JOURNAL OF MATERIALS SCIENCE **40** (2005) 1259–1263 LETTERS

Comparisons of thermal properties between inorganic filler and acid-treated multiwall nanotube/polymer composites

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Carbon nanotubes(CNT) have excellent physical properties, thus many applications based on these unique properties have been proposed, such as high-strength structural and high-performance functional polymer/CNT composites [1–4]. Although they are good candidates for structural, electrical and thermal applications [5, 6], the potential applications of carbon nanotubes are hindered by processing and manipulation difficulties owing to their insolubility and poor dispersion in common organic solvents and polymeric matrices [7, 8]. As-produced multi wall nanotubes (MWNTs) which can be produced at a relatively low cost and in increasing quantities significantly advanced by recent developments [9] are in the form of a web or an entanglement [10]. Generally, entangled nanotubes can not be easily dispersed in a polymer matrix. Hence, it is necessary to shorten the length of nanotubes and to get rid of nanotube entanglements.

In general, for pre-treatment of pristine MWNTs, three types of method are used—purification, shortening, and fluorination [11–15]. Basically, purification means the elimination of catalytic impurities and amorphous carbons. The most general method is oxidation; however, this method can introduce defects on the nanotubes, such as end cap opening and side wall defects. Next approach is shortening, and there are two possible methods—sonication and mechanical treatment. In this study, sonication was applied either in solvent or in concentrated sulfuric and nitric acid solution. This study investigates the dispersion of MWNTs in a polymer matrix, and the resulting thermal properties are discussed. Furthermore, thermal properties of composites that were dispersed with various particles having different aspect ratios are discussed.

A room temperature vulcanizing (RTV) silicone elastomer was used as the polymer matrix, because it is easy to handle and is a well-known material used in microelectronic packaging. The high purity MWNTs (> 95%, by ILJIN Nanotech Co., Korea) produced by CVD process were used in these experiments. Typically, tube diameters were in the range of 10–20 nm with tube lengths of 10–50 „ m. To reduce the size of nanotube entanglement, as-received MWNTs were sonicated at 30 Hz in toluene or in the solution of nitric and sulfuric acids. In this experiment, toluene was introduced as a thinner in order to control the viscosity of the silicone resin.

The composites were prepared as follows: the nanotube/toluene solution and silicone resins were mixed together in the homogenizer for 10 min. Subsequently, the mixed paste was placed in vacuum oven in order to evaporate the residual solvent. Finally, a 400-micron thick film was obtained which was subsequently cured at room temperature for 24 hrs. Thermal conductivity was measured by TC Probe which was manufactured by Mathis Instrumentals Ltd. The measurable range of the equipment was 0–10 W/mK [16]. Test specimen measured 3 mm £ 30 mm with thickness of 0.4 mm.

Fig. 1 shows SEM and TEM images of pure nanotube samples without matrix that have been sonicated for 9 hrs. A number of differences can be observed between sonications in toluene and in concentrated acid solution, such as shapes and sizes of clusters. During sonication in concentrated acid solution, the nanotubes were relaxed and lost original structures resulting in smaller clusters. These clusters are likely to be well dispersed in a polymer matrix. However, in the case of sonication in toluene (Fig. 1a and c), nanotubes appeared as bulky agglomerates with the diameters in several microns although they were sonicated for 9 hrs in toluene. Thus, it can be concluded that sonication in strong acid is more effective in shortening the MWNTs than sonication in toluene.

The effects of pre-treatment on the dispersion of MWNTs in a polymer matrix were investigated. MWNT/polymer composites were prepared as mentioned earlier and the SEM images of their fracture surfaces are shown in Fig. 2. For the composites which are only sonicated in toluene for 9 hrs, the overall dispersion is poor, as evidenced by the non-uniform distribution of the MWNTs. However, the specimen containing acid treated nanotubes is well dispersed in the entire range of the specimen characterized by small clusters or individual nanotubes. To improve the electrical and thermal conductivities, particle to particle network, namely percolation, is critical. Therefore, the acid treated sample is expected to exhibit low electrical and thermal conductivity thresholds because of their good dispersion.

