peaks for the antisymmetric stretching mode of siloxane (Si-O-Si) at 1,027 cm^{-1} and 1,107 cm^{-1} . However, at a high AEPTEs concentration (0.0300 M), the Si²⁺ peak increased, relative to those of Si¹⁺ and Si³⁺. It can be assumed that the unreacted AEPTEs molecule

remained incompletely cross-linked in the solution.

The presence of a C1s spectrum for the modified surface clearly indicated that the organosilane was grafted onto the MWCNT surfaces. Pristine MWCNTs showed their main binding energy peak at 284.6 eV, which was assigned to C-C. Two other peaks at 285.2 and 289.5 eV were assigned to C-OH and -COOH, respectively [11]. The C=O peak (286.5 eV) was too weak to allow for inclusion in the peak fitting. In addition, a new peak appeared at 283.2 eV (assigned as C-Si), which increased with AEPTEs concentration, while the C-OH peak decreased. This further suggested that the film undergoes cross-linking via intermolecular condensation of Si-OH groups on neighboring molecules to form siloxane or Si-O-Si bonds. We also confirmed this observation in the O1s peaks (Fig. 4d). The O1s spectrum is symmetrical and narrow, characteristic of a single O environment, as expected for a situation wherein all the oxygen-containing bonds are O-Si (532.6 eV) [12].

Based on the FT-IR spectra and XPS fitting results, the film structures can be understood as follows (Scheme): The MWCNT surfaces formed a network of O=C-O-Si-R bonds from silanization with AEPTEs. Consequently, MWCNTs were linked with Si-O-Si bonds and became well dispersed in the polymer network. This is a network similar to that of Si-O-Si-R, reported for AEPTEs-modified silica surfaces [8].

The dispersion of MWCNTs affects the electrical and mechanical properties of nanocomposite films. If MWCNTs are well dispersed in the polymer matrix, the amine group and MWCNT should encourage the formation of a percolation network, which can become a pathway for electrons in the film. Such nanocomposites should have enhanced conductivity. To examine their performance, we measured the current-voltage (I-V) characteristics of nanocomposite films that were set on a quartz substrate (10 mm × 10 mm). These characteristics were measured by the two-probe method within an applied voltage ranging from -1.0 to 1.0 V using a source meter (Keithley Model

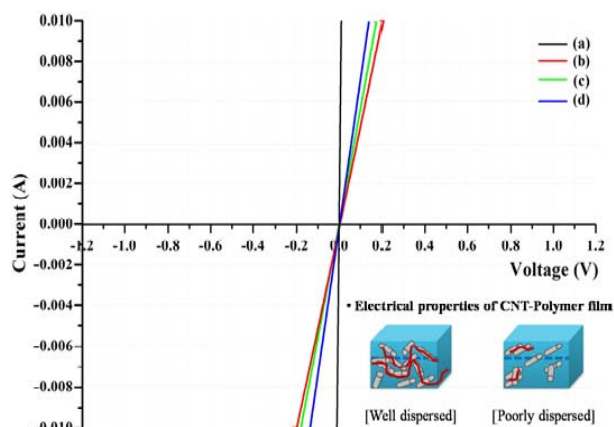


Fig. 5 I-V characteristics of composite films with different concentrations of AEPTEs: (a) pristine MWCNT, (b) 0.0196 M, (c) 0.0250 M, (d) 0.0300 M.

2400). As seen in Fig. 5, all samples exhibited a linear I-V relation under the experimental conditions, demonstrating their Ohmic nature. Pristine MWCNT (Fig. 5a) had a high gradient in the I-V plots, indicating a high electrical conductivity. Furthermore, the I-V slope increased with AEPTEs concentration (Fig. 5b-d). An AEPTEs concentration of 0.0300 M (Fig. 5d), gave the highest conductivity. This result suggests that the good dispersion of the CNTs in the polymer allowed for an electrical pathway in the polymer matrix, which enhanced the conductivity.

4. Conclusions

In conclusion, we synthesized nanocomposite films based on MWCNTs with a self-assembled aminosilane. The thickness of the synthesized nanocomposite films ranged from 50 to 70 μm with well-dispersed MWCNTs. Increasing the AETPES concentration from 0.0196 to 0.0300 M increased the amine content and the dispersion of the MWCNTs in the films. The MWCNT composites synthesized at an AETPES concentration of 0.0300 M exhibited the greatest dispersion among the three samples. The improved dispersion of MWCNTs likely resulted from an interaction between the amine groups of AETPES and the MWCNT surfaces.

Enhancing dispersion of CNTs with AEPTEs can create well-aligned electric pathways through polymer

matrices to improve their conductivity.

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