The electrical influences of various multiwalled carbon nanotubes with plasma modification and chemical oxidation in the polymer matrix

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Introduction

The Carbon nanotubes (CNT) with quasi-one-dimensional structure can be metallic or semiconducting depending on their structural parameters. This makes the CNT as central elements in composite materials for many electronic applications. They also have high stiffness and tensile strength, which make them preferable for the composites with desired mechanical properties. Unfortunately, it is difficult to obtain homogeneously dispersed CNT nanocomposites arises from the non-reactive nature of the CNT surface and the unavoidable bundle formation due to van der Waals attraction during synthesis. It is a key factor to reinforcement of composites that the CNT can disperse efficiently in the polymer matrix. According to the literatures, the size of fillers in the composite affects the properties of the composite. In our previous research, the CNT modified with maleic anhydride by plasma (mCNT) and the mCNT can have good dispersion in the polymer matrix. Therefore, we prepared two different sizes (0.05-0.2 μm, 0.8-1.5μm) of mCNT and discussed their influence in the polymer matrix. With various ratio of two different mCNT, we can obtain an optimum ratio when total contents of CNT in the polymer matrix were 1.0, 2.0 and 3.0 wt%. Moreover, the conductivity of the CNT/polymer can maintain 3×10^{-3} S/m.

Experimental

Materials

Multiwalled carbon nanotube (MWCNT) (diameter 10–90 nm, length 0.8–1.5 μm samples), which were prepared by chemical vapor deposition using an AlO_3-supported FeO_3 catalyst, were obtained from the Industrial Technology Research Institute in Taiwan. Joncryl 538, a hard acrylic polymer, was kindly supplied by S.C. Johnson (non-volatile content 45%, glass transition temperature 64°C).

Acid modification of MWCNT (aCNT) and acid–plasma modification of MWCNT (apCNT)

The MWCNT were washed with 60 wt% acid and 40 wt% nitric acid mixed acid by stirring at 50 ^{0}C for a period of 24 hr. then washed with deionized water, filtered and dried at 120 °C (aMWCNT, diameter 5–60 nm, length 0.05–0.2 μm samples). After acid treatment, MWCNTs were further plasma-modified with maleic anhydride as described above (apMWCNT).Then subsequently washed with deionized water, filtered and dried in 120 ^{0}C.

MWCNT/polymer nanocomposites

Using Joncrylic 538 as the polymer matrix, MWCNT/polymer nanocomposites were prepared using a modified MWCNT content of 0.0–2.5 wt.-% based on the polymer matrix with various mMWCNT/apMWCNT ratios.

Characteristic

The electrical conductivities of the polyimide/CNT nanocomposites were measured by an AutoLab PGSTA 30 with AC measurement according to ASTM D257 and the specimen was 2.54 mm in diameter and varied in thickness from 100 to 300 μm. A Hitachi S4100 field-emission scanning electron microscope (SEM) was used to observe the fractured surfaces of MWCNT/polymer nanocomposites with different
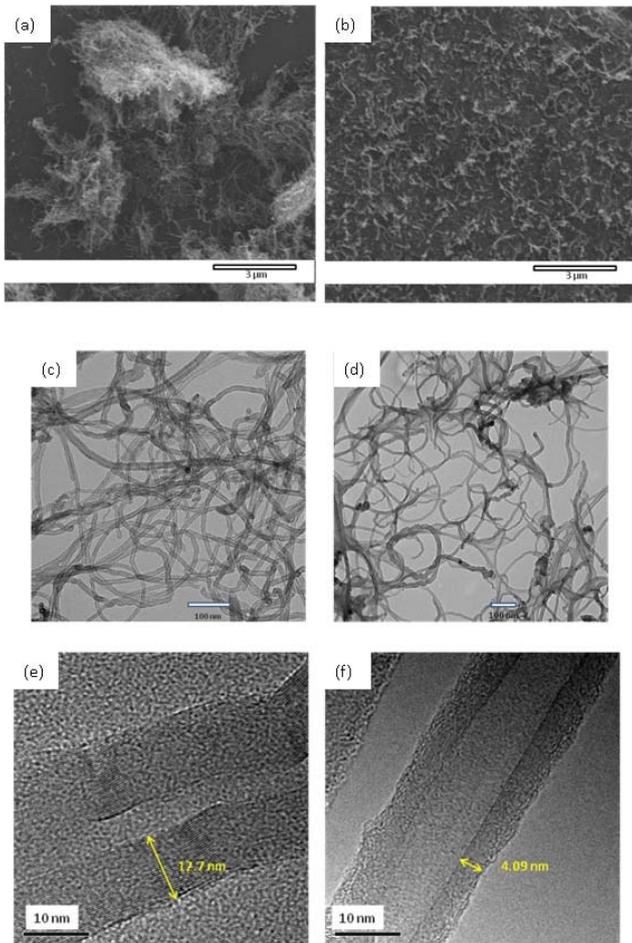
Fig. 1 TEM images of MWCNTs before and after various modifications.

MWCNT structure and the type of polymer. To investigate the electrical properties of the nanocomposites, we need to consider the effect of the MWCNT surface structure.

