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Preparation and characterization of conductive carbon nanotube-polyurethane foam composites

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Abstract Electrical, thermal, and morphological properties of the polyurethane foam (PUF)/multiwall carbon nanotube (MWCNT) composites were investigated with the MWCNT content. Electrical conductivity of the PUF/MWCNT composites increased rapidly from 0 to 0.23 S/cm at 0.1 php MWCNT content, then, the electrical conductivity did not change significantly with the increase of MWCNT content up to 0.5 phr because of the aggregation of the MWCNT when the amount of MWCNT was large (0.5 php). The PUF/MWCNT composite having low MWCNT contents (0.01, 0.05, and 0.1 php) showed lower thermal conductivity than that of the PUF/MWCNT composite having higher content (0.5 php). This is maybe due to that the PUF with the lower MWCNT contents (0.01, 0.05, and 0.1 php) showed smaller cell size than that of the PUF with the higher content of MWCNT (0.5 php). From the results of thermal conductivity and cell size of the PUF/MWCNT composites, it is suggested that reduction in cell size of the composite affects lowering the thermal conductivity of the PUF/MWCNT composites. Also, small amount (0.01, 0.05, and 0.1 php) of MWCNT may contribute to decrease the thermal conductivity of the PUF/MWCNT composites.

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Introduction

Conductive polymers and their composites are of great research interest because of their wide range of applications in batteries, sensors, electronics, etc. [1–4]. Polymer and multiwall carbon nanotube (MWCNT) composites show high electrical conductivity at low MWCNT concentration [5–9]. The low percolation threshold achieved in the polymer blend systems was attributed to the localization of the conductive fillers in one phase or at the interface of the composite [10]. During processing, the composite is in the state of melt, solution, or liquid, as in the case of epoxy. Flow or shearing applied to facilitate conductive filler dispersion both can disturb conductive network formation. At the same time, conductive nano fillers tend to reaggregate [2].

The polyurethane foam (PUF) is widely used as a thermal insulating materials in building, liquefied natural gas storage, transportation, and refrigeration industries. Thermal conductivity of PUF is influenced by thermal conductivities of blowing agent and solid polymer of PUF itself, and cell size of the PUF. When blowing agents and solid polymer are fixed, the improvement of thermal conductivity of the PUF can be achieved by reducing cell size of the PUF. Many researchers have extensively studied to improve thermal insulation property of PUF by reducing cell size and improving uniformity of the morphology in the PUF [11–20].

The foaming process can be explained by the nucleation and the cell growth mechanism [21, 22]. First of all, many bubbles are generated if there are many nucleation sites during the process and PUF have small and uniform cellular structure can be produced if coalescence of bubbles is prohibited by controlling reaction parameters or reducing surface tension of solution during the growth phase of PUF.

There are possible nucleation sites such as blowing agent in the polyol and diisocyanate compound, other dissolved gas or air bubbles hiding on the surface of the materials [23].

The low concentration of well-dispersed nano-particles in the polyurethane matrix may yield copious bubble nucleation by reducing the critical activation energy for nucleation. From the results of the recent investigations, nano-particles effectively reduced the cell size of the PUF during foaming process [24–26]. Especially, the presence of nano-particles resulted in a pronounced the improvement of electrical and thermal properties.

Studies of PUF and MWCNT composites are difficult to find by other researchers. Therefore, it is thought that electrically conductive PUF with the MWCNT is worth to study since the PUF has shown only the thermal insulating properties so far. In this study, we synthesized PUF/MWCNT composites with the MWCNT by treatment of milling and hydrogen peroxide (H_2O_2). Morphologies, electrical, and thermal conductivities of the PUF/MWCNT were measured by scanning electron microscopy (SEM), digital multimeter electrical conductivity analysis, and thermal conductivity analyzer, respectively.