Theoretically, the thermal resistance is caused by phonon scattering processes [17]. In order to increase

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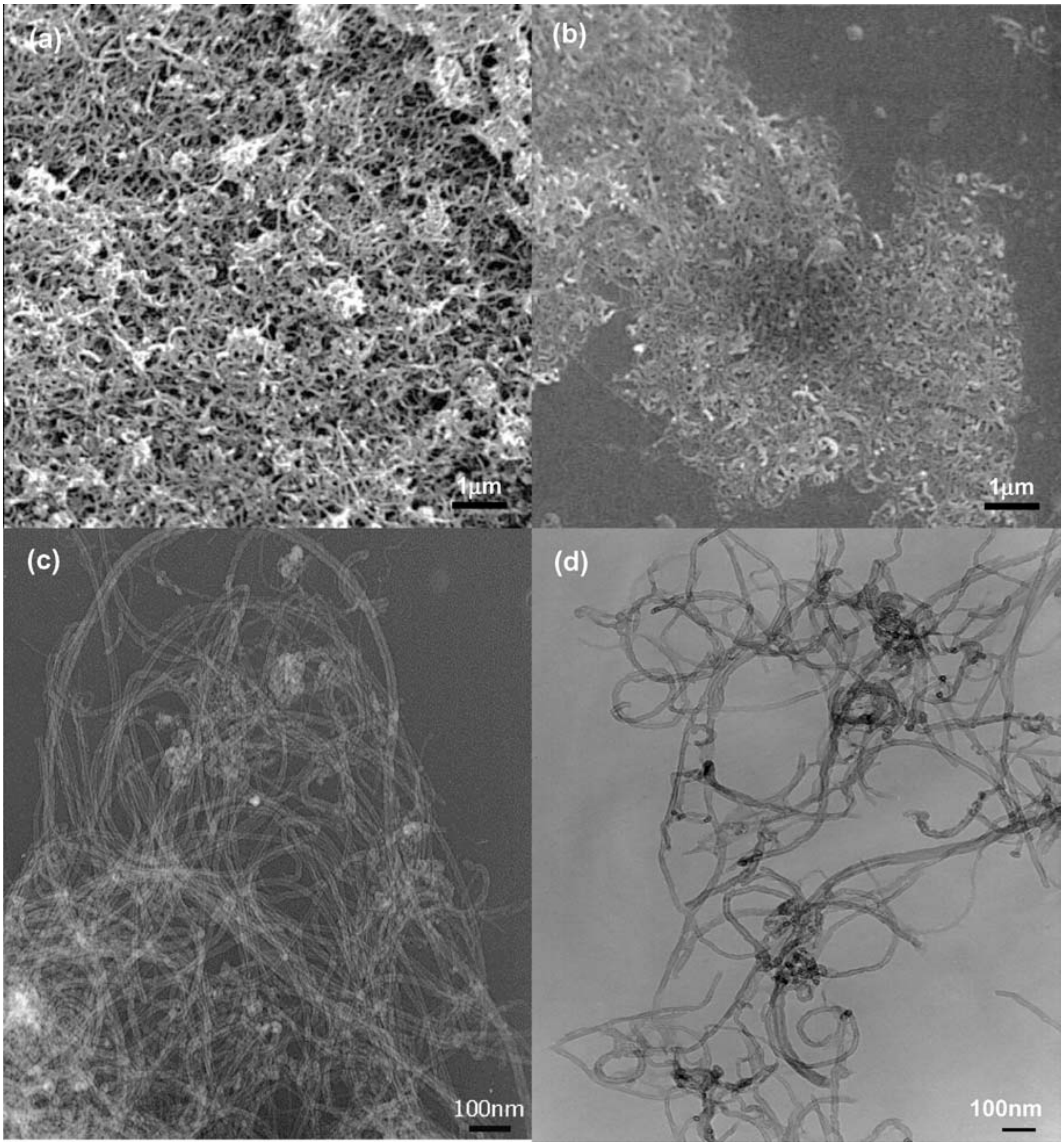


Figure 1 SEM and TEM images of multi wall nanotubes. (a) and (c) Sonication in toluene, and (b) and (d) sonication in concentrated acid solution.

