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Improvement of thermal conductivity of poly(dimethyl siloxane) using silica-coated multi-walled carbon nanotube

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Abstract In order to enhance the thermal conductivity of MWCNT filled poly(dimethyl siloxane) (PDMS) composites, the MWCNT was coated with silica layer by three step reactions. The composites filled with raw and silica-coated MWCNTs were prepared and the properties were investigated in terms of the curing characteristics, mechanical properties, and thermal conductivity. Due to the poor compatibility between raw MWCNT and PDMS, raw MWCNT showed poor dispersion uniformity and wettability in PDMS. On the other hand, due to the chemical affinity between silica/MWCNT and PDMS throughout the hydrogen bonding, the silica-coated MWCNT filled PDMS showed improved mechanical properties in terms of tensile strength and 100% modulus, and good interfacial compatibility than raw MWCNT incorporated PDMS. Finally, the good wettability of silica/MWCNT in PDMS resulted in higher thermal conductivity caused from the facile phonon movement at the interface even with the smaller MWCNT contents.

Keywords PDMS · Thermal conductivity · Carbon nanotube · Silica

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Introduction

Carbon nanotube (CNT) composites for enhanced properties have been widely explored in materials science and engineering, in which CNT is used as a reinforcing filler or conducting filler. Since the CNT shows the extremely high thermal and electrical conductivity, and mechanical strength, a great attention has been paid to the application of CNT in electronics [1–4]. As the electronic devices need multifunction and high performance in a limited size, the thermal management of products has become more important. For example, a small difference in operating temperature in the order of 10–15 °C can result in a two-fold reduction in the life time of a device [5]. CNT has the one-dimensional unique structure, which enables the composites filled with CNT to have low percolation threshold concentrations [6, 7]. By using this characteristics, CNT incorporated composites show the thermal conductivity enhancement at low concentrations [8–10].

The improvement of thermal conductivity of polymer composites has recently received much attention since they are widely used in electronic packaging [11–13]. The materials used to efficiently dissipate heat are referred as thermal interface materials (TIM), which provide an effective heat conduction path [14]. Various types of TIMs are now present such as elastomeric thermal pads, thermal greases, solders, and phase change materials [15]. Among them, elastomeric thermal pads are most widely applied for cooling power devices, such as chip sets and mobile processors. And poly(dimethyl siloxane) (PDMS; silicone rubber) is the most frequently adopted TIM matrix [16, 17] due to its unique properties including a wide range of service temperature, high flexibility, chemical resistance, electrical insulating property, resistance to ozone and corona, and so on [18, 19].

For PDMS, silica is an essential filler because it greatly increases the mechanical property of PDMS caused by the hydrogen bonding [20]. Hydroxyl groups in the silica generate the hydrogen bonding with oxygen atoms in PDMS main chains. Therefore, the addition of silica together with CNT in PDMS is expected to optimize the mechanical property and thermal/electrical conductivity. The method for the synthesis of the silica layer on CNT has been recently explored by our group [21, 22]. Silica on the surface of CNT is expected to provide not only the mechanical strength increment but also enhanced dispersibility of silica-coated CNT in the PDMS matrix by superior wettability. By increasing the wettability between the filler and matrix, phonon waves can easily move through the interface between CNT and PDMS [23]. Ultimately, the thermal conductivity of composites can be increased.

Recently, we have published the effect of dispersion uniformity of CNT in PDMS using a masterbatch technique where the thermal conductivity was improved by about 10% compared to the poor dispersion using a conventional compounding process [24]. However, carbon materials are usually incompatible with PDMS. Therefore, in this work, MWCNT was encapsulated with the silica layer for imparting improved wettability between CNT and PDMS matrix in order to investigate the effect on the thermal conductivity of the PDMS/CNT composite. Finally, it was found that the encapsulated silica layer significantly assisted phonon wave transfer through the interface of silica/MWCNT and PDMS by enhanced interaction. Therefore, the thermal conductivity and mechanical properties were increased.

Experimental

Materials

Poly(dimethyl siloxane) (Mw = 674,000 g mol^{-1}, 0.1 mol% vinyl group) was supplied from KCC Co. (Korea). MWCNT (Hanwha Nanotech Co. Ltd. (Korea)) synthesized via a chemical vapor deposition (CVD) method has more than 95% purity. The diameter of MWCNT was 10–50 nm and the length was 10–50 µm, respectively. The aspect ratio was approximately 1,000.

