Nuclear Science and Techniques **23** (2012) 156–162

Electrical and optical properties of MWNTs/HDPE composites in Terahertz region

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Abstract Optical and electrical properties of composites, prepared by filling of high density polyethylene (HDPE) with two kinds of multi-walled carbon nanotubes (MWNTs) differing in diameters, were explored by terahertz time-domain spectroscopy (THz-TDS) in the frequency range from 0.2 to 1.6 THz. It is found that composite with larger-diameter MWNTs possesses larger absorption coefficient and conductivity at the same concentration. The real part of the ac conductivity of the composites follows a power law dependence on frequency. And the power index is around 0.75 regardless of the MWNT concentration and diameter. The experimental data were analyzed with Cole-Cole equation under the assumption that the conductive clusters dispersed in the polymer matrix behave like dipoles and contribute mainly to the dielectric loss. It is found that both of the composites have similar values of relaxation time and distribution parameter. With increase of the MWNTs concentration, the relaxation time increases and tends to saturate at 0.7 ps after passing through the percolation threshold.

Key words Carbon nanotubes, Transport properties, Terahertz time-domain spectroscopy, Cole-Cole equation

1 Introduction

With rapid development of electronic devices, spectroscopy and imaging technology has come into the era of Terahertz (THz) electromagnetic spectrum. Terahertz time-domain spectroscopy (THz-TDS) has been acknowledged as a powerful tool for material studies due to its unique advantages such as non-destructive and non-contact measurements, and high signal-to-noise ratio at <3 THz[1]. It is of particular advantage for acquisition of optical constants compared to the complicated Kramer-Kronig transformation.

Due to their unique structure and physical properties, carbon nanotubes (CNTs) are important building blocks for prototype electron emission devices, nanocomposite materials, energy storage materials, nanoprobes, sensors and templates to fabricate one-dimensional nanowires[2]. Among potential applications of CNTs, their usage as reinforcing materials for polymers has received considerable attention because of their exceptional mechanical properties, low density and high electrical conductivity. The use of CNTs in conductive materials will significantly reduce the percolation threshold and the production cost as well[3], and such conductive composites can be applied in manufacturing electronic devices in terahertz region such as terahertz absorbers and EMI shielding materials[4]. Therefore, characterization of the composite in the terahertz range, extending from a few tens of GHz to a few THz, is of particular importance. The factors that may affect electrical and optical properties of CNTs-filled composites include the sample purity, the metallic to semiconducting volume fraction and doping level of the semiconducting tubes[2,5,6]. Also, the geometry of CNTs, such as the length or diameter, may affect the absorptive and electrical properties[5,7].

Supported by National Natural Science Foundation of China (10675157) and (10875161) and by the National Basic Research Program of China (Grant No. 2010CB832903)

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Received date: 2011-10-09

In this work, composites were prepared by filling of high density polyethylene (HDPE) at the molten sate with various amounts of multi-walled carbon nanotubes (MWNTs) of different diameters at the molten sate. As a widely used polymer with excellent chemical resistance, high impact strength, good fatigue and abrasive wear resistance, and of low absorption and constant index of refraction in THz region, HDPE is often used as a polymer matrix of composites in THz measurements[8]. The optical and electrical properties of pure HDPE and the composites were investigated by using a THz-TDS. It was found that the dielectric properties of the composites can be analyzed by using the Cole-Cole equation of dipole relaxation in combination with the microstructure variation with filler concentration.

2 Experimental

2.1 Sample preparation

Thin (Φ10–20 nm) and thick (Φ20–40 nm) MWNTs, in length of 1–2 μm, and the purity of ~95% in mass fraction, were purchased from Shenzhen Nanotech Port Co., Ltd. HDPE 7000F (ρ=0.956 g/cm^3) was from Mitsui Corp. Antioxidant Dilauryl thiodipropionate (DLTP:$C_{30}H_{58}O_4S$) was from Sanfeng Chemical Corp. Detailed description of filler dispersion process can be found in Ref.[9]. The samples were made by pressing the MWNT-filled HDPE to about 1 mm in thickness at 180°C. MWNT contents (*V*/*V*) of the composites were 1.10%, 2.22%, 3.37%, 4.53%, 5.72% and 8.79%.