Experimental

Materials

All the materials used in this study were obtained from commercial sources. Polymeric 4,4′-diphenylmethane diisocyanate (PMDI) was supplied by BASF Korea, Ltd. (Korea). The average functionality of PMDI was 2.7, and the NCO content was 31.5 wt%. The equivalent weight and viscosity of PMDI were 135.0 g/mol and 550 cps, respectively. Pentaerythritol-based polyether polyol (OH value = 470), supplied by KPC Co. (Korea), was used for the preparation of the nanocomposites. The multiwall carbon nanotube (MWCNT) was supplied by JEIO Co. (Korea). Air Products and Chemicals, Inc. (Hamilton, PA), was used as a catalyst. Poly(siloxane ether), used as a surfactant, was supplied by Osi Specialties, Inc. (Sistersville, WV). Other chemicals were used as received. The MWCNT was treated with ball-milling, then the MWCNT was functionalized by treating with the hydrogen peroxide (H_2O_2). The ball-milling was used to reduce the length of the MWCNT, with a 400 alumina-balls at 400 rpm for 1 h. Without reducing the length of the MWCNT, it was difficult to prepare the proper foam samples. For the H_2O_2 treatment of MWCNT, a 1.5 g sample of MWCNT was sonicated with 500 mL of 98% H_2O_2 at room temperature for 90 min. The concentration of the silane coupling agent was 0.1 parts per hundred grams of polyol by weight (php). Table 1 shows the chemical compositions for the preparation of polyurethane foam (PUF)/MWCNT composites.

Composite preparations

The rigid PUF sample was prepared by mixing both polyol and the polymeric 4,4′-diphenylmethane diisocyanate (MDI) at 25 °C using a mechanical stirrer. When the PUF sample is synthesized at high speed, the additives do not disperse homogeneously and the additives are aggregated each other. Therefore, the mixing was started from a speed of about 100 rpm and it was gradually increased to 3,000 rpm for 5 min when the MWCNT is added to polyol solution. The amount of MWCNT added was 0.01, 0.05, 0.1, 0.3, and 0.5 php. Then, distilled water, catalysts, and surfactant are added to polyol solution and they are mixed for 60 s at 3,000 rpm using the stirrer until the mixture becomes a homogeneous phase. After mixing, cyclopentane was put into the polyol mixture and mixed again for 10 s using brushless type at 3,000 rpm. Since cyclopentane is very volatile, it is stored in a refrigerator before mixing. After that, MDI is added into the polyol mixture prepared by the process mentioned above at the rotation speed of 5,000 rpm for 10 s at room temperature. Finally, the mixture is immediately poured into an open mold (250 mm × 250 mm × 250 mm) to produce free-rise foams, which is kept at room temperature for 10 min. The foam is then removed from the open mold and it is cured at room temperature for at least 1 day before characterization.

Thermal conductivity

Thermal conductivities of PUF/MWCNT composites were measured with a thermal conductivity analyzer (model TCA Point2, Anacon) according to ASTM C518. PUF sample was placed in the test section between two plates which are maintained at different temperatures during the test. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, dimension of the specimen was 200 mm × 200 mm × 25 mm (width × length × thickness). The thermal conductivities of three specimens per sample were measured and averaged.

Electrical conductivity

Measurements of volume electrical conductivity were carried out on the specimen of the PUF/MWCNT composite (15 mm × 15 mm × 5 mm) (width × length × thickness). The composite samples were pressed in the space between two conductive gold coated disc electrodes of 30 mm in diameter. The Pressure was 10 N. Both electrodes were connected to a power supply (Zahner mess Technic, Model

Table 1 Compositions of the materials used in the preparation of rigid polyurethane foam and carbon nanotube composites

Chemicals	Description	Weight (g)
MDI	4,4′-Diphenylmethane diisocyanate	143.0
Polyol	Polyether type	100.0
Surfactant	Silicone type	2.0
Blowing agents	Cyclopentane/Water	6.0/1.0
Catalyst	Amine type	1.5
Additive	MWCNT	0.01, 0.05, 0.1, 0.3, 0.5

IM6ex potentiostat) and a digital multimeter (Keithley, Model 2000 multimeter).

Morphology

Morphology of PUF/MWCNT composite was studied with a field emission scanning electron microscope (FE-SEM) (Hitachi Model S-4300SE, Tokyo, Japan). The samples were cryogenically fractured and the surface was coated with gold before scanning. The accelerating voltage was 25 kV.

