

Fabrication of Surfactant-Removed Polymer Composites with Single-Walled Carbon Nanotube Networks

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ABSTRACT: Polystyrene (PS) composites with a network of single-walled carbon nanotubes (SWNTs) were fabricated by using monodispersed PS microspheres. First, PS spheres and surfactant-dispersed SWNTs were mixed in water, then a hybrid cake was obtained by filtration via a microporous membrane and the SWNTs were filled within the spaces of packed polymer spheres. At this stage, the surfactants for dispersing SWNTs were totally removed from the composites by a thorough washing. Then the composite films with SWNT networks were obtained by

compression molding at 160°C. Structure of the composites had been characterized by transmission electron microscopy and scanning electron microscopy. The present SWNT composites showed a low percolation threshold of electrical conductivities. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 155–161, 2011

Key words: electrical conductivities; microspheres; nanocomposites; polystyrene; single-walled carbon nanotubes; surfactants

INTRODUCTION

Being a single layer of rolling graphite lattice cylinder with a diameter between 0.4 to 2 nm, single-walled carbon nanotube (SWNT) is one of the most amazing materials discovered in recent decades.¹ Nanostructure of carbon provides the SWNTs of high aspect ratio with extraordinary electrical and thermal properties and makes them good candidates for fabrication of nanometer-scale electronic devices, chemical and biological sensors, and polymeric composites.^{2,3} Among these applications, the polymeric composites have attracted much attention in recent years for their combination of the unique characters of SWNTs and the elasticity of polymers. However, poor solubility and dispersibility coming from strong van der Waals interactions between nanotubes impede incorporation of SWNTs into polymer matrixes.^{4,5} So covalent and noncovalent strategies have been applied to improve their solubility in solution and dispersibility in a polymer matrix, and much progress has been achieved during the past few years.^{6,7}

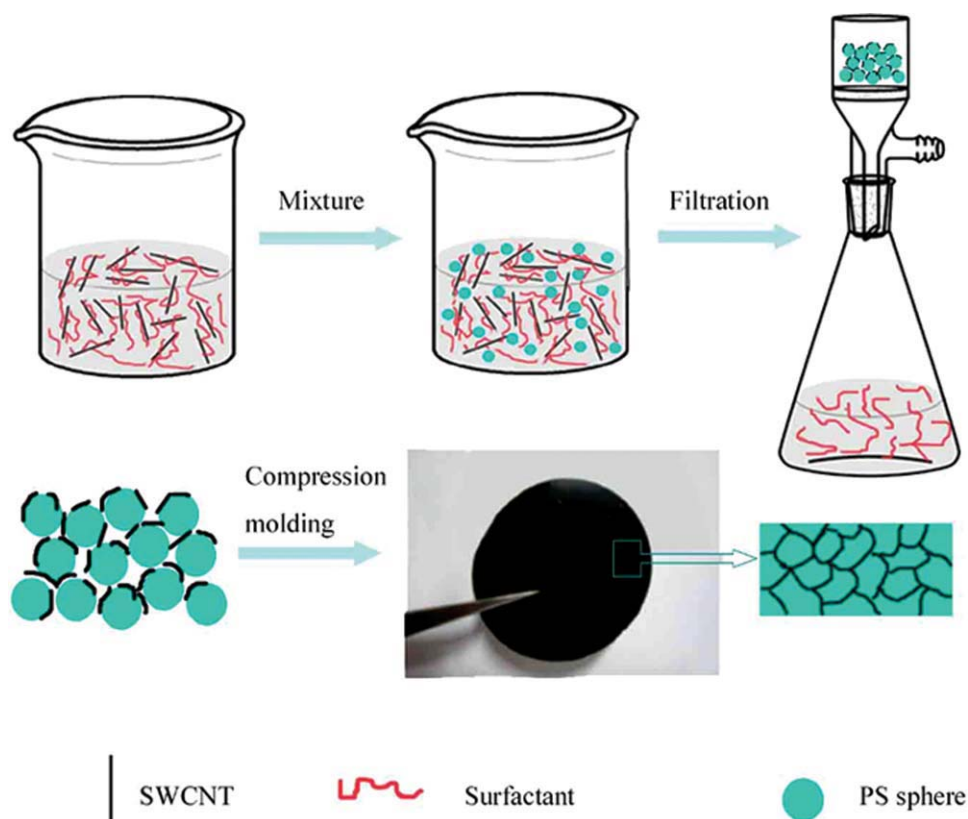
Although chemical modification is a common way to disperse SWNTs, it damages the nanotube lattice, reduces their strength and conductivity, and shortens their lengths considerably, leaving reactive groups on the nanotube surface which can cause further deterioration.^{8,9} In contrast, noncovalent modification of the tube surfaces with dispersants such as surfactants and polymers is a more attractive approach because not only the intrinsic properties are preserved but also the fabrication is much easier.^{7,10,11} Therefore, there are much works based on the latter approach to fabricate related composites and some promising results have been achieved.^{12,13} Tchoul et al. have prepared composites of SWNTs and polystyrene (PS) by evaporation of chloroform solutions of PS and SWNTs being noncovalently functionalized with conjugated polymers. They found that the percolation threshold of conductivity of thus produced composites was as low as 0.2 wt %.¹⁴

