

Polystyrene Composites Containing Crosslinked Polystyrene-Multiwalled Carbon Nanotube Balls

Soon-Min Kwon, Hun-Sik Kim, Don-Young Kim, Young Soo Yun, Hyoung-Joon Jin

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea

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ABSTRACT: Crosslinked polystyrene-multiwalled carbon nanotube (PS-MWCNT) balls, which act as conductive microfillers, were prepared by the *in situ* suspension polymerization of styrene with MWCNTs and divinyl benzene (DVB) as a crosslinking agent. The diameters of the synthesized crosslinked PS-MWCNT balls ranged from 10 to 100 μm and their electrical conductivity was about 7.7×10^{-3} S/cm. The morphology of the crosslinked PS-MWCNT balls was observed by scanning electron microscopy and transmission electron microscopy. The change in the chemical structure of the MWCNTs was confirmed by Raman spectroscopy and Fourier transform infrared spectroscopy. The mechanical and electrical properties of the

PS/crosslinked PS-MWCNT ball composites were investigated. It was found that the tensile strength, ultimate strain, Young's modulus, and impact strength of the PS matrix were enhanced by the incorporation of the crosslinked PS-MWCNT balls. In addition, the mechanical properties of the PS/crosslinked PS-MWCNT ball composites were better than those of the PS/pristine MWCNT composites. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3737–3744, 2008

Key words: polystyrene; multiwalled carbon nanotubes; conductive microfiller; suspension polymerization; solution casting

INTRODUCTION

To increase the inherent properties of polymers, many researchers have studied polymer composites with carbon nanotubes (CNTs), because CNTs are widely seen as the ideal candidate for use as a reinforcing filler in composite materials, due to their unique properties, for example, their very large aspect ratio (length/diameter) significantly larger than 1000,¹ high Young's modulus as high as 1 TPa,² stiffness, electrical and thermal conductivity, low density, and flexibility.³ Thus, CNTs offer many opportunities for the development of fundamentally new material systems.⁴ In many studies, polymer/CNT composites showed better properties than the pristine polymers, such as polystyrene (PS),^{3,5} poly(methyl methacrylate),⁶ polyethylene,⁴ and polycarbonate,² and can be used in various industrial fields. However, CNTs have two main problems. One is their poor dispersibility in various solvents or polymer matrices, because CNTs form aggregates due to the large van der Waals forces. The other is their poor interfacial adhesion with the polymer matrix in

the final products, which is required for good load transfer. Therefore, many methods have been proposed to solve these problems, such as the surface functionalization of the CNTs by acid-treatment, halogenation, alkylation, and grafted polymers which are miscible with the polymer matrix or novel self-assembling techniques.^{7–10} Although the tensile, electrical, and thermal properties of the polymer matrix in polymer/CNT composites were enhanced by the individual dispersion of the CNTs, the impact strength of the polymer matrix is slightly degraded at higher CNT concentrations.¹¹

PS, which is one of the most important thermoplastics, has now been manufactured industrially for some 80 years. Generally, PS can be polymerized through most polymerization methods, including free-radical and ionic polymerization, etc. Also, PS, as one of the general polymers, is inexpensive and easy to use in a wide range of industrial processes. Despite these advantages, PS is difficult to use in some special areas, such as engineering applications. Thus, PS is generally modified with other monomers or polymers through copolymerization or blend mixing. For example, acrylonitrile-butadiene-styrene terpolymer, styrene-acrylonitrile copolymer, or high-impact PS (HIPS) exhibit improved thermal resistance or impact strength due to such chemical or physical modifications. HIPS is a typical rubber-toughened polymeric material that is basically prepared by phase separation between a rubbery phase

Correspondence to: H.-J. Jin (hjjin@inha.ac.kr).

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such as polybutadiene (PB), to improve the impact strength and toughness, and a glassy phase such as PS.¹² Typically, the PB content is in the range of 5–15%. However, increasing the PB content for the purpose of improving the impact strength decreases the other properties, such as the tensile strength and surface gloss. In addition, controlling the heat of reaction and mix up is difficult, due to the increased viscosity of the solution in the polymerization process.

Among the various polymerization techniques, the suspension polymerization method, another name for which is the mini-bulk polymerization method, is used to fabricate polymers in the form of particles or balls and is a process in which water insoluble monomers, high stirring rates, and small amounts of surfactant (stabilizer) are used. The particle size is determined by the dispersed droplet phase, because the suspension polymerization takes place entirely in the dispersed monomer droplets. Also, a surfactant is used to produce a colloidally stable dispersion through adsorption, to promote the dispersion of the droplets and hinder the coalescence at the monomer droplet-water interface.¹³

In this study, we fabricated crosslinked polystyrene-multiwalled carbon nanotube (PS-MWCNT) balls, for use as reinforcing microfillers, using styrene dispersed MWCNTs and divinyl benzene (DVB) as a crosslinking agent via the *in situ* suspension polymerization method to simultaneously enhance the tensile and impact properties of the PS matrix. The crosslinked PS-MWCNT balls are miscible with the PS matrix and the micrometer-sized fillers inhibit the progression of cracks. In addition, we observed the morphology and structure of the prepared crosslinked PS-MWCNT balls and investigated the mechanical and electrical properties of their composites with commercial PS.