Results and discussion

Electrical conductivity

Figure 1a, b shows the scanning electron micrographs of the MWCNT before and after ball-milling for 1 h, respectively. From Fig. 1, the length of the MWCNT after milling was found to be 1.08 μm with standard deviation of 0.39 μm. For comparision, the length of the MWCNT before milling was about 3.50 μm. After milling of the MWCNT, it was able to prepare the PUF/MWCNT sample properly.

Figure 2 shows the electrical conductivity of the PUF/MWCNT composites with the MWCNT content. From Fig. 2, electrical conductivity of the PUF/MWCNT composites increases rapidly from 0 to 0.23 S/cm at 0.1 php MWCNT content. Then, the electrical conductivity does not change significantly with the increase of MWCNT content up to 0.5 php. When the amount of MWCNT is increased, the cells of the PUF composite are destroyed by the MWCNT. Therefore, the electrical conductivity of the PUF/MWCNT composite does not increase with the increase of the MWCNT content. This is also maybe due to that when the amount of MWCNT is large (0.5 php), the MWCNT is aggregated compared the amount of MWCNT is small (0.01 and 0.05 php). When the MWCNT is added more than 0.5 php, it was difficult to produce proper PU foam structure because of the MWCNT entanglement.

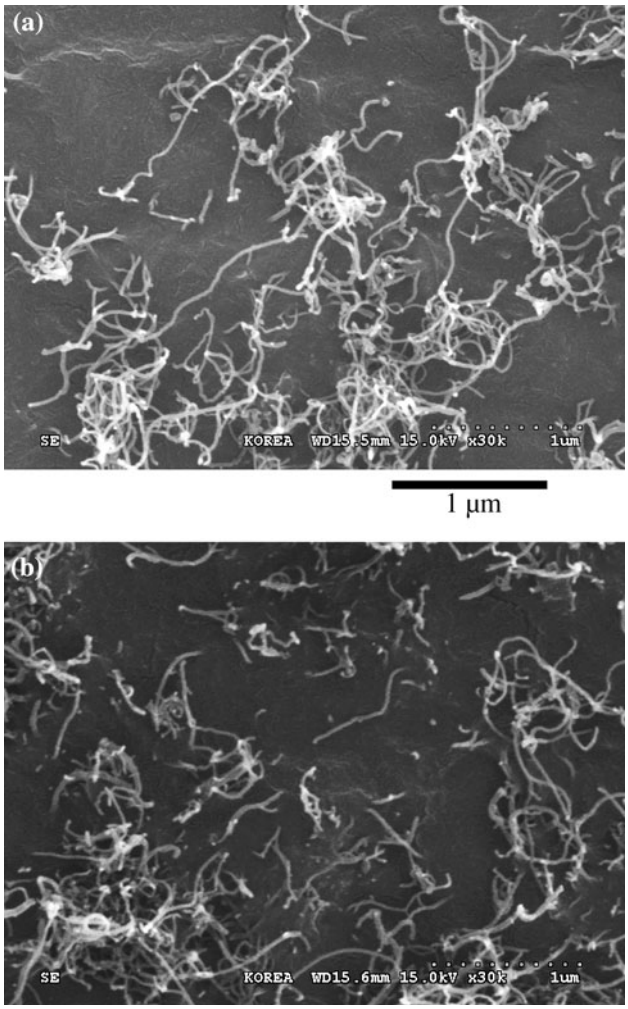

Fig. 1 Scanning electron micrographs of multiwall carbon nanotube (MWCNT): **a** before milling, **b** after milling

Thermal conductivity

Thermal conductivity is an important property in the thermal insulating materials. Figure 3 shows thermal conductivity of the PUF/MWCNT composites with the MWCNT content. From Fig. 3, thermal conductivity of the PUF without MWCNT shows 0.0210 kcal/mh°C, then the thermal conductivity decreases from 0.0210 to