It is believed that the formation of nanotube network is very important for the composites to display conductivity. Recently, Grunlan et al. have applied polyvinyl acetate emulsion to fabricate the polymer composite films of SWNTs with very low percolation threshold. During drying, Gum Arabic stabilized SWNTs were located between the spaces of polymer particles to form a network.^{15,16} Also, Regev et al. have applied the same approach to generate SWNT networks in PS matrixes.¹⁷ By such a latex procedure, fabrication of the network composites may be carried out easily and intrinsic properties of

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Scheme 1 Multistep process for preparation of PS/SWCNT composites by using monodispersed PS microspheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers were remained. However, in both systems, a large amount of surfactants were captured into the composite films which left the uncertainty for material properties. For the latter case, the size of PS latex was pretty small relative to the length of SWNT, which might be not helpful to form effective SWNT networks regarding the SWNTs of micrometer in length.

As we know, monodispersed polymer particles can pack closely because their uniformity of diameters. Recently, it was demonstrated that colloidal patterns on surface can be applied to fabricate and control nanotube networks of two-dimension.¹⁸ So, it would be interesting to utilize monodispersed microsized polymer particles to control the location and network of nanotubes in bulk composites, where both nanotubes and polymer matrix may keep their own properties. Moreover, the presence of surfactants in composites may be problematic for the properties of composites.^{19,20} However, it is difficult to remove the surfactants from composites once the materials had been obtained.

Herein, we report a fabrication of PS composites with SWNT networks based on monodispersed PS spheres of about 1 micrometer. Scheme 1 shows a schematic description of a multistep process for making PS/SWCNT composites by using monodis-

persed PS spheres and a filtration procedure. First, SWNTs were dispersed in an aqueous solution of surfactant and mixed with PS spheres. After water being removed by a filtration, the obtained cake of spheres and tubes was washed thoroughly with alcohol to remove the surfactants. Finally, the dried cake was processed by compression molding at 160°C. As a result, a composite film with nanotube network was obtained. By present procedure, the surfactants for nanotube dispersion including solvent may be removed easily by filtration before formation of PS film. We expected that the surfactant-removed polymer composites with SWNT network fabricated by this approach would be a model material for clarifying the instinctive properties of polymer composites with carbon nanotubes.

EXPERIMENTAL

Materials

Monodispersed PS microspheres were prepared by a surfactant-free process as described in literature and the average diameter of sample used in this experiment was 0.85 μm .²¹ Pluronic copolymer (Aldrich, $M_n = 13,440$, PEO 82.5 wt %), sodium dodecylbenzene sulfonate (SDBS, Chemical Reagent Beijing

Co.), and pristine SWNTs (Timesnano, prepared by chemical vapor deposition method, 90 wt % pure SWNTs, 1–2 nm in diameter and several micrometers in length) were used without further purification. A PTFE membrane (Jinteng Instrument Co., Tianjin, China) with a pore size of 0.22 μm was used to filter.

