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Dielectric properties of epoxy composites with modified multiwalled carbon nanotubes

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Abstract We report here a high dielectric percolative polymer nanocomposite, fabricated by a combination of triethylene-tetramine (TETA) modified multiwalled carbon nanotube (named as TETA-MWNT) within epoxy resin matrix. In this composite system, with various TETA-MWNT volume fractions, the dielectric constant (K) is well fitted by the scaling law of the percolation theory with the percolation threshold f_c is 0.042 and the critical exponent p is 0.786. At 1,000 Hz of room temperature, the value of the dielectric constant is as high as 421 with the TETA-MWNT content of 4.14vol%, which is almost 60 times higher than that of epoxy resin. In contrast, a simple blend of pristine MWNT in epoxy composite shows evident lower dielectric constant and much higher loss with the same volume fraction.

Keywords Multiwalled carbon nanotube · Epoxy resin · Dielectric properties · Percolation

Introduction

Polymeric materials with high dielectric constant are highly desirable for use as capacitors and charge-storage applications. Conductive filler particles in an insulating matrix are able to dramatically increase the dielectric constant when a network develops throughout the matrix. The transition from an insulating to a conducting composite as a function of filler concentration is known as percolation. The variation of the dielectric constant of the composite with the concentration f of the conductive filler has been predicted to follow a critical behavior, i.e., the well-known power law as following [1, 2],

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$$K \propto K_m (f_c - f)^{-p} \text{ for } f \leq f_c \tag{1}$$

where K and K_m are the dielectric constants of the composite and matrix, respectively, f is the volume fraction of the filler and f_c the critical volume fraction corresponding to the percolation threshold, p the dielectric critical exponent. The percolation threshold of the composites depends on the property of the conducting fillers, dispersion of conducting fillers in polymeric matrix and interaction between the fillers and the polymer [3–6]. One of the most popular conductive fillers is carbon nanotubes (CNTs). Depending on the polymer matrix and the processing technology as well as the type of nanotube material used, percolation thresholds between 0.05 and 10wt% have been observed experimentally for thin films [7–10].The incorporation of CNTs into polymer bulk materials will surely enhance their thermal and electrical properties [11, 12]. An enhancement of the compatibility between the CNTs and resin matrix can improve the electrical properties as well as mechanical properties of the composite materials. Because the nanotubes have a strong tendency to form stack assemblies and microaggregates, it is hard to disperse homogeneously between the nanotubes and the polymer through physical blending.

In order to overcome this problem, the pristine MWNT was chemically modified using triethylene-tetramine (named as TETA-MWNT) in our research. As amino group has a high chemical reactivity and can react with the epoxy, which enables a stress transfer between the polymer matrix and MWNTs, thus improving the compatibility of the two components, as well as offering the potential of obtaining good dielectric properties [13]. Furthermore, we also prepared the composite in which MWNTs were physically blended with epoxy resin (named as MWNT/EP) and found that TETA-MWNT/EP composite indeed exhibit better electric properties than MWNT/EP as well as more finely dispersed morphology.

Experimental

Materials

The MWNT produced by chemical vapor deposition (VCD) was obtained from Shenzhen Nanotech Port Co. and purified by thermal oxidation. A commercially available bisphenol A type epoxy resin (E51, Blue Star New Chemical Materials Co.) with the epoxy equivalent 196 g/eq and density of 1.10 g/cm^3 at 25 °C was used as matrix. Amine hardener 2-ethyl-4-methyl imidazole was distilled under reduced pressure. Triethylene-tetramine (TETA) was dried with NaOH and then distilled before use. Dimethylformamide (DMF) was dried with CaH_2 followed by distillation in vacuo prior to use.

Synthesis of TETA-MWNT

MWNT (0.5 g) was sonicated with 100 mL of a 3:1 (v:v) mixture of H_2SO_4 (98%)/HNO_3 (68%) at 40 °C for 3 h, the carboxylated MWNT was filtered and washed with deionized water until pH was 7 and dried in vacuum; 0.4 g of carboxylated

MWNT was stirred in 80 mL thionyl chloride ($SOCl_2$) and 4 mL DMF for 24 h at 70 °C and the unreacted $SOCl_2$ was removed under vacuum. The obtained acyl chlorination MWNT was washed five times with anhydrous tetrahydrofuran (THF) and vacuum dried. 0.4 g acyl chlorination MWNT was reacted with 100 mL TETA at 120 °C for 48 h. After cooling to room temperature, the solid was washed with ethanol to remove excess TETA. Finally, TETA-MWNT was obtained after drying the product under vacuum.