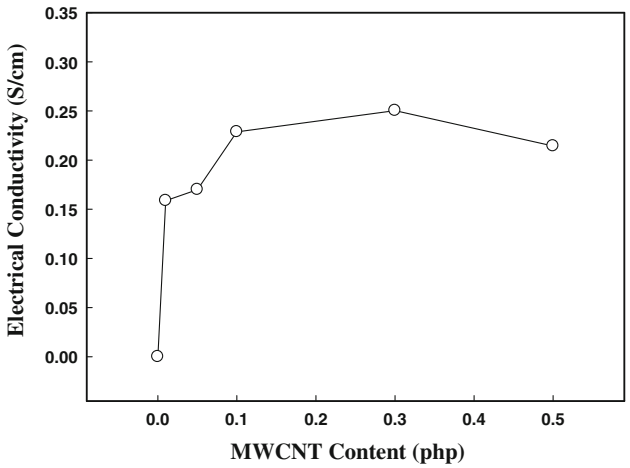

Fig. 2 Electrical conductivity of polyurethane foam and multiwall carbon nanotube (MWCNT) composites with MWCNT content

0.0202 kcal/mh°C at 0.01 php MWCNT content. At the 0.5 php MWCNT content, thermal conductivity of the PUF/MWCNT composite is increased to a value of 0.0209 kcal/mh°C. The behavior of the thermal conductivity of the PUF/MWCNT composites can be explained by the thermal conductivity of the MWCNT. The CNT has very high thermal conductivity, and singlewall carbon nanotube has a room temperature thermal conductivity along its axis of about 4,070 kcal/mh°C. However, when the MWCNT is added very small amount such as 0.01 php, the CNT absorbs the heats, instead of transmitting the heats. Therefore, thermal conductivities of the PUF/MWCNT composites at the low concentrations (0.01, 0.05, and 0.1 php) decreased compared that of the PUF composite without adding MWCNT.

From Fig. 3, thermal conductivity of the PUF/MWCNT composite having low MWCNT content (0.01 php) shows lower than that of the PUF/MWCNT composite having higher content (0.5 php) which are 0.0202 and

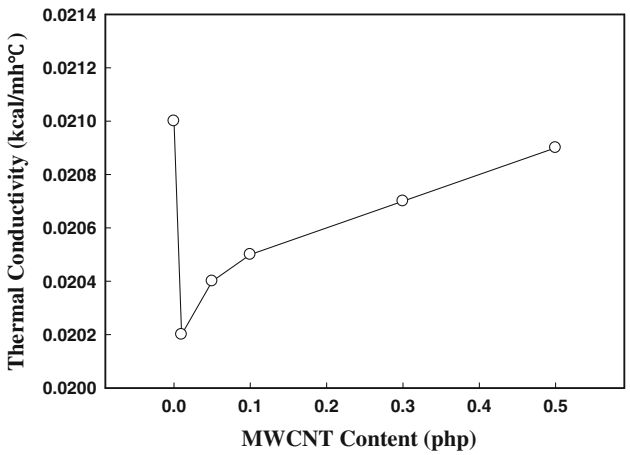

Fig. 3 Thermal conductivity of polyurethane foam and multiwall carbon nanotube (MWCNT) composites with MWCNT content

0.0209 kcal/mh°C, respectively. This is maybe due to that the cell size of PUF with the low MWCNT content (0.01, 0.05, and 0.1 php) would be smaller than the cell size of the PUF with the higher content of MWCNT (0.5 php). In our early studies, liquid-type silane additive will reduce surface tension of the polyol mixture which prohibits the coalescence of the cells, therefore, the cell size of the PUF will be decreased [27]. The cell size of the polyurethane foam is an important factor in the thermal conductivity of the PUF. Because the smaller cell size of PUF shows the lower thermal conductivity of the PUF [27–29].

Morphology

Figure 4a–f shows the scanning electron micrographs of the cryogenically fractured cross-sectional surfaces of the PUF containing 0.0, 0.01, 0.05, 0.1, 0.3, and 0.5 php MWCNT, respectively. From Fig. 4a, b, average cell size of the PUF/MWCNT composite is shown to decrease from 420 to 320 μm with the increase of MWCNT content from 0.0 to 0.01, respectively. For Fig. 4b–f, average cell size of the PUF is shown to increase from 320 to 440 μm with the increase of the MWCNT content. From Fig. 4b–d, it is observed that average cell size is more uniform and finer when the amount of the MWCNT is small such as 0.01, 0.05, and 0.1 php, respectively. MWCNT can act as a nucleation agent and serves as sites for the bubble growth with the formation of new bubbles in heterogeneous system where ultra fine solid particles are dispersed uniformly. As a result, whenever additives act as nucleating agents regardless of the phase, as the nucleating agent concentration is increased, the bubble size is decreased and the number of bubbles is also increased.

