

Sensing Behaviors of Polymer/Carbon Nanotubes Composites Prepared in Reversed Microemulsion Polymerization

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ABSTRACT: Polystyrene/carbon nanotubes composites were readily prepared by reversed microemulsion polymerization. Compared with the composites prepared by solution mixing, the uniform dispersion of carbon nanotubes in polymer matrix could be obtained more easily and the thermal and electrical properties of the as-prepared composites were also enhanced. The as-prepared composites were deposited onto a microelectrode array to fabricate a vapor sensor. The response for different organic vapors was evaluated by monitoring the change in the resistance of the

composites upon exposure to various gases. The change in resistance was of the order of about 10^3 for the composites prepared by reversed microemulsion polymerization. The chemical sensors based on the composites prepared by reversed microemulsion polymerization presented excellent reproducibility and reversibility in response. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1842–1847, 2011

Key words: reversed microemulsion polymerization; polystyrene; carbon nanotubes; composites; sensors

INTRODUCTION

A variety of composite materials, which combine with the advantageous properties of both materials, have attracted increasing interest to materials scientists due to their unique physicochemical properties from the viewpoint of scientific research and practical applications.^{1–4} It is well known that carbon nanotubes (CNTs) are one of the most promising materials in many fields because of their unique combination of mechanical, electrical, and thermal properties. The advantage of incorporating CNTs into polymers is that they can perform many differ-

ent functions, making it unnecessary to add on extra, bulky components.^{5,6} Considerable attention has been paid to the preparation of polymer/CNTs composites with the improved properties^{7–9} and the application in many fields, such as electronics, photonics, catalysis, sensors, and biotechnology.^{10,11}

The detection of organic vapors is an important task in many technological fields, such as industrial processes, clinical diagnosis, and environmental monitoring. The gas-sensing behaviors of the sensors based on polymer/CNTs composites depend on their size, surface area, environmental stability, and mechanical and electronic properties.^{12–14} However, because of the weak interaction between CNTs and polymer, the aggregations of CNTs in the composites inevitably take place, leading to the low solubility of the composites in ordinary organic solvent and nonrealization of the expected enhancement in properties. Better spatial distribution and improved solubility of CNTs in the matrices and solvents are the key requirements for harnessing the maximum benefits from CNTs in sensors. Recently many efforts have been made to improve the interaction between CNTs and polymer by chemical modification of the CNT surfaces.¹⁵ Windle and coworkers synthesized polypyrrole/CNTs composites by an electrochemical method and observed that the dopants of CNTs improved

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both strength and conductivity of polypyrrole.¹⁶ Poly(methyl methacrylate)/CNTs composites were produced using an *in situ* radial polymerization.¹⁷ Viswanathan et al. and Kong et al. have prepared polymer/CNTs composites by anionic polymerization¹⁸ and atom transfer radical polymerization,¹⁹ respectively. Our group and other researchers have also reported the polymer/CNTs composites fabricated by microemulsion polymerization.^{20–23}

Herein, we fabricated and characterized polystyrene (PS)/CNTs composites by reversed microemulsion polymerization. This polymerization method has some merit over other emulsion methods because it produces thermodynamically stable tens of nm size polymer particles and employs the advantage of surfactants throughout polymerization. In reversed microemulsion, a reverse micelle is defined as an aggregate of surfactant molecules containing a nanometer-sized water pool in the oil phase. A variety of methods have been exploited to prepare metal, ceramic, and polymeric nanomaterials in reversed emulsions system.^{24–27} In this work, The higher surface area in CNTs provided more sites for anchoring PS chains. The solubility, electrical, and thermal properties of the as-prepared composites were characterized. Furthermore, we describe the application of PS/CNTs composites as chemical sensors for detecting organic vapors.

EXPERIMENTAL

Materials

CNTs raw materials were purchased from Shenzhen Nano-Technologies Port Co. Ltd (Shenzhen, China). The raw materials were further purified to remove the impurity phases according to the reported procedure.²⁸ The monomer of styrene was distilled to remove the inhibitors. Cetyltrimethylammonium bromide (CTAB) and potassium persulfate (KPS) from Aldrich were used as received. The other reagents were of analytical grade and were used as received unless otherwise mentioned.