EXPERIMENTAL

Materials

MWCNTs (purity of 95%, supplied by Ijin Nanotech, Korea) produced by thermal chemical vapor deposition (CVD) were used in this study. Styrene (Samchun Pure Chemical, Korea) and DVB (80%, Aldrich) were used as the monomer and the crosslinking agent, respectively, and they were washed three times with a 10 mol % aqueous solution of sodium hydroxide and then stored in a refrigerator. Polyvinyl alcohol (PVA, $M_w = 77,000$ g/mol, DC Chemical, Korea) was used as a stabilizer without further purification. 2,2-Azobisisobutyronitrile (AIBN, Junsei, Japan) was used as an initiator and was dissolved in ethanol to remove the inhibitor, precipitated at -10°C , and stored in a refrigerator

before polymerization. PS ($M_w = 260,000$ g/mol, Scientific Polymer Products) was chosen as the polymer matrix for the composite. Chloroform (CHCl_3) was obtained from DC Chemical, Korea.

Preparation of crosslinked PS-MWCNT balls

To obtain the crosslinked PS-MWCNT balls, the styrene and pristine MWCNTs were reacted with DVB via *in situ* suspension polymerization. First, 1.5 wt % of the MWCNTs were loaded in a mixed solution containing 4.5 g of styrene and 10 mol % DVB. Ultrasound was then applied to the MWCNT dispersion using an ultrasonic generator (Kodo Technical Research, Korea) with a nominal frequency of 28 kHz and a power of 600 W for more than 8 h at 25°C . At the same time, 0.125–0.183 g of PVA was dissolved in 220 g of deionized water with weak stirring. Then, AIBN was dissolved in the styrene-DVB-MWCNTs mixed solution as an initiator. Under vigorous stirring, the styrene-DVB-MWCNTs mixed solution was dropped into the PVA dispersed deionized water and the reaction system was converted to an oil-in-water system. *In situ* suspension polymerization was carried out in a 500-mL round bottomed flask with mechanical stirring at 1600 rpm under a nitrogen atmosphere at 75°C for 5 h. When the *in situ* suspension polymerization was completed, the crosslinked PS-MWCNT balls were obtained. The withdrawn polymerization products were rinsed off with methanol and deionized water, and centrifuged repeatedly to remove the nonreacted styrene, DVB, and PVA. Then, the crosslinked PS-MWCNT balls were dried in a vacuum oven at room temperature for 24 h. To confirm that they were crosslinked by covalent bonds between the PS and MWCNTs, the crosslinked PS-MWCNT balls were compared with PS balls, crosslinked PS balls, and uncrosslinked PS-MWCNT balls synthesized by the same process via *in situ* suspension polymerization.

Preparation of composites

PS/crosslinked PS-MWCNT ball composites were fabricated by solution casting using chloroform. The PS/crosslinked PS-MWCNT ball composites were prepared with 0.5 and 1.0 wt % of the MWCNTs with respect to the crosslinked PS-MWCNT balls. Appropriate amounts of the crosslinked PS-MWCNT balls were loaded in 30 mL of chloroform and then dispersed by means of an ultrasonic generator. Then, 3 g of PS was dissolved in the chloroform dispersion of the crosslinked PS-MWCNT balls and stirred at room temperature for 24 h to obtain a homogeneous solution. The solution was then poured into a square-shaped mold and the chloroform was evaporated slowly at room temperature for more

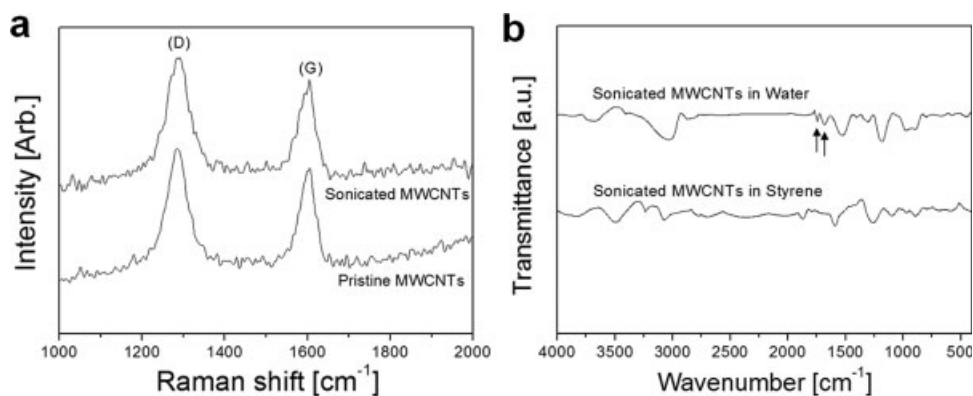


Figure 1 (a) Raman spectra of pristine MWCNTs and MWCNTs sonicated for 10 h in styrene and (b) FTIR spectra of MWCNTs after sonication for 10 h in water and in styrene, respectively.

