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Thermophysical Properties of Multi-Walled Carbon Nanotube-Reinforced Polypropylene Composites[1]

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The thermal conductivity and thermal diffusivity of chemically surface-treated multi-walled carbon nanotube (MWCNT) reinforced polypropylene (PP) composites were measured using the 3ω method in the temperature range of 90–320 K and photoacoustic (PA) spectroscopy at room temperature, respectively. Nine kinds of samples were prepared by the melt-blending of PP resins with the addition of 0.1, 0.5, and 2.0 mass% of non-treated, nitric acid (HNO_3)-treated, and potassium hydroxide (KOH)-treated nanotube contents, and compression-molded at 180°C into about 0.5 mm thickness composite films using the hot-press. The measured thermal conductivities are in the range from 0.05 to $0.6\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ and increase as the temperature increases and the CNT concentrations are increased. By the chemical treatment, the thermal conductivity of 0.5 and 2.0 mass% samples were enhanced by about a factor of two; however, the sample of 0.1 mass% did not change. This can be explained qualitatively by the effects of chemical treatment on the reinforcing ability for CNTs/polymer composites.

KEY WORDS: multi-walled carbon nanotube; nano-composite; photoacoustic spectroscopy; thermal conductivity; thermal diffusivity; three omega method.

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1. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 [1] and the realization of their unique physical properties, including mechanical, thermal, and electrical properties, many investigators have endeavored to fabricate advanced CNT composite materials that exhibit one or more of these enhanced properties [2]. For example, as conductive fillers in polymers, CNTs are quite effective compared to traditional carbon black micro-particles. CNTs possess one of the highest thermal conductivities known, more than $600\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$, which suggests their use in composites for thermal management [3]. A better understanding of the relationships between processing, interfacial optimization, and composite properties is a major goal of this area of research, which may lead to optimal reinforcement of polymer matrices with CNTs [4].

From the view point of the surface chemistry, the formation of oxygen functional groups on CNT surfaces as well as the improvement of diversity in the polymeric matrix by chemical treatment plays an important role in the reinforcing ability for CNTs/polymer composites [5–7].

Therefore, in this work, we performed chemical surface treatment with HNO3 and KOH to study the effect of acid and base interactions between the CNT fillers and the polymeric matrix on thermophysical properties of the CNTs/polymer composites. We measured the thermal conductivity and thermal diffusivity of the chemically treated CNT-reinforced polypropylene composites.

2. THEORETICAL CONSIDERATIONS

The thermal conductivity was measured by the 3ω method. The 3ω method has been widely utilized for the thermal conductivity measurement of bulk and film-type samples [8]. There are two kinds of modes in PA measurements to measure the thermal diffusicity, namely, front surface excitation (FSE) and rear surface excitation (RSE). In general, the PA signal from the RSE mode is weaker than that from FSE; therefore, especially for the case of a thin film sample that requires high frequency modulation, FSE is more sensitive than RSE [10, 11]. For the FSE mode of an opaque film on a backing material, the expressions for the amplitude variation of the PA signal can be derived from the Rosencwaig–Gersho (R–G) theory [11, 12] and the thermal diffusivity was obtained by this theory.

3. EXPERIMENTAL PROCEDURES

3.1. Sample Preparation

The MWCNTs produced by the chemical vapor deposition (CVD) were obtained from Nanotech Inc. Their purity is over 97%, the length and diameter were 10–50 μm and 15–30 nm, respectively. The MWCNTs were purified by the following method prior to use. The purification procedure was based on a mixture of concentrated nitric (HNO_3) and sulphuric acids (H_2SO_4) in a ratio of 1:3, respectively. In a typical experiment, 1 g of raw MWCNTs was added to 40 cm^3 of the acid mixture in a round-bottomed flask, and refluxed for 30 min. On cooling, the mixture was washed with distilled water on a sintered glass filter until the washings showed no acidity.

For the modification of MWCNT surfaces and diversity, the chemical surface treatment was performed with 10 mass% HNO_3 and KOH solutions at room temperature for 1 h using an apparatus, which were denoted by A-CNT and B-CNT, respectively (non-treated one was denoted as CNT). Prior to use, the residual chemicals were removed by Soxhlet extraction by boiling with acetone at 80°C for 2 h. Finally, the MWCNTs were washed with distilled water several times and dried in a vacuum oven at 90°C for 12 h.

