

Effective in-situ preparation and characteristics of polystyrene-grafted carbon nanotube composites

Jun Uk Park, Saehan Cho, Kwang Soo Cho¹, Kyung Hyun Ahn*, Seung Jong Lee and Seong Jae Lee²

School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea

¹*Department of Polymer Science, Kyungpook National University, Daegu 702-701, Korea*

²*Department of Polymer Engineering, The University of Suwon, Gyeonggi 445-743, Korea*

(Received March 1, 2005; final revision received April 27, 2005)

Abstract

As an effort to explore the effective use of carbon nanotubes as a reinforcing material for advanced nanocomposites with polymer matrices, multi-walled carbon nanotubes (MWNTs) were successfully incorporated into polystyrene (PS) via in-situ bulk polymerization. Various experimental techniques revealed that the covalent bonds formed between PS radicals and acid-treated carbon nanotubes are favorable resulting in an effective load transfer. The enhanced storage modulus of the nanocomposites suggests a strong possibility for the potential use in industrial applications.

Keywords : polystyrene/carbon nanotube composites, in-situ bulk polymerization, morphology, storage modulus

1. Introduction

Carbon nanotubes (CNTs) naturally exist in the form of aggregates due to strong van der Waals forces originating from their small size and large surface area. In particular, the thermal chemical vapor deposition method produces substantial amount of agglomeration because the entanglement of CNTs occurs during nanotube growth. This agglomeration leads to difficulties when attempting to utilize the CNT as reinforcing agents for polymer systems. To fully achieve the maximum potential of the nanotube composites, two issues should be considered. First is the state of dispersion of the CNT in the matrix polymer and second is the interfacial adhesion between the CNT and polymer matrix.

Although it has been reported that CNTs have poor interfacial bonding strength with polymer matrices, resulting in uncertainty in effective load transfer (Lau and Hui, 2002), many researchers have attempted to develop high performance CNT/polymer composites. Of the various methods to prepare the CNT/polymer composites, melt blending seems most promising because conventional resins can be directly utilized. For example, Paul and his coworkers (Potschke *et al.*, 2002) prepared multi-walled carbon nanotube (MWNT)/polycarbonate (PC) composites using a twin-screw extruder and monitored the change in prop-

erties with CNT content using rheometry. They elucidated the percolation threshold of MWNT/PC composites and confirmed that rheometry was a useful tool to check the reinforcement effect. Another preferred method for preparing CNT/polymer composites is direct polymerization. As an example, well-dispersed MWNT/epoxy composites were prepared using a surfactant, resulting in a 30% increase of elastic modulus with the addition of 1 wt% CNT (Gong *et al.*, 2000). However, the enhanced properties demonstrated in the above cases are generally limited due to severe CNT agglomeration and/or poor interfacial interactions between the CNT and polymer matrix.

To improve both the degree of CNT dispersion in a polymer matrix and the interfacial bonding strength, chemical functionalization of CNTs has been employed (Mitchell *et al.* 2002; Hill *et al.*, 2002; Qin *et al.*, 2004; Lin *et al.*, 2003). However, this approach requires many complicated steps in order to modify CNTs prior to composite preparation as well as the use of various environmentally unfavorable chemicals. To avoid these disadvantages and simplify the process for industrial applications, a preparation of MWNT/poly(methyl methacrylate) (PMMA) composites using in-situ process has been reported (Jia *et al.*, 1999; Park *et al.*, 2003), even though they speculated a newly-observed peak originating from the chemical bonds between CNT and PMMA matrix with insufficient evidence.

In this study, we prepared MWNT/PS composites via an effective in-situ bulk polymerization and characterized

*Corresponding author: ahnnet@snu.ac.kr
© 2005 by The Korean Society of Rheology

their properties. Acid treatments were performed to eliminate impurities and render chemically active sites in the MWNTs, and ultrasonication was applied to improve the degree of CNT dispersion throughout the medium. Gel permeation chromatography and Fourier transform infrared spectrometer results confirmed the possibility of chemical bond formation on the defects in CNT surface during the free radical polymerization. High-resolution transmission electron microscopy micrographs indicating a CNT coated with amorphous PS, convinced us that CNTs take part in free radical polymerization with radicals onto or from them resulting in enhanced compatibility and stress transfer between CNTs and PS. Rheological measurements also showed dramatically improved storage modulus of PS/CNT composites. Very recently, it was predicted that the covalent bond formation between alkyl radicals and CNTs is energetically favorable using a computational method (Mylvaganam and Zhang, 2004). Our experiments show that in-situ polymerization is a very simple and effective method to prepare CNT/polymer composites when employing PS as a matrix.