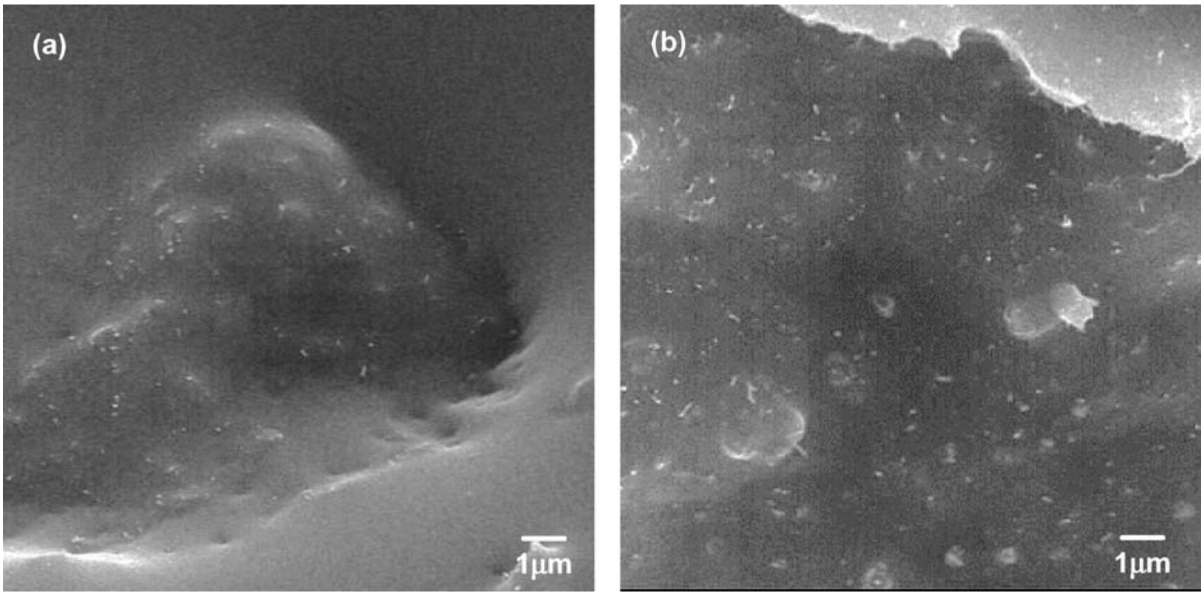


Figure 2 SEM images of fracture surface of MWNT/polymer composites. (a) Sonication in toluene, and (b) sonication in concentrated acid solution.

