

Surface Resistivity and Rheological Behaviors of Carboxylated Multiwall Carbon Nanotube-Filled PET Composite Film

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ABSTRACT: Multiwalled carbon nanotube (MWNT) nanocomposites with poly(ethylene terephthalate) (PET) were prepared via *in situ* polymerization. The refluxing time was more important factor than the sonication time for giving carboxylic groups onto the surface of MWNT. Acid-MWNT prepared was well dispersed in ethylene glycol, whereas the neat-MWNT agglomerated and sedimented at the bottom. The viscosity of the composites increased with the addition of MWNT, but PET/acid-MWNT composite showed lower viscosity than PET/neat-MWNT because of

the damage of MWNT by acid treatment and copolymerization effect by the reaction between carboxylic groups of MWNT and PET. PET/acid-MWNT composite film showed lower surface resistivity than PET/neat-MWNT composite film. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 900–904, 2006

Key words: polyester; nanotube; nanocomposite film; surface resistivity; rheology

INTRODUCTION

Carbon nanotubes (CNTs) have attracted much attention from worldwide, because they show superior physical and electrical potentials, which allow them to be applied to hydrogen storage,¹ chemical sensors,^{2,3} nanoelectronic devices,^{4,5} and flat-panel field-emission displays.^{6–8} Multiwalled carbon nanotubes (MWNTs) are reported to be always electrically conductive and have an electrical conductivity of approximately 1.85×10^3 S/cm.⁹ Polymer/MWNT composites can form the conductive path at a relatively very low content, owing to their high aspect ratio of 100–1000 and high specific surface areas when compared to the use of composites filled with carbon black or carbon fibers. Therefore, their use in various applications, such as antistatic film, electromagnetic shielding materials, etc., has long been anticipated. Recently, Gojny *et al.*¹⁰ have reported that the oxidized MWNT led to a reduced agglomeration resulting from the improved interaction between the nanotubes and epoxy resin. Kim *et al.*¹¹ reported that the oxidized MWNT are well purified, but their crystalline struc-

tures are partially damaged, resulting in the considerable influence on the electrical properties of the MWNT/epoxy composites. The influence of MWNT on electrical properties of polypropylene¹² and poly(methyl methacrylate)¹³ was studied.

Poly(ethylene terephthalate) (PET) has found a variety of application such as fiber, bottles, films, and engineering plastics in automobiles and electronics because of its low cost and high performance. To facilitate the development of PET/MWNT composite for antistatic film, the dispersion of MWNT in PET matrix is a key factor.

In this study, we tried to facilitate the dispersion of MWNT through the reaction between PET and the carboxylic groups obtained by the acid treatment of MWNT during *in situ* polymerization. The various acid treatment conditions with sonication and refluxing time were performed. The reaction was investigated in terms of complex viscosity, storage modulus (G'), and loss modulus (G''). The surface resistivity was measured for the antistatic film application of PET/MWNT nanocomposites.

EXPERIMENTAL

Materials

Nanotubes (MWNT) used in this work were manufactured by CVD process and supplied from Iljin Nanotech (Korea; degree of purity is > 97%, length: 10–50

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μm , diameter: 10–20 nm). Dimethyl terephthalate (DMT) and ethylene glycol (EG) were obtained from SK Chemicals and DaeJung, respectively. Titanium isopropoxide was used as a catalyst.

Preparation of acid-MWNT

Acid-MWNTs were prepared in a mixture of concentrated nitric and sulfuric acids in a ratio of 1:3. After sonication for 1 h, the mixture was refluxed for 30 min at 100°C. On cooling, the mixture was washed with distilled water on a sintered glass filter until the washings showed no acidity. The solution obtained was quenched at -84°C for 6 h, and then dried in a freeze drier for 5 days.

Preparation of PET/acid-MWNT

PET/acid-MWNT nanocomposites were prepared by *in situ* polymerization. Acid-MWNT prepared was first mixed with EG and the sonication was performed for the dispersion. In a small scale batch reactor, 100 g of DMT, 65 g of EG mixture containing 1 g of MWNT and catalyst were mixed. This mixture was first heated to 190°C in a silicone oil bath. This temperature was maintained for 2 h. The temperature was then increased to 210°C where it was maintained for 2 h. The reaction temperature was progressively increased to 280°C. Then the pressure was reduced to a specified level and maintained for 0.5–1 h. The pure PET and PET/MWNT nanocomposite were also prepared by the same method for comparison.

