The Preparation of Multi-walled CNT–PMMA Nanocomposite

D. W. Seo¹, W. J. Yoon¹, S. J. Park¹, M. C. Jo² and J. S. Kim¹*¹

¹Department of Chemical and Bio Engineering, Kyungwon University, Seongnam, Korea
²Department of Chemical Engineering, Dongseo University, Busan, Korea
*e-mail: jskim@kyungwon.ac.kr
(Received November 15, 2006; Accepted December 11, 2006)

Abstract

Multi-walled carbon nanotube-poly methyl methacrylate (MWNT/PMMA) nanocomposite has been prepared by in situ polymerization of MMA dispersed with MWNTs. The MWNTs were functionalized by nitric acid and sulfuric acid treatment, and this was confirmed by FTIR spectrometer. The solution mixture of MWNTs and MMA was partially polymerized at 80°C, followed by the addition of AIBN and polymerization at 50°C. The MWNT-PMMA composite was prepared by casting the pre-polymer on the glass plate, and the optical properties have been studied using UV-vis spectrometer. The acid treated MWNTs were well dispersed in MMA with fairly good dispersion stability, while flocculation and sedimentation was observed from raw MWNTs in MMA.

Keywords: MWNT, nanocomposite, dispersion, FTIR

1. Introduction

Since the discovery of the carbon nanotubes (CNTs) by Iijima in 1991 [1], there have been lots of interests in the preparation and characterization of CNT-polymer composites because of their novel physical properties such as high aspect ratio, good electrical conductivity, good mechanical strength, and high thermal stability [2]. Transparent conductive nanocomposites can be produced with extremely low volume content of the CNTs. Lots of applications of CNTs have been developed including field emission array, nano transistor, electrochemical energy storage, and chemical and biological sensors. Despite these advantages, there are several limitations for the application of CNTs due to poor dispersion properties in most organic and aqueous solvents, which lead to the agglomeration and segregation of CNTs. Hence, many researches on CNT-polymer nanocomposites are mainly focused on the improvement of dispersion properties of CNTs in the polymer matrix [3, 4].

Several researches have been reported to improve the dispersion properties including the surface treatment, chemical purification, solution mixing, melt blending, and direct polymerization in the presence of CNTs or in-situ polymerization [5-7]. The as-prepared carbon nanotubes by catalytic reaction should be purified because they usually contain a large amount of impurities. CNTs can be purified by several methods including oxidation by mineral acids and gas phase oxidation to remove catalytic particles and carbonaceous byproducts, respectively. Usually HNO₃ aggressively attack the CNT wall, while HCl is found to be passive with respect to the attack on the tube wall [8].

Raman scattering can be used as a probe of disorder in the carbon nanotube wall. The disorder in the graphene structure of the tube wall leads to the appearance of a dispersive broad band [9]. FTIR spectroscopy can be used to identify the functional groups attached to CNTs. The carboxyl group and hydroxyl group after acid treatment can be identified.

In this study, we have prepared MWNT/PMMA nanocomposites via in situ polymerization. MWNTs were purified by acid treatment, and the tube wall functionalization and disorder were studied by FTIR and Raman spectroscopy, respectively. The dispersion property of the MWNT in MMA has been studied, and the optical property and morphology of the composite depending on the CNT contents were studied.

2. Experimental

2.1. Materials

The multi-walled carbon nanotubes (MWNTs) produced by chemical vapor deposition (CVD) were purchased from Nanotech Co., Inc. The mean diameter of the MWNTs was about 12 nm with the purity of 97%. Methyl methacrylate (MMA, provided by Aldrich), α,α’-azobisisobutyronitrile (AIBN, Junsei chemical Co., Ltd.), and stearic acid (Yakuri pure chemical Co., Ltd.) were used as received. Sulfuric acid (H₂SO₄, 96.1%) and nitric acid (HNO₃, 10.4%) were purchased from Duksan pure chemical Co., Ltd. and used as received.
22. Functionalization of MWNTs

The raw MWNTs as received contain amorphous carbon. Oxidation in air at high temperature is a simple and efficient purification method to remove the amorphous carbon. The MWNTs were heated in air at 380°C for 2 h with the ramp rate of 5°C/min. The heat-treated MWNTs (1 g) were chemically treated by refluxing in 300 ml of acid solution mixture of H2SO4 and HNO3 (3:1 by volume) at 80°C for 8 h under vigorous stirring. The acid-treated MWNTs were then filtered, rinsed several times with methanol and distilled water, and dried using freeze-dryer.

