Preparation and Characterization of Thermally Conductive Polystyrene/Carbon Nanotubes Composites

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ABSTRACT: Thermally conductive polystyrene (PS)/multi-walled carbon nanotubes (MWNTs) nanocomposites was prepared through a simple solution-evaporation method assisted by ultrasonic irradiation. To enhance the dispersion of MWNTs in PS, MWNTs were chemically functionalized with poly(styrene-*co*-maleic anhydride) (SMA) (MWNT-*g*-SMA), which had benzene group and exhibited strong affinity with PS. The thermal conductive properties of PS increased and the mechanical properties decreased in presence of MWNTs, while by addition of MWNT-*g*-SMA, the properties of the composites can be improved to some extent. The thermal conductivity can reach 0.89 W/m K for the composite with 33.3 vol % MWNT-*g*-SMA, which was four times higher than that of neat PS. A linear increase of the thermal conductivity was observed with increasing MWNTs-*g*-SMA content, and the Maxwell–Eucken model and the Agari model were used for theoretical evaluation. Compared with MWNT-OH, MWNT-*g*-SMA with larger diameter exhibited diffused boundary with the PS matrix, resulting from the strong interfacial bonding of the two phases. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2336–2342, 2010

Key words: polystyrene (PS); multiple-wall carbon nanotubes (MWNT); poly(styrene-*co*-maleic anhydride) (SMA); thermal conductive composites

INTRODUCTION

In recent years, the polymer composite materials with high thermal conductivity have attracted more and more attentions. General-purpose plastics, such as polyethylene, polypropylene, polystyrene (PS), etc., have already been widely used for electronic packaging. The new applications of dissipating the heat and maintain the operating temperature require new composites with high thermal conductivity.[1,2] By addition of thermal conductive fillers to plastics, the thermal behavior of polymers can be improved remarkably.

Varying kinds of fillers, such as metal, metal oxide, carbon black, carbon fiber, etc. have been applied to prepare the thermal conductive polymer composites with a component of 30–45 vol % polymer and 55–70 vol % filler. The thermal conductivity of these composites would be in the range of 1–4 W/m K.[3–11] Recently, polymer/carbon nanotubes (CNTs) nanocomposites have gained intensive interest because of their unique and valuable properties in mechanical, electronic, and thermal conductive properties compared with the pristine polymers.[6–11] One of the advantages of CNTs with high thermal conductivity of about 3000 W/m K at room temperature makes it as an ideal filler for the thermal conductive applications. However, the research on the topic of thermal conductive properties of CNTs/polymer composites, which is still needed, is far too less than those studies on the mechanical and electronic properties of the composites.[12–13]

The key point on the achievement of thermal conductive polymer/CNTs composites is the well dispersion of CNTs in the polymer matrix. CNTs are greatly influenced by Van der Waals attraction due to the small size and large surface area of nanoparticles. The force gives rise to the aggregates and makes the dispersion of CNTs in the polymer matrix difficult, resulting in poor mechanical, electronic, and thermal conductive properties. In this case, the improvement of the interaction between CNTs and polymer is of great importance not only for the dispersion of CNTs but also for the final properties of the composites.[6]

PS is a kind of general-purpose plastic with excellent dielectric property, good dimensional stability, low mold shrinkage, good chemical resistance, easily processing property, and low cost. It is widely used in the electronics industry, food packing, kitchen appliance, etc. In this work, multi-walled carbon nanotubes (MWNTs) were chemically functionalized for the purpose of the improvement of the dispersion in PS matrix. The PS/MWNTs composites were

studied in terms of thermal conductivity and morphology properties.

EXPERIMENTAL

Materials

The materials used in this research included: PS, 143E, was produced by BASF-YPC Co., (Germany); MWNTs containing hydroxyl groups (MWNT-OH) with an average diameter of 50 nm and a hydroxyl group content of 1.8 wt % was purchased from Chengdu Institute of Organic Chemistry (China), poly(styrene-co-maleic anhydride) (SMA) with a maleic anhydride content of 18 wt % was kindly provided by Petrochemical Research Institute of Shanghai (China); other chemical agents are all commercial grade products and used without further purification.

Sample preparation

Surface modification of MWNT-OH

Firstly, a certain amount of MWNT-OH was sonicated in dimethyl benzene. Then SMA was added and the mixture was heated up to 120°C, and kept at this temperature for 24 h. When the reaction was over, the grafted MWNT products (MWNT-g-SMA) were collected by centrifugal and washed by acetone.

