Dielectric Properties of MWNTs/HDPE Composites in Terahertz Region Studied with Reverse Effective Medium Approach

[1]Wang Zhenqiang, [1]Chen Xiliang* , [1,2]Liu Wei*
[1]*Yellow River Conservancy Technical Institute, Kaifeng 475003, Henan, China.*
[2]*Kaifeng Key Laboratory of Green Coating Materials, Kaifeng 475003, Henan, China.*
466548592@qq.com*

(Received on 21st May 2018, accepted in revised form 2nd August 2019)

Summary : Optical properties of composites MWNTs/HDPE were explored by terahertz time-domain spectroscopy (THz-TDS). It was found that with the increasing of frequency from 0.4 to 2 THz the absorption coefficient increases gradually whereas the refractive index decreases. Furthermore, composites with thick MWNTs possesses larger absorption coefficient and index of refraction compared to that with the thin MWNTs at the same concentration. The dielectric properties of the MWNTs were extracted with reverse effective medium approach (REMA) from that of the composites. The results of the absorption coefficient and refractive index for MWNTs calculated from different concentrations coincides well with each other. The extracted results were then analyzed with the Drude model combined with a localized Lorentz absorption.

Keywords: multi-walled carbon nanotubes; dielectric properties; Terahertz time-domain spectroscopy (THz-TDS); effective medium approach

Introduction

Carbon nanotubes (CNTs) have numerous potential applications in emission displays, microscopy tips, and high-capacity hydrogen storage medium et al. due to their unique structures and physical properties. Recently, possibilities for using of the CNTs as electronic devices including high-frequency interconnects between transistors [1], terahertz emitters as well as absorbers at GHz even at THz region were considered [2]. So it is of great significance to study the electrical conductivities and optical behaviors of CNTs in terahertz region from both fundamental and technological points of views. Ugawa [3] and his collaborators measured the reflection spectrum of a single-walled carbon nanotubes film. The real conductivity was then obtained through the numerical process of Kramer-Kronig transformation. It was found that there was a clear plasma edge on the reflection spectrum and a low-frequency localized conductivity peak around 4 THz. The real part of the ac conductivity and dielectric constants were further found to be quite weakly temperature-dependent, which was consistent with the results of microwave spectroscopy test. The doping and hydrogenation effects of SWNTs on their infrared optical behavior were explored by Kang [4], with terahertz time domain spectroscopy (THz-TDS). The absorption and conductivities after doping or hydrogenation significantly decreased due to the fact that the number of free carriers decreases for bonding change from sp^2 hybridization to sp^3.

CNTs have strong absorption to terahertz wave, therefore the believable measurement bandwidth of the spectrum will be greatly reduced. The samples for THz-TDS test are usually prepared with very small thickness from tens nanometers to hundreds of micrometers by growing or spraying CNTs on absorption-free substrates [3, 4]. The samples are considered as composite composed of CNTs and air when calculating their dielectric constants. The contribution of air to the dielectric constants should be deducted from that of the composites, which is generally obtained via fitting the experimental data to effective medium approximation with adjustable geometrical factor and concentration as fitting parameters. As the concentration of CNT is not known exactly, the precision of the obtained dielectric constants of pure CNTs may be questionable. An alternative method is required to analyze the dielectric properties of the conductive particles with accurately fixed volume content.

High density polyethylene (HDPE) is a kind of non-polar polymers with superior mechanical and insulating properties. It is suitable for using as matrix of the composites for THz measurements due to its weak absorption and low refractive index in terahertz band [5]. We have prepared MWNTs/HDPE composites previously by dispersing the MWNTs in HDPE at molten state assisted by mechanical shearing, which ensure homogeneously distribution of MWNTs within the polymer matrix. The components MWNTs and HDPE were weighed before carefully in order to acquire the volume fractions of MWNTs in the composites. The optical properties of the composites

*To whom all correspondence should be addressed.

were measured with THz time domain spectroscopy and analyzed with Cole-Cole equation [6]. However, the dielectric properties of the pure MWNTs were still unknown. In this article, the optical properties of MWNTs particles were extracted using reverse effective medium approach (REMA) with a known volume concentration. The extracted dielectric constants from composites with different concentrations were found coincide well with each other.

