Synthesis of Functionalized Carbon Nanotubes/Phenolic Nanocomposites and Its Electrical and Thermal Conductivity Measurements

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The phenolic resins (PR) was reinforced with carbon nanotubes (CNTs) to improve its electrical, thermal and mechanical properties with CNTs in different contents. The results indicate that by adding multi wall carbon nanotubes (MWNTs) up to 10% in weight, the thermal conductivity of the nanocomposites can increase from 0.612 to 1.473 W m\(^{-1}\) K\(^{-1}\) while the electric conductivity increase significantly from 0 to 135.52 ms. In order to further disperse the MWNTs in PR, two different methods to modify MWNTs, such as carboxyl MWNTs (c-MWNTs) and surfactant (sodium dodecyl sulfate, or SDS) modified MWNTs (SDS-MWNTs), were adopted. The transmission electron microscopy (TEM) images reveal that the length of the c-MWNT becomes much shorter, while the length of SDS-MWNT has no significant change. Measurements by ultraviolet–visible (UV–vis) spectrophotometer indicate that for MWNTs dispersion in alcohol the absorption spectrum of c-MWNTs dispersion is much higher than both the SDS-MWNTs and the as-grown MWNTs dispersion. In addition, with better dispersion of SDS-MWNTs in PR, both the electrical and the thermal conductivity of SDS-MWNT/PR nanocomposites are found higher. However, the lower thermal conductivity of c-MWNTs/PR composites may be attributed to shortening of the MWNTs by the attack of acidic treatment.

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1. Introduction

Polymers with addition of small amount of carbon nanotubes (CNTs) to become conducting polymers have combined many advantages of plastics, e.g., flexibility, low temperature process, with advantages of conductivity either in metallic or semiconducting regimes. This has significantly widened the area of application for a polymer.\cite{1,2} Adding carbon black, however, carbon fiber or metal wire in polymer to produce conducting polymer has been developed\cite{3} long time ago. However, the percentage of adding these kinds of materials is relatively high, and is about 20 to 40% of the polymer. Therefore, the mechanical properties of the polymer can be significantly decayed. For example, the material lacks ductility that it becomes difficult to be drawn into fiber. For nanomaterials, however, the percentage of adding these materials into polymer can be small. Not only the electrical property, but also the mechanical property is expected to be significantly improved.

One class of these polymer materials that can be added with CNTs is phenolic resins (PR). The PR has many applications in various areas, such as in electronics, automotive, adhesive and additive for the improvement of thermoplastics.\cite{4} However, the degree of dispersion of CNTs in polymer becomes a major concern which has a detrimental effect on the resulting property of composite materials. Current work attempts to use different functionalized CNTs to improve degree of dispersion of CNTs in PR. The resulting electrical and thermal conductivity of the nanocomposites which combine PR with different functionalized CNTs are measured and presented.

2. Experiments

2.1 Material preparation

The phenolic powder synthesized by polymerizing process of the phenol and formaline is supplied from Kuen Bong Chemical Industry. It has a specific gravity of 0.337 and melting point of 84°C. The carbon nanotubes used are the multi-wall carbon nantobes (MWNTs), which were supplied from Conyuan Biochemical. The MWNTs have the diameter of 20–40 nm, the length of 5–15 μm and the degree of purity greater than 95–98%. The MWNTs were functionalized with different methods. The MWNTs can be soaked in ethanol consisting of 1 wt% sodium dodecyl benzene sulfonate (SDS) with sonication and becomes SDS-MWNTs. Functionalization of MWNTs with surfactant, SDS, is a nondestructive, noncovalent exohedral binding process. The nanotubes can be transferred to the aqueous phase in the presence of surface-active molecules of SDS. The MWNTs dissolved in methanol at 1 mg/10 ml is added with 1% SDS surfactant under sonication for 30 min. After centrifugation, the supernatant decanted and the remaining solid was dried in oven to form SDS-MWNTs.

The MWNTs can also be acidic treated, which is boiled in sulfuric acid with nitric in a ratio of 1 : 3 by volume. 0.532 g of untreated MWNTs were suspended in 40 ml of acid mixture (sulfuric acid and nitric in the molar of 1 : 3). The reaction was carried out at 50°C and magnetic stir for 3 h. The reaction temperature is much lower and reaction period adopted is much shorter than the ones reported in refs. 5–7. This time period selected has been tested, and the results show, as discussed in the following, that the time is short enough to minimize the damage of the solvent attack to the nanotubes, but allow carboxylic groups attach the nanotube surface. The sample was filtered using a 0.47 μm filter membrane and was washed until the pH value was around 7.0. The nanotubes were filtered from the water, and dried in oven at 100°C under vacuum to form carboxylated MWNTs (designated as c-MWNTs).

