Rheological and Electrical Properties of PS/Multi-Walled Carbon Nanotube Nanocomposites Prepared by Latex Technology

Myung-Hwan Kang, Won Jin Noh, and Seong Jae Lee

Department of Polymer Engineering, The University of Suwon, Gyeonggi 445-743, Korea

ABSTRACT

Rheological and electrical properties of latex-blended polystyrene (PS)/multi-walled carbon nanotube (MWNT) nanocomposites were investigated, and the effects of nanotube treatments, nanotube length and PS particle size were considered. Pronounced effect of MWNT incorporation was observed, resulting in increased rheological properties and electrical conductivity when compared to unmodified PS.

INTRODUCTION

Since their discovery, carbon nanotubes (CNTs) have been extensively studied due to excellent properties, such as elastic modulus, electrical conductivity and thermal stability.[1,2] These special properties make CNTs preferred candidates to be used to fabricate the nanocomposites with higher properties. However, it has been well known that as-produced CNTs are very difficult to be dispersed in polymer matrices as CNTs have large aspect ratio and surface area and possess large van der Waals forces between themselves, which can lead to the formation of aggregates or bundles that are tightly bound. Therefore, the dispersion of CNTs and incorporation of CNT individuals into polymer matrices is one of the most important tasks to optimize the effective utilization of polymer/CNT nanocomposites.

Traditionally, the incorporation of CNTs into polymers has been achieved by solution blending of nanotubes in dissolved or dispersed polymers,[3] in-situ polymerization of nanotube-laden monomer suspensions[4] and melt mixing of nanotubes with polymers.[5] Another approach to incorporate CNTs in polymer matrices has been presented by the use of latex technology.[6] Successful applications of this technology must be strongly dependent on the availability of colloidal particles with highly monodisperse state. Among various colloidal particles, PS colloids can be used in many areas because the highly monodisperse PS particles are easily synthesized by various polymerization techniques, such as emulsion polymerization, dispersion polymerization and seeded polymerization.

We first synthesized the monodisperse PS particles and then prepared the PS/MWNT nanocomposites by the use of latex technology, and investigated their electrical properties as well as rheological properties since rheology could be used as a tool to quantify from a global average of the degree of dispersion across the whole sample. In this study, the effects of various factors such as nanotube treatments, nanotube length and PS particle size on the rheological properties were considered to enhance the electrical conductivity of the PS/MWNT nanocomposites.

EXPERIMENTAL
Synthesis of PS particles

Two types of PS particles with uniform size (500 nm and 5 μm) were synthesized by emulsifier-free emulsion polymerization and dispersion polymerization, respectively.

Styrene monomer was purified by vacuum distillation, and 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. For preparing small particle, 40 ml of styrene and 0.3676 g of potassium persulfate were taken inside the reactor containing 43.2 ml ethanol and 360 ml of water. Polymerization was carried out at 70 ^{o}C for 24 h with the agitation speed of 300 rpm. Large PS particle was prepared with 20 g of styrene, 0.8 g of polyvinyl pyrrolidone and 105 g of butanol. Polymerization was carried out in the presence of 0.2 g of AIBN at 70 ^{o}C for 24 h with 120 rpm.

Nanotube treatments

The MWNTs used in this study were purchased from Hanwha Nanotech (CM-100, Korea), which were synthesized by a catalytic chemical vapor deposition process. Acid-treated MWNTs were prepared by the following procedure. The MWNTs of 1 g were introduced and treated in 100 ml of HNO_3 and H_2SO_4 (1:3 by volume) at 70 ^{o}C for 24 h in an ultrasonic bath under a reflux process. After centrifugation, the upper liquid part was decanted and the lower solid part was thoroughly washed with deionized water. Ultrasound-treated MWNTs were prepared by an ultrasonicator with a probe of 13 mm in tip diameter (VC-505, Sonics, USA). Ultrasonication generated by a frequency of 20 kHz was imposed at 20 W for 30 min. In order to prevent the temperature rise of the suspension, the beaker was placed in an ice bath during ultrasonic treatment.

Preparation of nanocomposites

After a sufficient dispersion of MWNTs in deionized water, the MWNT suspension was homogeneously mixed with suitable amount of PS latex while keeping either ultrasonication for 30 min or mechanical mixing for 3 h again depending on the treatment method, and then abruptly frozen with liquid nitrogen. The aqueous moiety in the frozen mass was removed with a freeze-dryer (FD-1000, Eyela, Japan). Lastly, the PS/MWNT nanocomposites so obtained were compressed into 1~2 mm thick disk-type samples with diameter of 25 mm at 180 ^{o}C for 5 min using a hot press. The samples were used for measuring the rheological and electrical properties.