23. Preparation of MWNT-PMMA Nanocomposite

The acid-treated MWNT were dispersed in methyl methacrylate (MMA) monomer. The MWNTs in MMA was then ultrasonicated at a frequency of 28 kHz, with a power of 600 W for 5 h at 25°C [10]. After dispersion, 0.04 wt% AIBN and 0.05 wt% stearic acid was added to the MWNT/MMA mixture. The MWNTs concentration was varied as 0, 0.005, 0.01, and 0.05 wt% with respect to MMA to investigate the effect of MWNT concentration on the properties of the composites. MWNTs dispersed MMA was partially polymerized in a three-neck Pyrex reactor at 80°C for 1 h and 30 min. The solution became viscous as the reaction proceeded. The 0.04 wt% AIBN was added again to the partially polymerized mixture, and the mixture was cast on the glass plate for further polymerization at 50°C for 24 h.

24. Characterization

Raman spectroscopy (LABRAM HR, Jobin-Yvon) and FTIR (TENSOR 27, Bruker optics) spectroscopy were used for the analysis of raw MWNTs and acid-treated MWNTs. FTIR spectra was obtained in the transmission mode at the range of 4000-1000 cm⁻¹ at room temperature. Raman spectra were obtained using an Argon ion laser operating at 514.5 nm with a CCD detector. The spectrum presented is an average of five spectra recorded at different regions of the sample. The images of the MWNTs and MWNT-PMMA nanocomposites were obtained by field emission scanning electron microscopy (FE-SEM; Hitachi S-4700, Hitachi) under an acceleration voltage of 15 kV. UV-vis spectra for the nanocomposites were obtained by using UV-vis spectrometer (CARY 100 CONC, Varian) in the range of 250-800 nm with a resolution of 1 nm and exposure time of 0.5 s. The dispersion properties of raw MWNTs and acid-treated MWNTs in MMA were investigated using Turbiscan (TURBISCAN LAB EXPERT, Formulation).

3. Results and Discussion

3.1. Structural analysis

Fig. 1 shows the Raman spectra of raw MWNTs and acid-treated MWNTs. Both spectra had the similar shape, indicating that the acid-treatment process did not affect the graphitic structure of the MWNTs. The figure also shows a strong band at 1580 cm⁻¹ (G mode) and a disorder induced band at 1349 cm⁻¹ (D mode) [11]. G band is the characteristics of graphitic phase corresponding to in-plane vibration of C atoms which indicates the presence of crystalline graphitic carbon in MWNTs. D band has been attributed to disorder induced features such as defects generated in the graphitic planes of MWNTs due to curvature and presence of amorphous defects in graphitic structure. By comparing the I_D/I_G ratios, the degree of disorder of MWNTs can be measured [12]. The I_D/I_G ratio of the raw MWNTs and acid-treated MWNTs was 1.16 and 1.11, respectively, this tells that the acid-treatment increased the degree of disorder of MWNTs and improved the dispersion properties. The radial breathing mode (RBM) Raman frequencies (1-350 cm⁻¹) were not observable, which means that the inner tube of the MWNTs was bigger than 2 nm. The RBM frequency measurement using several laser energies can be used to characterize the ratio of metallic to semiconducting single walled carbon nanotubes which is dependent on their chirality [13]. Generally MWNTs show average properties and tend to be semimetallic as parent graphite.

The functionalization of the MWNTs by acid treatment was characterized using FTIR as shown in Fig. 2. The peak at 1560 cm⁻¹ which can be seen in both raw MWNTs and acid treated MWNTs was attributed to the vibration of carbon skeleton of the MWNTs. The strong absorption band at 1687 cm⁻¹ was in correspondence to acid carbonyl (C=O) stretches, and the broad band at 3394 cm⁻¹ was attributed to −OH stretching in carboxylic acid group [14]. The peak at 2404 cm⁻¹ was attributed to the contaminated CO₂ asymmetric stretching. The FTIR spectra result indicates that carboxylic acid groups have been attached to the surface of MWNTs.
3.2. Morphology study

The morphology of the MWNTs and MWNT-PMMA has been characterized by FE-SEM. Fig. 3 presents FE-SEM images of raw and acid treated MWNTs and PMMA and MWNT-PMMA composite. MWNTs were dispersed in methanol and then dropped on glass plate and dried. The figure shows that the diameter of the MWNTs ranges from 10 to 30 nm. Many entangled clusters of MWNTs with amorphous carbon are observed from the photograph of raw MWNTs. Fig. 3(b) shows clean MWNTs without amorphous carbon were prepared by the acid treatment. Fig. 3(c) and (d) show the fractured surface of the PMMA and MWNTs (0.05 wt%)-PMMA composite. It is hard to distinguish between them. The individual MWNTs were not observable, which may be attributed to their small size and good dispersion in PMMA matrix.