2. Experimental section

The MWNT (Iljin Nanotec, Korea) has a length of 10-50 μm , a diameter of 10-20 nm, and the purity as received was over 97%. It was treated by refluxing in an acid solution of 96.1% H_2SO_4 and 10.4% HNO_3 (1:3 by volume) at 140°C for 60 min for purification. Acid treatment is known to induce defects and introduce $-\text{COOH}$ groups on the surface of MWNT (Goh *et al.*, 2003), resulting in useful sites for chemical functionalization and good compatibility with organic solvents. MWNTs were dispersed in a vacuum-distilled styrene medium. The suspension was stirred with a magnetic bar in an ultrasonicator (Kyungil Ultrasonic, Korea) for 3 h at 20°C. It is known that ultrasonication leads to the formation of defects in the CNT structure. Although these defects may slightly reduce the mechanical strength of MWNTs, they also increase the anchoring sites on the surface of tubes. The polymer matrix can bind to these sites providing for effective load transfer from polymer to CNTs (Lu *et al.*, 1996).

The polymerization experiments were carried out in a three-neck Pyrex reactor. The mechanical stirrer, nitrogen inlet and refluxing condenser were connected to one of the 3 necks. Formulated CNT contents are 0, 0.1, 0.5 and 1 wt% with reference to styrene. The initiator, 2,2'-azobisisobutyronitrile (AIBN), purified by recrystallization from methanol, was charged into the reactor just before the start-up of polymerization at the fixed concentration of 0.1 mol% with reference to styrene. The system was maintained at 70°C for 48 h, including an agitation period maintained at 100 rpm for the first 6 h. In addition, a 0.1 wt% CNT/PS composite was prepared via suspension polymer-

ization for scanning electron microscopy (SEM, Jeol JSM-6700F, Japan). This was done in order to observe the degree of CNT dispersion in PS matrix because the SEM image of the fractured surface may represent local or distorted morphology. The procedure of suspension polymerization is not explained here. Rheological measurements were performed using a strain-controlled rotational rheometer (RMS800, Rheometric Scientific, USA). Dynamic frequency sweep tests were conducted to elucidate the microstructure of PS/CNT composites in a frequency range of 0.1-100 rad/s at 200°C using a 25 mm parallel plate geometry. The chemical structure of PS/CNT composites was characterized by a Fourier transform infrared spectrometer (FT-IR, Bomem MB-100, Switzerland). In order to measure the molecular weight of the PS, PS/CNT composites were dissolved in THF (tetrahydrofuran) and then filtered through syringe filter consisting of PTFE (polytetrafluoroethylene) membrane (0.2 μm). The molecular weight of the acquired free PS was determined by a gel permeation chromatograph (GPC, Waters 515 HPLC, USA) to examine the effect of CNTs on polymerization. The MWNT morphology was characterized by a high-resolution transmission electron microscope (HR-TEM, Jeol JEM-4010, Japan) to confirm the chemical attachment of PS chains on the surface of CNT.

3. Results and discussion

To transfer mechanical loads effectively from matrix to CNTs, both issues stemming from the dispersion and the interfacial bonding have to be solved. Many researchers have attempted to enhance the interfacial compatibility between CNTs and polymer matrices (Mitchell *et al.*, 2002; Jia *et al.*, 1999; Park *et al.*, 2003; Chen *et al.*, 2001; Velasco-Santos *et al.*, 2002). However, there is few literature regarding the π -bond attack of CNT by radicals. Jia *et al.* (1999) and Park *et al.* (2003) studied the PMMA/CNT composites and concluded that CNTs take part in the PMMA polymerization and that a strong binding interface is formed between PMMA and CNTs. They speculated that the FT-IR peak at around 1660 cm^{-1} might result from a C-C bond between CNT and PMMA. This may be controversial because of the interference with the alkane chain backbone of common polymers. Nevertheless, an increase in two peaks, 1630 and 991 cm^{-1} , with CNT content is observed in Fig. 1. Exact peak assignment indicates that these two peaks originate from a C=C bond and an aryl C-H bond observed in styrene, not in PS. This fact demonstrates that CNTs participate in the PS polymerization and consume initiator, AIBN, resulting in more unreacted monomers. Therefore, two peaks characterizing styrene monomer are getting stronger as CNT content increases, and the relative amounts of unreacted monomers are characterized by the two peaks in FT-IR spectra. The results of