Preparation of sheet samples for electric measurement

A certain amount of TETA-MWNT was dispersed in 5 mL acetone and sonicated for 1 h. Then the suspension of TETA-MWNT in solution was added into epoxy resin, and the mixture was stirred by further ultrasonic treatment for 3 h. The solution was removed from the mixture under vacuum before the hardener added. Then the homogeneous mixture was cured 2 h at 140 °C. The final samples were cut into small pieces of 10 × 10 mm and around 1 mm thick. The MWNT/EP composite samples were prepared as the mentioned processing above. For electrical measurement, gold electrodes with 3.0 mm radius were sputtered on the center of both surfaces of each sample.

Characterization

FT-IR spectra were recorded with a Bruker Vector-22 FT-IR spectrometer. Raman spectroscopy was performed using a JY-T64000 spectrometer on powder samples of pristine and TETA functionalized MWNT over a scanning range of 1,200–2,000 cm^{-1} with incident laser excitation wavelength of 514.5 nm. Elemental analyses were performed with a CHN-O-Rapid Heraeue elemental analyzer. The fractured cross-sections of the composites were observed with a LEO 1,550 field-emission scanning electron microscopy (FESEM). Dielectric properties of samples were measured using an Agilent 4194A Impedance Analyzer in the frequency ranges of 1 kHz–20 MHz. All of the samples were measured at room temperature and the results were the typical values of reproduced experiments.

Results and discussion

IR spectra of the raw MWNT, amino-functionalization MWNT and cured TETA-MWNT/EP composites are shown in Fig. 1. The significant increase at 3,420 cm^{-1} in spectrum (b) indicates the appearance of NH_2 group. Peaks at 2,925 and 2,850 cm^{-1} are attributed by stretch modes of C–H bond of methylene groups and 1,124 cm^{-1} with C–N stretching bond. The 1,648 cm^{-1} peak was assigned to $C = O$ stretch mode and 1,502 cm^{-1} peak is due to the appearance of N–H bond. The disappearance of 3,420 cm^{-1} peak of NH_2 groups and the appearance of 1,033 cm^{-1} to the $C–N^+$ stretching vibration in graph (c) indicate the reaction of amino group at the TETA-MWNT with epoxy group at the matrix.

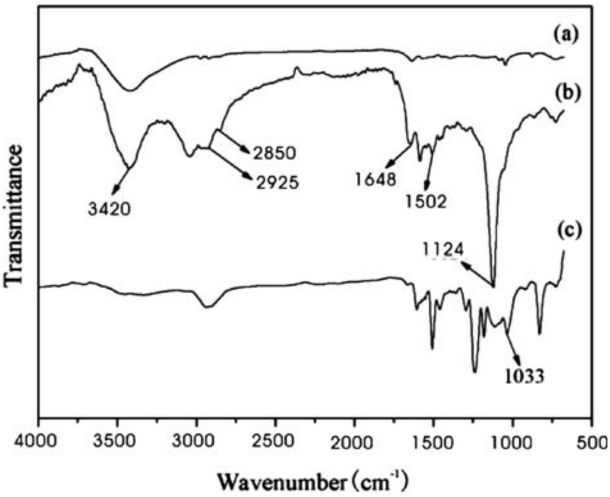

Fig. 1 FTIR spectra of (**a**) pristine MWNT (**b**) TETA-MWNT and (**c**) TETA-MWNT/EP

Figure 2 shows the Raman spectrum of the MWNT and TETA-MWNT. Both spectra have the same pattern, revealing that treating the surface with TETA does not affect the graphite structure of the MWNT. Such chemical functionalization of the MWNT can be used to produce carboxylic acid and amino groups at local defects in the curved grapheme sheets and tube ends. The presence of two broad bands at 1,350 and 1,580 cm^{-1}, usually referred as to D (disorder, sp^3 banding) and G (graphitic, sp^2 banded carbon) bands. The value of intensity ratio between the G- and D-bands (I_G/I_D) serves as a measure of the graphitic ordering and indicates the approximate crystalline size in the hexagonal plane. Comparing the I_G/I_D ratios of the samples, which are 1.33 for MWNT and 1.08 for TETA-MWNT, reveals that chemical modification of MWNT increases defects scattering on sidewall of nanotubes due to covalent functionalization [14, 15].