Preparation of PS/MWNT-g-SMA composites

A simple solution-evaporation method assisted by ultrasonic irradiation was applied. The grafted MWNTs(MWNT-g-SMA) were dispersed in tetrahydrofuran (THF) by introduction of ultrasonic irradiation. Then PS was dissolved in the dispersion system at 60°C, and stirred for 6 h. The mixture was dried in the vacuum oven at 65°C for 24 h, and finally put into a mold and hot pressed at 190°C and 10 MPa.

Measurements

Fourier-transform infrared spetrum

The functionalized MWNTs sample was analyzed with Nicolet-560 Fourier transform infrared spectrometer (FTIR, USA).The pellet sample was prepared by pressing the mixture of MWNTs and KBr powder.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed with a TA2950 thermobalance equipment from TA Co.(USA) with the flow rate of 50 mL/min under air atmosphere. The samples of about 10 mg were heated from ambient temperature to approximately 800°C at a heating rate of 10°C/min. All samples were dried in the heating oven at 80°C for 2 h before the measurement.

Transmission electron microscope

The morphology analysis of the MWNTs sample was performed with JEM-100CX Transmission electron microscope (TEM, Japan). in solution. The MWNTs sample was diluted with ethanol and then dropped on a copper grid. The operating voltage was 20 KV.

Scanning electron microscopy

The surface morphology analysis of the tensile fractured samples was performed with JEOL JSM-5900LV scanning electron microscopy (SEM, Japan). The operating voltage was 20 KV.

Thermal conductive property

The thermal conductive properties of the composites were measured with a Hot Disk thermal analyser (Hot Disk AB, Uppsala/Sweden), which is based upon a transient technique. The measurements were performed with bulk specimens ($20 \times 20 \times 4$ mm^3) by putting the sensor (3 mm diameter) between two similar slabs of material. The sensor supplied a heat-pulse of 0.03 W for 20 s to the sample and the associated change in temperature was recorded. The thermal conductivity and thermal diffusivity of the individual samples were obtained by fitting the data according to Gustavsson et al.[14]

Mechanical property measurement

The tensile strength of the samples was measured with a 4302 material testing machine from Instron Co. (USA) according to ISO527/1-1993 (E). The test speed was 5 mm/min, and the sample length between benchmarks was 25 mm.

The notched charpy impact strength of the samples was measured with ZBC-4B impact testing machine from Xinsansi Co. (Shenzhen of China) according to ISO179-1993 (E).

RESULTS AND DISCUSSION

Functionalization of MWNT-OH

The effective use of CNTs in polymer composites requires excellent nanotube distribution and dispersion. It is necessary, therefore, to make a suitable modification on the surface of MWNT-OH so that they can be more evenly dispersed into PS matrix, resulting in a strong interfacial bonding between the two phases. In this work, SMA with benzene group
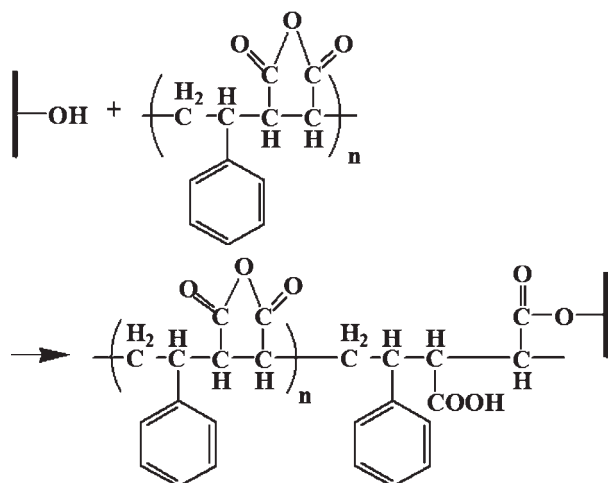
Figure 1   Functionalization of MWNT-OH with SMA.

was grafted onto MWNT-OH, which exhibited strong affinity with PS. The chemical reaction of MWNT-OH and SMA was shown as Figure 1.