than 96 h until the composites were completely dry. The PS/crosslinked PS-MWCNT ball composites were denoted as PS- x -cMWCNTs, where x indicates the MWCNTs concentration with respect to the crosslinked PS-MWCNT balls. For comparison, PS films and PS/pristine MWCNT composites were prepared using the same processes. The PS films were fabricated using only PS dissolved in chloroform, and the PS/pristine MWCNT composites were fabricated with 0.5 and 1.0 wt % of the pristine MWCNTs. The PS films and PS/pristine MWCNT composites were designated as PS-f and as PS- x -pMWCNTs, respectively, where x indicates the pristine MWCNT concentration. However, otherwise, it seems strange to say, for example, that PS is fabricated from PS or to refer to PS composites (i.e., containing only PS).

Characterization

The functional groups of PS and the structure of the samples were verified using Fourier transform infrared spectroscopy (FTIR, VERTEX 80v, Bruker Optics, Germany). Each spectrum of the samples was acquired by the accumulation of 64 scans with a resolution of 4 cm^{-1} and spectral range of $4000\text{--}400\text{ cm}^{-1}$. The presence of sp^2 hybridized carbon in the MWCNT samples was confirmed through the examination of the E_{2g} mode or G band (stretching vibrations in the basal plane of crystalline graphite), the so-called D band (indicating the level of defects in the graphitic material) and the I_G/I_D ratio (the intensity ratio of the D band to the G band which is usually used for the assessment of the purity and crystallinity of CNTs) by Raman spectroscopy (RFS-100/S, BRUKER, 1064 nm excitation, Germany). The morphology of the balls and composites was observed using field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan) at an accelerating voltage of 15 kV after pre-coating the samples with a homogeneous Pt layer

by ion sputtering (E-1030, Hitachi, Japan). To confirm that the MWCNTs were present not only inside the balls, but also on their surface, the internal structures of the crosslinked PS-MWCNT balls were observed by transmission electron microscopy (TEM, CM200, Philips) at an accelerating voltage of 100 kV. All of the ultrathin sections were microtomed using an MTX ultramicrotome (Tucson, AZ) with a diamond knife. Thermogravimetric analysis (TGA, Q50, TA instruments, UK) was used to measure the MWCNT content in the crosslinked PS-MWCNT balls. TGA was performed at a heating rate of $20^\circ\text{C}/\text{min}$ from room temperature to 600°C under a dynamic nitrogen flow of $10\text{ cm}^3/\text{min}$. The optical microscope used in this study was an Olympus BX 51. To measure the electrical conductivity of the crosslinked PS-MWCNT balls, they were prepared in the form of disc-type pellets with a thickness of 0.7 mm by applying a pressure of 1 ton at room temperature using a Carver laboratory press (Model 3912, Carver, Wabash, IN). The electrical resistances of the composites and the crosslinked PS-MWCNT balls were measured by a four-probe method with a resistivity meter (Hiresta-up MCP-HT450, Mitsubishi Chemical, Japan). The tensile properties of the samples were determined following the ASTM D638 (type I) test procedures and were measured using a Universal Testing Machine (UTM, Model 5569, INSTRON) at room temperature. The strain rate was $10\text{ mm}/\text{min}$ under a load of 1 kN and 30% humidity. At least five measurements were averaged to collect the tensile property of a given sample. The un-notched Izod impact strength was measured using the ISO 180/1U procedure and a pendulum impact testing machine (Resil 25, CEAST, Italy). The samples were held by a vertical cantilever beam, and the faces of the samples were impacted by a single swing of the pendulum. At least five tests were performed for each analysis at room temperature, and the average value was calculated and reported.

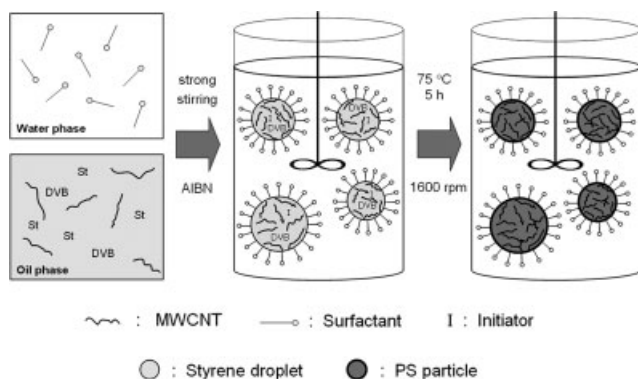


Figure 2 Schematic diagram of fabrication process of the crosslinked PS-MWCNT balls via *in situ* suspension polymerization.