2.2 THz-TDS Measurements

The terahertz time domain spectroscopy apparatus is composed of a laser generator and the optical arrangement. The laser was mode-locked Ti:sapphire system that provides 80-fs pulses at a central wavelength of 800 nm, with an average power of 700 mW and a repetition rate of 80 MHz. Measurements were all carried out under nitrogen atmosphere to eliminate the effects of water vapor.

2.3 Atomic force microscopy analysis

All scanning probe microscope measurements were performed in dynamic force modulation (DFM) mode using an atomic force microscopy (SPA-400) unit coupled with a SPI-3800 control station (Seiko Instruments). Cantilevers with an Al-coated tip (NSC35/Al BS, MikroMasch) having a normal spring constant of 4.5 N·m^{-1} and resonance frequency of 120–190 kHz were used as received. The scanning range was 10 μm×10 μm.

2.4 DC conductivity measurements

DC conductivity was determined by measuring the dc resistance using two-probe method as described in Ref.[10]. A PC68 digital electrometer were used to measure high resistance samples (resistance>10^8 Ω) and a LCR (HIOKI 3522-50) electrometer to measure conductive samples (resistance<10^8 Ω).

3 Results and discussion

The time domain transmission spectra of the composites filled with thin MWNT are shown in Fig.1a. Compared to the reference of N_2, the THz signal attenuates obviously with increasing concentrations of the filler. The phase delay for passage of the signals through the samples increases gradually with the MWNT contents. From the frequency-domain spectra (Fig.1b), the power decreases strongly with increasing contents of the filler, which can be attributed to the strong absorption of the filler to the THz wave.

The complex transmission coefficient $T(\omega)$ of the sample can be calculated by Eq.(1)

$$T(\omega)=\frac{S_{\text{sam}}(\omega)}{S_{\text{ref}}(\omega)}=\frac{2\tilde{n}_{\text{sam}}\cdot 2\tilde{n}_{\text{ref}}}{\left(\tilde{n}_{\text{sam}}+\tilde{n}_{\text{ref}}\right)^2}\cdot \exp\left[-i\left(\tilde{n}_{\text{sam}}-\tilde{n}_{\text{ref}}\right)\frac{\omega\cdot d}{c}\right]\cdot FP(\omega) \tag{1}$$

where, S is the Fourier transformed amplitude of the output THz wave form; d is the sample thickness; and c is the velocity of light in free space; $\tilde{n}=n-ik$ is the complex refractive index, n is the refractive index and k is the extinction coefficient; the subscripts of sam and ref denote sample and reference; and $FP(\omega)$ is the Fabry-Pérot factor, which refers to the backward and forward reflections in the sample, as the sample is strongly absorptive and thick enough, it can be considered as negligible, i.e. $FP(\omega)=1$[11]. The absorption coefficient can be calculated by

$\alpha(\omega)=2\omega k/c$, where the angular frequency $\omega=2\pi f$ and f is the circular frequency in Hz.

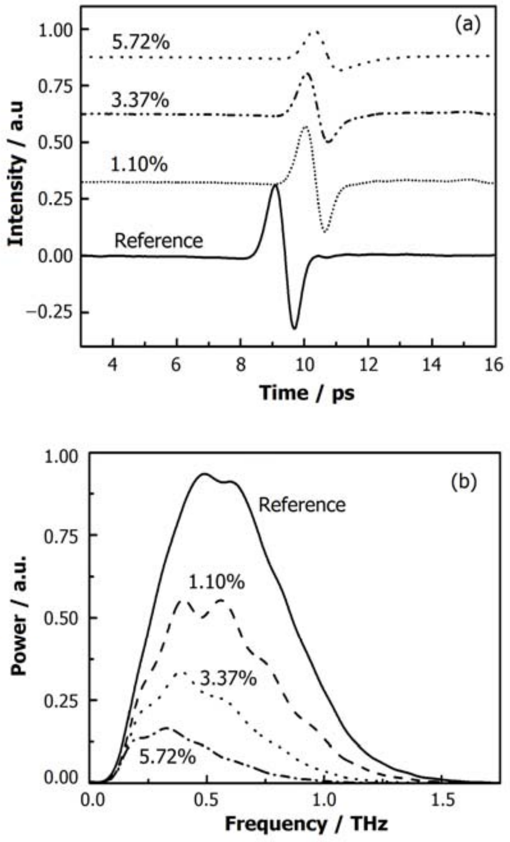

Fig.1 THz time-domain wave forms (a) and frequency-domain spectra (b) of the reference and samples filled with different volume concentrations of thin MWNT.