For generating the hydroxyl groups on MWCNT, potassium permanganate ($KMnO_4$), methylene chloride, and methanol were purchased from Samcheon Chemical Co. Korea. Tetrapropyl ammonium bromide (TPABr) was received from Aldrich. Acetic acid was purchased from Duksan Chemical Co., Korea. For endowing the good interactions between MWCNT and silica precursor, a silane coupling agent, aminoethylaminopropyl trimethoxysilane (AEAPS) was purchased from Shin-Etsu Chemical Co., Japan. Ethanol, ammonium hydroxide (27% in water), and tetraethylorthosilicate (TEOS) from Samchun Chemical Co. were used for the fabrication of silica shell on MWCNT.

Preparation of the composites

Surface modification of the pristine MWCNT by silica was performed by three-step reactions [22]: (1) hydroxylation of MWCNT by an oxidant, $KMnO_4$, with the aid a phase transfer catalyst, TPABr, at room temperature, (2) coupling reaction between the hydroxyl groups on MWCNT and nitrogen containing AEAPS, and (3) sol–gel process of TEOS on the surface of AEAPS-modified MWCNT. With the high shear from two-roll mill, pristine and surface modified MWCNT were dispersed within the PDMS matrix. After the compounding process, roll milled PDMS was cured at 170 °C for 10 min using 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (DHBP, Akzo Nobel, The Netherlands) as a curing agent.

Characterization

A scanning electron microscopy (SEM) (S-4300, Hitachi) was used to observe the morphology of MWCNT and prepared composites. Thermogravimetric analysis (TG) was performed at a heating rate of 20 °C min^{-1} under atmospheric condition on TGA/SDTA 851. Thermal conductivity of prepared silicone pads was measured using QTM-500 (Kyoto electronics, Japan) and curing test was performed by using rubber process analyzer (RPA 2000, Alpha Technologies, USA) by following the ASTM D6204-99. Mechanical test was performed on Instron 5569® with a crosshead speed of 50 mm min^{-1}.

Results and discussion

By following the process reported by our group [22], MWCNT was successfully coated by the silica layer. Discernible differences can be found from the SEM morphology in Fig. 1. Silica shell on the MWCNT can be identified in Fig. 1b. Raw MWCNT in Fig. 1a shows the smooth surface compared with silica-coated MWCNT. The surface hydroxyl groups developed by permanganate together with a phase transfer catalyst, TPABr, are subsequently reacted with AEAPS to give amine group-terminated MWCNT. The opulent basic amine groups on modified MWCNT can activate acidic precursor (TEOS) by acid–base interaction with an assist from a basic catalyst (ammonium hydroxide). Due to the strong chemical attraction, MWCNT was evenly coated with silica and the thickness of silica shell can be readily controlled by adjusting the amounts of reagents. In TG thermograms as shown in Fig. 2, the MWCNT is completely decomposed above 700 °C under atmospheric condition and the silica is stable above 800 °C [25]. Therefore, it is possible to measure the amount of silica in silica-coated MWCNT above 650 °C, which is about 80 wt%. It is noted that the raw MWCNT started to decompose above 400 °C, while the silica-coated MWCNT started to decompose from the beginning of the experiment. The reason is because of the decomposition of hydroxyl groups and silane coupling agent attached for the fabrication of silica layer. Therefore, during the TG analysis, these functional groups were decomposed under 400 °C [22].