RESULTS AND DISCUSSION

Although the degree of damage to the CNTs caused by their sonication in water varies as a function of the time and power, this procedure could significantly damage the CNT framework.¹⁴ In this study, the pristine MWCNTs were sonicated in styrene to obtain a good dispersion. Thus, we confirmed the structural alteration of the MWCNTs by Raman spectroscopy. [Fig. 1(a)] The ratio of the intensity of the G-band to the D-band (I_G/I_D ratio) has been widely used to evaluate the defects in MWCNTs. The I_G/I_D ratio of the pristine MWCNTs is 0.86 and that of the MWCNTs sonicated in styrene for 10 h is 0.84. Therefore, it can be inferred that the pristine MWCNTs were physically damaged by their sonication in styrene, resulting in a slight decrease in their degree of crystallinity. However, in this study, this reduction in the degree of crystallinity of the MWCNTs is negligible when considering their original outstanding properties. Also, we investigated the functional groups on the surface of the MWCNTs after their sonication for 10 h by FTIR spectroscopy. [Fig. 1(b)] The FTIR spectrum of the MWCNTs sonicated in water revealed the characteristic adsorption

peaks at 1746 and 1686 cm^{-1} due to the C=O stretching vibrations. However, the MWCNTs sonicated in styrene did not exhibit these peaks. This indicates that the damage induced by their sonication in water caused the MWCNTs to be broken and that the sidewalls of the opened MWCNTs were oxidized by water, whereas the MWCNTs sonicated in styrene were only broken but not oxidized. Figure 2 presents a schematic diagram of the *in situ* suspension polymerization process used for fabricating the crosslinked PS-MWCNT balls. Generally, suspension polymerization is carried out in an oil-in-water system and all of the polymerization reactions take place in the dispersed monomer droplets which act as the oil phase. Thus, in this study, DVB as a cross-linking agent is dissolved in styrene to induce the formation of crosslinking bonds between the PS molecules. The MWCNTs were dispersed in styrene and were found to be present on the inside of the final PS balls. If a sufficient amount of them was used, the MWCNTs were not only embedded inside the PS balls but also present on their surface. We synthesized crosslinked PS-MWCNT balls by the *in situ* suspension polymerization of the styrene monomer in which the MWCNTs (1.5 wt % of MWCNTs) were dispersed. The surface and inner morphologies of the crosslinked PS-MWCNT balls were observed by FESEM and TEM. Figure 3 shows the FESEM images of the crosslinked PS-MWCNT balls. The crosslinked PS-MWCNT balls were successfully prepared with a spherical shape, and their diameters ranged from 10 to 100 μm . [Fig. 3(a)] The MWCNT content of the crosslinked PS-MWCNT balls was 4.3 wt % as determined by TGA. Figure 3(b) shows a larger magnification image of the surface morphology, which indicates that the MWCNTs were wholly present on the surface of the crosslinked PS-MWCNT balls. Figure 4 shows the TEM images of the crosslinked PS-MWCNT balls. Numerous MWCNTs were observed by TEM on the surface of the crosslinked PS-MWCNT balls, as shown in Figure 4(a). These results confirmed those provided by the FESEM images. Figure 4(b) shows the center

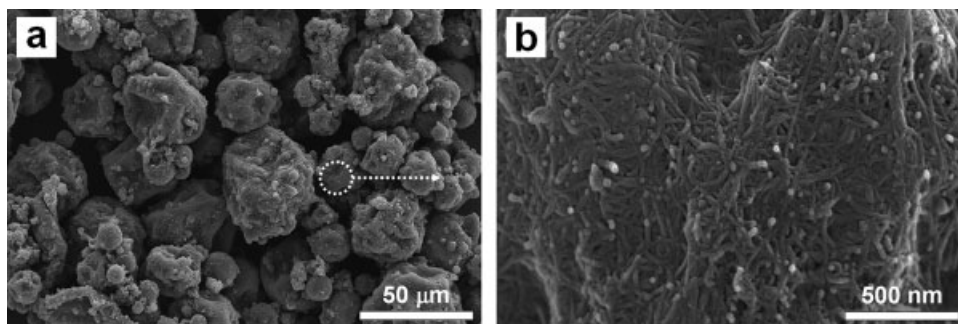


Figure 3 FESEM micrographs of (a) the crosslinked PS-MWCNT balls (b) with a higher magnification.

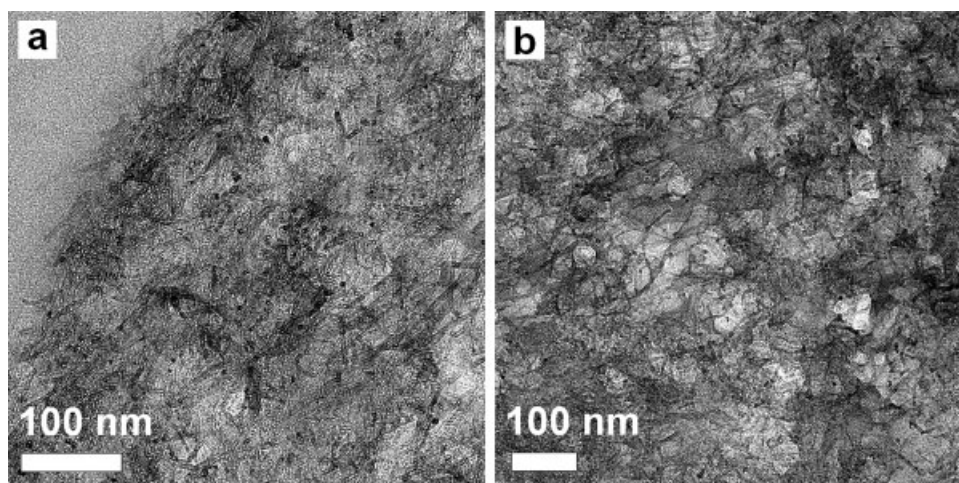


Figure 4 TEM images of (a) the surface part and (b) the center part of the crosslinked PS-MWCNT balls.