Some researchers have reported that the length of fillers can be controlled to influence the properties (mechanical, thermal, electrical, etc.) of nanocomposites [1]. Therefore, we considered adjusting the mMWCNT/apMWCNT ratio to control the conductivity of the nanocomposites. We added different MWCNT size ratios to the polymer matrix and the conductivity of these nanocomposites is shown in Fig. 3. For mMWCNT, conductivity increased in the range 0.0–1.0 wt.-% MWCNT content; with further increases in mMWCNT content the conductivity remained constant or even decreased slightly. Nanocomposites containing apMWCNT exhibited a similar trend. According to our previous research, when the MWCNT content exceeds a critical value, the huge surface area and van der Waals' forces mean that the

MWCNT contents. Transmission electron microscopy (TEM) images were obtained using a Hitachi HF-2000 field-emission TEM instrument at an acceleration voltage of 200 kV. The detailed structure and chemical composition of MWCNTs were analyzed by X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). XRD data were recorded on a Rigaku RINT2000 instrument with Cu K_α radiation (λ=1.54056 Å). A scanning speed of 4°/min and sampling width of 0.02° were used for 2θ from 20° to 80° at 40 kV and 30 mA. XPS data were recorded using an ESCA PHI 1600 instrument at a base pressure of 5×10^{-10} Torr.

Results and discussion

More detail experimental results for the XPS were showed in our previous research. We do not describe in this paper. The amount of O 1s on the MWCNT surface can influence the MWCNT–polymer compatibility. Consequently, the dispersion of aMWCNT, apMWCNT and mMWCNT in the polymer matrix was better than that of bMWCNT, as confirmed by TEM images (Fig. 1). However, the properties of MWCNT/polymer nanocomposites depend on the
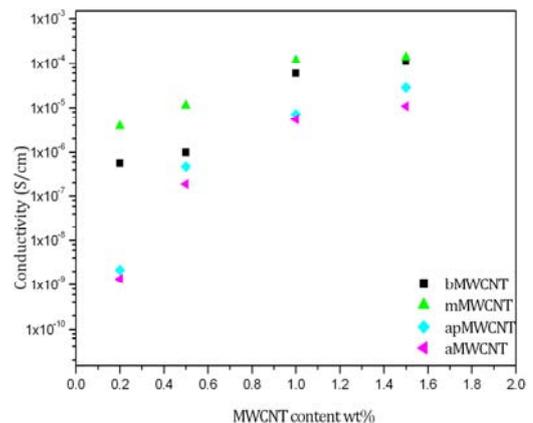

Fig. 2 The conductivity after acid treatment (aMWCNT and apMWCNT) was lower than for bMWCNT.

MWCNTs tend to cluster. Once MWCNTs start to aggregate, the charge cannot be transferred effectively and the conductivity of the nanocomposites may decrease. For different MWCNT size ratios, short MWCNTs can fill the gaps caused by long MWCNT clusters, leading to more effective charge transfer and increasing the conductivity of the nanocomposites, the TEM patterns of MWCNT dispersion are shown as Fig. 1 However, short MWCNTs (apMWCNT) may form clusters of a different type and the conductivity will not further increase with MWCNT content.
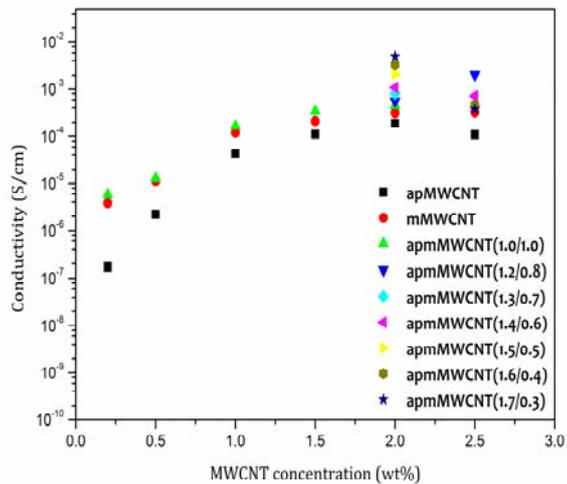
Fig. 3 The conductivity of these nanocomposites.

To obtain the optimum conductivity, only a small amount of apMWCNT (15% of the total MWCNT content) was required to fill the gaps. For a total MWCNT content of 2.0 wt.-%, a greater proportion of mMWCNT led to more gaps due to mMWCNT clusters, so approximately 40% apMWCNT was used to fill these gaps and obtain the optimum conductivity. However, the conductivity may break down for apMWCNT content higher than the critical value owing to the formation of clusters of a different type.

Conclusion

In the present study, we proposed a specific concept to increase the loading of MWCNT in a polymer matrix. Two types of MWCNT are used in our system, mMWCNT and apMWCNT. mMWCNT (plasma-modified with maleic anhydride) exhibited good dispersion in the polymer matrix and the properties of MWCNT/polymer nanocomposites were improved. apMWCNT exhibited good dispersion, but decreased the electrical properties. Therefore, we adjusted the mMWCNT/apMWCNT ratio to control the conductivity of the MWCNT/polymer matrix. The optimum conductivity was of the order of 10^{-3} S/cm for a total MWCNT content in the polymer matrix of 2.0 or 2.5 wt.-%.

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