Figure 5 shows average cell size of the PUF/MWCNT composites with the MWCNT content. From Fig. 5, it is observed that the reduction in cell size of the PUF/MWCNT composites is more effective when the MWCNT content is small (0.01, 0.05, and 0.1 php). From Fig. 5, the decrease in cell size is maybe due to that the MWCNT acted as a nucleation agent and served as sites for the bubble growth with the formation of new bubbles in PUF, especially when the MWCNT content was small (0.01, 0.05, and 0.1 php). Figure 6 shows the relation between the thermal conductivity and cell size of PUF and MWCNT composites. From the results of thermal conductivity and cell size of the PUF/MWCNT composites, it is suggested that reduction in cell size of the composite affects lowering the thermal conductivity of the PUF/MWCNT composites.

Conclusions

The electrical and thermal conductivities of the PUF/MWCNT composites were investigated with the MWCNT

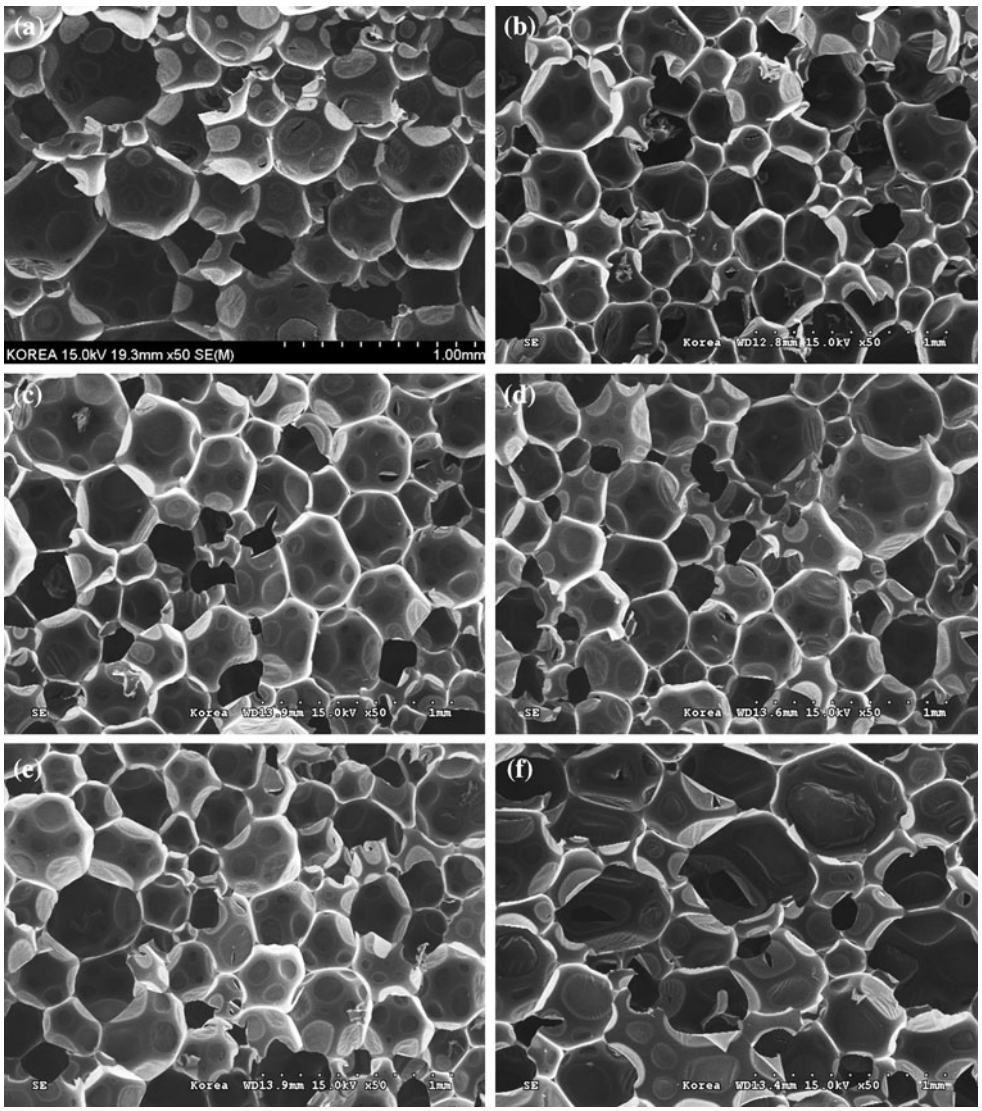

Fig. 4 Scanning electron micrographs of polyurethane foam and multiwall carbon nanotube (MWCNT) composites with MWCNT content (php): **a** 0, **b** 0.01, **c** 0.05, **d** 0.1, **e** 0.3, **f** 0.5

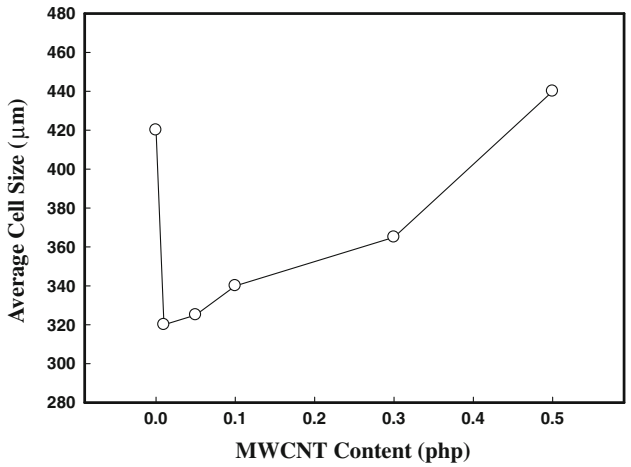

Fig. 5 Average cell size of polyurethane foam and multiwall carbon nanotube (MWCNT) composites with MWCNT content

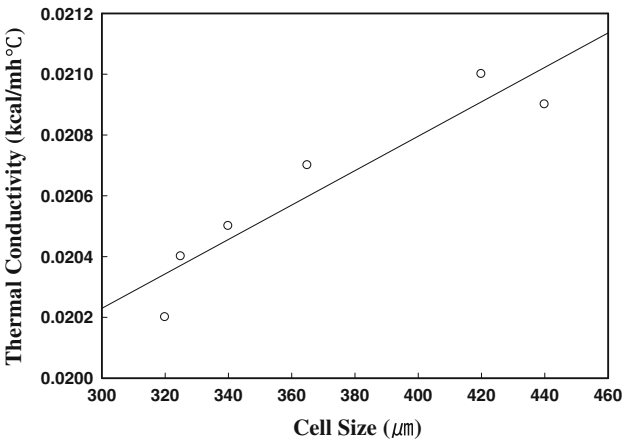