Experimental

Materials

Two kinds of raw MWNTs with diameters of 10-20 nm (thin MWNTs) and 20-40 nm (thick MWNTs) were purchased from Shenzhen Nanotech Port Co., Ltd. The length of the nanotubes is 1-2 μm, density is 1.75 $g \cdot cm^{-3}$, and the purity is about 95% in mass fraction according to the manufacturer's specifications. HDPE 7000F is from Mitsui Corporation with density of 0.956 g/cm^3 and MFI of 0.05 g/10min.

Sample preparation

Dispersion of fillers was carried out by using a Haake internal mixer working at 150°C for 15 minutes with a rotating speed of 50 rpm. Prior to mixing, the resin particles and the fillers were all dried at 60°C under vacuum for 24 hours. The pure HDPE and the mixed compounds were then compressing-molded into discs at 160°C under a pressure of 15 MPa. The thickness of the samples was about 0.5mm. The volume concentration of MWNTs φ is determined by the following equation:

$$\varphi = \frac{W_{MWNT} / \rho_{MWNT}}{W_{MWNT} / \rho_{MWNT} + W_{HDPE} / \rho_{HDPE}} \qquad (1)$$

where W and ρ refer to the weight and density of the corresponding material, respectively. The calculated volume concentration according to Eq.1 of the samples are 1.10%, 2.20%, 3.37%, 4.53%, 5.72%.

THz-TDS setup and 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 800nm with an average power of 700 mW and a repetition rate of 80 MHz. The femtosecond pulse was split into two beams, a pumping beam and a probing beam. THz pulse was generated by illuminating a photoconductive antenna (LT-GaAs) with the pumping beam and then focused transmitting through the sample. The probe beam passes through a ZnTe crystal in co-line with the THz pulse. The THz wave signal that carries the information of the sample was obtained via electro-optical sampling at each delay time between the pumping and probing pulses. All the measurements were carried out under nitrogen atmosphere to eliminate the effects of water vapor.

Computational Methods

The refractive index (n) and extinction coefficient (k) could be theoretically calculated with complex refractive index ñ (=n-ik) from the analysis of spectrum in time domain as described in Ref[6]. And then the absorption coefficient and dielectric constant could be obtained.

The dielectric constant of composites could be calculated with effective medium theory (EMT) if the dielectric constant and volume fraction of each individual components are known. EMT could also be used reversely to calculate the dielectric constant of one component given dielectric constants of the composite and the other component. This reverse EMT has been found applicable to the absorption of ZnO nanostructures composites in the infrared portion of electromagnetic wave [7]. The effective dielectric constants ε_{eff} of the composite satisfy the following equation:

$$\varepsilon_{eff} = \varepsilon_i \frac{[D + f(1-D)]\varepsilon_m + (1-D)(1-f)\varepsilon_i}{D(1-f)\varepsilon_m + (fD + 1 - D)\varepsilon_i} \qquad (2)$$

where ε_i and ε_m are the dielectric constant for HDPE and MWNT, respectively. f is the filling factor and D is the geometrical factor of the Maxwell-Gamett (MG) model, respectively. The geometrical factor D with a value range from 0 to 1 depends on the particle shape as well as the particle orientation to the THz beam. D is related to the screening parameter κ through $\kappa=(1-D)/D$. κ=2 and D=1/3 for spheres. κ approaches infinity and D~0 for needlelike particles with their rotation axes perpendicular to the light incidence.

The frequency-dependent dielectric function of MWNTs can be represented by the Drude model combined with Lorentz harmonic oscillators as shown by the following equation:

$$\varepsilon_{CNT}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} + \sum_j \frac{\omega_{p,j}^2}{(\omega_j^2 - \omega^2) - i\Gamma_j\omega} \qquad (3)$$

The first and second terms correspond to Drude model for conductive metals. ε_∞ stands for the frequency-independent dielectric constant, ω_p is the plasma frequency and Γ is the damping rate of the charge carriers. The inverse of Γ is the carrier collision time τ. The third term represents a Lorentz oscillator caused by phonon mode. $\omega_{p,j}$, ω_j, Γ_j are the oscillator strength, center frequency, spectral width of the Lorentz oscillators for the localized absorption.