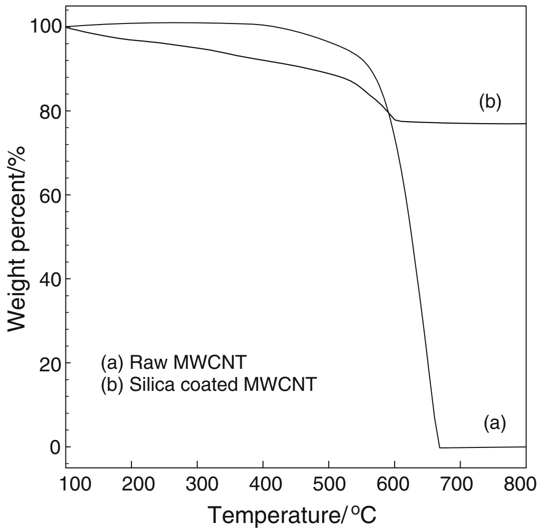

Fig. 2 TGA thermograms of (*a*) pristine MWCNT and (*b*) silica-coated MWCNT

In order to investigate the dispersibility and the wettability of MWCNT in the PDMS matrix, the prepared PDMS composite pads containing 0.5 phr pristine and silica-coated MWCNT were cryogenically fractured and the morphology of the cross section was examined. In Fig. 3a, the MWCNT was observed out of matrix. Due to the poor wettability between the PDMS and pristine MWCNT, the protruded MWCNT appears at the cross section. Also, MWCNT is not uniformly dispersed in PDMS. On the other hand, silica-coated MWCNT is well dispersed. More importantly, the bare surface of the MWCNT is hardly observed. Due to the excellent wettability between silica layer and PDMS, the silica-coated MWCNT is not pulled out. This result implies that the interfacial interaction would be good enough to give enhanced thermal conductivity and mechanical properties.

Curing test of the raw and silica-coated MWCNT incorporated PDMS was performed using the RPA2000®. Each phr for the silica-coated MWCNT indicates the amount of the sum of the silica and net MWCNT. In Fig. 4a, the maximum torque of pristine MWCNT incorporated PDMS increases from 2.6 to 3.4 dNm with the increment of

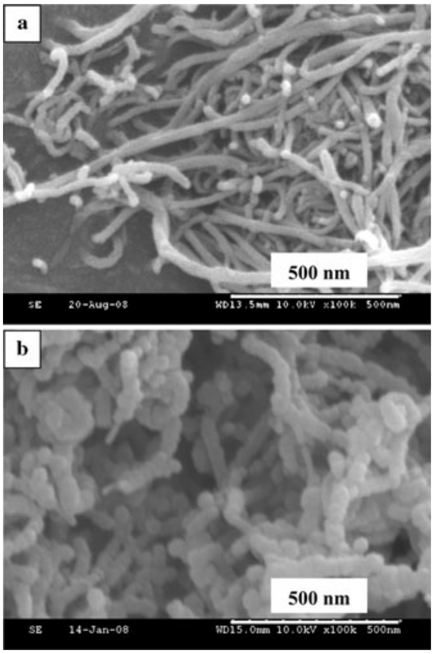

Fig. 1 SEM microphotographs of **a** raw MWCNT and **b** MWCNT with silica shell

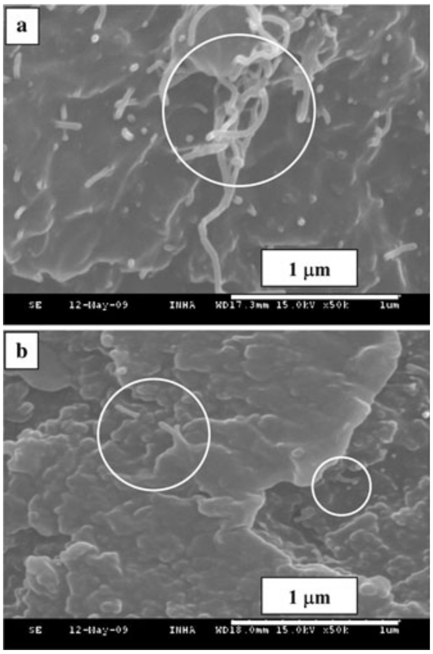

Fig. 3 SEM microphotograph of **a** 0.5 phr pristine MWCNT incorporated PDMS and **b** 0.5 phr silica-coated MWCNT incorporated PDMS

the amount of MWCNT from 0.1 to 2.0 phr. Due to the reinforcing effect of MWCNT on various polymer-based nanocomposites [26, 27], the maximum torque of the composite naturally increases. In the MWCNT incorporated PDMS nanocomposites, the reversion is not observed for prolonged time span because PDMS has excellent thermal stability at high temperatures. Silica-coated MWCNT incorporated PDMS shows a higher maximum torque at the same MWCNT concentration attributed to the improved reinforcement effect throughout hydrogen bonding between silica layer on MWCNT and PDMS. Also, the scorch time of the silica-coated MWCNT filled composites is shorter than that of pristine MWCNT filled PDMS at the same concentration of MWCNT. With improved interfacial property, i.e., wettability, the heat supplied from the surface of the composites can easily penetrate into the center of the composite. Eventually, the temperature of the composite is rapidly increased so that the crosslinking reaction starts fast, resulting in the reduction in scorch time. Also, this result is related to the fact that the silica-coated MWCNT has a higher thermal conductivity.

