Effect of Fe₃O₄ loading on the conductivities of carbon nanotube/chitosan composite films

Jason Marroquin¹, H. J. Kim², Dong-Ho Jung³ and Kyong Yop Rhee*¹

¹Department of Mechanical Engineering, College of Engineering, Kyung Hee University, Yongin 446-701 Korea
²Ocean Development System Laboratory, Korea Research Institute of Ships and Ocean Engineering, Taegon 305-600, Korea
³Industrial Liaison Research Institute, Department of Mechanical Engineering, Kyung Hee University, Yongin 446-701, Korea

Received 12 February 2012
Accepted 19 March 2012

*Corresponding Author
E-mail: rheeky@khu.ac.kr
Tel: +82-31-201-2565

Open Access
DOI: http://dx.doi.org/10.5714/CL.2012.13.2.126

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Abstract

Nanocomposite films were made by a simple solution casting method in which multi-walled carbon nanotubes (MWCNT) and magnetite nanoparticles (Fe₃O₄) were used as dopant materials to enhance the electrical conductivity of chitosan nanocomposite films. The films contained fixed CNT concentrations (5, 8, and 10 wt%) and varying Fe₃O₄ content. It was determined that a 1:1 ratio of CNT to Fe₃O₄ provided optimal conductivity according to dopant material loading. X-ray diffraction patterns for the nanocomposite films, were determined to investigate their chemical and phase composition, revealed that nanoparticle agglomeration occurred at high Fe₃O₄ loadings, which hindered the synergistic effect of the doping materials on the conductivity of the films.

Key words: nanocomposite films, multi-walled carbon nanotubes, magnetite nanoparticles, electrical conductivity

1. Introduction

Carbon nanotubes (CNTs) are one-dimensional nanomaterials that are considered as ideal reinforcing agents for polymer matrices because of their unique structure and properties [1,2]. Electrically conductive composites filled with CNTs have attracted increasing attention for a variety of applications, such as static-charge dissipation [3], electromagnetic interference shielding [4], and actuators [5]. However, CNTs are often in bundles or they are entangled because of very strong intertubular van der Waals attractions, which is the current bottleneck in their application [6].

Chitosan (CS) is a linear polysaccharide synthesized by the deacetylation of chitin, a natural polymer found in the exoskeleton of crustaceans. CS is widely used in biomedical applications, drug delivery, food industry, biotechnology, pharmaceuticals, biomedicine, packaging, wastewater treatment, cosmetics, etc. [7,8]. Another advantage of CS is its solubility in acidic aqueous media. Natural polymers modified with suitable nanofillers have now found potential applications as electrochemical sensors and electrodes [9-13]. CS can be made to possess amphiphilic properties giving it a unique capacity to solubilize hydrophobic CNTs in aqueous solution [14,15]. A key characteristic of the CNT/CS composite is its conductivity, as defined by the charge transfer from one conductive particle to another. Because conduction of electrical charge is established when a network of conductive CNTs reaches a critical percolation threshold density that provides direct electrical contact between particles, the effective conductivity of a CNT/CS composite depends upon many factors, such as size, shape, density, and distribution of CNTs within the CS matrix, as well as chemical interactions between the two materials [16-18].

A Fe₃O₄/CNT/CS composite is expected to have diverse properties because each component contributes different chemical and physical properties to the composite. A Fe₃O₄/CNT/CS composite may find applications in drug delivery, tumor treatment, enzyme en-
Effect of Fe$_3$O$_4$ on the conductivities of composite films

1. Introduction

Engineering, batteries, electro-magneto rheological fluids, electromagnetic shielding and magnetic recording. In this study, Fe$_3$O$_4$/CNT/CS nanocomposite films were prepared by the solution casting method. The main objective was to investigate the synergistic effect of Fe$_3$O$_4$ and CNTs on the electrical properties of the nanocomposites. The films were prepared with different concentrations of Fe$_3$O$_4$ at fixed quantities of CNTs in order to determine the optimal metal loading for improving conductivity. Subsequently, the electrical conductivity and X-ray diffraction (XRD) patterns were determined for the nanocomposite films.

2. Experimental

CS (average molecular weight = 350 000 gmol$^{-1}$, 90% degree of deacetylation) was purchased from Sigma Aldrich. Raw multi-walled CNTs (MWCNTs, CM-95), synthesized using the chemical vapor deposition method, were purchased from Hanwha Nanotech Co., Ltd., Korea. The MWCNTs had diameters of 10-15 nm, tube length of 10-20 µm and a purity of 95%. Magnetite (Fe$_3$O$_4$) nanopowder, (<50 nm particle size [transimission electron microscopy], ≥98% trace metals basis) was purchased from Sigma Aldrich. Acetic acid was used to dissolve CS in distilled water.