part of one of the crosslinked PS-MWCNT balls, which indicates that the MWCNTs were embedded within them. From the results of FESEM and TEM, we consider that the prepared crosslinked PS-MWCNT balls are mainly constructed with MWCNTs both in the interior and on the surface.

The FTIR spectra were analyzed to prove the successful progress of the polymerization from styrene to PS and the interaction between the PS and MWCNTs. Figure 5 shows the FTIR spectra of the PS balls, crosslinked PS balls, uncrosslinked PS-MWCNT balls, and crosslinked PS-MWCNT balls. The crosslinked samples were polymerized with DVB as a crosslinking agent. Ring C—C stretching vibrations were observed in the region of 1625–1430 cm^{-1} . The FTIR spectrum of the PS exhibits the characteristic adsorption peaks at 3082, 3059, and 3025 cm^{-1} , due to the C—H stretching vibrations of an aromatic compound, and the adsorption peaks attributed to $-\text{CH}_2-$ symmetric and asymmetric stretching vibrations at 2922 and 2848 cm^{-1} , respectively.¹⁵ Compared with the FTIR spectra of the PS balls and crosslinked PS balls, a new peak at about 1665 cm^{-1} was observed in the FTIR spectra of the PS-MWCNT balls, regardless of the presence or absence of DVB as a crosslinking agent. This indicates the existence of C—C bonds between the MWCNTs and the polymer.¹⁶ Namely, during the progress of the *in situ* suspension polymerization, radicals created by the initiator were transferred to the surface of the MWCNTs, causing them to open their π -bonds. These opened π -bonds of the MWCNTs can be linked with the styrene, oligomer, and PS, which results in their grafting with the PS and consequent strong interfacial adhesion caused by the covalent bonding between the MWCNTs and the PS. In addition, the PS molecules are crosslinked with each other due to the DVB. Thus, the prepared crosslinked PS-MWCNT balls are successfully polymer-

ized via *in situ* suspension polymerization and are linked by covalent bonding between the PS and the MWCNTs, as well as being crosslinked between the PS molecules.

The electrical conductivity of the crosslinked PS-MWCNT balls was measured by the four-probe method at room temperature and was found to be about 7.7×10^{-3} S/cm. Thus, we expect that the crosslinked PS-MWCNT balls would provide good reinforcing properties in the polymer matrix, by acting as a conductive microfiller, which is miscible with PS.

We prepared PS/crosslinked PS-MWCNT ball composites by solution casting from dilute solution. As a control experiment, we prepared PS/pristine MWCNT composites by the same method. The concentrations of MWCNTs were 0.5 and 1.0 wt %. Figure 6 shows that the crosslinked PS-MWCNT balls were well dispersed in the PS matrix, so that the

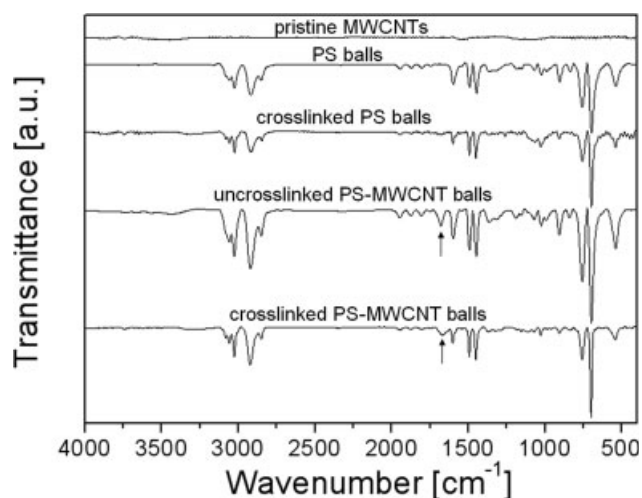


Figure 5 FTIR spectra of the pristine MWCNTs, the PS balls, the crosslinked PS balls, the uncrosslinked PS-MWCNT balls, and the crosslinked PS-MWCNT balls.