Reversed microemulsion polymerization

KPS aqueous solution was added to the mixture of CTAB and CHCl_3 (mass ratio $m(\text{CHCl}_3)/m(\text{CTAB})/m(\text{H}_2\text{O}) = 7.5/2/2$) in a three-necked round-bottom flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until polymerization was finished. The mixture was stirred for 1 h until it became homogeneous. A different content of CNTs was added to the homogeneous solution and was sonicated for more than 2 h. Then styrene was

added. The mass ratio of CNTs/styrene was 2, 5, 8, 10, 12, 15, and 20%. The solution was stirred in an oil bath at 70°C for about 12 h. The sample had no odor, indicating that no monomer remained. The dispersion was added to methanol, and the mixture was allowed to stand overnight. The precipitation was filtered, washed with large amount of methanol and water, and dried in a vacuum at room temperature. For comparison, the composites by solution mixing were prepared by ultrasonication of CNTs and PS for 2 h in toluene.

Characterization

Transmission electron microscopy (TEM) analysis was carried out on a JEM-200 TEM CX instrument. Thermogravimetric analysis (TGA) of the composites was carried out on a TA Instruments 2100 thermogravimetric analyzer with a heating rate of 10°C/min. The glass transition temperatures of the composites were determined by differential scanning calorimetry (DSC) using Perkin–Elmer model DSC-2C system. Electrical conductivities the composites were measured by a conventional four-probe method. The sensing behavior of the PS/CNTs composites was characterized by measuring its resistance change upon exposure to various organic vapors at room temperature. The sensors were fabricated by coating 0.5 mL of the ethanol solution containing 0.1 wt % composites onto an interdigitated gold microelectrode (7 fingers on 1 cm × 1 cm resin substrate). The sensor was then dried in a vacuum oven at room temperature. It was finally mounted in a testing chamber (1000 mL) with gas inlet/outlet and electrical feed-through. The chamber was flushed with high-purity N_2 until the electrical resistance reached a steady value. Then, a certain amount of vapor was injected into the testing chamber with a syringe. The resistance change of the sensor was monitored at room temperature with a source meter connected to a computer. The response of the sensors was defined as the ratio of $(R - R_0)/R_0$, in which R_0 was the initial resistance of the composites before test and R was the time-dependent resistance of the composites exposed to the test gas.

RESULTS AND DISCUSSION

Figure 1 showed the typical TEM image of PS/CNTs composites prepared by reversed microemulsion. Before the reaction, the CNTs were hollow ropes with a rather smooth surface. Their diameter was in the range of 5–10 nm. After the reaction, the surface of the PS/CNTs composites is rougher, and the diameter of the PS/CNT composites further increases to 15–30 nm, which indicated that PS was coated onto the surface of CNTs.

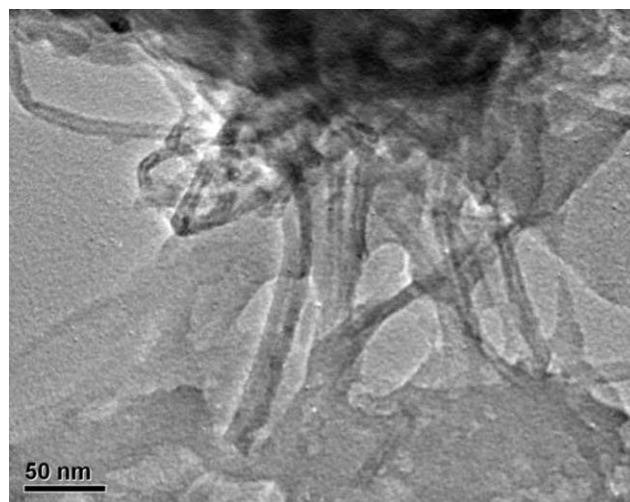


Figure 1 TEM image of PS/CNTs composites.

More changes in intrinsic polymer properties are expected to be brought about by the addition of CNTs. However, direct mixing of CNTs and PS leads to little change in the glass transition temperature of the PS matrix, as reported by Viswanathan.¹⁸ In our reversed microemulsion polymerization, as shown in Table I, the addition of a low amount of CNTs 2 wt % increased the glass transition temperature of the matrix from 105 to 111°C. Meanwhile, the temperature at 10 wt % loss of the composites also increases with the increase of CNTs concentration in the composites (Table I), as measured by TGA.