Measurements

The solution viscosity of the composites was measured by using a mixed solvent of phenol/1,1,2,2-tetrachloroethane. The infrared spectra of acid-MWNTs with acid-treatment conditions were recorded using a Fourier transform infrared spectrometer (FTIR-300E, Jasco). Dynamic rheological measurements were performed using a rotational rheometer (PHYSICA Rheo-Lab MC120). The measurements were carried out in an oscillatory shear mode using the parallel plate geometry. Before any measurements, all samples were allowed to relax at the measuring temperature for 2 min and then sheared at a low shear rate (0.01 s^{-1}) for 3 min under a nitrogen atmosphere. Frequency sweeps were performed from 0.1 to 100 rad/s. Morphology of nanocomposites was examined by scanning electron microscopy (SEM, S-4300, Hitachi). The surface resistivity of PET, PET/MWNT, and PET/acid-MWNT nanocomposite films were measured by electrometers (R8340A, ADVANTEST, JP)

TABLE I
Classification of MWNT With Respect to the Acid Treatment Conditions

MWNT	Sonification (hr)	Refluxing (hr)	Refluxing temperature ($^\circ\text{C}$)
S1 ^a -R0.5 ^b	1.0	0.5	100
S1-R1	1.0	1.0	100
S1-R3	1.0	3.0	100
S2-R0.5	2.0	0.5	100
S3-R0.5	3.0	0.5	100

S, sonication; R, refluxing.

^a sonication time, ^b refluxing time.

RESULTS AND DISCUSSION

Fourier transform infrared spectrometry

Concentrated aqueous acids are known to introduce acidic groups onto the surface of CNTs.^{14–18} It is expected that the carboxyl groups on the MWNT surface will be reacted with PET, resulting in good dispersion of MWNT. To increase the carboxyl group concentration on the external walls and the end caps in the MWNT, the various acid treatment conditions were performed. The FTIR spectra of neat-MWNT and acid-MWNT with the acid treatment conditions (see Table I) are shown in Figure 1. The peaks at 1740 and 1200 cm^{-1} are in correspondence to C=O and C—O stretching, respectively, indicated the existence of carboxyl groups in acid-MWNT.¹⁹ The peaks at 1400 cm^{-1} are associated with the carbonic C—C stretch.¹¹ For S1-R1 and S1-R3, the characteristic peaks were not observed. It indicates that the excessive refluxing time do not give the functional group onto the surface of MWNT, but cut the length of MWNT seriously. For the acid-MWNT with different sonication time for refluxing time of 0.5 h, most of the characteristic peaks are found. So it is concluded that the refluxing time is more important factor than sonication time for giving carboxylic groups onto the surface of nanotubes. The treatment condition of acid-MWNT used for PET/acid-MWNT nanocomposites is fixed as a S1-R0.5.

Dispersibility

Figure 2 shows the dispersibility of neat-MWNT and acid-MWNT in EG after being stored for 10 days. The dispersibility of acid-MWNT is remarkably changed after acid treatment. In EG, neat-MWNT agglomerate and sediment at the bottom, but acid-MWNT is well dispersed.

SEM morphology

PET, PET/neat-MWNT, and PET/acid-MWNT nanocomposites were prepared by *in situ* polymerization and the solution viscosity values ranged from 0.70 to