Preparation of PS/SWNT composites

SDBS and Pluronic copolymer have been proved as efficient dispersants for the SWNTs,⁷ and they are soluble in ethanol or mixture of ethanol and water in which PS is not soluble. To disperse SWNTs in SDBS aqueous solution, 100 mg of SDBS and 20 mg of SWNTs were charged into a 50 mL flask with 20 mL of deionized water, and the mixture was sonicated for 1 h, followed by centrifugation at 3600 rpm for 30 min, resulting in a homogeneous black solution. To estimate the exact amount of SWNTs in the solution, the precipitates were collected and washed by 100 mL of water, 200 mL of acetone, and 200 mL of ethanol to remove the surfactants. The dried impurities in nanotube samples were weighted and the amount of nanotubes in solution was calculated. The process of dispersing SWNTs in Pluronic aqueous solution was similar to that of SDBS, except that the amount of Pluronic was 400 mg for every 20 mg of SWNTs.

As-prepared PS spheres in water were then added to the solution of surfactant-stabilized SWNTs. After sonication for 15 min, the mixture was transferred into a filter carefully and water was removed drop by drop to give a composite cake. After this procedure, the sample was washed with 200 mL of water and 200 mL of anhydrous ethanol to remove all the surfactants. After dried for 12 h under vacuum at 60°C, homogeneous opaque black film was obtained by compression molding under ambient conditions in the mold at 160°C and 4 MPa pressure for 2 min.

Characterization

Fourier-Transform Infrared (FTIR) spectra were recorded by a deuterate triglycine sulfate (DTGS) detector on a Bruker EQUINOX 55 spectrometer and processed by the Bruker OPUS program. Samples were prepared by milling with potassium bromide (KBr) to form a very fine powder and then compressed into a thin pellet. Transmission electron microscopy (TEM) images were obtained using a Hitachi H-800 instrument operated at an accelerating voltage of 100 kV. The images were recorded by a digital camera. To explore dispersion of SWNTs in matrix, the samples were embedded in epoxy and cured at 40°C overnight. Thin sections (50–100 nm) were obtained using Leica Ultracut UCT ultramicro-

tome and a diamond knife at room temperature. Scanning electron microscopy (SEM) images were obtained using a JSM 6700F instrument operated at 5.0 kV. A cross section of the final composites was obtained by breaking the film in liquid nitrogen. For SEM observations, dried specimens were placed carefully on a conducting glue and then coated with gold to make them conductive. Electrical conductivity was measured using a standard four-point method. Parallel copper lines in 1 cm length and with 1 cm interval were adhered to the composite film with silver conductive paint, and all conductivity measurements were performed at room temperature.

RESULTS AND DISCUSSION

Preparation of surfactant-removed PS composites with SWNT network

To check generality of this method, we applied SDBS and Pluronic copolymers as the surfactants to disperse SWNTs in the experiment. Both surfactants are soluble in alcohol and therefore, they could be removed by washing the as-prepared hybrids of spheres and nanotubes on the filters directly with alcohol. Compared with that of the neat PS (Fig. 1 line A), IR spectra of the composites before and after removal of SDBS were showed in Figure 1(B,C),

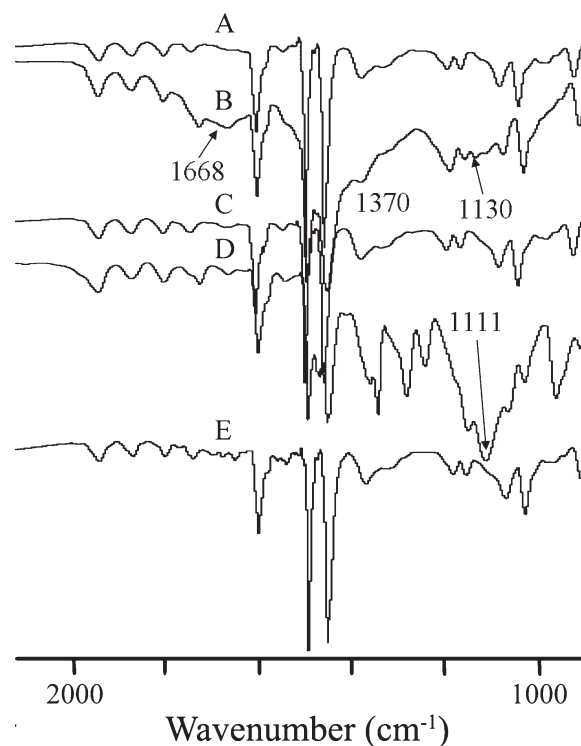


Figure 1 FTIR spectra of different stages of sample preparation. A: pure PS, B and C: hybrids with and without SDBS, D and E: hybrids with and without Pluronic.