The structure of MWNT-g-SMA was confirmed by comparison of FTIR spectra of MWNT-g- SMA with MWNT-OH, as shown in Figure 2. For MWNT-OH, the wide absorption band at 3430 cm^{-1} was attributed to the presence of hydroxyl groups (—OH) on the surface of MWNT. For MWNT-g-SMA, the new absorption peak at 1750 cm^{-1} was attributed to the carbonyl group on the molecules of SMA. The absorption peak at 1129 cm^{-1} was attributed to the stretching vibration of C—O—C group, and the absorption peaks at 1548–1455 cm^{-1} and 692.60 cm^{-1} were attributed to the fine structure of the double bonds and bending vibration of C—H group on the benzene ring of SMA, respectively. The result indicated that SMA has been grafted on to MWNT-OH successfully.
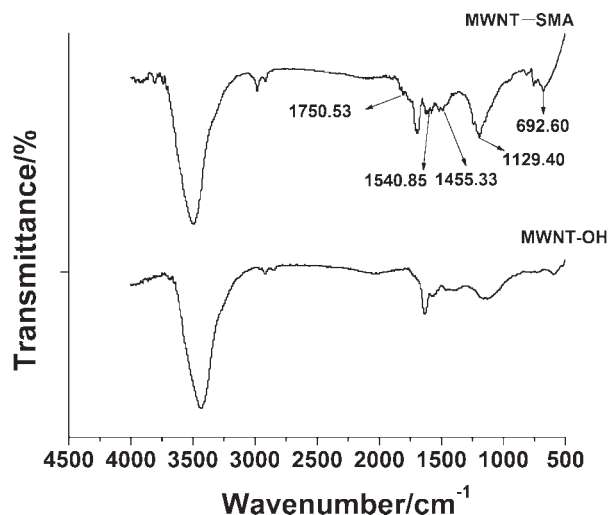

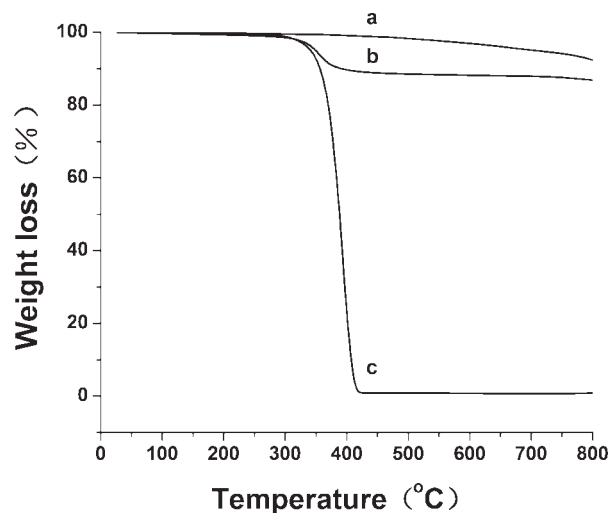Figure 2   FTIR spectrum of MWNTs.

Figure 3   TGA thermograms of MWNT functionalized with SMA (a) MWNT-OH, (b) MWNT-g-SMA, and (c) SMA.

Further evidence of the structure of MWNT-g-SMA has been provided by TGA. As shown in Figure 3, an obvious step of almost totally 100% weight loss in the thermogram of pure SMA sample was observed at 329–382°C, while there was almost no any weight loss for MWNT-OH sample in this temperature range, and 7.5% weight loss can be observed in the range of 480–718°C. Between these two extremes, a tiny step was observed at 329–382°C for MWNT-g-SMA sample and the weight loss was 12%, resulted from the grafted SMA.

Moreover, the percentage of carbon atoms in MWNTs grafted with the SMA can be estimated from the two-step weight loss of the samples according to the following equation.

$$GE \frac{W_1}{W_1 + W_2} \times 100\%$$

where GE was graft ratio, W_1 and W_2 were the weight loss and the weight of the residue of MWNT-g-SMA, respectively. Therefore, the graft ratio of SMA onto MWNT-OH can be calculated to be 4.5%.

The morphology of MWNTs was observed by TEM, as shown in Figure 4. It can be seen that the nongrafted MWNTs entangled densely in ethanol solution. In contrast, MWNT-g-SMA presented less agglomeration and its external diameter seemed to be increased remarkably, indicating that a uniform SMA layer has been formed around the sidewalls of MWNTs.