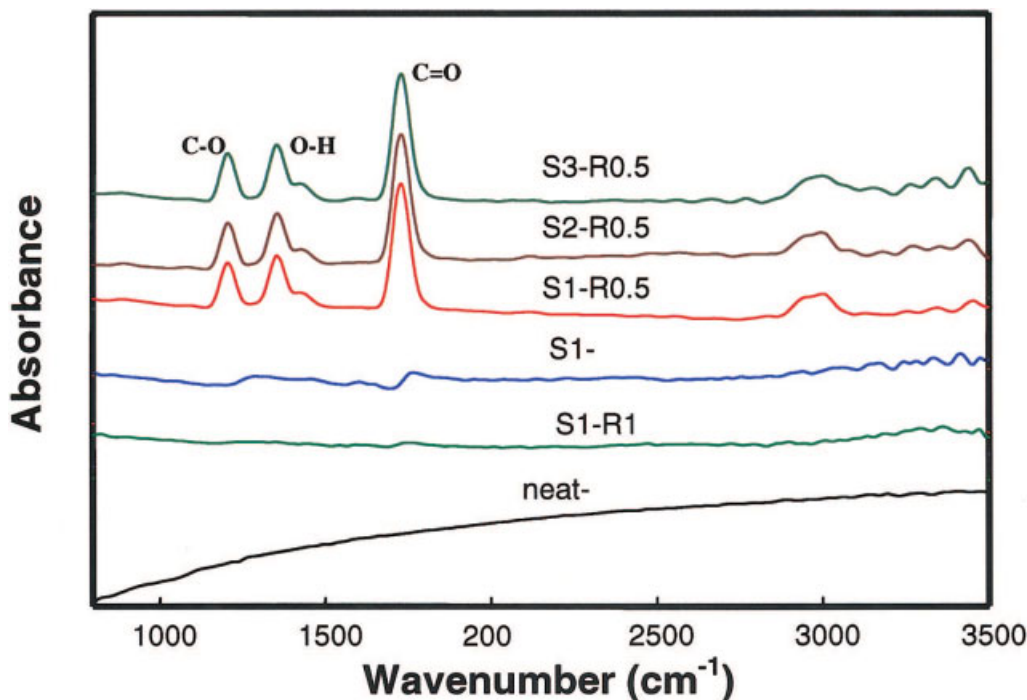


Figure 1 FTIR spectra of neat-MWNT and acid-MWNT after acid treatment with acid mixtures (symbols are listed in Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

0.76 dL/g, depending on the MWNT content. Figures 3(a) and 3(b) show SEM morphology of neat-MWNT and acid-MWNT, respectively. Because of van der Waals interactions, neat-MWNTs are aggregated and curved. In addition, metal particles and amorphous carbon are seen. It is well known that HNO_3 is very efficient in dissolving metal particles and removing amorphous carbon. After acid treatment, the decrease in van der Waals force may have occurred, as shown in Figure 3(b). Figures 3(c) and 3(d) show SEM morphology of PET/neat-MWNT and PET/acid-MWNT nanocomposite containing 1 wt % of nanotubes, respectively. For PET/neat-MWNT nanocomposites, the

neat-MWNT aggregates were inhomogeneously dispersed in PET matrix. In contrast to neat-MWNT, acid-MWNT was well dispersed and showed a homogeneous phase. It is thought that the acid groups on the surface of acid-MWNT might have reacted with PET during *in situ* polymerization, resulting in good dispersion of acid-MWNT.

Rheological properties

Rheological behavior is used to estimate the effect of the filler at high frequency and the information about the percolation state of MWNT within the composite

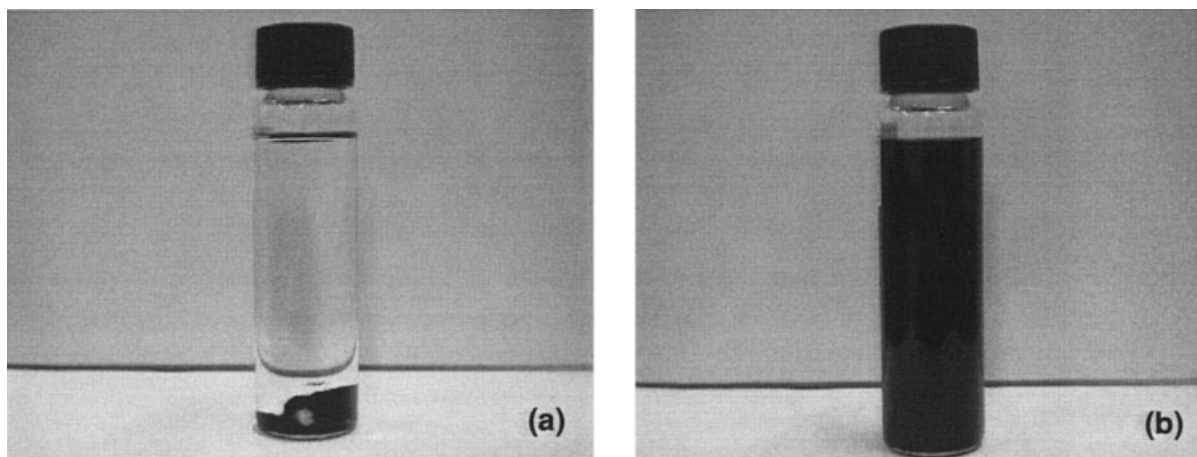


Figure 2 Dispersibility behavior of (a) neat-MWNT and (b) acid-MWNT in EG after being stored for 10 days.