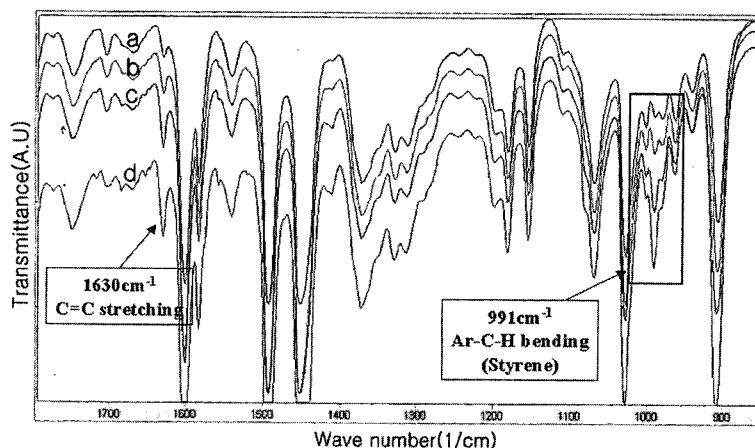


Fig. 1. FT-IR spectra of PS/CNT composites by in-situ bulk polymerization: (a) PS, (b) PS/CNT 0.1 wt%, (c) PS/CNT 0.5 wt%, and (d) PS/CNT 1 wt%.

Table 1. GPC results of PS prepared by in-situ polymerization with and without CNT

	PS	CNT 0.1 wt%	CNT 0.5 wt%	CNT 1 wt%
M_w	271,600	323,900	375,800	427,100
M_n	105,000	117,700	127,700	137,000
Polydispersity index(M_w/M_n)	2.59	2.75	2.94	3.45

GPC analysis give definitive information about the role of CNTs during polymerization, as summarized in Table 1. As the CNT content increases, the molecular weight of the PS monotonically increases, which is indicative of initiator consumption by the CNTs.

Fig. 2 shows a CNT cross-section covered by amorphous

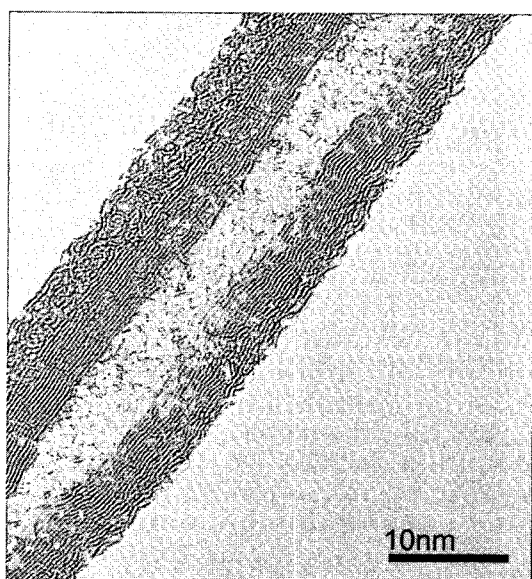


Fig. 2. HR-TEM micrograph of PS/CNT composite by in-situ bulk polymerization.

materials thought to be unextracted PS that has been grafted to the CNT, which could be considered as a clear evidence for the formation of a chemical bond between CNT and PS. The CNT overlaid with PS confirms that the interaction between CNT and PS is not a physical contact but strong adhesion due to chemical bonds.

Two SEM micrographs in Fig. 3 show the dispersion state of CNTs in the PS matrix and the interfacial bonding between CNTs and matrix. The sample in Fig. 3(a) was prepared by suspension polymerization to investigate the morphology of PS/CNT composites as prepared. It clearly shows that a homogeneous dispersion of CNTs is achieved throughout the PS matrix. A fractured sample, prepared from bulk polymerization in Fig. 3(b) indicates how CNTs play a role as a reinforcing agent in the PS matrix. The CNTs align perpendicularly to the crack direction and sustain the crack like bridges. One nanotube, as indicated by an arrow marked in Fig. 3(b), is found to be broken rather than just pulled out of the matrix. These reinforcing and breakage phenomena indicate favorable interfacial nature between PS and CNTs originating from chemical bonds.