The content of amino group on the surface of MWNT after chemical modification was determined using an elemental analyzer, with the testing values of C, 71.91; H, 3.41; O, 19.03; N, 5.66, respectively. The analyzed results show that one of 15 carbon atoms in the MWNTs was aminated.

The morphology of fractured of MWNT/EP and TETA-MWNT/EP composites are shown in Fig. 3. The raw MWNTs are easily aggregated in epoxy matrix while very good dispersion of chemical functionalization MWNTs can be found in epoxy composites, which can be seen from the comparison of the low magnification SEM images of Fig. 3a and b. It can be said that the increase of the polarity between the nanotubes and the reaction of amino group with epoxy group contribute to greatly improvement of compatibility in the TETA-MWNT/EP composite. Moreover, we cannot see any extraction trace in Fig. 3d and the fractured TETA-MWNTs are embedded in epoxy resin tightly while some of the raw MWNTs are pulled out in

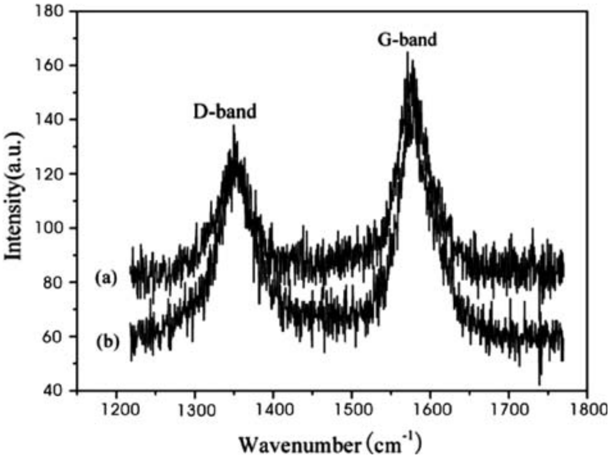

Fig. 2 Raman spectra of (**a**) pristine MWNT and (**b**) TETA-MWNT

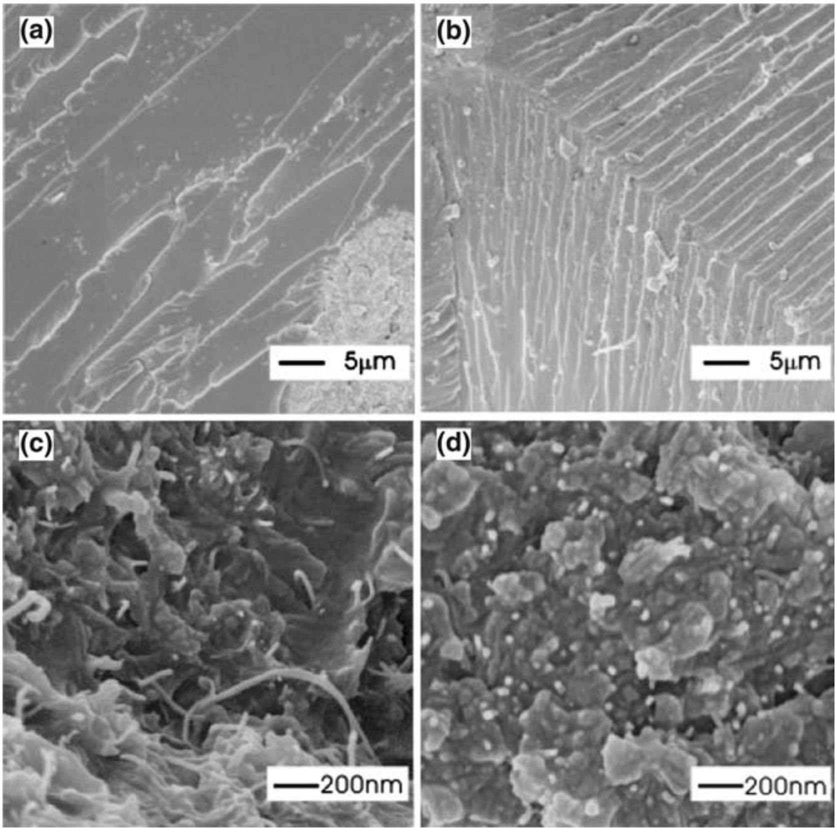

Fig. 3 FESEM micrograph of fractured surface of (**a**) MWNT/EP, (**b**) TETA-MWNT/EP, (**c**) MWNT/EP and (**d**) TETA-MWNT/EP composites with nanotube fraction of 4vol%