3.3. Dispersion properties and Transmittance

Fig. 4 presents the transmission and backscattering flux intensities of the raw MWNT/MMA and acid-treated MWNT/MMA suspension measured by Turbiscan. This apparatus allows the investigation of the dispersion stability and homogeneity of the suspension via periodical turbidity scan over sample height. The cylindrical glass cell containing MWNTs dispersed MMA was placed in the apparatus and completely scanned by a light source (wavelength $\lambda = 880$ nm). The detection head scanned the entire length of the cell (about 50 mm), acquiring transmission and backscattering data from each 40 $\mu$m, and repeated every 30 min for 24 h. Both the intensity of the transmitted and backscattered light increased with elapse of time. As the transmission flux was not nil, the partial reflection of the light crossing the sample by the face of the measurement cell interfered with the backscattering.
For this reason, only transmission flux could be taken into account. The lower transmission flux intensity at the bottom part (5-12 mm) of raw MWNT-MMA sample indicates the flocculation and coalescence of MWNTs, while acid-treated MWNT-MMA sample shows more stable transmission flux, which means that the MWNTs are well dispersed in MMA with fairly good dispersion stability.

Fig. 5 shows the time variation of the delta transmission flux of raw MWNTs and acid-treated MWNTs in MMA. Delta transmission is the averaged relative transmission values with respect to the initial transmission value. The raw MWNTs shows higher transmission flux than acid-treated MWNTs, which means that more aggregates are formed from raw MWNTs. Between 4 h and 24 h, the transmission flux increase for raw MWNTs and acid-treated MWNTs was 0.27%/h and 0.18%/h, respectively. This indicates that the dispersion stability of the latter was higher. This shows that carboxylic acid groups produced on the surface of MWNTs by the acid-treatment enhance the dispersity and stability of MWNTs in MMA.

Fig. 6 shows the optical microscope image of the MWNT-PMMA composites. Partial polymerization was necessary to produce composites without agglomeration of MWNTs. AIBN was added twice to enhance the polymerization. If the partial polymerization was not enough to show high viscosity, MWNTs were agglomerated and black sediment of MWNTs was observed at the bottom. With the addition of 0.05 wt % MWNT, the transmittance of the composite becomes very low. The UV-vis spectra provide quantitative information concerning the transmittance of the composite. Fig. 7 shows the UV-vis spectra of MWNT-PMMA composite in transmittance mode. The percent transmittances at 300 nm, 400 nm, 500 nm, and 600 nm are tabulated in Table 1.

### Table 1. The transmittance of MWNTs-PMMA nanocomposites

<table>
<thead>
<tr>
<th>Sample (MWNT wt%)</th>
<th>Transmittance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 nm</td>
</tr>
<tr>
<td>0</td>
<td>19.0</td>
</tr>
<tr>
<td>0.005</td>
<td>16.2</td>
</tr>
<tr>
<td>0.01</td>
<td>3.2</td>
</tr>
<tr>
<td>0.05</td>
<td>–</td>
</tr>
</tbody>
</table>

MWNT/PMMA nanocomposites with various concentrations...
of MWNTs have been prepared via in-situ polymerization process. The acid treatment of the MWNTs produced carboxylic acid group on the surface of MWNTs and this was confirmed by Raman and FTIR spectrometer. The acid treatment increases the degree of disorder hence improves the dispersion properties. The turbidity scan shows that acid-treated MWNTs were well dispersed in MMA, and the dispersion stability was fairly good, while flocculation and coalescence behavior was observed from raw MWNTs in MMA with poor dispersion stability. UV-vis spectra show that higher MWNTs concentration significantly decreases the transmittance of the MWNT-PMMA nanocomposites. The SEM images of MWNT-PMMA composite show that the MWNTs are homogeneously dispersed in PMMA matrix with smooth interface. Partial polymerization was necessary to produce composites without agglomeration of MWNTs.

Acknowledgement

This work was supported by RIC of Kyungwon University.

References