Morphology of PS/MWNTs composites

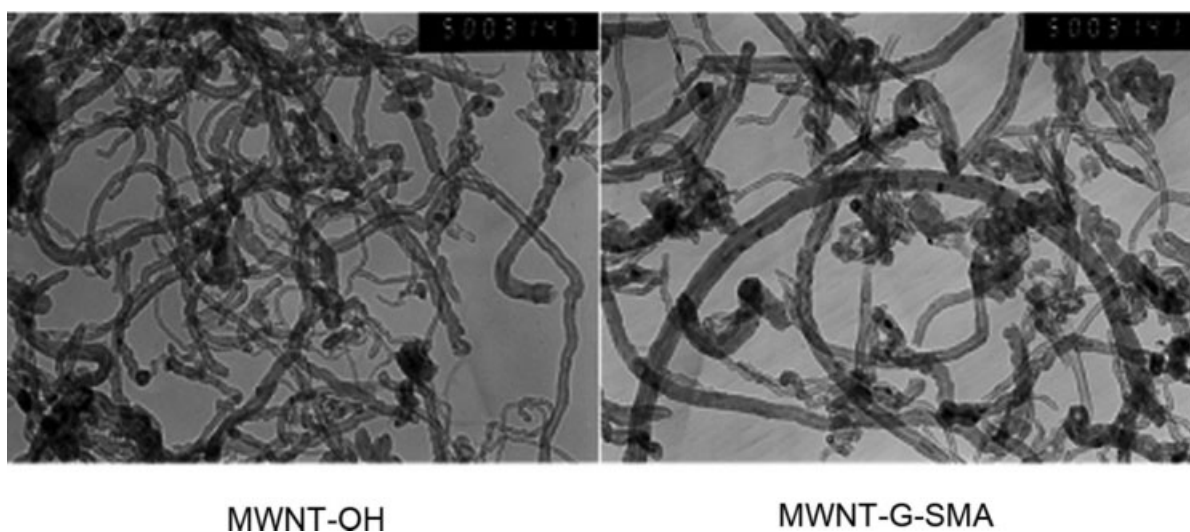The morphology of PS/5 vol % MWNT composites was observed by SEM. As shown in Figure 5, it was

Figure 4 TEM images of MWNT-OH and MWNT-*g*-SMA (magnification: 50000X).

found that both MWNT-OH and MWNT-*g*-SMA with fibril-like morphology dispersed uniformly in PS matrix and there was no obvious aggregation. Compared with MWNT-OH, the diameter of MWNT-*g*-SMA in the composite was relatively large, and the boundary of the two phases was diffused, indicating of the formation of the strong interfacial bonding of the two phases.

Effect of surface modified MWNTs on the property of PS/MWNTs composites

The thermal conductive properties of various PS samples were shown in Figure 6. It can be seen that the thermal conductivity of PS improved obviously by addition of 5 vol % MWNT-OH, while further improved by using 5 vol % MWNT-*g*-SMA, resulting from the improved dispersion of MWNT in PS ma-

trix and enhanced miscibility of the two phases, which facilitated to form the conductive network.

The mechanical properties of various PS samples were shown in Figure 7. It can be seen that the tensile and impact strength of PS decreased by addition of 5 vol % MWNT-OH. However, the mechanical properties of the composites can be improved to some extent by addition of 5 vol % MWNT-*g*-SMA, and especially the impact strength was close to that of the neat PS, resulting from the enhanced interfacial bonding between the two phases.

Effect of content of MWNTs on the thermal conductive property of PS/MWNTs composites

The thermal conductive properties of PS/MWNT-*g*-SMA composites versus MWNT-*g*-SMA content were shown in Figure 8. For the investigated system,
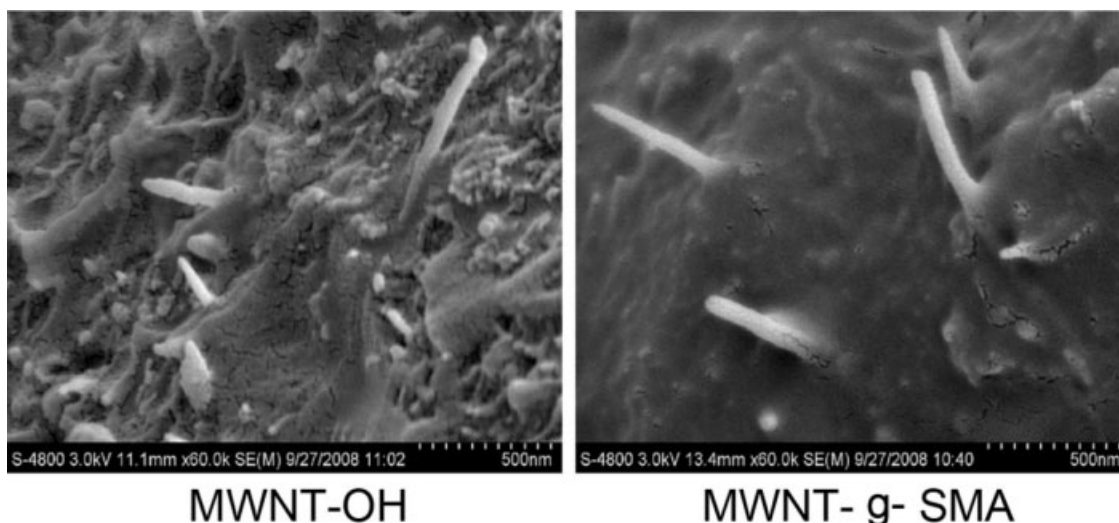