2.2 Characterization techniques

The surface morphology of the functionalized MWNTs is studied with field emission gun transmission electron microscope (FEG-TEM; Philips Tecnai G2 F20). The
Raman spectrometer (Jobin Yvon/Labram HR) is used to study the defects and structure change of functionalized MWNTs. In addition, Fourier transform infrared spectroscopy (FTIR; Integrated Scientific Services Thermo/Nicolet) is used to study the attached functional groups on the MWNT surfaces. The capability of MWNTs dispersion in polymer can also be studied by adding MWNTs in organic solvent. After sonication, the light absorption of the solvent added with MWNTs is measured by ultraviolet–visible (UV–vis) spectrophotometer (U-3010) and is used to indicate the degree of MWNTs dispersion in the polymer. The pressed composites are characterized by high resolution thermal field emission scanning electron microscopy (FE-SEM) using a JEOL-7000F. The electrical resistance of the PR composites is measured by four point probe (ELCHEMA CM-308). Seven different locations on the sample surface were selected for measurements. From the size of the sample, the resistivity of the composite can be calculated. The thermal conductivity of the nanocomposites is measured by thermal conductivity meter (Laser Flash LFA-447 Modify ASTM E1461). The system uses Xe laser to emit a light beam on the surface and causes a temperature rise of the sample. The diffusivity of the nanocomposites was first calculated from the heat conduction equation in the solid by the temperature rise of the sample surface with the given light heat flux imposed on the surface. From further measurements of density and specific heat of the nanocomposite, the conductivity of the nanocomposites can be calculated and obtained. More details on the methods of measurements can be found in ref. 9.

The TEM images reveal, as shown in Fig. 1, that the length of c-MWNTs has become much shorter and the ends of the c-MWNTs have been opened, while the length of SDS-MWNT has no significant change and the ends of SDS-MWNTs are still closed by the catalysts. It appears that wrapping of the MWNTs by SDS does not damage the surface and entire structure of the nanotubes. In addition, the temperature and duration of the acidic treatment for the case of 50 °C c-MWNTs has been controlled in such a way that damage on the MWNTs has been minimized. The Raman spectrum, as shown in Fig. 2, indicates that Raman shifts for the pristine MWNTs are almost the same as that for the SDS- and c-MWNTs. This suggests that functionalization of MWNTs by SDS or acidic treatment at 50 °C does not damage the structure of MWNTs.

![Fig. 1. TEM images of the (a) MWNTs, (b) c-MWNTs, and (c) SDS-MWNTs.](image)

![Fig. 2. (Color online) Raman spectrum of MWNTs, SDS-MWNTs, and c-MWNTs.](image)

![Fig. 3. (Color online) UV–vis spectrum of the MWNTs, SDS-MWNTs, and c-MWNTs dispersed in alcohol.](image)

The degree of dispersion of the functionalized MWNTs in ethanol, which is a blending solvent during mixing with phenolic resins, was tested by absorption of UV–vis, as shown in Fig. 3. The greater absorption of c-MWNTs in the solvent suggests a better dispersion of c-MWNTs in this solvent. It is expected that dispersion of c-MWNTs in the phenolic resins will be very good, and better electrical and thermal conductivity can be obtained.

The FTIR spectrum for the various kinds of nanotubes, as shown in Fig. 4, is used to check and see if the functional groups have attached to the nanotube surface. The peaks appearing in the range of 1550–1573 cm⁻¹ are attributed to the C=C bond of the nanotube structure. Despite of the damage, all the nanotubes still maintain their carbon network structure. For the 50 °C c-MWNTs, the peaks appearing in the vicinity of 1710 and 1050 cm⁻¹ account for C=O and C–O stretching mode of the carboxylic groups, respectively. The peak appearing at 3630 cm⁻¹ accounts for O–H stretching mode of the carboxylic groups. It appears that the COOH group has attached on the surface of the MWNTs. For SDS-MWNTs, the peaks appearing at 2944 and 2912 cm⁻¹ are the unsymmetric and symmetric stretching mode of the alkyl (–CH₂–) group.
2.3 Synthesis of MWNTs/phenolic resin nanocomposite

The pristine or functionalized MWNTs is first added into ethanol and sonicated for two and half hours. Then, the powder material of PR is then blended into the mixed solvent and stirred for 12 h until they are well mixed. The MWNTs/phenolic mixture is heated to 75 °C to remove the solvent. The sample is placed into a mold preheated up to 125 °C for hot impress. The pressure imposed is 1000 psi. The ramp speed is 10 °C per 20 min. until the sample reaches 170 °C. After pressure is maintained there for 20 min, the temperature of the sample is allowed to drop gradually into the ambient condition. The size of the sample can be 8 × 8 × 0.5 or 20 × 8 × 0.5 mm$^3$ for both electric resistivity and thermal conductivity measurements.