Results and Discussion

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

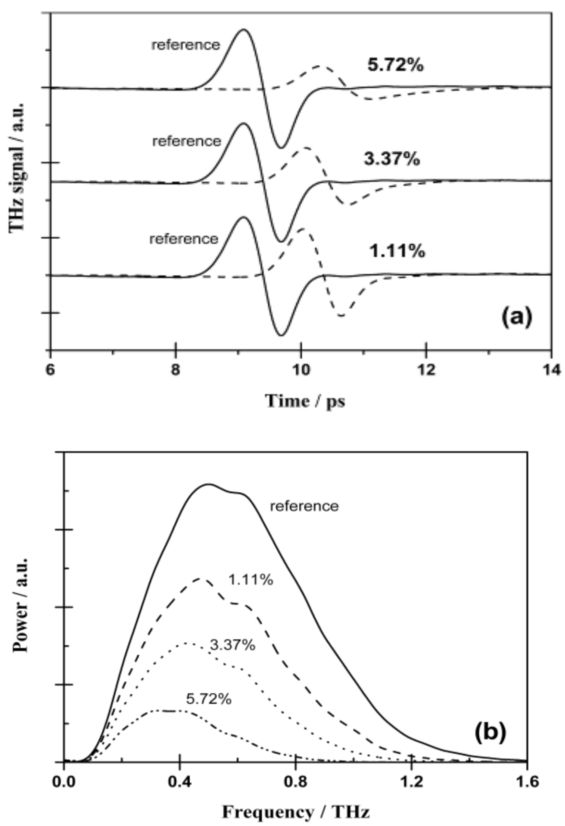

Fig. 1: Time-domain wave forms (a) and frequency-domain spectra (b) for the reference and composites filled with thin MWNTs at different concentration.

Pure HDPE is nearly transparent over the entire frequency range measured and the absorption coefficient α is found to be less than 5 cm^{-1} and changes negligible as shown in Fig.2a. The real part of refractive index (Fig.2b) of the HDPE has a constant value of about 1.52 in the frequency region between 0.4-2.0 THz, which agrees well with the result of literature [5]. For composites with 2.20% MWNTs, with increasing of frequency, the absorption coefficient of the composites increases monotonously whereas the refractive index decreases. The composite with thick MWNTs possesses larger absorption coefficient and refractive index than that with thin MWNTs at the same filler concentration.

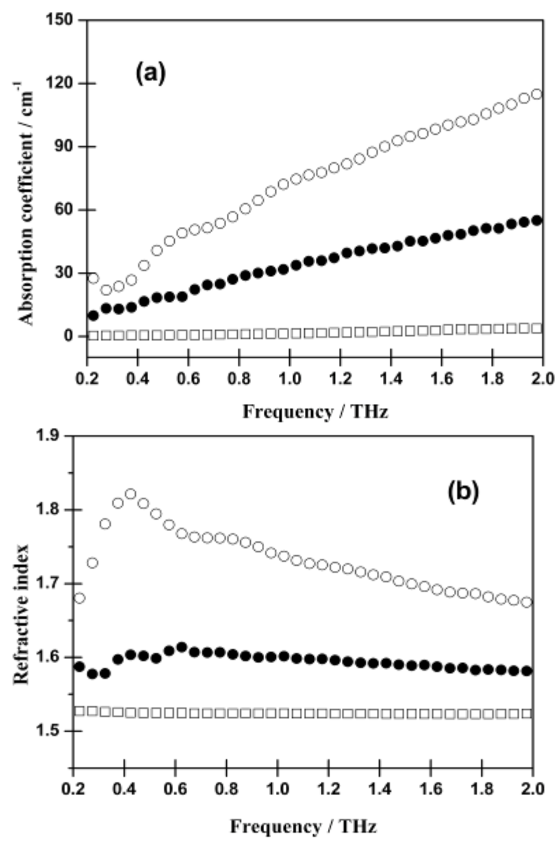

Fig. 2: The frequency dependence of α (a) and n (b) for HDPE(□) and composites filled with 2.20% thin-MWNT(●) and thick-MWNT(○) , respectively.

Fig. 3 shows the index of refraction and absorption coefficient of MWNTs extracted using Eq.2 with a geometrical factor D=0.01 [3, 8], from the measurements for the composites at different loadings. It can be seen that both n and α extracted for different loadings coincide very well for thin and thick

MWNTs. The extremely small differences between different samples may be caused by measurement errors in sample thickness and the inhomogeneous distribution of the MWNT clusters. The value of *D* is close to zero. It implies that most of the MWNTs oriented with their axis parallel to the THz fields, which can be caused by the shear mixing and compressing process. As shown in both panels in Fig.3, the fitted data (solid lines) with a single localized absorption has a reasonable agreement with the experimental data.