Sample characterization

The morphology of PS particle and freeze-dried PS/MWNT nanocomposite powder were observed by using the scanning electron microscopy (FE-SEM: JSM 6700F, Jeol, Japan). The rheological properties of nanocomposite samples were investigated with a stress-controlled rotational rheometer (MCR 300, Paar Physica, Germany) in a small-amplitude oscillatory shear mode using parallel plate geometry. Frequency sweeps between 0.03 and 100 s^{-1} were carried out at specified strain. The strain amplitude was imposed to 3% throughout the measurements, after confirming that the amplitude was within the linear viscoelastic range. All measurements were conducted at a constant temperature of 210 ^{o}C. Electrical properties were measured by a digital multimeter (Fluke 189, USA). After polishing the sample to eliminate the polymer-rich layer, silver electrodes were attached on both sides and then the resistance of the sample was measured. The electrical conductivity of the sample was calculated from the relationship,

$$\sigma = 1/\rho = d/RS \qquad (1)$$

where σ is the electrical conductivity, ρ is the resistivity, R is the resistance, d is the sample thickness, and S is the cross-sectional area of the sample.

RESULTS and DISCUSSION

The average diameter of PS particles synthesized by an emulsifier-free emulsion polymerization was c.a. 500 nm. The PS particles showed well-ordered monodisperse

spherical pattern. The number-average and weight-average molecular weights were 45,000 g/mol and 229,000 g/mol, respectively.

For the freeze-dried composite samples of PS particles and MWNTs, the codes PS/P-CNT, PS/A-CNT, PS/U-CNT and PS/AU-CNT were used for the latex-blended samples of PS and as-produced MWNT, PS and acid-treated MWNT, PS and as-produced MWNT with ultrasonic treatment, and PS and acid-treated MWNT with ultrasonic treatment, respectively. The FE-SEM micrographs of freeze-dried PS/MWNT nanocomposite powder prepared at 3% MWNT are shown in Figures 1 and 2.
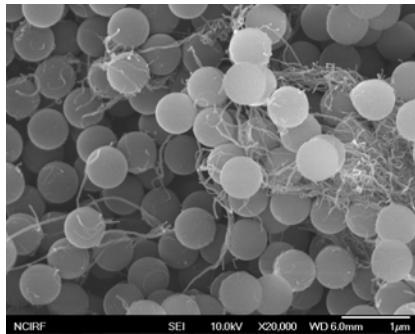
Figure 1. SEM micrograph of freeze-dried PS/U-CNT nanocomposite powder.
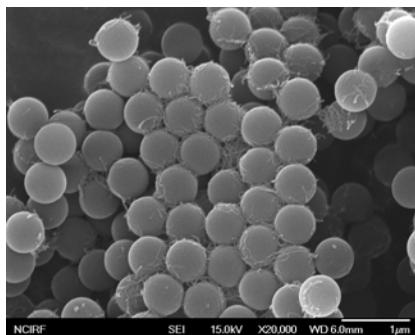

Figure 2. SEM micrograph of freeze-dried PS/AU-CNT nanocomposite powder.

Figure 1 shows the dispersion state of as-produced MWNTs with ultrasonic treatment in freeze-dried nanocomposite powder. Long individual nanotubes are dispersed across PS particles, which reveals

ultrasonication can assist to disperse MWNTs from bundles and prevent re-aggregation of MWNTs by electrostatic repulsion. The morphology of acid-treated MWNTs with ultrasonic treatment is shown in Figure 2. The PS/AU-CNT nanocomposite shows relatively regular hexagonal structure of the PS microspheres well-dispersed with chopped nanotubes. This kind of morphology seems to be formed reflecting that the physical cutting due to ultrasonic action to the MWNTs damaged and weakened by strong acid treatment is responsible for uniform dispersion.
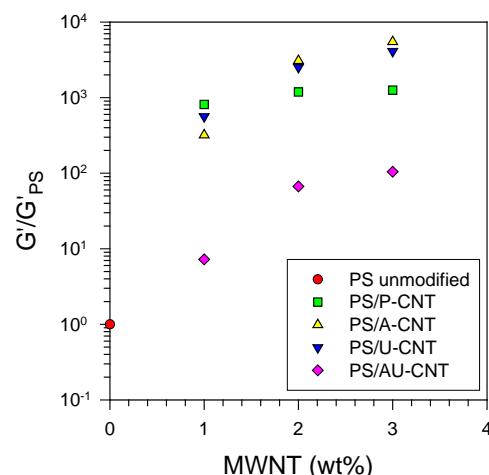

Figure 3. Relationship between MWNT content and normalized storage modulus of PS/MWNT nanocomposites with that of unmodified PS at a frequency of 0.03 s^{-1}.