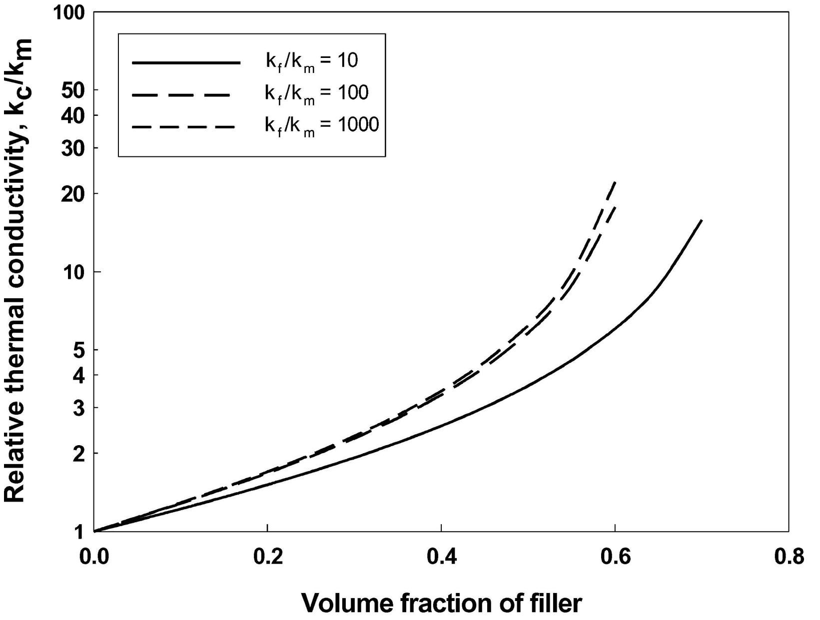


Figure 3 Relative thermal conductivity as a function of volume fraction of filler.

thermal conductivity, phonon scattering has to be minimized. Materials with high thermal conductivities can be obtained by using fillers with high intrinsic conductivities. However, as discussed by Bigg [18], when the intrinsic thermal conductivity of the filler is 100 times greater than that of the polymer matrix, there is no significant improvement in the thermal conductivity of the composite. This phenomenon is illustrated in Fig. 3, where k_{f}, k_{m} and k_{c} are the thermal conductivities of filler, matrix and composite, respectively. On the contrary, the aspect ratio of the filler is a more important parameter that dictates the conductivities of a composite, because the fillers with large aspect ratios easily form the bridges between them, known as conductive network. The formation of random bridges or networks from conductive particles facilitates electron and phonon transfer leading to high conductivities. Therefore, if higher thermal conductivities are desired, the use of fillers with higher aspect ratios is recommended. With their aspect ratios ranging from 100 to 1000, MWNTs are one of the best candidates for this purpose. This principle can be applied to most other fields concerned with electrical and thermal conductivities.

The effect of MWNT dispersion on thermal conductivity was investigated and the resulting curves are shown in Fig. 4a. In the case of acid treated nanotubes, higher thermal conductivity was obtained as compared to the case of untreated ones. Furthermore, additional information can be obtained from Fig. 4b plotted with respect to the measuring positions. In the case of untreated samples, a dip in the conductivity curve can be observed. This indicates a non-homogeneous dispersion in the bulk region of the composites and the shape of the curve can be used to assess the degree of dispersion. The TC probe measurement was made over a relatively large area of 3 mm £ 30 mm with thickness of 400 „ m. However, more detailed information on dispersion can be obtained if a smaller size is measured. From the figure, it is suggested that the degree of dispersion can be indirectly predicted by measuring the thermal conductivity. Thermal or electrical conductivity is prone to be a useful means to measure the degree of either local or bulk dispersion.