Figure 5 SEM micrographs of PS/5 vol % MWNT composites (magnification: 60000X).
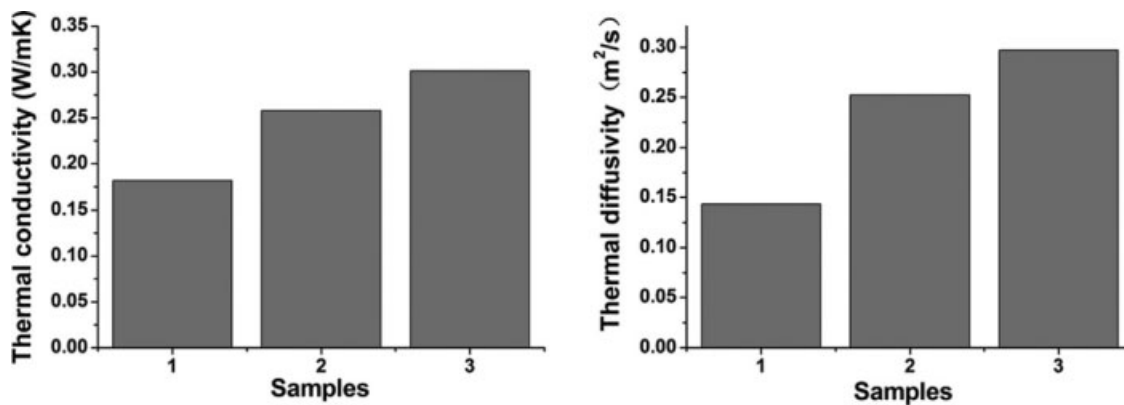
Figure 6 Comparison of thermal conductive properties of PS samples (1: PS 2: PS/5 vol % MWNT-OH 3: PS/5 vol % MWNT-g-SMA).

the thermal conductivity and thermal diffusivity increased linearly with an increase of the content of MWNT-g-SMA. No threshold was observed. The thermal conductivity was improved from the value of 0.18 W/m K for neat PS to the value of 0. 89 W/m K for the composite with 33.3 vol % MWNT-g-SMA.

Many theoretical and empirical models have been proposed to predict the thermal conductivity of two-phase mixtures. The Maxwell-Eucken model was used here to evaluate the thermal conductivity of the composites.

Maxwell-Eucken model

$$\lambda = \frac{\lambda_p[2\lambda_p + \lambda_f + 2V_f(\lambda_f - \lambda_p)]}{2\lambda_p + \lambda_f - V_f(\lambda_f - \lambda_p)}$$

where λ, λ_p and λ_f are the thermal conductivity of composites, polymer and filler, respectively; and V_f is the volume fraction of filler.

As shown in Figure 9, it was clear that the experimental data did not agree with Maxwell–Eucken model very well, and the experimental data were always higher than those predicted. The model

assumed that the shape of the filler was sphere, and the dispersion state of filler was confined to common dispersion state of the filler in the composites. However, the present case that the MWNT-g-SMA possessed fiber structure and the much better dispersion state of MWNT-g-SMA in PS matrix formed through surface modification and ultrasonic irradiation mixing was obviously beyond the presuming limits of the models, resulting in the improvement of the thermal conductivity of the composites.