The good wettability is necessary for the enhanced mechanical properties of composites. Figure 5 shows the tensile strength, elongation at break, and 100% modulus of the composites filled with pristine and silica-coated MWCNTs. Tensile strength of the composites increases with increasing raw MWCNT and the opposite result is observed for the silica-coated MWCNT since the stiffness of the composites is greater as seen in the increase in 100% modulus due to the excellent reinforcing effect. Accordingly, the elongation at break significantly is reduced for silica-coated MWCNT filled PDMS due to the increased stiffness. These phenomena are often obtained with strongly reinforcing fillers in most polymer composites. Consequently, these results suggest that the silica layer on the surface of the MWCNT gives superior interactions with PDMS.

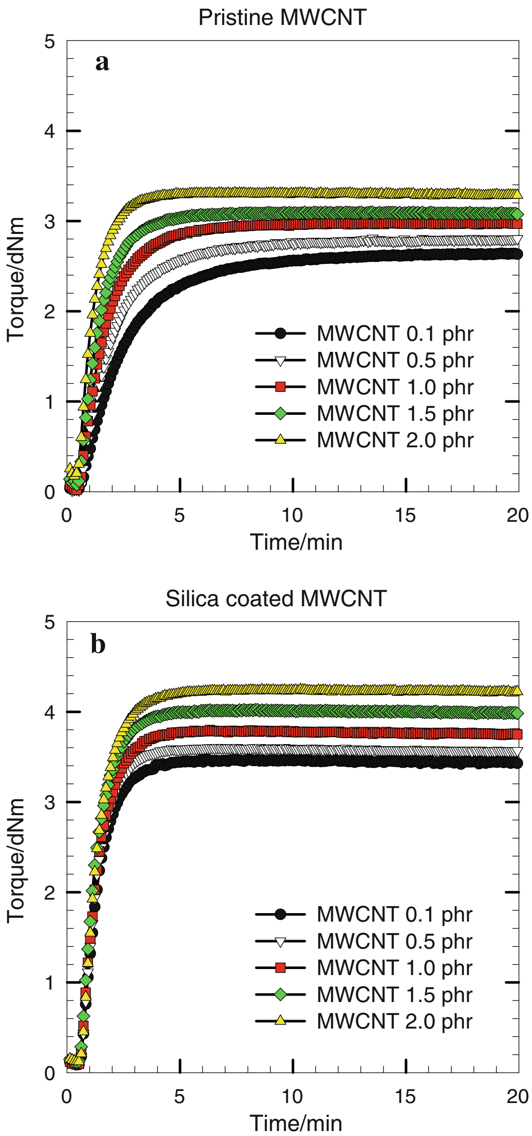

Fig. 4 Cure curves of 0.1, 0.5, 1.0, 1.5 and 2.0 phr. **a** Pristine MWCNT incorporated MWCNT and **b** silica-coated MWCNT incorporated PDMS at 170 °C

Thermal conductivity of the composites is represented in Fig. 6. Thermal conductivities of both raw and silica-coated MWCNTs filled PDMS composites are linearly increased with the amount of MWCNT as expected. Zeng et al. also reported the linear thermal conductance enhancement of MWCNT-palmitic acid nanocomposite with the low incorporation of MWCNT [28]. Herein, for raw MWCNT incorporated PDMS, the thermal conductivity increases from 0.208 (0.1 phr) to 0.230 W m^{-1} K^{-1} (2.0 phr). Although MWCNT has excellent thermal conductivity about 3,000 W m^{-1} K^{-1}, the result shows only 10% enhancement when 2 phr pristine MWCNT is added. As the raw MWCNT aggregates in the PDMS matrix, it gives poor dispersibility and prevents the percolation of MWCNT in the matrix. Finally, the thermal conductivity of the composite is lowered than expectation. It is noted that the thermal conductivity of 0.1 phr MWCNT incorporated PDMS is expected to be 0.24 W m^{-1} K^{-1} [29] according to a following thermal conductivity model;

$$\frac{K_e}{K_m} = 1 + \frac{fp}{3}\frac{K_C/K_m}{p + \frac{2a_K}{d}\frac{K_C}{K_m}} \qquad (1)$$

where a_K is Kapiza radius. Also d, p, and f are the diameter, aspect ratio (1000 for MWCNT), and volume fraction of MWCNT, respectively.