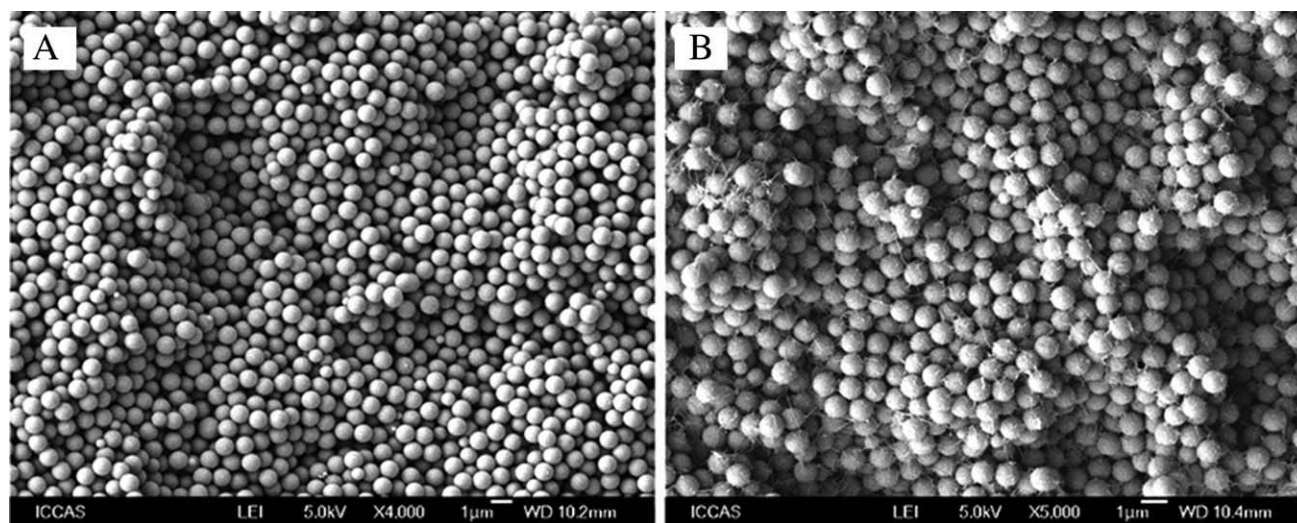


Figure 2 SEM images of cross section of (A) PS spheres and (B) PS sphere/SWNT hybrids with 2 wt % of SWNTs.

respectively. Before removal of surfactants, the peaks of symmetrical stretching of S=O at 1130 cm^{-1} was found, meanwhile the peak of C—C aromatic stretching at 1668 cm^{-1} and the peaks of saturated C—H bending between 1370 and 1500 cm^{-1} were broadened and strengthened obviously because the existence of SDBS. After washing process, these peaks from SDBS disappeared as shown in Figure 1 line C, indicating removal of SDBS. For the Pluronic case, the presence of unique C—O stretching peaks at 1111 cm^{-1} (line D) demonstrated that Pluronic molecules were incorporated in the sample. However, these peaks disappeared (line E) after washing with ethanol. These results proved the efficiency of present procedure to remove the surfactants in the composites which is meaningful for properties of the polymer composites.

SWNTs of different contents ranging from 0.4 to 6 wt % were hybridized with PS spheres by the present approach and then the surfactants were removed by washing with alcohol. SEM was used to identify morphologies of the precomposites after drying. As a comparison, monodispersed PS spheres without SWNTs were collected with the same procedure. As shown in Figure 2(A), PS spheres packed closely and the spaces between spheres were several hundreds nanometers. A representative morphology of the hybrid was shown in Figure 2(B), where the cross section of the as-prepared PS spheres hybridized with 2 wt % SWNTs was presented. The SWNTs were located in the interstitial spaces of PS spheres and the overall dispersion was uniform. This result implies that it was possible to fabricate polymeric composites with SWNT networks using the hybrids of polymer microspheres and SWNTs.