Figure 3 shows the normalized storage modulus measured at a frequency of 0.03 s^{-1} for the nanocomposites as a function of MWNT content. The modulus of PS/P-CNT nanocomposite at content 1 wt% abruptly reaches to 800 times higher than that of unmodified PS and then levels off for further addition. The moduli of both PS/A-CNT and PS/U-CNT nanocomposites at content 1 wt% are also significantly larger than that of unmodified PS and continue to increase for further addition. When compared with the PS/A-CNT and PS/U-CNT nanocomposites, the PS/AU-CNT nanocomposite having

good dispersion but short nanotube length shows relatively small increase of storage modulus although this also continues to increase with MWNT content.

Electrical properties of the PS/MWNT nanocomposites also depend sharply on the CNT content. Figure 4 shows the effect of various nanotube treatments on the electrical conductivity of the nanocomposites. Conductivities of the PS/A-CNT and PS/AU-CNT nanocomposites were lower than the other two. It seems that the chemical degradation of MWNTs such as tube bending and surface damage is responsible for reduced electrical response. In particular, rheological and electrical properties of the PS/AU-CNT nanocomposite were not increased much due to severe breakup of nanotubes. Although the PS/P-CNT nanocomposite shows higher conductivity than the PS/U-CNT counterpart at lower MWNT content, the PS/U-CNT nanocomposite seems better because it gives better CNT dispersion than the PS/P-CNT nanocomposite at higher MWNT content as seen in Figure 3.
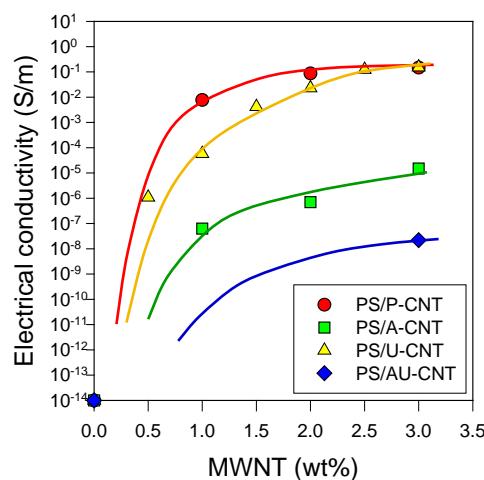

Figure 4. Effect of nanotube treatments on electrical conductivity of PS/MWNT nanocomposites.

The effect of CNT length on rheological properties was examined. Figure 5 shows the result of storage modulus as a function of frequency. Here, two types of acid-treated MWNTs were used. The lengths of longer MWNT (L-CNT) and shorter MWNT (S-CNT) were 0.97±0.28 μm and 0.70±0.39 μm, respectively. Although the lengths of the two MWNTs are not that different, the PS/L-CNT nanocomposite showed much higher storage modulus than the PS/S-CNT counterpart. It can be explained that longer CNTs have more chance to be contacted and to be entangled.
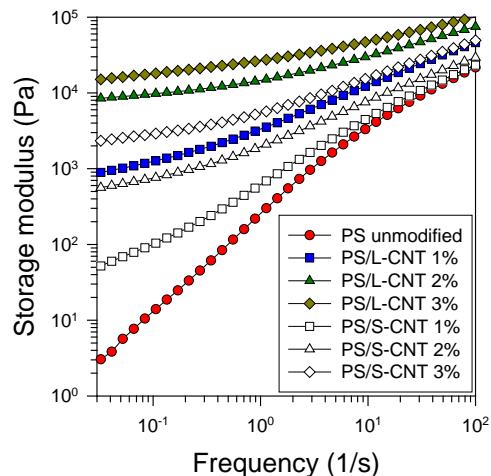

Figure 5. Effect of MWNT content on storage modulus of PS/L-CNT and PS/S-CNT nanocomposites.

The effect of PS particle size on rheological and electrical properties was investigated. The average diameters of small and large PS particles were 500 nm and 5 μm. The number-average and weight-average molecular weights of 5 μm PS particles were 26,000 g/mol and 87,000 g/mol, respectively, which were lower than those of 500 nm PS particles. Figure 6 shows a dispersion state of large PS particles and as-produced MWNTs with ultrasonic treatment in freeze-dried composite powder. Morphology showing the small PS particles and U-CNT dispersion state was shown in Figure 1. (Note the magnifications of two images are different.) The PS (5 μm)/U-CNT nanocomposite showed distinctly improved rheological

properties (Results not shown here). In comparison with the PS (500 nm)/U-CNT nanocomposite, it is speculated that a network structure connected by CNT-CNT brides could be formed with ease because the specific surface area of larger PS particles is small.
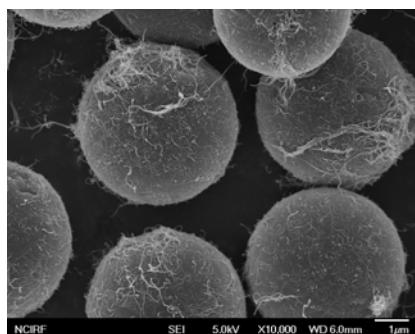