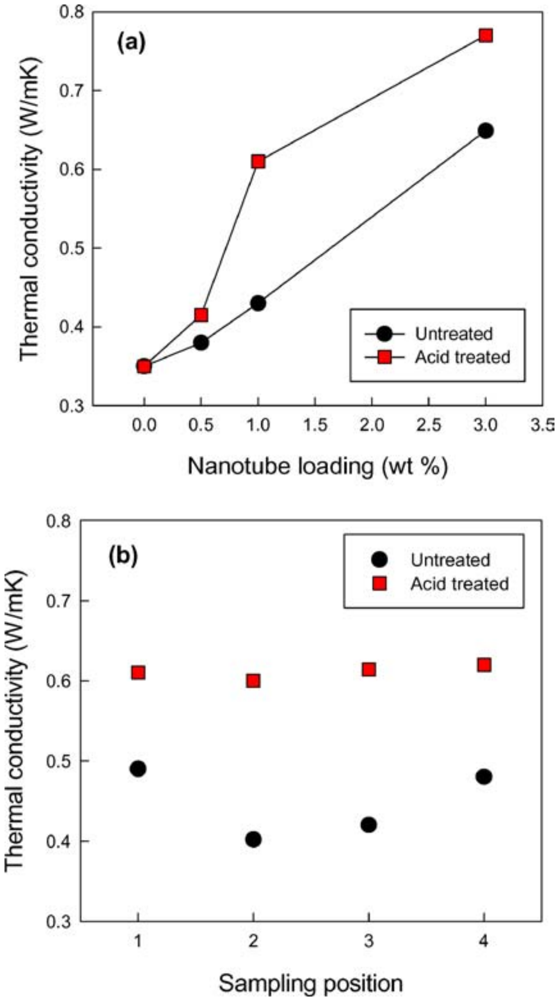
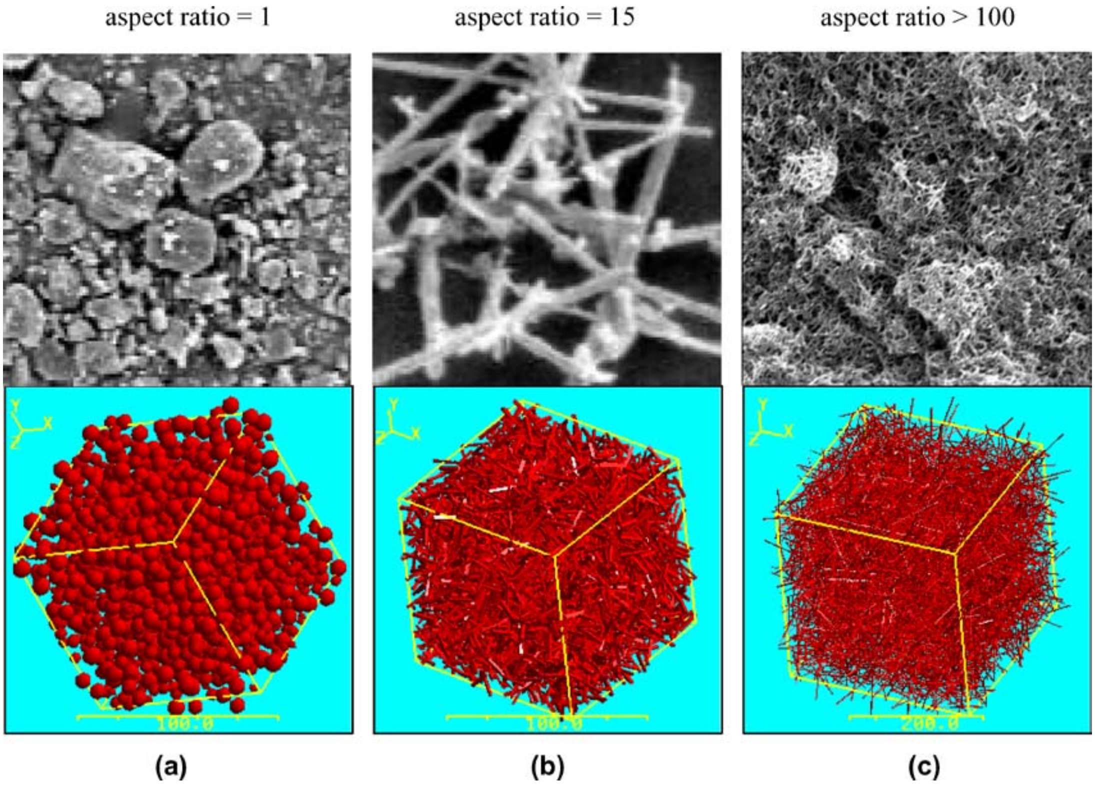


Figure 4 Thermal conductivity of the composites, (a) for the various nanotube contents, and (b) for the various sampling positions (nanotube loading of 1 wt%).



(a) (b) (c)

Figure 5 SEM images of conductive particles and estimated particle packing by using packaging software considering aspect ratio of fillers. (a) Aluminum nitride, (b) silicon carbide and (c) multiwall nanotubes.