A critical issue in nanocomposites fabrication and processing is the uniform distribution and dispersion of nanofillers in the polymer matrices. CNTs are often agglomerated in the form of bundles as a result of very strong van der Waals interactions.²⁹ With the increase of CNTs, the color of the composites prepared by reversed microemulsion and solution mixing turned darker. For the composites prepared by solution mixing, only after one day the black precipitation appeared, presumably containing CNTs, from the dispersion solution of PS/CNTs composites after sonication for 2 h. However, PS/

TABLE I
Temperature at 10 wt % Loss of the Composites with Different CNTs Concentration Prepared by Reversed Microemulsion Polymerization

CNT concentration (wt %)	Temperature at 10 wt % loss (°C)	Glass transition temperature (°C)
0	325	105
2	343	111
5	356	112
10	363	112
15	365	113
20	366	113

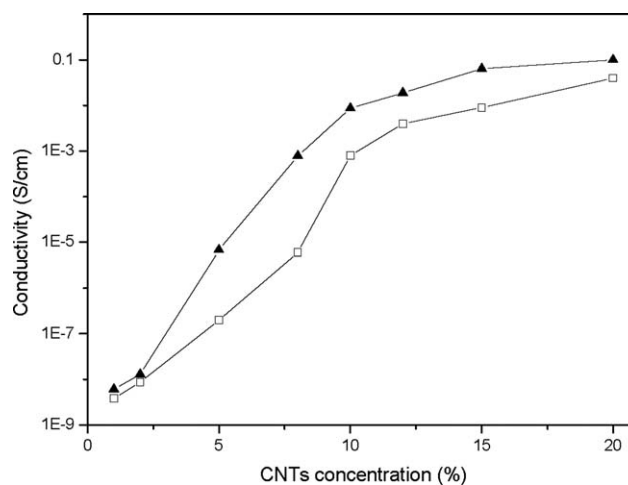


Figure 2 Conductivity of PS/CNTs composites. (▲) by reversed microemulsion polymerization; (□) by solution mixing.

CNTs composites prepared by reversed microemulsion formed a uniform dark dispersion in the ordinary organic solvent. The solution was still stable and no obvious precipitates could be observed even after more than 5 weeks. This suggested CNTs might participate in the polymerization of monomer and have strong interfacial interaction with attached polymer chains that impede flocculation and depletion aggregation phenomena in the process of reversed microemulsion polymerization. However, the interaction between PS and CNTs prepared by direct mixing is weak, which could be accounted for the separation of CNTs from the PS/CNTs solution after the cease of sonication.

The conductivities of the PS/CNTs composites were shown in Figure 2. The increase of the conductivities is typical of a percolation behavior. According to the percolation theory,³⁰ the data of conductivity versus the concentration was fitted as follows:

$$\sigma = \sigma_0(f - f_c)^t \quad (1)$$

where σ represents the conductivity of the composites; σ_0 is a constant; t is the critical exponent; f is the volume concentration of CNTs and f_c is the volume concentration of CNTs at the percolation threshold. The densities of CNTs and PS were assumed to be 2.04 g/cm³ and 1.18 g/cm³, respectively.²⁰ For the composite prepared by reversed microemulsion polymerization, the values of f_c and t were about 1.1 vol % and 3.81. While for those prepared by solution mixing, the values of f_c and t were about 4.5 vol % and 3.66. The values of t for both systems were similar to that in the previous report.³¹ The smaller volume concentration at the percolation threshold for the composites prepared by reversed microemulsion polymerization indicated that CNTs