CS nanocomposite films containing Fe$_3$O$_4$ and CNTs were prepared by the solution casting method [19]. The concentrations of the functional additives (Fe$_3$O$_4$ and CNT) were changed in order to evaluate the synergistic effect of Fe$_3$O$_4$ and CNTs in the nanocomposite films. Electrical conductivities of the films were measured at room temperature using a ring probe method with a high resistivity meter (MCP-HT 450, Mitsubishi). Wide angle XRD patterns of the Fe$_3$O$_4$/CNT/CS nanocomposite films were recorded with a Rigaku Rotaflex (RU-200B) X-ray diffractometer using Cu Kα radiation with a Ni filter. The tube current and voltage were 300 mA and 40 kV, respectively, and 20 angular regions between 0 and 40° were explored.

3. Results and Discussion

The CS composites were characterized in relation to their conductivity as a function of the CNT to Fe$_3$O$_4$ ratio. This was important because the establishment of a highly conductive CNT/CS film requires a network of effective tube-tube contacts. The quality of such a network is ultimately defined by the nanotube concentration and the relative extent of homogeneous (i.e., well-distributed within the matrix) to heterogeneous distribution (i.e., formation of aggregates). The nanotube dimensions limit the effectiveness of electron tunneling across tube-tube contacts. It was also expected that Fe$_3$O$_4$ addition would be beneficial to the electrical conductivity of the CNT and the subsequent composite because of the inherent electrical conductivity of Fe$_3$O$_4$.

Furthermore, the nanoparticles could facilitate electron transfer between nanotubes while being dispersed in the polymer matrix because the composite would acquire more conductive channels and subsequently, a higher metallic character.

Fig. 1a shows how the effect of Fe$_3$O$_4$ loading, expressed as a weight percentage relative to the carbon nanotube (CNT) content, affects the conductivity of (a) 5% CNT/chitosan (CS), (b) 8% CNT/CS, and (c) 10% CNT/CS nanocomposite films.

![Fig. 1. Effect of Fe$_3$O$_4$ loading, expressed as a weight percentage relative to the carbon nanotube (CNT) content, on the conductivity of (a) 5% CNT/chitosan (CS), (b) 8% CNT/CS, and (c) 10% CNT/CS nanocomposite films.](http://carbonlett.org)

![Fig. 2. X-ray diffraction patterns of chitosan (CS), carbon nanotubes (CNTs), Fe$_3$O$_4$, and the nanocomposite films.](http://carbonlett.org)
of CS, one main peak was observed at 2θ = 20° (maximum intensity) corresponding to a characteristic peak of CS chains aligned through intermolecular interactions [19]. The characteristic sharp peak of CNTs at 2θ = 26° represents C (002), which is attributed to the ordered arrangement of concentric cylinders of graphitic carbon in the nanotube [16]. This crystalline peak is not present in the nanocomposite samples, suggesting the dispersion of CNTs into the CS matrix (17). XRD patterns for the Fe$_3$O$_4$/CNT nanoparticles displayed characteristic peaks (20 = 30.1°, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6°). These peaks are consistent with those found in the Joint Committee on Powder Diffraction Standards (JCPDS) database (PDF No. 65-3107). Patterns for the Fe$_3$O$_4$/CNT/CS composites revealed the presence of such peaks, indicating that the Fe$_3$O$_4$ particles in the composites were pure Fe$_3$O$_4$ with a spinel structure.

Fig. 3 clearly shows how increasing Fe$_3$O$_4$ loading in the composites resulted in increasing corresponding peak intensities. The figure further shows that neither the CNTs nor CS induced a phase change in Fe$_3$O$_4$. Furthermore the results show how the increase in Fe$_3$O$_4$ concentration broadened the main peaks, specifically the (400) peak above a Fe$_3$O$_4$ to CNT ratio of 1:1, which indicates a higher average particle size of Fe$_3$O$_4$ due to increased agglomeration of the nanoparticles. The average particle size, calculated using Scherrer’s formula, was approximately 30.79 nm and 46.61 nm for the 1:1 and 2:1 ratios of Fe$_3$O$_4$ to CNT, respectively. Hence the decrease in conductivity at higher Fe$_3$O$_4$ to CNT ratios was attributed to the agglomeration of the nanoparticles, which hindered the effectiveness of the conductive channels between CNTs; this consequently reduced the conductivity percolation threshold of the composites.

4. Conclusions

Fe$_3$O$_4$/CNT/CS nanocomposite films were successfully prepared using a simple solution casting method. A synergistic effect of Fe$_3$O$_4$ and CNTs on the electrical conductivity of the nanocomposite films was observed, where by an optimal loading of Fe$_3$O$_4$ resulted in a ratio of 1:1 relative to the CNT content of the nanocomposite film. XRD patterns revealed that higher Fe$_3$O$_4$ to CNT ratios increased the agglomeration of the Fe$_3$O$_4$ nanoparticles, which hindered the synergistic effect on the conductivity.

Acknowledgements

This work was financially supported by the National R&D project of “Development of Energy Utilization of Deep Ocean Water” supported by the Korean Ministry of Land, Traffic and Maritime Affairs.

References

Effect of Fe₃O₄ on the conductivities of composite films