Pure HDPE is nearly transparent in terahertz region and the absorption coefficient is less than 5 cm^{-1} over the entire frequency range as shown in Fig.2a. The real part of refractive index (Fig.2b) of the HDPE is about 1.52 and remains almost constant in the whole frequency range, which is in good agreement with the literature value[8]. For MWNTs/HDPE composites, due to the strong absorption of MWNT to THz wave, the signal-to-noise ratio is reduced markedly. As a result, the dynamic range of the spectrometer is greatly reduced. For the composite containing 2.22% MWNT, the believable bandwidth is 0.2−1.7 THz. As for the composites, both the absorption coefficient and refractive index increases with the filler content. With increasing frequency, absorption coefficient of the composites increases whereas the refractive index decreases. Also, the absorption coefficient and refractive index of the composite with thick MWNTs are larger than that those of the composite with thin MWNTs at the same filler concentration (Fig.2).

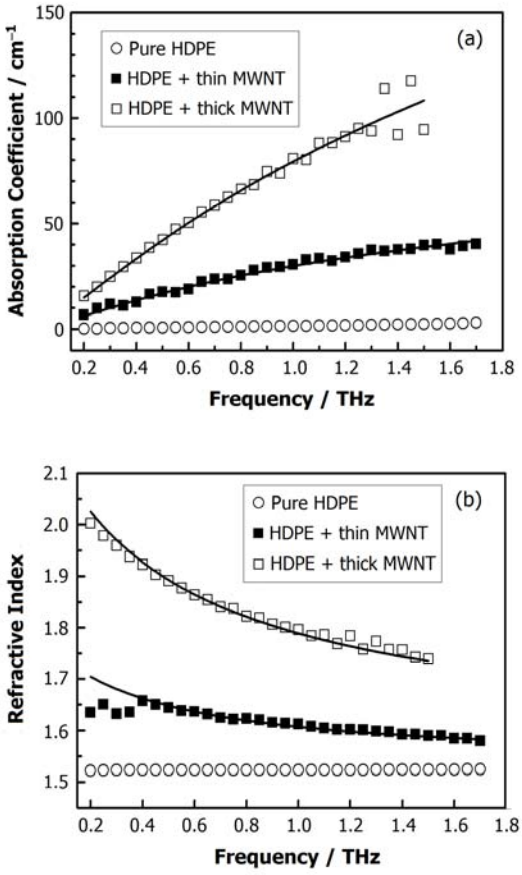

Fig.2 Absorption coefficient (a) and refractive index (b), as a function of frequency, for pure HDPE and composites filled with thin and thick MWNT at concentration of 2.22%. The solid lines are fittings by using Cole-Cole equation.

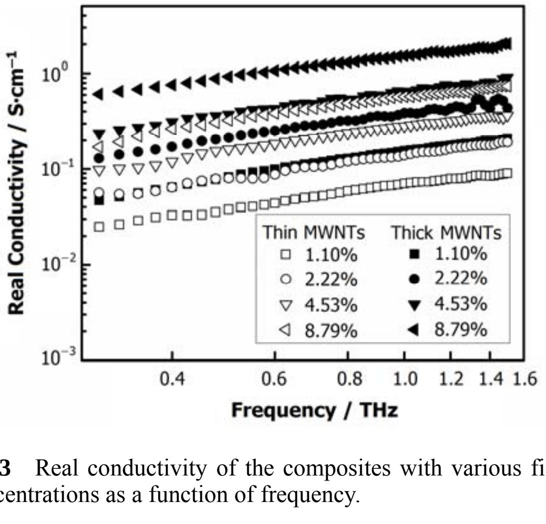

Fig.3 Real conductivity of the composites with various filler concentrations as a function of frequency.