Fig. 6 Relation between thermal conductivity and cell size of polyurethane foam and multiwall carbon nanotube (MWCNT) composites with MWCNT content

content. Electrical conductivity of the PUF/MWCNT composites increased rapidly from 0 to 0.23 S/cm at 0.1 php MWCNT content. Then, the electrical conductivity does not change significantly with the increase of MWCNT content up to 0.5 phr. This is maybe due to the aggregation of the MWCNT when the amount of MWCNT is large (0.5 php).

The PUF/MWCNT composite having low MWCNT contents (0.01, 0.05, and 0.1 php) showed lower thermal conductivity than that of the PUF/MWCNT composite having higher content (0.5 php). This is maybe due to that the PUF with the lower MWCNT contents (0.01, 0.05, and 0.1 php) showed smaller cell size than that of the PUF with the higher content of MWCNT (0.5 php). The decrease in cell size is maybe due to that the MWCNT acted as a nucleation agent and served as sites for the bubble growth with the formation of new bubbles in PUF, especially when the MWCNT content was small (0.01, 0.05, and 0.1 php). From the results of thermal conductivity and cell size of the PUF/MWCNT composites, it is suggested that reduction in cell size of the composite affects lowering the thermal conductivity of the PUF/MWCNT composites. It is also suggested that small amount (0.01, 0.05, and 0.1 php) of MWCNT may contribute to decrease the thermal conductivity of the PUF/MWCNT composites.

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