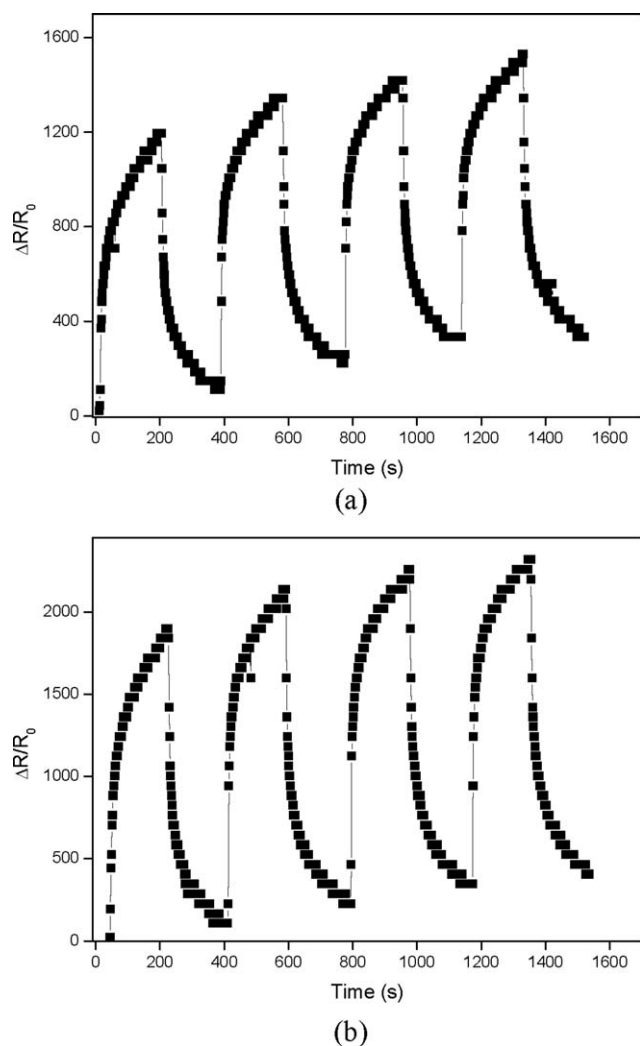


Figure 3 Reversibility in the response of PS/CNTs composite (CNTs 10 wt %) prepared by polymerization to (a) THF and (b) chloroform vapors.

formed better electrical conductive channel in the PS matrix in the process of reversed microemulsion polymerization than in solution mixing.

The reversible responses of the composites prepared by reversed microemulsion polymerization (CNTs 10 wt %) for periodic exposure to THF (230 mbar) and chloroform (130 mbar) vapors were shown in Figure 3. Upon exposure to the vapor, the swelling of the polymer matrix occurred due to the absorption of organic vapors, which increased the distance between the nanotubes and resulted in the disconnection of CNTs conductive channel. It was observed that there was a significant decrease of conductivity. After the subsequent removal of the vapor, the conductivity was found to recover due to the desorption of the absorbed molecules from the polymer matrix and reconnection of the separated CNTs in the composites. But the lost conductivity could not be completely compensated in this case, perhaps due to the inevitable presence of some re-

sidual vapors in the polymer matrix. The cyclic test presented similar responses more than four times. These manifested that the composites prepared by reversed microemulsion polymerization can be expected to be a good candidate for gas sensors.

The effect of the CNTs concentration on the sensing behavior was further studied. As shown in Figure 4, the composites prepared both by reversed microemulsion polymerization and by solution mixing showed the maximum responses at certain concentration of CNTs. In the case of low amount CNTs, tunneling effect contributed to the conduction in the composites to most extent besides the direct internal contacts. Though swelling upon exposure to vapor, the increase of the resistance due to destruction of the limited conduction paths built by the direct internal contacts should be less significant. While for high CNTs concentration, the excessive CNTs inevitably aggregated. It was difficult to destroy the conduction paths completely during the swelling of polymer matrix. Only at certain concentration, the conduction paths were mainly constructed by the bridged CNTs, which were easy to be broken down by the polymer swelling, and the maximum change of resistance appeared. As shown in Figure 4, the maximum response of the composites prepared by solution mixing appeared at higher CNTs concentration, and the maximum response was lower than that of the composite prepared by reversed microemulsion polymerization, which could be attributed to the poor dispersion of CNTs and the lower conductivity of the composites prepared by solution mixing. While during reversed microemulsion polymerization, the monomers were able to penetrate into the aggregated CNTs and result in better dispersion of CNTs in the subsequent polymerization. Lower concentration of CNTs was enough to construct conductive paths in