The real conductivity $\sigma'(\omega)$ of the composites can be evaluated from absorption coefficient (α) and refractive index (n) through $\sigma'(\omega)=c\alpha(\omega)n(\omega)\varepsilon_0$, where ε_0 is the free space permittivity. As shown in Fig.3, log-log plot of the real conductivity of the composites is chosen to characterize the function of frequency. The $\sigma'(\omega)$ follows a power law frequency-dependence with a power index of 0.75±0.03 for all the composites regardless of the concentration and MWNTs diameter. This value is very close to S=0.7±0.04 for carbon black filled composites at high frequencies up to 0.6 THz[12].

The real conductivity can be resulted from three processes: (a) polarization effects between clusters[13], (b) anomalous diffusion within each cluster[14] and (c) dc conduction through the filler network. The electrical conduction through the conducting paths formed by the filler network dominates at higher filler concentration in the low frequency range. At high frequency range, the frequence-dependent ac conductivity mainly comes from the effects of polarization between clusters and the anomalous diffusion within cluster. The former can be considered by making an analogy between the conductive clusters and an equivalent circuit that has capacitance between the different clusters. With the increase of the frequency, the current passing through each capacitor increases resulting in the increased conductivity of the composites. The theoretical predictions based on the intercluster polarization gives an exponent value of 0.72[13]. In addition to the intercluster polarization effects, the anomalous diffusion inside the clusters also contributes to the conductivity. At high frequencies, electrons will scan a distance $L_\omega \sim \omega^{-1/(2+\theta)} < \xi$, where ξ is the correlation length of the system, θ=1.5 is a for the 3-dimensional systems according to the percolation theory[14]. On these scales the conducting clusters are self-similar fractals. Since the conductivity $\sigma(\omega)$ increases when L_ω decreases, it can be seen that the conductivity will increase with increasing ω. The typical index value for the anomalous diffusion according to Gefen *et al.* [14] is about 0.58. The measured values (0.75) in this work are closer to the predictions of the intercluster polarization model for the measured frequency range. It implies that the intercluster polarization may be the dominant conductive mechanism under the present experimental conditions.

The filler concentration dependence of $\sigma'(\omega)$ at 1THz is shown in Fig.4. The conductivity of the two composites increases linearly with the filler concentrations. At the same filler concentration, composite with thick MWNTs is of larger conductivity, having a 2.6-fold conductivity increase with a two times increase in MWNTs diameter. Considering that the dc conductivity is very small even at the highest filler concentration (<1%, see Fig.1), the large increase in conductivity with diameter is mainly a response of the ac conductivity, i.e. the intercluster polarization.

The magnitude of intercluster polarization is related to the cluster size, cluster number density, charge-carrier density and charge-carrier mobility inside clusters. As a whole, it depends mainly on the total charge-carrier number and the charge carrier mobility. As at the same filler concentration the total number of carbon atoms and therefore the total number of charge carriers for the two kinds of composites is equivalent, it seems that the large difference in conductivity is a result of the difference in charge-carrier mobility.

As can be expected, at the same volume fractions, the total tube number of thin MWNTs is much more than thick MWNTs since the two types of MWNTs are of the similar length. As a consequence, the thin MWNT will form more tube-tube junctions than thick MWNTs do at the same concentration within the matrix when aggregates into clusters. In Ref.[15], Hu *et al.* studied the conductivities of the carbon nanotubes networks and suggested that the overall conductance of the nanotubes networks is limited by the intertube resistance of $10^8\ \Omega$, about 4 orders of magnitude larger that the resistance of the tube themselves. And the same ratio is obtained comparing the mobility of single nanotubes ($10^5\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$)[16] with that of networks (between 10 and $10^2\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$)[15]. So the averaged mobility of the charge carriers and the conductivity will be reduced rapidly when the nanotubes junctions form. In this work, the diameter of the thick MWNTs is twice of that of the thin MWNTs and thus the number of thin MWNTs is 4 times that of thick MWNTs at the same filler concentration. As a result, more junctions will form within the thin MWNTs clusters, which act as a potential barrier and make the carriers difficult to move onto the interface between clusters. Consequently, the conductivity due to the intercluster polarization will be reduced.