For the processing of the composite, PP was melt-blended with the addition of several nanotube concentrations specified as mass% in the polymer: 0.1, 0.5, and 2.0%. The temperature of the mixing system was determined to be 190°C with a thermocouple, and the blending time was 10 min. The mixed samples were compressed under a pressure of about 8 MPa at 210°C for 10 min using a hot-press. The thickness of the specimen is 0.5 mm. The samples were cut into pieces to measure the thermal conductivity and diffusivity in the thickness direction of the MWCNTs/PP composites.

We embedded 0.1, 0.5, and 2.0 mass% of each CNTs (A-CNT, B-CNT, and CNT) into PP matrix; therefore, nine different composites were prepared.

3.2. Thermal Conductivity and Diffusivity Measurements

The thermally evaporated gold metal strip line for the heater and thermometer is about 20 μm wide and 3 mm long. The electrical resistance of the gold layer was controlled to about 10–30 Ω by controlling the evaporation time. The metal strip line is functioning as both the heater and the thermometer for detecting the 3ω signal. The thermal conductivity of the chemically surface-treated MWCNT-reinforced composites was measured in the temperature range between 90 and 320 K by nearly the same process as used in our previous experiments [9].

In the PA experimental setup for thermal diffusivity measurements, the heating beam from an Ar^+ laser is absorbed by the sample placed in the PA cell. The beam is modulated by an acousto-optic modulator (AOM) whose modulation frequency can be varied from a few Hz to 350 Hz. The beam size on the sample surface is fixed by a condensing lens and iris to be 10 mm.

For detection and amplification of the PA signal, we used a half-inch (1.27 cm) microphone (B&K 2639) whose sensitivity is $40\,\mathrm{mV{\cdot}Pa^{-1}}$ and amplifier, respectively. A dual-phase lock-in amplifier (EG&G 5302) is used to analyze the phase and amplitude of the signal. Figure 3 also shows the design of the PA cell. To minimize the stray effect and other background noise, the cell was made of plexiglass, whose absorption is negligible. There are two chambers in the cell, one for the sample and the other for the microphone. The two chambers are connected by a narrow channel. The amplitude of the PA signal was measured by changing the modulation frequency of AOM.

4. RESULTS AND DISCUSSION

The measured thermal conductivities of chemically surface-treated and non-treated MWCNT-reinforced composites are shown in Fig. 1. We repeated the measurements five times for each sample, and the reproducibility and accuracy were within 10%. As the temperature increases, the thermal conductivity of all the samples increases. This is the common trends for most all dielectric and polymer materials because the dominant thermal carrier is a phonon; however, the unique difference is that the thermal conductivity was enhanced by CNT fillers.

The thermal conductivity of the sample also increases as the concentration of nanotubes increase; therefore, when the CNT concentration is 0.1 mass%, the thermal conductivity is the smallest and becomes the largest at 2.0 mass%. These can be explained by the model of Choi et al. [13] and Nan et al. [14]. They calculated the enhancement of the thermal conductivity with the addition of CNT on polymer matrix. From their work, the addition of 0.1 mass% CNT does not change the thermal conductivity; however, for the addition of 0.5 and 2.0 mass% CNT, the thermal conductivity increases abruptly by a factor of more than two and it depends on the ratio of the thermal conductivity of CNT and matrix material λ_c/λ_m(λ_c and λ_m are the thermal conductivity of the composite and matrix material, respectively). For our case, we can assume that $\lambda_c \geqslant 600\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, $\lambda_m = 0.4\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and $\lambda_c/\lambda_m \geqslant 1500$; therefore, the thermal conductivity will be enhanced by a factor of two and twelve at 0.5 and 2.0 mass%, respectively [14]. But the results in the figures show that it was enhanced by