The hybrids of PS spheres and SWNTs were fabricated into composite films by thermo-compression at

160°C . During this process, PS spheres fused and merged into a bulk material and meanwhile the SWNT network was expected to form in PS matrix. As the three-dimensional image of SWNT network was difficult to obtain, the composite was microtomed into a thin slice with thickness of 50–100 nm for TEM analysis. Although the PS spheres were pretty uniform, PS domains had been deformed during thermal treatment instead of keeping spherical shape and the microtomed thin slices gave an information of random network structure of composites. Shown in Figure 3(A,B) are representative TEM images of composite slices with 0.4 and 1.6 wt % SWNTs. The gray areas are neat PS phases and the isolated dark spots or fibers are attributed to the SWNTs and their bundles. From the sample with less tube content [Fig. 3(A)], it was observed that the PS matrix was hybridized with SWNT islands loosely. The network structure was found more clearly with increase of SWNT concentration as shown in Figure 3(B). The areas of neat PS matrixes ranged from submicro- to micrometers were surrounded by SWNT rich arrays. These results from thin slices implied that the composites should have such a structure that the continuous polymer phases are filled with the netting of carbon nanotubes like that of reinforced concretes. And this result is similar with the report from Grunlan's group recently.¹⁶

Furthermore, SEM was applied to identify SWNT morphology in the polymer matrix. As a comparison, a fracture section of the pure PS film compressed using the same PS sphere without SWNTs was observed by SEM [Fig. 4(A,B)]. The fracture surface was rough and showed plateau areas of several square micrometers. Figure 4(C) showed the fracture section of the composite sample where the SWNTs connected and formed networks. From the magnified

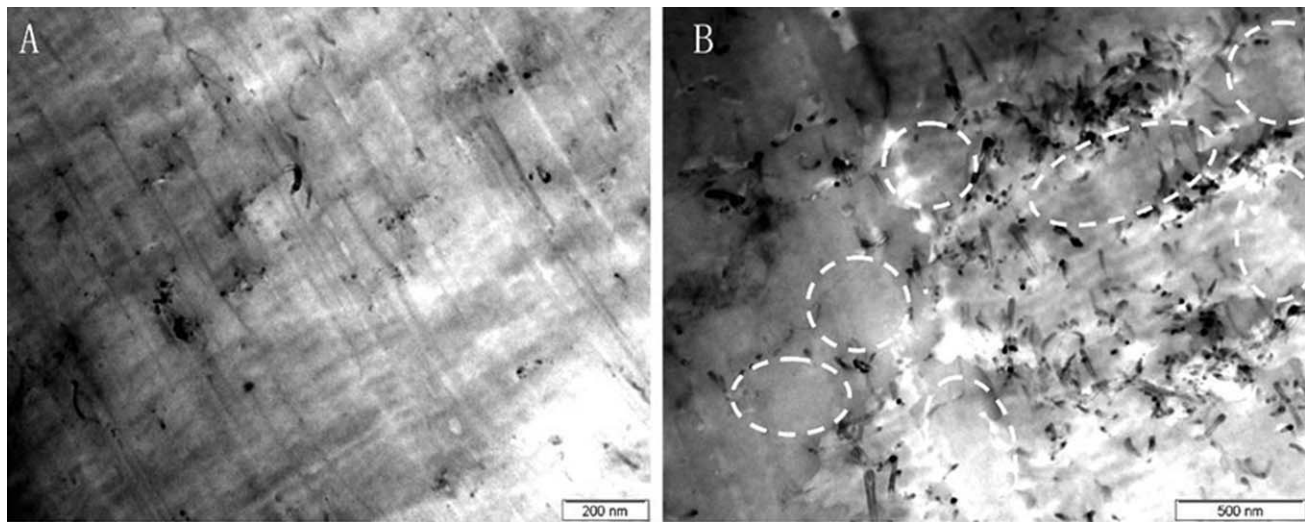


Figure 3 TEM images of microtomed sections of polymer composites containing (A) 0.4 wt % and (B) 1.6 wt % of SWCNTs.

view [Fig. 4(D)], it was clearly indicated that the knobbed areas were breakage of neat PS domains, and the SWNTs dispersed between these areas and

connected with each other. The results indicated that the PS/SWNT composite of network structure was successfully fabricated.