For comparison, three types of conductive fillers were used, namely, MWNT, silicon carbide(SiC) whisker and aluminum nitride(AlN) powder, which have different shapes and aspect ratios as shown in Fig. 5. As for the intrinsic thermal conductivities of the fillers, which are listed in Table I, the conductivity of multi-wall nanotube is greater than that of AlN by more than 10 times, and the conductivity of SiC whisker is half of that of AlN. The aspect ratios of AlN, SiC, and MWNT are approximately one, fifteen, and more than one hundred, respectively. The effect of the aspect ratios of conductive fillers is shown in Fig. 6. This plot shows the thermal conductivity as a function of volume concentration (vol%) which is calculated from the material density. For AlN and SiC having the same volume content (30 vol%), the conductivity of SiC is higher than that of AlN, although the filler conductivity of SiC is only half of that of AlN. However, MWNT has a much higher conductivity compared to the others, even in presence of nanotube loading below 2 vol%. It is due to conductive network as shown in lower half of Fig. 5c. The cubic boxed figures which were captured by using commercial packaging software [19] show the conductive network considering their aspect ratios and dimensions, although the MWNT particles were assumed as rigid rods. In the figure, it can be inferred that the conducting path or network is the most important factor over the intrinsic conductivity of particles and loading concentration. In conclusion, carbon nanotube is the best candidate as a filler in thermally conductive composites. In addition, to obtain high thermal conductivity with relatively low cost, the hybrid systems using two or more conductive particles are more considerable. These systems can provide synergetic effects and cost reduction simultaneously, because they could achieve percolation using small amount of carbon nanotubes.

From the study of the thermal properties of MWNT/polymer composites, which were prepared by solution process, it can be concluded that sonication in concentrated acid solution is more effective for nanotube shortening, good dispersion and high conductivity. Thermal conductivities were increased significantly at a low loading content of nanotubes as low as 2 vol% in the case of well-dispersed multi wall nanotube/silicone composite. In addition, carbon nanotube polymer composites exhibited the threshold more than 10 times as low as that of general conducting filler composites.

TABLE I Physical properties of conductive fillers and matrix

Materials	Diameter	Density (g/cm^3)	Length („ m)	Intrinsic thermal conductivity at *RT* (W/mK)
MWNT	10–20 nm	1.75 [20, 21]	10–50	3000 [8]
SiC	1–2 „ m	3.2	10–15	85
AlN	5–10 „ m	3.26	5–10	150–220
Silicone resin	–	1.04	–	0.35

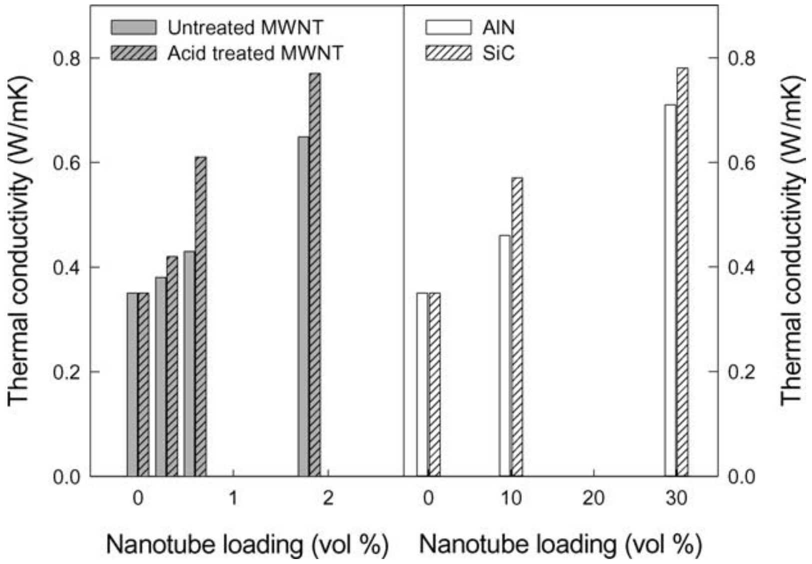


Figure 6 Thermal conductivity of the composites for the various conducting fillers and loading concentrations.

From the result of dispersion versus conductivity, the degree of dispersion can be indirectly predicted from the conductivities.

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*Received 2 June
and accepted 22 July 2004*