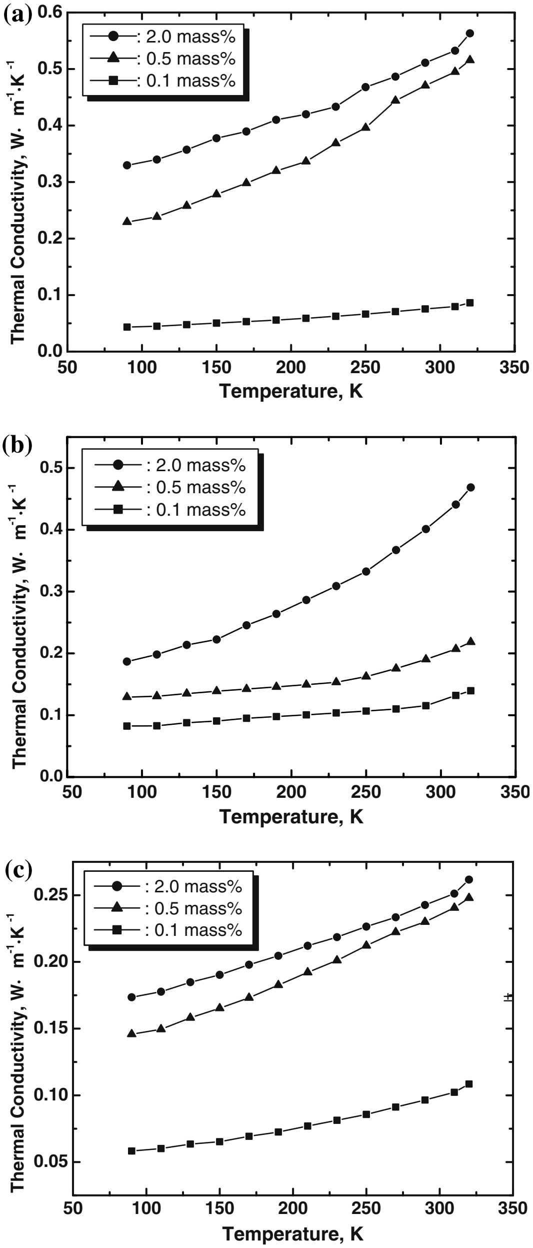

Fig. 1. Thermal conductivity of MWCNT-reinforced composites (a) HNO_3-treated (A-CNTs), (b) KOH-treated (B-CNTs), and (c) non-treated (CNTs).

a factor of about two at 0.5 and 2.0 mass%. The trends are qualitatively similar and the quantitative differences could be due to the interfacial thermal resistance between the PP matrix and nanotubes, the local aggregation, and the twist of the nanotubes in the composites.

Since CNTs are chemically inert, activation of their surface by the formation of oxygen functional groups is an essential prerequisite for tight binding to matrix. The activated CNTs had several times the specific surface area and pore volume than those of the normal CNTs [7]; therefore, the acid- and base-treated CNT composites show at least twice the thermal conductivity than that of the untreated CNT at higher CNT concentrations. The samples treated by HNO_3 and KOH show no large differences in thermal conductivity.

Figure 2 shows the microphotographs of HNO_3-treated (A-CNT), KOH-treated (B-CNT), and non-treated (CNT) samples for 2.0 mass% MWCNT samples. The envelopes of the grain surfaces in Fig. 2a, b are quite clear compared to Fig. 2c, and this is caused by the chemical treatment of nanotubes; however, the difference of the structures between Fig. 2a and 2b is not clear at present. For further quantitative investigation, a microscopic study will be required. From this result, the chemical treatment of the surface of CNTs enhances the thermal conductivity and diffusivity as well as the thermo-mechanical properties of CNT-reinforced composites.

In order to obtain the thermal diffusivity of the samples, the amplitude variation of the PA signal for each sample was measured by changing the modulation frequency from a few Hz to 350 Hz. Figure 3 shows the measured amplitude variation of the PA signal for 3 different HNO_3-treated samples by changing the modulation frequency. As the modulation frequency increases, the signal from all the samples quickly decreases and approaches zero, and the signal behavior of the non-treated and KOH-treated samples was similar.

The measured amplitudes were analyzed using a parameter estimation (PE) technique. A nonlinear PE algorithm NL2SOL developed by Dennis et al. [15, 16] was used in this work.

Table I shows the obtained thermal diffusivities of all the MWCNT samples by PA spectroscopy. The accuracy was within 5%. As was seen above, the thermal diffusivity shows the same trends as the thermal conductivity. This behavior can be explained by the relation of $\lambda = \rho\alpha C_P$, where ρ is the density, α is the thermal diffusivity, and C_p is the specific heat capacity of the sample. Here ρ and C_p can be assumed to be constant for all the samples. The thermal diffusivity was also enhanced by the embedding of the nanotubes into the PP matrices.