Effective load transfer due to enhanced interfacial bonding strength and good dispersion can be elucidated by rheological measurements. Fig. 4 shows the rheological behavior of PS/CNT composites prepared from in-situ bulk polymerization. Only the storage modulus G' is shown here because the reinforcing effect is more pronounced in this property than others (Potschke *et al.*, 2002; Mitchell *et al.*,

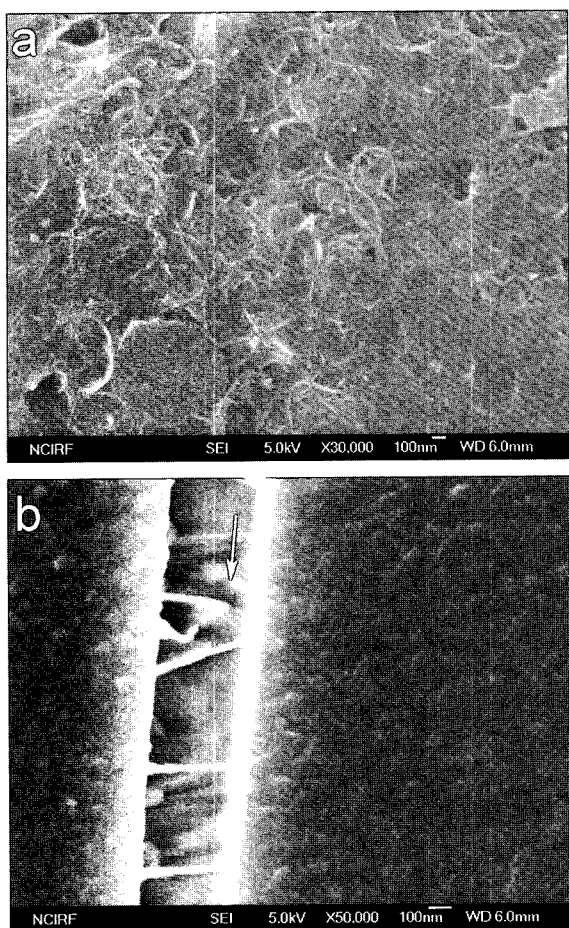


Fig. 3. SEM micrographs of PS/CNT 0.1 wt% composites produced by in-situ polymerization: (a) prepared by suspension polymerization and (b) prepared by bulk polymerization.

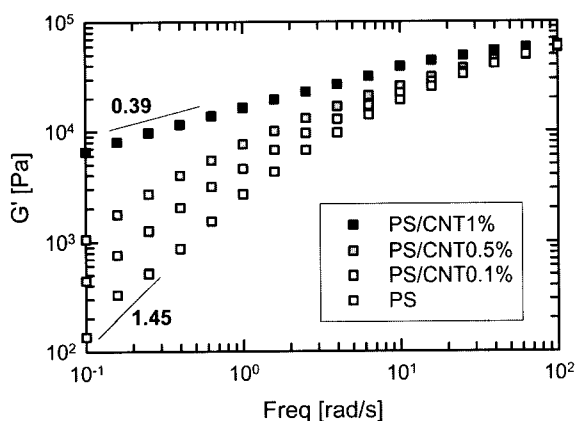


Fig. 4. Storage moduli G' of PS/CNT composites by in-situ bulk polymerization as a function of frequency at 1% strain and 200°C.

2002; Krishnamoorti and Giannelis, 1997). The G' of the composites in the terminal region increases dramatically by

nearly two orders of magnitude with only 1 wt% CNT addition at a frequency of 0.1 rad/s. The terminal slopes of the composites also decrease from 1.45 to 0.39 with increasing CNT content. Such an enhanced storage modulus and non-terminal behavior of the PS/CNT composites indicates that the material properties are changing from liquid-like to solid-like behavior as the CNT content increases (Krishnamoorti and Yurekli, 2001; Reichert *et al.*, 2001). Obviously, this effect is the result of a combined effect of enhanced chemical bonding and good dispersion. High frequency behavior also indicates a well-dispersed state. The values of G' at high frequency are similar for all systems, which means that all segments of PS chains thermodynamically behave in a similar manner independent of the presence of CNTs. With small CNT contents, the homogeneously dispersed CNTs do not affect the dynamics of matrix chains, even if a strong interfacial adhesion between CNTs and matrix exists. On the other hand, poor dispersion forming clusters may substantially influence the dynamics of polymer chains that are confined within a cluster. Further research on this subject is under investigation.

In summary, PS/CNT composites were successfully prepared via an in-situ polymerization method. The composites showed good interfacial adhesion because the participation of CNTs in PS polymerization generates new chemical bonds between CNT and PS by a π -bond opening. All the experimental findings were clearly characterized by FT-IR, GPC and HR-TEM. The SEM micrographs showed well-dispersed state of CNTs in PS matrix and effective load transfer mechanism. Finally, the enhanced properties of composites ascribed to good dispersion and effective load transfer were verified by the rheological measurements of PS/CNT composites depending on CNT content.