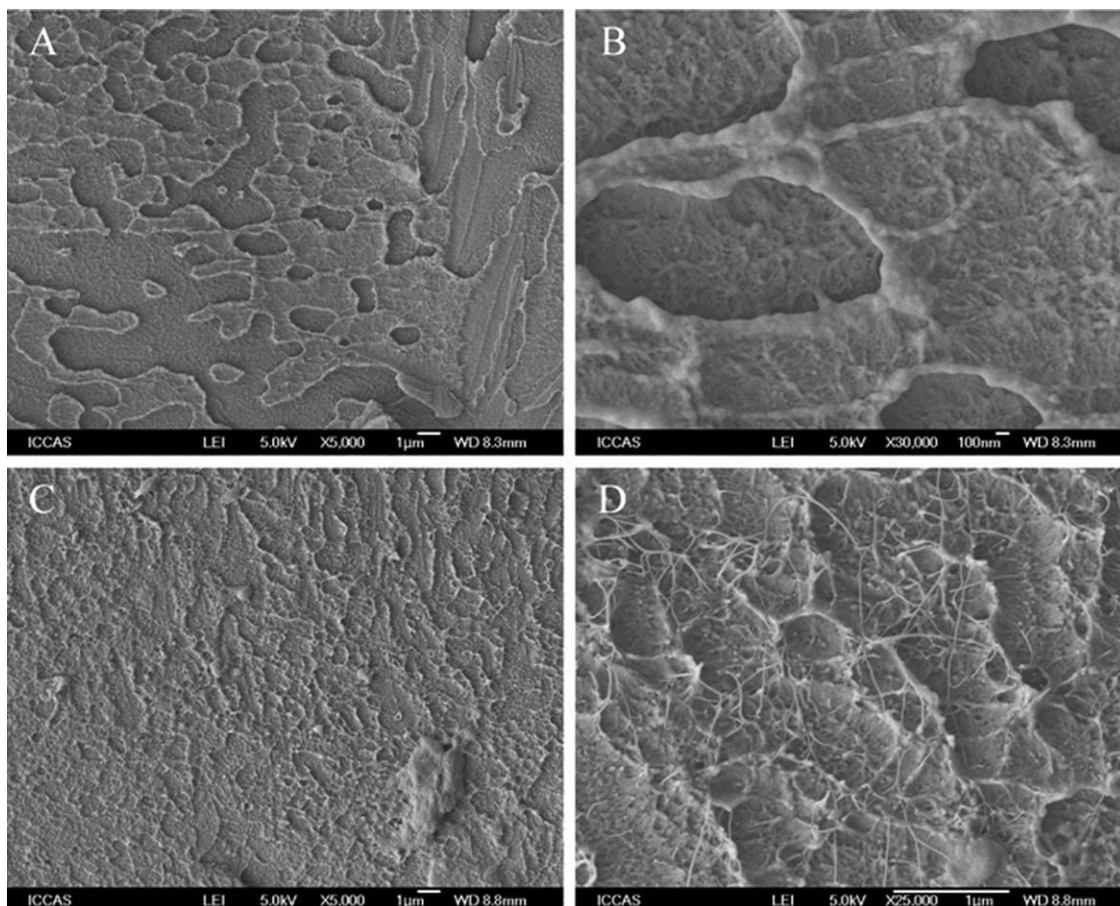


Figure 4 SEM images of the fracture sections of (A) pure PS film and (B) its magnification, (C) composites containing 1.6 wt % of SWNTs and (D) its magnification.