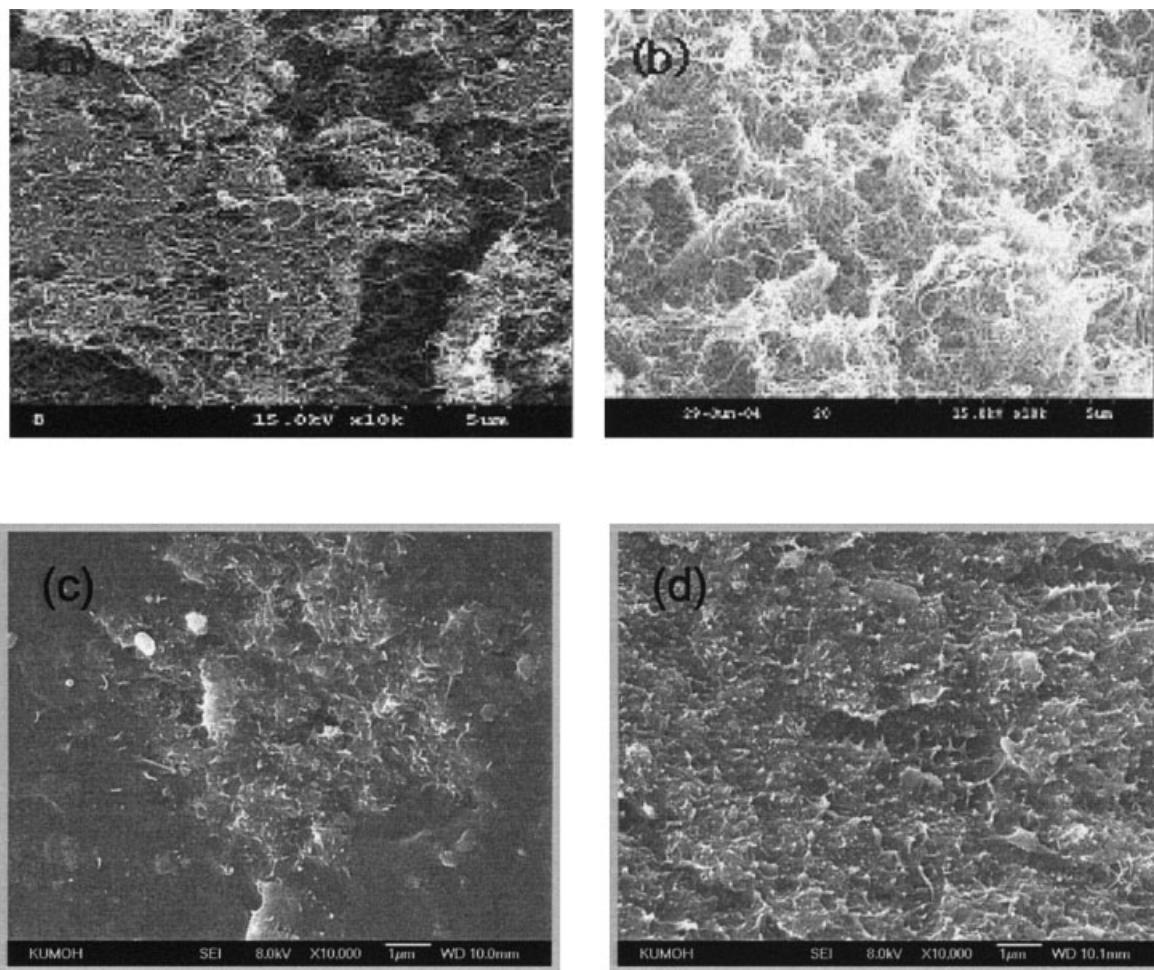


Figure 3 SEM photographs of (a) neat-MWNT, (b) acid-MWNT, (c) PET/neat-MWNT composite containing 1 wt % of neat-MWNT, and (d) PET/acid-MWNT composite containing 1 wt % of acid-MWNT.

can be obtained. The frequency dependence of the shear storage modulus G' , the loss modulus G'' , and the complex viscosity are shown in log–log plots in Figure 4. It was measured at 265°C. It is clearly seen that the addition of neat-MWNT as well as acid-MWNT to PET leads to an increase in complex viscosity and the viscosity does not depend on the nanotube content. However, the magnitude of enhancement of viscosities between PET/neat-MWNT and PET/acid-MWNT nanocomposites is quite different. The viscosity of PET/neat-MWNT nanocomposite containing 0.5 wt % nanotube shows the higher value than the nanocomposite containing 1.0 wt % nanotube. It indicates that the agglomeration of neat-MWNT occurred as shown in Figure 3(c), resulting in decrease in viscosity. The same result is observed in PET/acid-MWNT nanocomposite. It is interesting to note that the viscosity of PET/acid-MWNT nanocomposite is lower than that of PET/neat-MWNT nanocomposite. The decrease in viscosity of PET/acid-MWNT nanocomposite may arise from the damage of nanotube by acid treatment and the copolymerization effect due to the

reaction between the carboxylic groups of acid-MWNT and PET. The effect of nanotubes on the viscosity is most pronounced at low frequencies and the relative effect diminishes with increasing frequency because of shear thinning. It is well known that the interconnected structures of anisometric fillers result in a plateau region in the plot of $\log G'$ versus $\log G''$ at low frequencies. As the nanotube content increases, the nanotube–nanotube interactions begin to dominate, eventually lead to the percolation. However, in this experimental nanotube content (up to 1 wt %), the plateau region is not observed at low frequencies as shown in Figure 4(b).