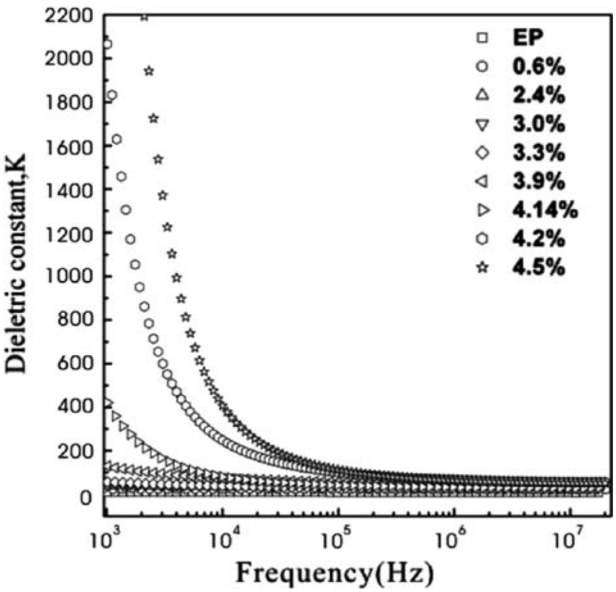

Fig. 4 Frequency dependence of dielectric constant *K* of TETA-MWNT/EP composites with different MWNT contents

the fractured process in Fig. 3c. The well compatibility of TETA-MWNT in epoxy matrix can improve the electrical properties of the composites.

Figure 4 presents the dielectric constant as a function of frequency at room temperature with different volume fractions of the TETA-MWNT. The measurements show that the dielectric constant *K* is almost independent of frequency when the filler contents are low ($f \leq 3.9$vol%), the *K* values decrease rapidly with the frequency when the contents are higher than 3.9vol%. For example, the dielectric constant of the composites with 4.14vol% of CNTs fillers decreases from 421 to 30 and for the composites with 4.2vol%, it is from 2,066 to 58 in the same range of 1 kHz–20 MHz. The increased dielectric dispersion of the composites is due to the presence of space charge polarization in the composite [16–18].The large difference of dielectric constant between the insulator polymer matrix and conductive filler will cause Maxwell–Wagner (MW) polarization, which results in large low frequency dielectric dispersion of the composites [19, 20]. For CNTs filler used here, the conduction mechanism is through the hopping transport of carries, which results the dielectric constant in the neighborhood of percolation threshold reducing rapidly with frequency, $\varepsilon(\omega) \sim \omega^{s-1}$, where s is a constant of approaching toward 1, ε decreases with the frequency, as has indeed been observed experimentally. When the concentration of CNT in the composites is higher than percolation threshold, the composites are electrically conductive, but when the concentration is lower than percolation threshold, the composites act as insulators.

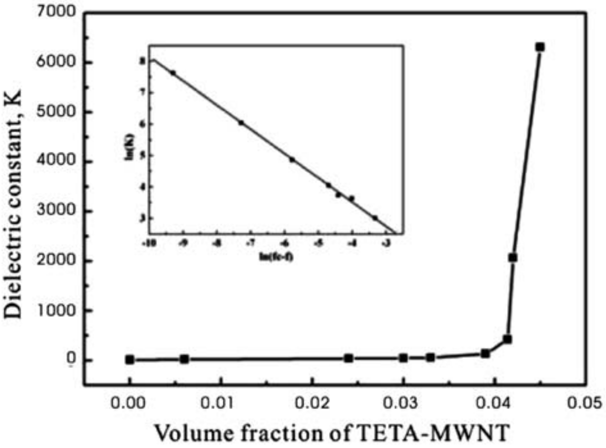

Fig. 5 Dielectric constant (*K*) of TETA-MWNT/EP composites as a function of the MWNT volume fraction (*f*), measured at room temperature at 1 kHz. The inserted plot in a log–log scale shows that the *K* values are well fitted by the scaling law of the percolation theory with a percolation threshold $f_c = 0.042$ and an exponent $p = 0.786$

Summarizing the data in Fig. 4, the dielectric constant at 1,000 Hz as a function of the volume fraction of TETA-MWNT in the composites, yields the data in Fig. 5. The dielectric constants vary very little with the MWNT content up to 3.90vol%. The *K* value increases significantly as high as 2,066 while the filler fraction is 4.2vol%. Fitting the data in formula (1) yields $f_c = 0.042$ and $p = 0.786$ (see inset in Fig. 5). The critical exponent *p*, which was considered to be universal, namely, depended only on the spatial dimension of the composites [21]. At 4.14vol% (in the neighborhood of the percolation threshold 4.2vol%), the dielectric constant of the sample is as high as 421, which is about 60 times higher than that of epoxy matrix and the dielectric loss is only 0.80 (see Fig. 6).