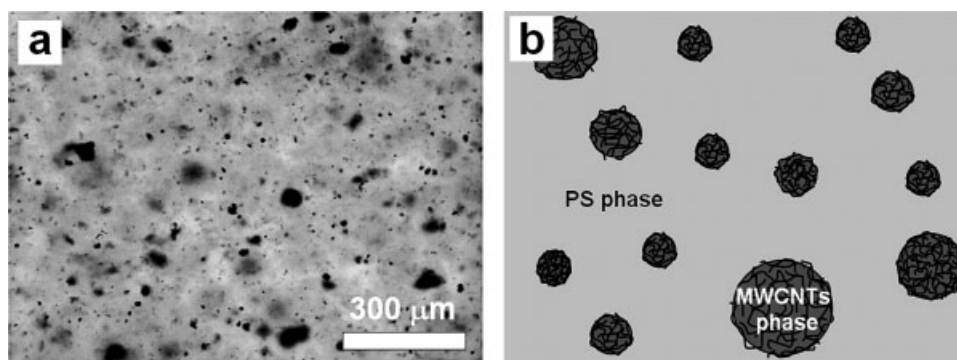


Figure 6 (a) Optical micrograph and (b) schematic diagram of the PS/crosslinked PS-MWCNT ball composites.

composite films were separated into two different phases. Because of their miscibility with the PS matrix, an improvement in load transfer can also be achieved by using the crosslinked PS-MWCNT balls.¹⁷ When compared with the PS/pristine MWCNT composites, we expected that the PS/crosslinked PS-MWCNT ball composites would be more effective in reinforcing the PS matrix, due to the improvement in their dispersion and load transfer.

The electrical conductivity of the PS/pristine MWCNT composites were 3.5×10^{-7} and 4.1×10^{-7} S/cm and those of the PS/crosslinked PS-MWCNT ball composites were 4.7×10^{-7} and 1.2×10^{-5} S/cm at MWCNT contents of 0.5 and 1.0 wt %, respectively. Comparing the PS-1.0-pMWCNTs with the PS-1.0-cMWCNTs, the latter exhibited better electrical conductivity than the former, due to the homogeneous distribution of the crosslinked PS-MWCNT balls in the PS matrix.

In an attempt to examine the reinforcing effects of the crosslinked PS-MWCNT balls, the tensile strength and impact strength of the composites were measured by a UTM and impact tester, respectively. Figure 7 shows the stress–strain curves and Table I summarizes the tensile properties of the samples. The tensile strength, ultimate strain, and Young's modulus of the PS/crosslinked PS-MWCNT ball composites were increased upon the incorporation of the crosslinked PS-MWCNT balls. The tensile strength, ultimate strain, and Young's modulus of the PS-1.0-cMWCNTs were increased by 24.0, 63.6, and 19.7%, whereas those of the PS-1.0-pMWCNTs were decreased by 2.3, 13.6, and 5.2%, when compared with the corresponding values of the PS-f, respectively. The poorer reinforcing effect of the pristine MWCNTs was attributed to their poor dispersion and weak interfacial adhesion in the PS matrix. Generally, the tensile strength, ultimate strain, and Young's modulus of a polymer are not simultaneously increased in polymer/CNT composites. In the case where the crosslinked PS-MWCNT balls were used as a reinforcing filler, however, the tensile

strength, ultimate strain, and Young's modulus of the polymer were simultaneously increased, so the toughness of the polymer was increased by the introduction of the crosslinked PS-MWCNT balls. Also, the impact strength of the samples exhibits the same tendency, as shown in Table I. The impact strength of the PS-1.0-pMWCNTs was about 2.9 kJ/m^2 . However, that of the PS-1.0-cMWCNTs was about 4.3 kJ/m^2 which represents an increase of 16.2% when compared with that of the PS-f. The increase of the impact strength is caused by the inherent properties of the MWCNTs and the improved interfacial adhesion between the polymer and MWCNTs. When impact damage is induced in the polymer/MWCNT composites, the damaged areas tend to magnify the stress locally due to development of cracks in the composite matrix. However, this detrimental effect induced by impact loading is hindered by the presence of the crosslinked PS-MWCNT balls in the composite matrix, due to the so-called crack shielding effect, and the impact stress is adsorbed by the crosslinked PS-MWCNT balls

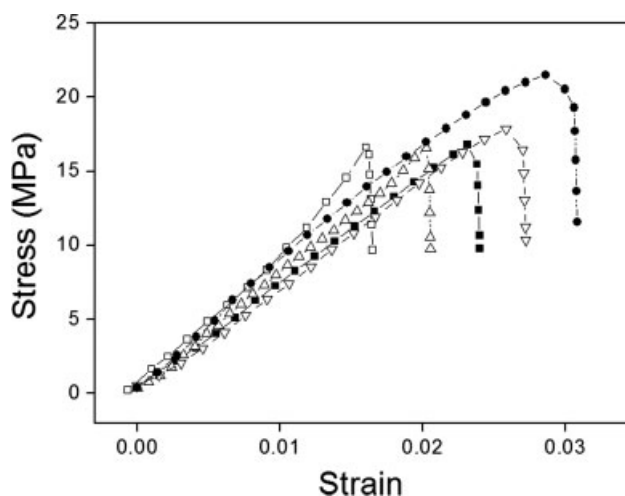


Figure 7 Stress–strain curves of PS-f (■), PS-0.5-pMWCNTs (□), PS-1.0-pMWCNTs (△), PS-0.5-cMWCNTs (▽), and PS-1.0-cMWCNTs (●).