The model of Agari was further applied to investigate the effect of the type of the MWNT-g-SMA on the thermal conductivity of the composites, which considered the effect of the dispersion state by introducing two factors C_1 and C_2:

$$\log \lambda = V_f C_2 \log \lambda_f + (1 - V_f) \log(\lambda_p C_1)$$

where λ, λ_p, and λ_f are the thermal conductivity of composites, polymer, and filler, respectively, V_f the volume fraction of filler, C_1 a factor relating to the structure of polymer, such as crystalinity of matrix, and C_2 is a factor relating to the measure of ease for the formation of conductive chains of filler. According
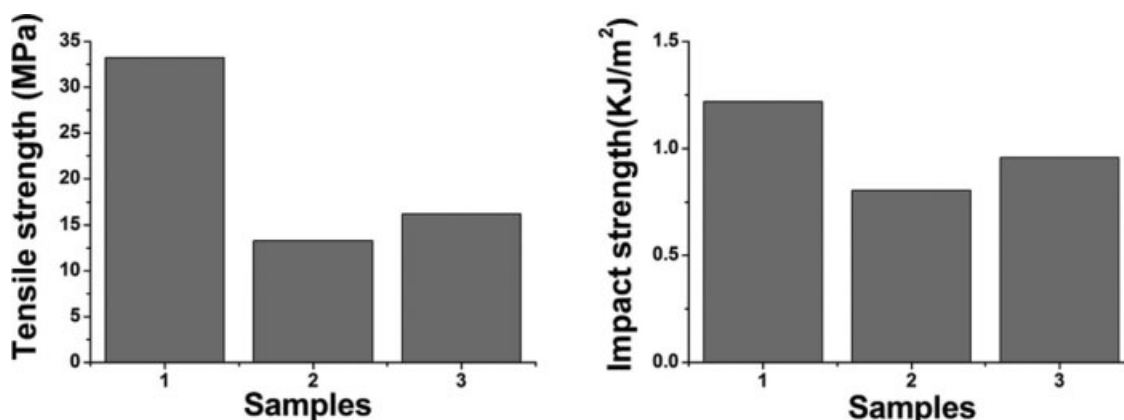

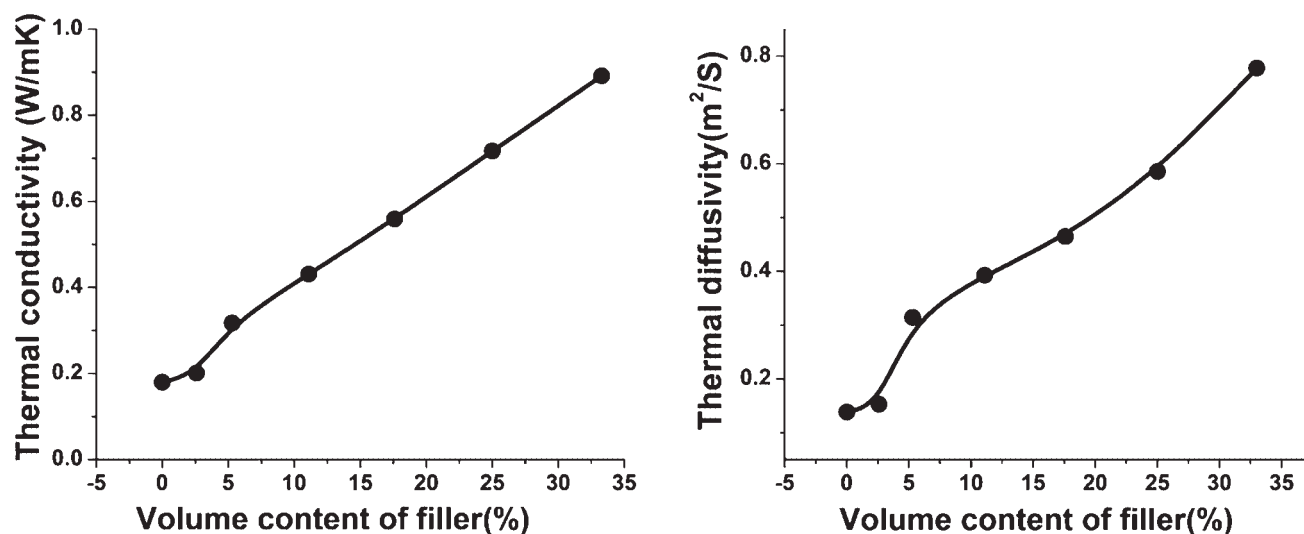**Figure 7** Comparison of mechanical properties of PS samples (1: PS 2: PS/5 vol % MWNT-OH 3: PS/5 vol % MWNT-g-SMA).