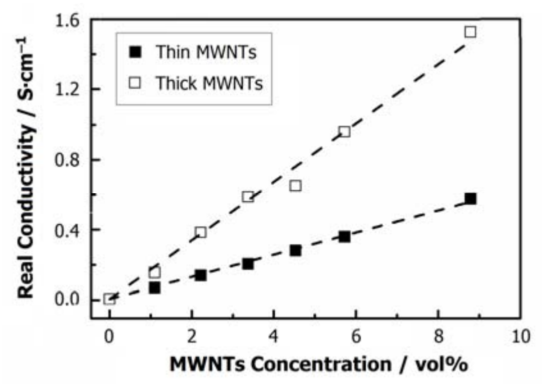

Fig.4 Ral conductivity as a function of filler concentration at 1 THz for composites containing thin and thick MWNTs.

In the MWNTs-filled composites, the MWNTs will aggregate into clusters. Under an alternative electric field the charges move inside the clusters, which make the clusters behave like dipoles. At high filler concentrations some of these clusters can connect to each other to form conducting networks. Therefore the dielectric behavior of the composites can be described by the Cole-Cole equation by taking into account the contributions from dc conduction, i.e.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\beta}} + \frac{\sigma_0}{i\omega\varepsilon_0} \qquad (2)$$

where $\varepsilon^*(\omega)$ is the complex permittivity, ε_s and ε_∞ are the static and optical permittivity, respectively, τ is the relaxation time and σ_0 is the dc conductivity. The parameter β measures the width of the underlying relaxation time distribution with a value ranging between 1 and 0. The larger the value of β, the broader the distribution is. It is easily seen that Eq. (2) yields Debye expression when $\beta=0$.

The fitting of absorption coefficient and refractive index of the samples at a filler concentration of 2.22 Vol% using Eq.(2) were depicted as solid lines in Fig.2 and the parameters obtained are summarized in Table.1. It can be seen that for both of the two composites non-zero β values of similar size are obtained, indicating a broader distribution of the relaxation time. Calame[17] found by a numerical simulation that systems containing isolated clusters with few inclusions exhibit a nearly Debye response with a single time constant whereas those containing clusters with more branch-like inclusions display a wide distribution of relaxation time. As stated above, the attractive interactions between the nanotubes make them tend to agglomerate even in the presence of surfactant. The observed distribution of relaxation times partially reflects the shape and size distribution of the clusters[18].

Table 1 Fitting parameters for composites with 22% MWNT.

Filler	diameter / nm	β	ε_∞	ε_s	$\Delta\varepsilon$	τ (ps)
MWNT-A	10–20	0.28	2.34	3.19	0.85	0.42
MWNT-B	20–40	0.33	2.35	5.01	2.66	0.40

The concentration dependence of the relaxation time was shown in Fig.5a. At low concentrations, the relaxation time increases with increase of filler concentration and tend to saturate at high concentrations. The saturation phenomenon is particularly clear for the composite with large diameter MWNTs above the percolation threshold. These phenomena may be related to the aggregation of clusters and the formation of percolating networks at high concentrations, which is consistent with the dc conductivity measurements in Fig.5b.

At very low concentrations of MWNTs, the conductivity increases gradually with MWNTs contents. A significant increase in conductivity in the order of 10^6 S/cm for thick MWNTs filled composites is observed at about 5 Vol%. This stepwise change in conductivity is a result of the formation of an interconnected structure of carbon nanotubes above a critical content regarded as an electrical percolation threshold. At the concentrations above this critical content the conductivity will further increase with the MWNTs concentration due to formation of more conducting paths and improved conducting network.

In the thin MWNTs-filled composites, however, the conductivity is much lower than that of thick MWNTs and no percolation threshold is observed up to the highest filler concentration. As stated above, the MWNTs tend to aggregate into clusters within HDPE matrix. The sizes of these clusters vary greatly with filler concentrations.