TABLE I
Mechanical Properties of PS and Composites

Sample codes	Tensile strength σ_{\max} (MPa)	Ultimate strain ε_{\max}	Young's modulus (MPa)	Impact strength (kJ/m^2)
PS-f	17.0 ± 1.0	0.022 ± 0.010	720.8 ± 39.6	3.7 ± 0.3
PS-0.5-pMWCNTs	17.3 ± 0.8 (2%)	0.015 ± 0.003 (-31.8%)	723.8 ± 22.7 (0.4%)	3.0 ± 0.2 (-18.9%)
PS-1.0-pMWCNTs	16.6 ± 0.7 (-2.3%)	0.019 ± 0.006 (-13.6%)	683.1 ± 24.0 (-5.2%)	2.9 ± 0.5 (-21.6%)
PS-0.5-cMWCNTs	17.9 ± 0.7 (5%)	0.028 ± 0.002 (27.3%)	820.7 ± 19.5 (13.9%)	4.0 ± 0.2 (8.1%)
PS-1.0-cMWCNTs	21.0 ± 0.6 (24%)	0.036 ± 0.007 (63.6%)	863.0 ± 31.2 (19.7%)	4.3 ± 0.4 (16.2%)

due to the high modulus and flexibility of the MWCNTs.¹⁸ Thus, at the same concentration of MWCNTs, the crosslinked PS-MWCNT balls exhibited a better reinforcing effect in the polymer matrix than the pristine MWCNTs.

The fracture surfaces of the composites after the tensile test were observed by FESEM. Figure 8(a,b) show the fracture surface of the PS-1.0-pMWCNTs. The poor dispersion and weak interfacial adhesion of the MWCNTs in the PS matrix can be clearly observed. The MWCNTs were apparently pulled out of the PS matrix, which is an indication that the PS-1.0-pMWCNTs exhibited poor tensile load transfer. Figure 8(c,d) show the fracture surface of the PS-1.0-cMWCNTs, where the sphere morphology of the crosslinked PS-MWCNT balls can be seen to act as a conductive microfiller. When compared with the PS-1.0-pMWCNTs, the strong interfacial adhesion of the MWCNTs in the PS matrix can be observed, due to presence of the PS-g-MWCNTs. The MWCNTs on the fracture surface were disturbed by the tensile loading force, due to the good interfacial adhesion between the PS matrix and the crosslinked PS-

MWCNT balls. Thus, the crosslinked PS-MWCNT balls were shown to act as a conductive microfiller which enhances their reinforcing effects, resulting in the improved electrical and mechanical properties of the polymeric composites, due to the homogeneous distribution and good interfacial adhesion of the crosslinked PS-MWCNT balls. Also, these electrically conductive and micrometer sized balls can be used as particles on electrorheological particles, due to their electrical conductivity in the range of 10^{-9} to 10^{-1} S/cm.¹⁹

CONCLUSIONS

In this study, we successfully synthesized cross-linked PS-MWCNT balls using MWCNTs dispersed in styrene before its polymerization and DVB as a crosslinking agent by *in situ* suspension polymerization. Also, we prepared PS/crosslinked PS-MWCNT ball composites by solution casting from chloroform to investigate the ability of the crosslinked PS-MWCNT balls to act as a conductive microfiller reinforcing the polymer matrix. The prepared cross-