Presented in Fig. 6 is the dielectric loss *D* as a function of the frequency with different CNTs volume fractions. As the existence of MW polarization, the loss values of TETA-MWNT/EP composite decrease with the frequency, especially at low frequency. When the filler fractions are higher than 4.14vol%, the dielectric loss increases rapidly, with the feature associated with the approach of percolation. The inserted plot fits well with the theoretical percolation threshold (see Fig. 5).

In order to compare the dielectric property of epoxy nanocomposite with amino-functionalization MWNT to pristine MWNT, dielectric constant *K* and dielectric loss *D* of the two composite systems were measured at room temperature, with the fillers content of 4.14vol%. From Fig. 7 we can see that the dielectric constant of MWNT/EP composite is visibly lower than TETA-MWNT/EP material, while the dielectric loss is much higher than TETA-MWNT/EP. The result is due to the poor dispersion of raw MWNTs in epoxy matrix, so the physical blends of the two components may easily form conductive pathways. Meanwhile the

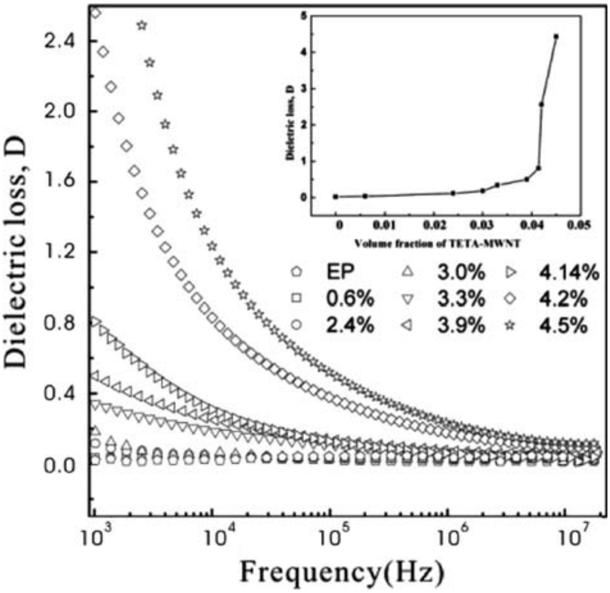

Fig. 6 Frequency dependence of dielectric loss *D* of TETA-MWNT/EP composite with different MWNT contents. The inserted plot is the loss of the composite with different TETA-MWNT contents

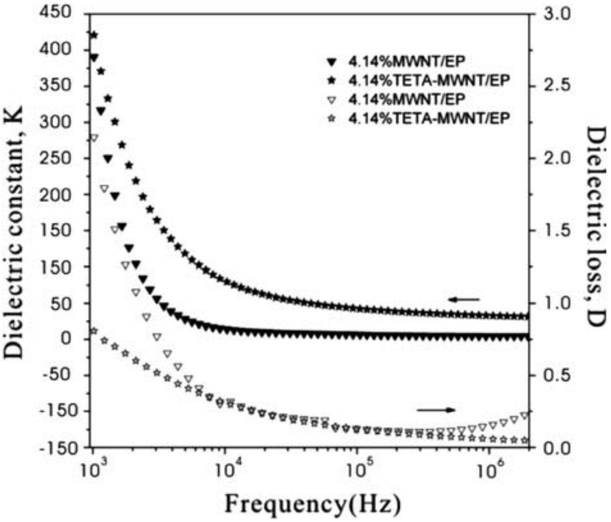

Fig. 7 Dielectric constants and dielectric loss of TETA-MWNT/EP and MWNT/EP composites as a function of frequency

amino-functionalization MWNT significantly increased the compatibility between the epoxy and the CNTs, which improve the dielectric constant and decrease the loss of the composite.

Conclusions

Epoxy resin composites filled with triethylene-tetramine functionalized MWNTs were prepared. According to the scaling law, the theoretical percolation threshold f_c was 0.042 and the critical exponent p was 0.786, fitting well with the experimental results. Due to the improvement of the compatibility of TETA-MWNT with epoxy matrix, the value of the dielectric constant is as high as 421 with the TETA-MWNT content of 4.14vol% at 1,000 Hz, which is almost 60 times higher than that of epoxy matrix and also evidently higher than MWNT/EP composites, while the loss is much lower than MWNT/EP.

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