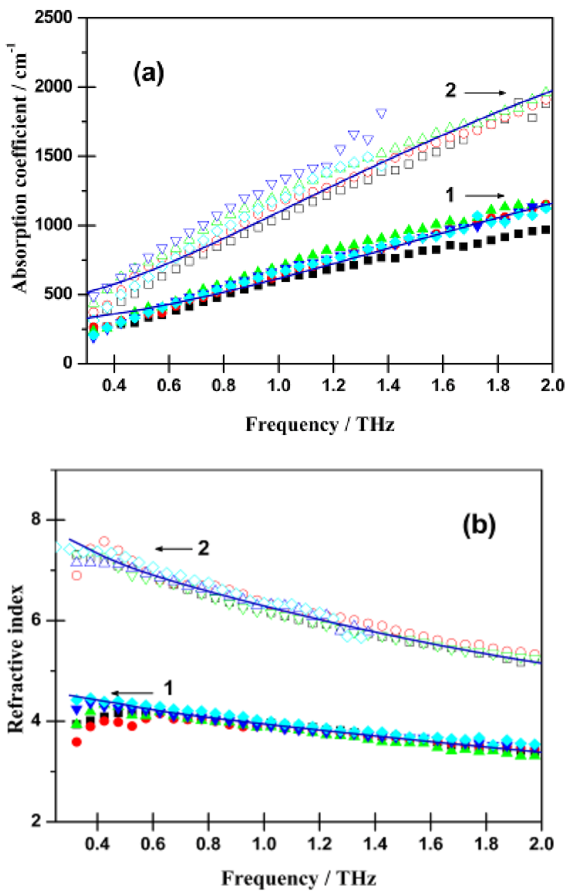

Fig. 3: α (a) and n (b) obtained by MG fitting as a function of frequencies for thin-MWNT (1) and thick-MWNT (2), respectively. ■□: 1.10%, ●○: 2.20%, ▲△:3.37%, ▼▽:4.48%, ◆◇:5.72%. The solid lines are fittings with Drude-Lorentz model.

The parameters used for fitting to Eq.3 are listed in Table-1. The plasma frequency for the MWNTs is in the order of 10-30 THz, which is similar to that obtained in the Ref. [8]. However, the value is smaller compared to the previously reported one [3]. This discrepancy is believed due to the different samples of carbon nanotubes and therefore the different conductivities. Furthermore, the plasma frequency for thick MWNTs is about twice that of the thin MWNTs; the oscillator strength of the thick MWNTs was also larger than that of the thin MWNTs. ω_p is proportional to square root of the conductivity, so the conductivity of the thick MWNTs was larger than that of the thin one according to the fitting results. In fact, carbon nanotubes do not exist in a single way but tend to aggregate together to form conductive networks in polymer matrix. The resistance of these networks containing two distinct sources: the resistance along the nanotubes itself and the resistance due to the tube-tube cross junctions. Previous measurements [9] have shown that the resistance of the mats is dominated by the resistance of these inter-tubes junctions, which may be as high as 4 orders in magnitudes larger than the resistance of the nanotubes itself. For the same volume concentration of MWNTs with similar length, the thin CNT possess large number of tubes in the conductive networks, so more junctions form in the networks and lead to the less conductivity compared with the thick one. The fitted damping rates were $\Gamma_p/2\pi$=13.55 and 34.13 THz, which correspond to the charge collision times of 12 and 4.7 *fs* for the thin and thick MWNTs, respectively. The Fermi velocity υ_F of the electrons for graphite is about 8.5×10^5m/s, and then the scattering length is estimated at 10 and 4 nm for thin and thick MWNTs, respectively. These values is very small when compared to some literature values [10], but it is reasonable for multi-walled carbon nanotubes if considering the aggregating effects and unavoidable defects in the nanotubes. CNTs could be considered as a network formed by cross junctions. These cross junctions act as a scattering center and determine the collision time [10]. Moreover, the nanotubes prepared by CVD-grown method have a large number of defects. These defects, such as stacking mismatch, amorphous phases of carbon and chemical impurities, could reduce the scattering length of the electrons to as short as a few nanometers.

Table-1: The parameters used for theoretical analysis with MG and DL model.