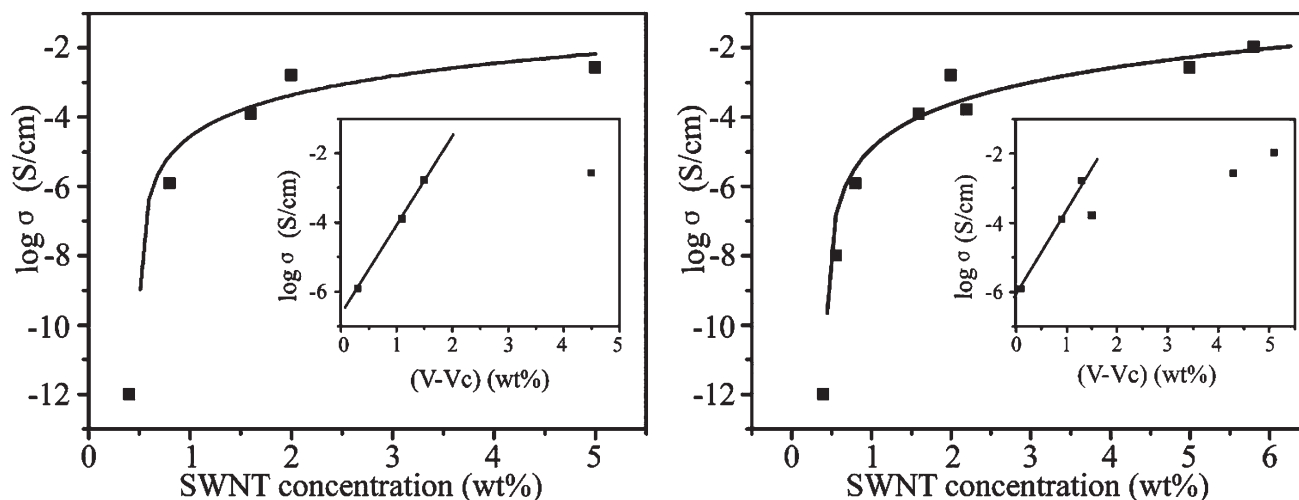


Figure 5 Volume conductivity of PS/SWCNT composites as a function of SWCNT content (A: SDBS system; B: Pluronic system).

Properties of PS/SWCNT composites

Electrical conductivity of the SWCNT composites fabricated by present procedure was measured using a standard four-point method. Figure 5 shows the effect of SWCNT content on the volume conductivity of PS/SWCNT composites. As we know, neat PS is an insulated material with a conductivity of about 1×10^{-12} S/cm. In contrast, there was a drastic increase in the electrical conductivity for the composites when the SWCNT content reached around 0.8 wt % in both SDBS and Pluronic system, indicating that the percolation threshold for formation of a conductive SWCNT network in the PS matrix is reached.

To study this result theoretically, the classical percolation theory is introduced,²² the conductivity follows a power law relationship as shown in eq. (1)

$$\sigma \propto (V - V_c)^c \quad (1)$$

where V is volume fraction of filler, V_c is volume fraction of percolation threshold, and c is critical exponent. c is related to system dimension and generally ranges from 1.6 to 2.0 by theoretical predication.²³

Herein, mass fraction of SWCNT was chosen instead of volume fraction because the density of nanotubes can only be roughly estimated and is similar with the volume fraction.²⁴ As shown in Figure 5, the electrical conductivity of PS/SWCNT composites agrees with the percolation behavior given by eq. (1). The best fitting to the experimental values resulted in V_c of 0.005 and c of 2.4 in SDBS system and 0.0072 and 2.04 in Pluronic system. These results meant the formation of three dimensional percolating network of a low percolation threshold at SWCNT loading of 0.5 wt % in SDBS system and 0.7 wt % in Pluronic system. According to Garboczi's results, the

percolation threshold for overlapping needles with an aspect ratio between 100 and 1000 is in the range of 0.1–1%.²³ As shown in the insets of Figure 5, at a higher concentration, $\log \sigma$ deviated from the straight line of conductivity versus $(V - V_c)$ of SWCNTs. This might be due to formation of the SWCNT bundles during fabrication where the SWCNTs reaggregated after the surfactants being washed away (shown in Fig. 3(B)). In this case, SWCNT bundles behaved more like multiwalled carbon nanotubes (MWNTs) because of their thicker diameter, where the conductivities of similar concentrations of MWNT fillers were lower than that of SWCNT.²⁵ It should be mentioned that the properties of polymer/SWCNT composites were decided not only by the dispersion state coming from fabrication methods but also the SWCNTs used (purity, defect density, and dimensions), so the difference of experiment results from different lab could be accepted.

CONCLUSIONS

We have successfully fabricated a kind of model PS/SWCNT composites by using PS spheres and filtration procedure. SDBS and Pluronic copolymer were used as dispersants of SWCNTs during fabrication, respectively, and they had been effectively removed by washing with solvents. After a compression molding, novel nanocomposites in which SWCNTs were woven into the continuous polymers were obtained and have showed a low percolation threshold of electrical conductivities. It is noteworthy that the size of SWCNT networks can be tuned by using PS microspheres of different size, implying that further understanding the properties of surfactant-free nanocomposites of polymer/SWCNT is feasible.

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