Acknowledgement

The authors gratefully acknowledge the Korean Science and Engineering Foundation (KOSEF) for the financial support through the Applied Rheology Center, an official engineering research center (ERC) in Korea.

References

- Chen, R. J., Y. Zhang, D. Wang and H. Dai, 2001, Noncovalent Sidewall Functionalization of Single-Walled Carbon Nanotubes for Protein Immobilization, *J. Am. Chem. Soc.* **123**, 3838.
- Goh, H. W., S. H. Goh, G. Q. Xu, K. P. Pramoda and W. D. Zhang, 2003, Crystallization and dynamic mechanical behavior of double- C_{60} -end capped poly(ethylene oxide)/multi-walled carbon nanotube composites, *Chem. Phys. Lett.* **379**, 236.
- Gong, X., J. Liu, S. Baskaran, R. D. Voise and J. S. Young, 2000, Surfactant-Assisted Processing of Carbon Nanotube/Polymer Composites, *Chem. Mater.* **12**, 1049.

- Hill, D. E., Y. Lin, A. M. Rao, L. F. Allard and Y. P. Sun, 2002, Functionalization of Carbon Nanotubes with Polystyrene, *Macromolecules* **35**, 9466.
- Jia, Z., Z. Wang, C. Xu, J. Liang, B. Wei, D. Wu and S. Zhu, 1999, Study on poly(methyl methacrylate)/carbon nanotube composites, *Mater. Sci. Eng.* **A271**, 395.
- Krishnamoorti, R. and E. P. Giannelis, 1997, Rheology of End-Tethered Polymer Layered Silicate Nanocomposites, *Macromolecules* **30**, 4097.
- Krishnamoorti, R. and K. Yurekli, 2001, Rheology of polymer layered silicate nanocomposites, *Curr. Opin. Colloid Interface Sci.* **6**, 464.
- Lau, K. T. and D. Hui, 2002, Effectiveness of using carbon nanotubes as nano-reinforcements for advanced composite structures, *Carbon* **40**, 1605.
- Lin, Y., B. Zhou, K. A. S. Fernando, P. Liu, L. F. Allard and Y. P. Sun, 2003, Polymeric Carbon Nanocomposites from Carbon Nanotubes Functionalized with Matrix Polymer, *Macromolecules* **36**, 7199.
- Lu, K. L., R. M. Lago, Y. K. Chen, M. L. H. Green, P. J. F. Harris and S. C. Tsang, 1996, Mechanical Damage of Carbon Nanotubes by Ultrasound, *Carbon* **34**, 814.
- Mitchell, C. A., J. L. Bahr, S. Arepalli, J. M. Tour and R. Krishnamoorti, 2002, Dispersion of Functionalized Carbon Nanotubes in Polystyrene, *Macromolecules* **35**, 8825.
- Mylvaganam, K. and L. C. Zhang, 2004, Chemical Bonding in Polyethylene-Nanotube composites: A Quantum Mechanics Prediction, *J. Phys. Chem. B* ASAP article.
- Park, S. J., M. S. Cho, S. T. Lim, H. J. Choi and M. S. Jhon, 2003, Synthesis and Dispersion Characteristics of Multi-Walled Carbon Nanotube Composites with Poly(methyl methacrylate) Prepared by In-Situ Bulk polymerization, *Macromol. Rapid Commun.* **24**, 1070.
- Potschke, P., T. D. Fornes and D. R. Paul, 2002, Rheological behavior of multiwalled carbon nanotube/polycarbonate composites, *Polymer* **43**, 3247.
- Qin, S., D. Qin, W. T. Ford, D. E. Resasco and J. E. Herrera, 2004, Functionalization of Single-Walled Carbon Nanotubes with Polystyrene via Grafting to and Grafting from Methods, *Macromolecules* **37**, 752.
- Reichert, P., B. Hoffmann, T. Bock, R. Thomann, R. Mulhaupt and C. Friedrich, 2001, Morphological Stability of Poly(propylene) Nanocomposites, *Macromol. Rapid Commun.* **22**, 519.
- Velasco-Santos, C., A. L. Martinez-Hernandez, M. Lozada-Casou, A. Alvarez-Castillo and V. M. Castano, 2002, Chemical functionalization of carbon nanotubes through an organosilane, *Nanotechnology* **13**, 495.