When the silica-coated MWCNT is incorporated in the PDMS matrix, thermal conductivity is greatly improved, compared to that of raw MWCNT. For example, the thermal conductivity of composites shows the 10% improvement at 0.1 phr silica-coated MWCNT. Thermal conductivity of silica-coated MWCNT incorporated PDMS is also

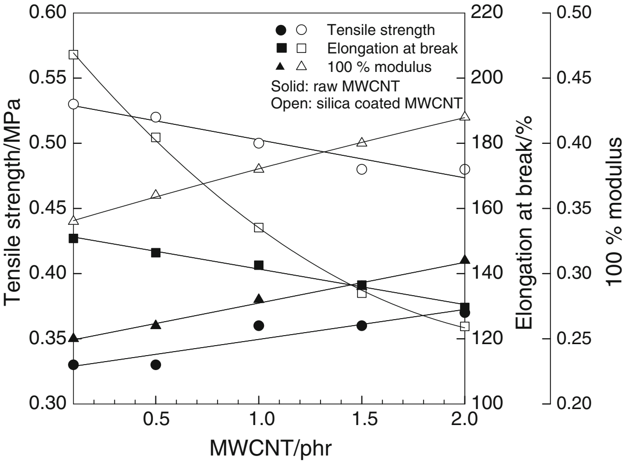

Fig. 5 Tensile strength, elongation at break, and 100% modulus of raw and silica-coated MWCNT incorporated PDMS with different concentrations of MWCNT (*solid*: raw MWCNT, *open*: silica-coated MWCNT)

increased as the amount of silica-coated MWCNT increases since the net amounts of silica and MWCNT correspondingly increase. In spite of the low thermal conductivity of the amorphous silica around 1.3 W m^{-1} K^{-1}, the thermal conductivity of silica-coated MWCNT incorporated PDMS shows the higher values than the raw MWCNT incorporated PDMS, implying that the improved wettability is the major factor to enhance the thermal conductivity of this system. As the silica has good wettability and compatibility with PDMS matrix, phonon waves easily pass through the interface between silica/MWCNT and PDMS. As a result, the thermal conductivity of the composites is increased for the silica-coated MWCNT incorporated PDMS. It is noted that the lower slope for the silica-coated MWCNT filled PDMS is simply ascribed to the reduced net amount of MWCNT in silica-coated MWCNT.

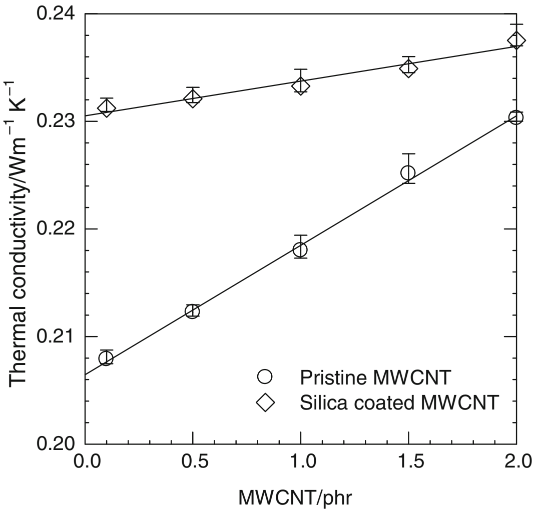

Fig. 6 Thermal conductivity of pristine MWCNT and silica-coated MWCNT incorporated PDMS composites

Conclusions

Surface modification of the pristine MWCNT by silica layer was performed by three step reactions: (1) hydroxylation of MWCNT by an oxidant with the aid a phase transfer catalyst at room temperature in order to minimize the structural damage of MWCNT, (2) coupling reaction between the hydroxyl groups on MWCNT and amino group containing silane coupling agent (AEAPS), and (3) sol–gel process of TEOS on the surface of AEAPS-modified MWCNT. The surface modification of MWCNT by silica was confirmed by SEM. TG analysis revealed that silica content was about 80 wt%. After compounding with PDMS, raw and silica-coated MWCNTs incorporated PDMS composites were tested in terms of curing reaction, interfacial property, mechanical properties, and thermal conductivity. Due to the poor compatibility between carbon atoms in MWCNT and silicon atoms in PDMS, raw MWCNT showed poor dispersion uniformity and wettability in PDMS. On the other hand, due to the chemical affinity between silica/MWCNT and PDMS throughout the hydrogen bonding, the silica-coated MWCNT filled PDMS showed improved mechanical properties in terms of tensile strength and 100% modulus, and good interfacial compatibility than raw MWCNT incorporated PDMS. Ultimately, the good wettability of silica/MWCNT in PDMS resulted in higher thermal conductivity even at a smaller net amount of MWCNT originating from the facile phonon movement at the interface.

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