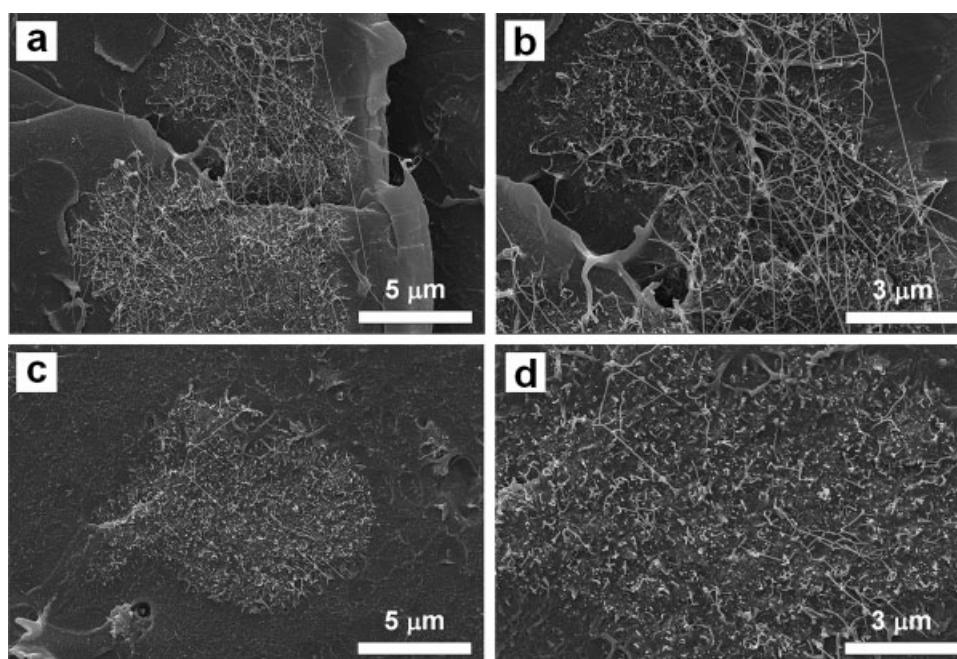


Figure 8 FESEM micrographs of fractured surfaces in composites after tensile test: (a) PS-1.0-pMWCNTs (b) with a higher magnification, and (c) PS-1.0-cMWCNTs (d) with a higher magnification.

linked PS-MWCNT balls have a spherical shape and their diameters ranged from 10 to 100 μm . The FESEM and TEM micrographs confirmed that the MWCNTs were present both in the interior and on the surface of the crosslinked PS-MWCNT balls, so they were mainly constructed with the MWCNTs. Through TGA measurements, we found that the amount of MWCNTs included in the crosslinked PS-MWCNT balls was about 4.3 wt %. The crosslinked PS-MWCNT balls exhibited an electrical conductivity of about 7.7×10^{-3} S/cm and, when used as conductive microfillers, they were better distributed in the composites made with commercial PS than the pristine MWCNTs. The electrical conductivity of the PS/crosslinked PS-MWCNT ball composites was 1.2×10^{-5} S/cm at an MWCNT content of 1.0 wt %. The mechanical properties of the PS/crosslinked PS-MWCNT ball composites at an MWCNT content of 1.0 wt %, viz. their tensile strength, ultimate strain, Young's modulus, and impact strength, were improved by 24.0, 63.6, 19.7, and 16.2%, respectively, when compared with the PS matrix. This indicates that the crosslinked PS-MWCNT balls were homogeneously distributed and had good interfacial adhesion with the PS matrix. Thus, it was confirmed that the prepared crosslinked PS-MWCNT balls act as a conductive microfiller reinforcing the polymer matrices.

References

1. Yerushalmi-Rozen, R.; Szleifer, I. *Soft Matter* 2006, 2, 24.
2. Jung, R.; Park, W.-I.; Kwon, S.-M.; Kim, H.-S.; Jin, H.-J. *Polymer* 2008, 49, 2071.
3. Hsiao, C.-C.; Lin, T. S.; Cheng, L. Y.; Ma, C.-C. M.; Yang, A. C.-M. *Macromolecules* 2005, 38, 4811.
4. Zhu, D.; Bin, Y.; Matsuo, M. *J Polym Sci Part B: Polym Phys* 2007, 45, 1037.
5. Chang, T.-E.; Kisliuk, A.; Rhodes, S. M.; Brittain, W. J.; Sokolov, A. P. *Polymer* 2006, 47, 7740.
6. Kwon, S.-M.; Kim, H.-S.; Myung, S. J.; Jin, H.-J. *J Polym Sci Part B: Polym Phys* 2008, 46, 182.
7. Hirsch, A.; Vostrowsky, O. *Top Curr Chem* 2005, 245, 193.
8. Qin, Y.; Shi, J.; Wu, W.; Li, X.; Guo, Z.-X.; Zhu, D. *J Phys Chem B* 2003, 107, 12899.
9. Hwang, G. L.; Shieh, Y.-T.; Hwang, K. C. *Adv Funct Mater* 2004, 14, 487.
10. Mylvaganam, K.; Zhang, L. C. *J Phys Chem B* 2004, 108, 15009.
11. Zou, Y.; Feng, Y.; Wang, L.; Liu, X. *Carbon* 2004, 42, 271.
12. Lee, S. J.; Jeoung, H. G.; Ahn, K. H. *J Appl Polym Sci* 2003, 89, 3672.
13. Ramirez, J. C.; Herrera-Ordóñez, J. *Eur Polym J* 2007, 43, 3819.
14. Heller, D. A.; Barone, P. W.; Strano, M. S. *Carbon* 2005, 43, 651.
15. Kim, S. H.; Son, W. K.; Kim, Y. J.; Kang, E.-G.; Kim, D.-W.; Park, C. W.; Kim, W.-G.; Kim, H.-J. *J Appl Polym Sci* 2003, 88, 595.
16. Jia, Z.; Wang, Z.; Xu, C.; Liang, J.; Wei, B.; Wu, D.; Zhu, S. *Mat Sci Eng A-Struct* 1999, 271, 395.
17. Wang, M.; Pramoda, K. P.; Goh, S. H. *Polymer* 2005, 46, 11510.
18. Seo, M.-K.; Lee, J.-R.; Park, S.-J. *Mat Sci Eng A-Struct* 2005, 404, 79.
19. Goodwin, J. W.; Markham, G. M.; Vincent, B. *J Phys Chem B* 1997, 101, 1961.