Diameter	*D*	ε_∞	$\omega_p/2\pi$	$\Gamma_p/2\pi$	$\omega_{p\,j}/2\pi$	$\omega_j/2\pi$	$\Gamma_j/2\pi$
10-20nm	**0.01**	2.3^2	**9.43**	**13.55**	**17.68**	**5.31**	**16.39**
20-40nm	**0.01**	2.9^2	**24.82**	**34.13**	**30.35**	**5.37**	**16.84**

Fitting results also predict a localized absorption for both two kinds of MWNTs around 5THz. This value is somewhat different but still comparable to the results of Ugawa [3]. This localized absorption at low frequencies was firstly regarded as electron transitions across the small energy gap of metallic nanotubes [3]. However, it is not consistent with the previous reports [3] that the absorption is temperature independent. So Jeon *et al*. [12] have suggested that phonon resonance absorption is an alternative explanation of the localized absorption at low frequencies. The fitting result also shows a large value of the spectral width, which maybe due to the wide distribution of the MWNTs in size.

Conclusions

The buck optical properties of MWNTs/HDPE composites were measured in the terahertz region. The refractive index and absorption coefficient all increased as the increase of filler concentration. Compared with the thin MWNTs, the thick MWNTs are more effectively in improving the absorption and refractive index because they have less tube-tube cross junctions and higher conductivity. By choosing a proper geometrical factor, the dielectric response of the MWNTs was extracted from that of the composites and HDPE with the REMA. The extracted dielectric constants from composites with different concentrations were found coincide well with each other. The extracted dielectric constants were analyzed with the Drude model combined with a localized Lorentz absorption. Fitting results indicated that both of the MWNTs possess the electronic properties and phonon response in terahertz region.

Reference

1. Z. Jun, Z. Jinglei, F. Chen, Design of refracting reflecting infrared detection optical system with high spatial resolution, *J. Infra. Las. Engi.*, **42**, 1280 (2013).
2. R. Rungsawang, V. G. Geethamma, E. P. J. Parrott, Terahertz spectroscopy of carbon nanotubes embedded in a deformable rubber, *J. Appl. Phys*, **103**, 123503 (2008).
3. Ugawa A., Rinzler A. G., Tanner D. B., Far-infrared gaps in single-wall carbon nanotubes, *J. Phys Rev B*, **60**, 11305 (1999).
4. C. Kang, I. H. Maeng, S. C. Lim, K. H. An, Terahertz optical and electrical properties of hydrogen-functionalized carbon nanotubes, *J. Phys Rev B*, **75**, 85410 (2007).
5. C. Xiliang, C. Xin, Z. Zhiyong, THz-TDS spectra study of polymer materials with different polarity, *J. Infra. Mil. Wav.*, **32**, 150 (2013).
6. C. Xiliang, C. Xin, Z. Zhi-yong, Electrical and optical properties of MWNTs/HDPE composites in Terahertz region, *J. Nucl Sci Tech*, **23**, 156 (2012).
7. J. B. Baxter, C. A. Schmuttenmaer, Conductivity of ZnO nanowires, nanoparticles, and thin films using time-resolved terahertz spectroscopy, *J. Phys Chem B*, **110**, 25229 (2006).
8. X. Xu, L. Song, Y. Shi, Y. Yang, S. Xie, Light-induced dielectric transparency in single-walled carbon nanotube films, *J. Chem Phys Lett*, **410**, 298 (2005).
9. L. Hu, D. S. Hecht, G. Grüner, Percolation in Transparent and Conducting Carbon Nanotube Networks, *J. Nano Lett*, **4**, 2513 (2004).
10. J. Han, Z. Zhu, Z. Wang, W. Zhang, L. Yu, L. Sun, The conductivity of single walled nanotube films in Terahertz region, *J. Phys Lett A*, **310**, 457 (2003).
11. T. Kampfrath, L. Perfetti, K. Volkmann, C. M. Aguirre, Optical resonanse of single-wall carbon nanotube sheets in the far-infrared spectral range from 1 THz to 40THz, *J. Phys. Stat. Sol.(B)*, **244**, 3950 (2007).
12. T. I. Jeon, K. J. Kim, C. Kang, Terahertz conductivity of anisotropic single walled carbon nanotube films, *J. Appl. Phys. Let.*, **80**, 3403 (2002).