Consequently, the results of chemical modification on CNT surfaces show that acid-treated CNT (A-CNT) surfaces lead to an increase of

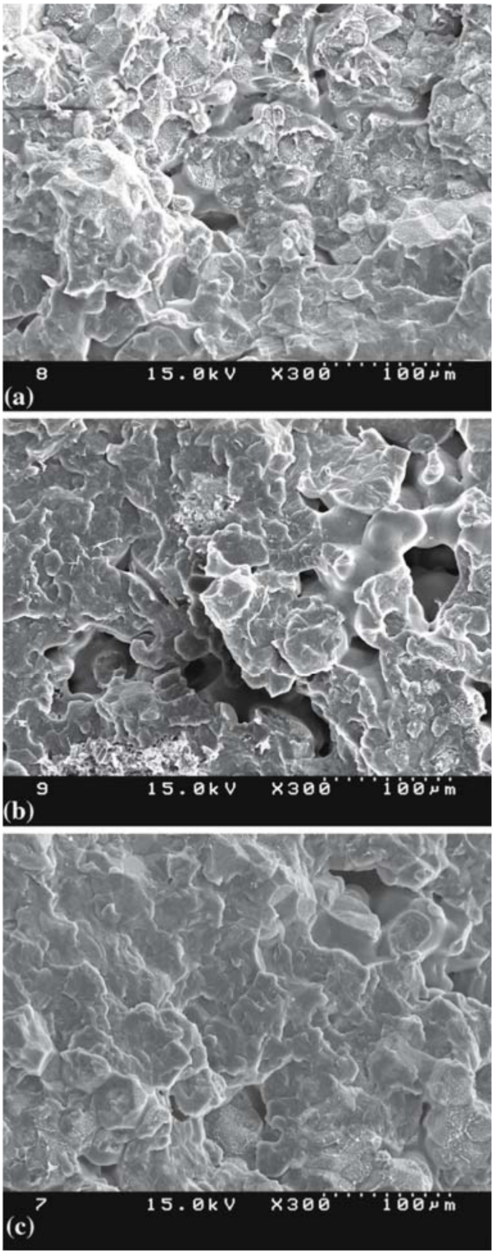

Fig. 2. Microphotographs of 2.0 mass% MWCT (a) HNO_3-treated (A-CNTs), (b) KOH-treated (B-CNTs), and (c) non-treated (CNTs).

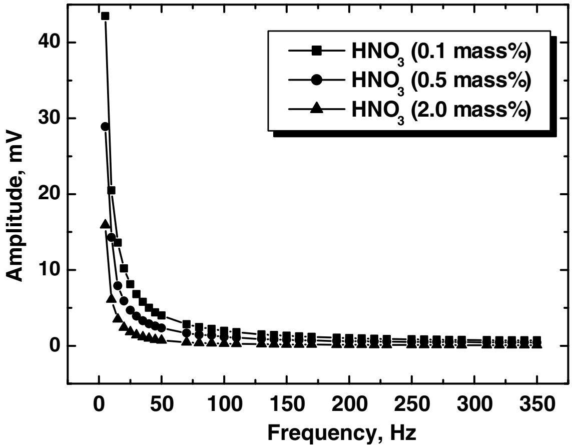

Fig. 3. Amplitude variation of the PA signal as a function of the modulation frequency.

Table I. Thermal Diffusivity ($cm^2 \cdot s^{-1}$) of the Samples by Photoacoustic Method

Specimens (mass%)	HNO3treated (A-CNT)	KOH treated (B-CNT)	Non-treated (CNT)
0.1	1.251 ± 0.050	1.149 ± 0.057	0.757 ± 0.030
0.5	1.530 ± 0.061	1.348 ± 0.067	0.769 ± 0.023
2.0	1.888 ± 0.075	1.495 ± 0.045	0.814 ± 0.033

acidic functional groups, compared to the base-treated CNT (B-CNT) or non-treated CNT (CNT) surfaces. Therefore, A-CNT-reinforced polypropylene matrix composites exhibit the highest thermal conductivity and thermal diffusivity. This result is probably interpreted as a result of the intermolecular interactions between the polymer matrix and the CNT fillers. It is then concluded that the chemical modification of CNTs appear to be one of the possible methods to increase the dispersivity and to improve the polymer-filler interactions for the resulting thermal behaviors of the CNT-reinforced polymer composites when a nonpolar organic matrix is considered in a composite system.

5. CONCLUSIONS

The thermal conductivity and thermal diffusivity of surface-treated CNT-reinforced polypropylene composites were measured by the 3ω and photoacoustic methods, respectively. By increasing the concentration of

CNTs, the thermal conductivity and diffusivity also increase. Both the acid-treated and base-treated samples show an enhancement of a factor of two in thermal diffusivity and thermal conductivity compared to the untreated samples because of the increase of the specific surface area and pore volume of nanotubes. A more detailed and microscopic investigation will be carried out soon.

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