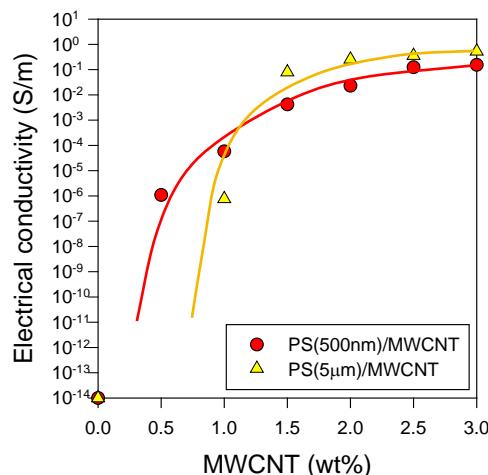Figure 6. SEM micrograph of freeze-dried PS (5μm)/U-CNT nanocomposite powder.

Figure 7. Effect of PS particle size on electrical conductivity of PS/MWNT nanocomposites.

Electrical conductivities of the PS (5 μm)/U-CNT and PS (500 nm)/U-CNT nanocomposites are shown in Figure 7. With low content of MWNTs, the electrical conductivity of the PS (500 nm)/U-CNT nanocomposite was higher than that of the PS (5 μm)/U-CNT counterpart. At the MWNT content of 1 wt% and above, on the contrary,

the opposite result could be obtained. Since the electrical conductivity is affected by dispersion and distribution state of CNTs, it is speculated that good dispersion of MWNTs and poor homogeneity in matrix might give higher electrical conductivity.

CONCLUSIONS

The PS/MWNT nanocomposites were prepared via latex technology and the effects of treatment method, nanotube length and PS particle size on rheological and electrical properties were investigated. Two different sizes of PS particles were synthesized by emulsifier-free emulsion polymerization and dispersion polymerization. The MWNTs were used unmodified or surface-modified.

The PS/MWNT nanocomposite prepared by the combined treatment of acid and ultrasonication showed superior dispersion state of MWNTs. However, the combined effect caused severe breakup of nanotubes. As a result, the increases of rheological and electrical properties with MWNT content were not substantial.

Rheological properties of the PS/MWNT nanocomposites were increased as the nanotube length increased. It can be explained that longer CNTs have more chance to be entangled so that they are likely to form network structure rather easily.

The effect of PS particle size on electrical properties was different depending on the MWNT content. With lower MWNT content, the nanocomposite prepared by smaller particle showed higher electrical conductivity, but the opposite result was produced as the content increased. It is speculated that smaller particles are effective at lower CNT content due to the homogeneous dispersion of CNTs, but larger particles are more effective at higher content because densely connected CNT path could be formed.

REFERENCES
1. Treacy, M.M.J., Ebbesen, T.W., and Gibson, J.M. (1996), "Exceptionally high Young's modulus observed for individual carbon nanotubes", *Nature,* **381**, 678-680.

2. Yu, J., Lu, K., Sourty, E., Grossiord, N., Koning, C.E., and Loos, J. (2007), "Characterization of conductive multiwall carbon nanotube/polystyrene composites prepared by latex technology", *Carbon,* **45**, 2897-2903.

3. Safadi, B., Andrews, R., and Grulke, E.A. (2002), "Multi-walled carbon nanotube polymer composites: synthesis and characterization of thin films", *J. Appl. Polym. Sci.,* **84**, 2660-2669.

4. Kim, S.T., Choi, H.J., and Hong, S.M. (2007), "Bulk polymerized polystyrene in the presence of multi-walled carbon nanotubes", *Colloid Polym. Sci.,* **285**, 593-598.

5. Potschke, P., Fornes, T.D., and Paul, D.R. (2002), "Rheological behavior of multiwalled carbon nanotube/polycarbonate composites", *Polymer,* **43**, 3247-3255.

6. Regev, O., ElKati, P.N.B., Loos, J., and Koning, C.E. (2004), "Preparation of conductive nanotube-polymer composites using latex technology", *Adv. Mater.,* **16**, 248-251.