As shown by AFM images (Fig.6), at lower concentration (1.1 vol%) the clusters have diameters of about 0.1-0.2 μm. The diameter of the clusters at the concentration of 5.72 Vol% is found to be about 0.5 μm, more than two times that of the composites at the concentration of 1.1 vol%. The increase of relaxation time at lower filler contents can be understood by the fact that with increasing cluster size the charge carriers have to take more time to reach the interfacial surface of the clusters under the external field.

At high concentrations, however, percolating structure will form and parts of the clusters are not isolated any more. Further increase of the concentration results in formation of more conducting paths, hence the improved dc conductivity, but the size of isolated clusters will be little influenced. Besides, it was reported that change in cluster shape could also influence the relaxation time[18]. An increment in relaxation time was observed with the cluster shape changing from spherical to prolate spheroid.

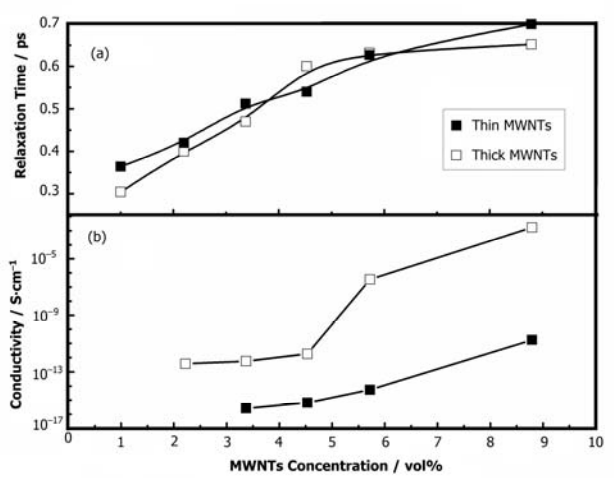

Fig.5 Relaxation time (a) and dc conductivity (b) *vs.* filler concentration for composites containing thin and thick MWNT.

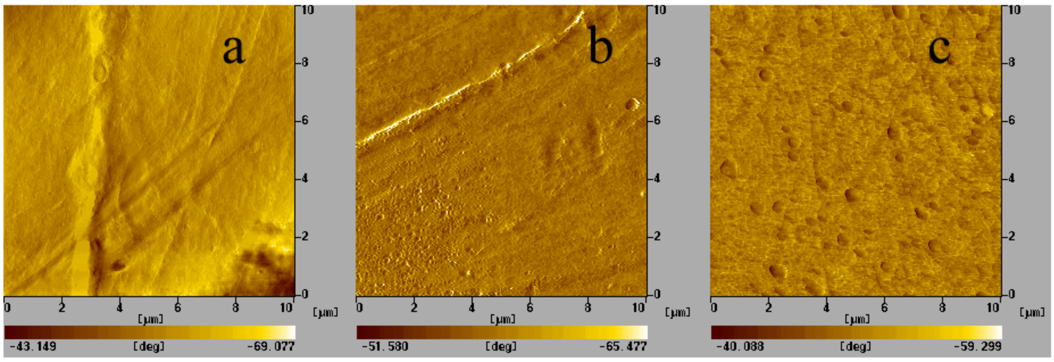

Fig.6 AFM images of pure HDPE (a) and HDPE/thick MWNT composites at content of 1.1 vol% (b) and 5.72 vol% (c).

4 Conclusion

HDPE-based composites containing MWNTs with different diameters were characterized with THz-TDS. It is demonstrated that the composite containing MWNTs with larger diameter possesses higher conductivity and refractive index, and is more effective in absorption to THz waves. The real conductivity follows the interfacial polarization model and was proportional to $\omega^{0.75}$. The power index has no relationship to the concentration and diameter of MWNTs. Assuming that the conductive particles dispersed in the matrix behave like dipoles at THz field. The experimental data were analyzed with Cole-Cole equation of dipole relaxation. The fitting indicated that the relaxation time has a distribution, which is correlated to the distribution of cluster size and shapes. Furthermore, it is found that the relaxation time increases with the increasing of filler concentration at low concentrations, a phenomenon that is attributed to the increasing of the size and the changing of the shape of the conductive clusters. At higher concentration, however, formation of dc conductive paths inhibited the growth of the isolated clusters and therefore resulted in the saturate of the relaxation time.

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