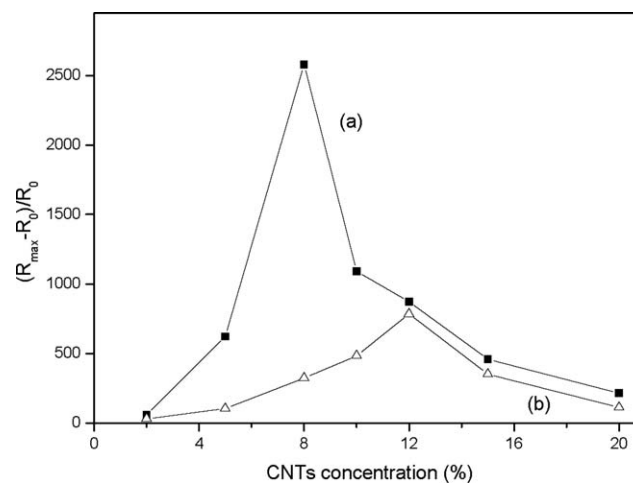


Figure 4 The effect of CNTs concentration on the sensing behaviors upon exposure of toluene. (■) prepared by reversed microemulsion polymerization; (△) prepared by solution mixing.

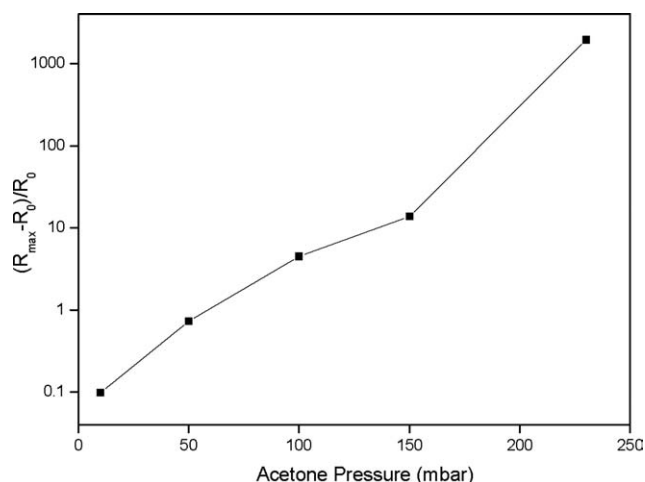


Figure 5 The response of the PS/CNTs composite (CNTs 8 wt %) prepared by reversed microemulsion polymerization to the partial acetone vapor pressure.

the composites, which was in accord with the result in Figure 2.

Figure 5 showed the response of the PS/CNTs composites to the partial vapor pressure at a given time (200 s). With the increase in the vapor pressure, the response of the resistance increased. When it was close to the vapor pressure of acetone at room temperature, a sharp increase in response was observed. The data in Figure 5 were semilog plots of the partial pressure dependence of the maximum resistance change, which was like the behavior of the polymer/carbon black composite.³² The sensor responses of PS/CNTs composites prepared by reversed microemulsion polymerization in various organic vapors were presented in Table II. The PS/CNTs composites showed high response to the organic vapors with different physicochemical parameters, such as acetone, toluene, tetrahydrofuran, chloroform, benzene etc., which were higher than those of the PS/CNTs composites (CNTs 20 wt %) prepared by solution mixing and those of the polymer/metal nanoparticles composites.^{33,34}

CONCLUSIONS

In summary, PS/CNTs composites with improved thermal and electrical properties were prepared in

TABLE II
Sensor Response of PS/CNTs Composite (CNT 8 wt %) Prepared by Reversed Microemulsion Polymerization

Different vapors	$(R_{\max} - R_0)/R_0$
Acetone	1.95×10^3
Toluene	2.58×10^3
THF	4.28×10^3
Ethyl acetate	3.34×10^3
Chloroform	2.83×10^3
Benzene	6.56×10^3

reversed microemulsion polymerization. The composites have better solubility in ordinary solvents than that of PS/CNTs prepared by direct solution mixing. The as-prepared PS/CNTs composites were readily integrated into the sensor device and were utilized as chemical sensors to detect organic vapors. Compared with the composites prepared by solution mixing, the composites prepared by reversed microemulsion polymerization showed a lower percolation threshold and significantly improved sensor performances. The ability to perceive chemical vapor may provide the feasibility for multifunctional sensors. Polymer/CNTs could be expanded to potential applications in the fields of actuators, switches, and memory cells.

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