Figure 8 Effect of the volume content of MWNT-*g*-SMA on the thermal conductive property of PS/MWNT-*g*-SMA composites.

to Agari model, the closer C_2 values is to 1, the more easily conductive chains are formed in composites. Therefore, the thermal conductivity of composites may vary with the dispersion state of fillers, even if for the same composition of the composites. By fitting the experimental data into the model (as shown in Fig. 10), a possible explanation of the dispersion state of filler in composites could be obtained. C_1 and C_2 for PS/MWNT-*g*-SMA system were 1.667, 0.258, respectively. It was observed that the value of C_2 was far below 1, which indicated that the conductive channels could not form in the composite.

CONCLUSIONS

PS was compounded with MWNTs, which possess high thermal conductivity and large aspect ratio,
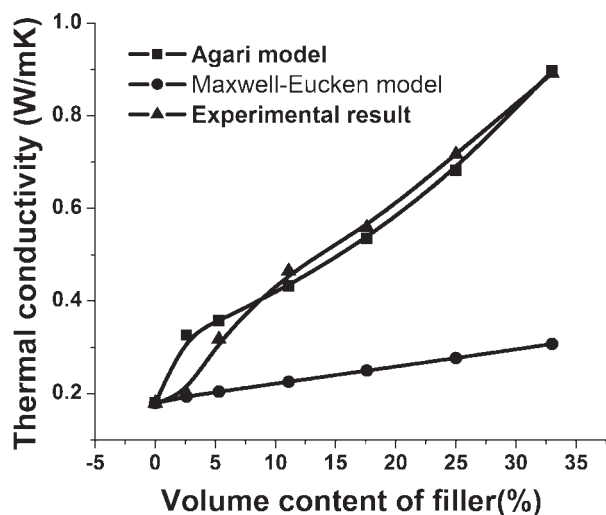
and the thermal conductive composites were prepared. To improve the dispersion of MWNTs in PS matrix, a simple solution-evaporation method assisted by ultrasonic irradiation was applied. Furthermore, MWNT was chemically functionalized with SMA (MWNT-*g*-SMA), which exhibited strong affinity with POM due to their similar molecular structure. The structure and the morphology of MWNT-*g*-SMA were characterized through FTIR, TGA, and TEM analysis. The thermal conductivity and the mechanical properties of the composites were investigated, which showed that the thermal conductive properties of POM increased and the mechanical properties decreased in presence of MWNT-OH, while by addition of MWNT-*g*-SMA, the properties of the composites can be improved to some extent. A linear increase of the thermal conductivity was observed with increasing MWNTs-SMA content, and the Maxwell–Eucken model and
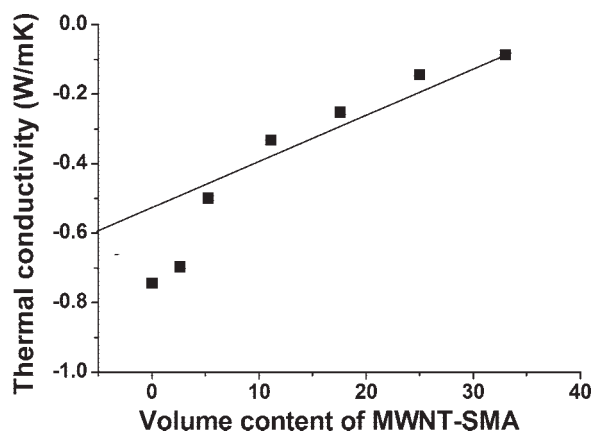

Figure 9 Comparison of experimental and predicted thermal conductivity of PS/MWNT-*g*-SMA composites.

Figure 10 Logarithms of thermal conductivity of PS/MWNT-*g*-SMA composites.

the Agari model were used for theoretical evaluation. It was observed that the value of C_2 was far below 1, indicating that the conductive channels could not form in the composite. However, SEM result indicated that both MWNT-OH and MWNT-g-SMA with fiber shape dispersed uniformly in PS matrix. Compared with MWNT-OH, MWNT-g-SMA presented relatively large diameter and the boundary with the matrix was diffused, exhibiting the strong interfacial bonding of the two phases.

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