Surface resistivity

To know the application for PET antistatic composite film, the surface resistivity (Ω) of PET, PET/neat-MWNT, and PET/acid-MWNT nanocomposite film was measured and listed in Table II. The films were made by hot press and its thickness ranges from 150 to 170 μm . To be used for antistatic film, the surface

resistivity value should be less than $10^{10} \Omega$. The surface resistivity value of PET film has more than $10^{15} \Omega$ so that PET itself cannot be used as an antistatic film. The composite films show less than $10^{10} \Omega$; PET/acid-MWNT film has lesser value than the PET/neat-MWNT film. It was confirmed that acid-MWNT is well dispersed in PET matrix in comparing with neat-MWNT.

CONCLUSIONS

Acid-MWNTs were prepared with the sonication and refluxing times. The refluxing time was more important factor than the sonication time for giving carboxylic groups onto the surface of MWNT. Acid-MWNT was well dispersed in ethylene glycol in comparison with neat-MWNT. In this work, we prepared PET composites containing neat-MWNT and

TABLE II
Surface Resistivities of PET, PET/neat-MWNT, and PET/acid-MWNT Composite Film

Composite samples	Surface resistivity (Ω)
PET	7.5×10^{15}
PET/neat-MWNT (0.5 wt%)	1.8×10^9
PET/acid-MWNT (0.5 wt%)	3.8×10^8

acid-MWNT by *in situ* polymerization. It was expected that carboxylic groups on the external walls and the end caps of MWNT participate in the reaction during polymerization, resulting in homogeneous phase. However, concentration of the carboxylic groups prepared was very small, and so the concentration could not be measured by direct method. The decrease in complex viscosity of PET/acid-MWNT composite, in comparison with PET/neat-MWNT, resulted from the reaction even though there must be damage of MWNT by acid treatment. The application of PET composite for antistatic film was confirmed by measuring surface resistivity.

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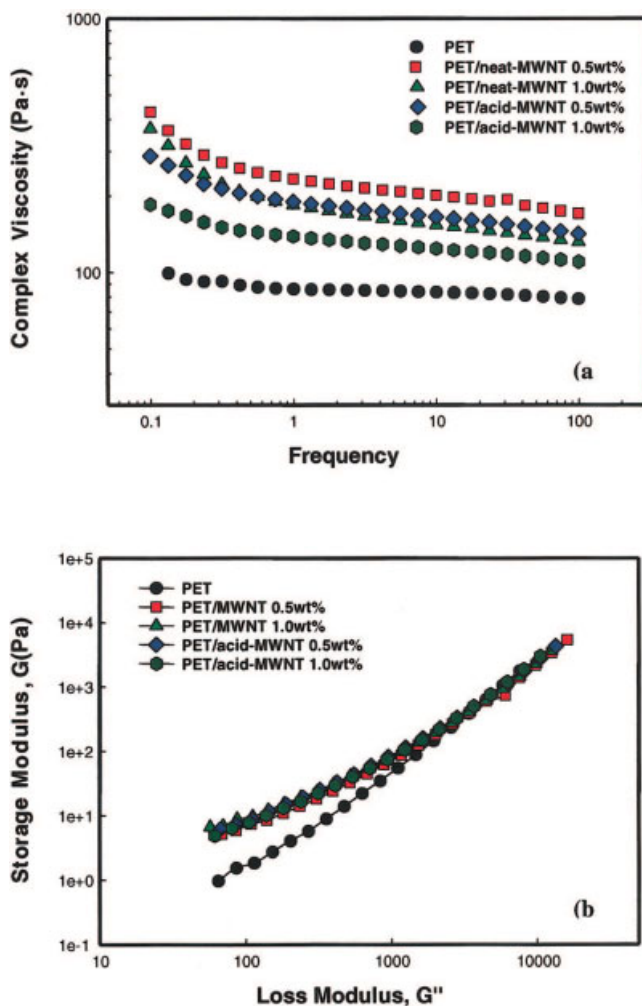


Figure 4 Complex viscosities (a) and plot of $\log G'$ versus $\log G''$ (b) for PET, PET/neat-MWNT, and PET/acid-MWNT composites with respect to frequency. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]