The SEM images of the PR blended with MWNTs show that the material is composed of fibril distributed homogeneously, as shown in Fig. 5(a). After hot-press, the fibril is distributed homogeneously in the material, no clustering or agglomeration of CNTs has been found on the surface. It appears that the hot-pressing process does not cause agglomeration of CNTs. For comparison, the sample without MWNT is also photographed as shown in Fig. 5(b). The surface of the sample without MWNT is very smooth and flat, and does not have fibril structure. In addition, the surface is very shiny that the SEM picture is not readily taken.

3. Electrical and Thermal Aspect

The electrical resistivity of pure PR is around $10^{11}$–$10^{12}$ Ω cm for volume resistivity. However, the resistivity of PR can vary significantly with different process of fabrication into solid sample, as shown in Fig. 6 for comparison with data published in ref. 11. After adding small amount of pristine MWNTs into the PR matrix, the electrical resistivity decreases rapidly, as shown in Fig. 6. The current data show that the rate of decrease in resistivity becomes mild until the content of MWNTs is greater than 0.75%. It appears that the sharp decrease in the resistivity is attributed to the formation of an interconnected structure of MWNTs. This simply means that a very high percentage of electrons are permitted to transfer through the specimen due to the creation of an interconnecting conductive pathway.

For SDS-MWNTs/PR composites, the electrical resistivity can become lower when the amount of the MWNTs becomes greater due to the better dispersion of the nanotubes. However, the wrapping of SDS outside the nanotubes can decrease the electrical conductivity and increase the resistivity. This explains that adding small amount of the SDS-MWNTs into phenolic resins may not increase the electrical conductivity so much as that of adding the pristine MWNTs. However, for the c-MWNTs/PR composites, better dispersion of the nanotubes in the composites, as mentioned previously, can not make the electrical resistivity greater, as shown in Fig. 6. This may be due to the shortening of the nanotubes, as shown in Fig. 2 by the acidic treatment, which has an effect to decrease the electrical conductivity.

Fig. 4. (Color online) FT-IR spectra of the nanotubes.

Fig. 5. SEM picture of the hot-pressed sample for (a) MWNTs/PR and (b) neat PR.

Fig. 6. (Color online) Resistivity variation with MWNT contents for MWNTs/PR composites.
Figure 7 shows comparison for the thermal conductivity of the pristine MWNTs, the SDS- and the c-MWNT composites. It appears that better dispersion of SDS-MWNTs in the composites can make the thermal conductivity of the composites material higher. However, the wrapping of the SDS outside the nanotubes does not have too much effect on the thermal conductivity. It appears that wrapping of SDS on the nanotube surface can have much greater effect on the electrical conductivity than on the thermal conductivity. It has been found that the electron transport in the composites is dominated by tunneling of electrons between neighboring nanotubes. The wrapping of SDS over the nanotubes can create an insulation layer over the nanotubes. This can significantly reduce the conductivity of electron and increase the resistivity in the composite, especially when the amount of the nanotubes is small in the composite.

For thermal transport, however, the wrapping of SDS over the nanotubes does not have too much effect on the heat transfer since the thermal transport is caused by the lattice vibration which propagates as wave and is explained by phonon transport or scattering through the entire material.

The thermal conductivity for the c-MWNTs/PR composites is not much different from the pristine MWNTs/PR composites. Although the functionalized nanotubes have a much better dispersion in the composites, the size of the nanotubes has significantly reduced. It appears that the increase of dispersion of the nanotubes in the composites which can lead to increase in the thermal conductivity has offset the effect of shortening of the nanotubes which can reduce the thermal conductivity of the composites. Similar phenomenon for electrical resistivity of the c-MWNTs/PR composites is also observed as discussed previously.

4. Conclusions

We have data for pristine MWNTs/PR composites with MWNTs up to 10% in weight, the electric conductivity can increase significantly from 0 to 135.52 ms while the thermal conductivity of the nanocomposites increase from 0.612 to 1.473 W m⁻¹ K⁻¹. However, current data is presented with MWNTs up to 2.5% in the composite. With better dispersion of SDS-MWNTs in PR, both the electrical and the thermal conductivity of SDS-MWNT/phenolic nanocomposites are found higher. However, both the electrical resistivity and the thermal conductivity of c-MWNTs/PR composites are not much different from the pristine MWNTs/PR composites. This is attributed to the fact that in the composites better dispersion of the c-MWNTs is offset by the effect of shortening of the MWNTs due to the acidic treatment.

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