Optical properties of carbon materials filled HDPE composites in THz region

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Abstract The optical and electrical properties of several composites, formed by filling the high density polyethylene (HDPE) with similar amount of carbon black (CB), multi-walled carbon nanotubes (MWNT) and fullerene (C_{60}), respectively, were characterized using a THz-TDS setup. It was found that the optical parameters and the details of their variation with frequency differ significantly for different kinds of carbon materials. The results are analyzed by using Cole-Cole formula of dipole relaxation under the assumption that carbon particles dispersed in the matrix behave like dipoles and contribute mainly to the dielectric loss in the THz frequency range. Fitting results indicate that MWNT and CB filled composites have a broader distribution of the relaxation time compared with C_{60} which possesses a nearly single relaxation time. Compared with CB and C_{60} , MWNT filled composite possesses the larger relaxation strength due to its higher electron density and larger conductive clusters. The real part of conductivity for three kinds of composites all follows power law behavior with respect to frequency but the exponents are quite different. These phenomena may be related to the special properties of the fillers as well as their particulate structures, such as aspect ratio, particle size, and aggregate structure, etc.

Key words THz-TDS, Carbon materials, Dielectric properties

1 Introduction

Terahertz (THz) light, ranging from far infrared (IR) to microwaves (0.1–10 THz), is of great importance in view of the chemical and physical processes in this frequency region. Terahertz time-domain spectroscopy (THz-TDS) is a powerful technique developed in the past decades^[1]. Advantages of the THz-TDS at frequencies below 3 THz include non-destructive, non-contact and higher signal-to-noise ratio than IR^[2]. Particularly, optical constants can be obtained without using complicated numerical process of Kramer-Kronig transformation. The technique has been widely used in studies of optical and electrical properties of conductive materials in the terahertz band^[3-5].

Conductive composites, obtained by mixing polymer resins with carbon black (CB), graphite,

carbon fiber, etc., can be used in many fields, such as gas sensors, electromagnetic interference-shielding materials, and PTC materials for circuit protection and cables^[6-8]. temperature-controlled heating The composites are of diverse electrical conductivity, light weight, good corrosion resistance and excellent mechanical properties. Carbon nanotubes (CNTs) have been considered as a kind of promising filler for developing new generation composite materials of mechanical unique electrical and properties. Composites filled with CNTs have much higher conductivity and lower percolation threshold than those filled with CB, graphite and carbon fibers, due to the higher electrical conductivity and larger aspect ratio of CNTs^[7]. C₆₀ is a new class of carbon-based solids which exhibit a wide variety of unusual physical and chemical properties. It was well known that the

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electronic and vibrational properties of solid C_{60} are strongly connected to the properties of the molecule itself^[9].

In this work, three kinds of fillers of different structures, i.e. CB, multi-walled carbon nanotubes (MWNT), and C_{60} , were added to HDPE at the molten state. Optical and electrical properties of the composites were investigated with a THz-TDS setup. The results were analyzed with Cole-Cole model of dipole relaxation, assuming that carbon particles within the matrix behave like dipoles under the terahertz electric field and contribute mainly to the dielectric loss in the THz frequency range.

2 Experimental

2.1 Materials

MWNTs, from Shenzhen Nanotech Port Corp. Ltd. of $\Phi 20-40 \text{ nm} \times 1-2 \mu \text{m}$ in size, were in purity of about 95% in mass fraction. The CB was acetylene black in beaded form of 40 nm in size, provided by Jiaozuo Xinda Corp., with DBP value of 3.2 mL·g⁻¹. The C₆₀ was from Puyang Chemical Reagent Corp. HDPE 7000 F of 0.956 g·cm⁻³ was from Mitsui Corp. Antioxidant DLTP (Dilauryl thiodipropionate, C₃₀H₅₈O₄S) was from Sanfeng Chemical Corp.

2.2 Sample preparation

HDPE/CB composites containing 8%–9% (V/V) carbon particles were prepared at 150°C by 15-min blending in a Haake mixer at 50 r/min. Antioxidant DLTP (about 1% in mass fraction) was added to prevent sample oxidation. Prior to the mixing, the HDPE granules and fillers were vacuum-dried at 60°C for 24 h. The mixture were heated to 160°C and compressed into disks at 15 MPa.

Thickness of the MWNT and CB discs was about 0.25 mm, because MWNTs and CB are good absorbers in THz band and a thick sample would reduce the amplitude of transmission spectrum greatly, and so would the bandwidth with believable results. As C_{60} and HDPE absorb weakly in THz range, the HDPE and C_{60} /HDPE samples were about 2.5 mm in thickness.

2.3 THz-TDS setup and measurements

THz tests were performed on a Z-1 THz-TDS system with a SNR (Signal-to-Noise Ratio) of 5000. The laser, a mode-locked Ti: sapphire system, provides 80 fs pulses at a central wavelength of 800 nm with an average power of 700 mW and a repetition rate of 80MHz. The fs pulses were divided into a pumping beam and a probing beam. The pumping beam illuminated a photoconductive antenna on a GaAs wafer to generate photoelectrons, which were accelerated by a high voltage of the antenna. A transient photocurrent generated free-space radiation. The THz pulses were focused at the normal incidence onto the reference and sample surface. The transmission signals were detected in a ZnTe crystal via electro-optical sampling and recorded by a lock-in amplifier. The time delay between the pumping and probing pulses was controlled by a motorized transition stage. All the measurements were carried out under N₂ atmosphere to eliminate the effects of water vapor.

3 Results and discussion

The transmission spectra, in time and frequency domains, of HDPE and the composites are shown in Fig.1. HDPE is nearly transparent in THz region, and amplitude of the transmission spectrum was almost the same as the N₂ reference (Fig.1a). The amplitude of electric current was obviously attenuated with the CBor MWNT-added samples due to strong absorption of the particles. The spectrum amplitude of C₆₀ filled composite reduced, too, but the reduction was not as evident as that of MWNT and CB. Phase delay was observed for both the pure HDPE and composites when the THz signals passed through the samples. Fig.1 (b) is the frequency-domain spectra of the samples after Fourier transformation. The spectrum of HDPE was the same as the reference, and amplitude reductions were observed with the carbon-added HDPE due to absorption of the fillers to the THz waves. The believable frequency range of the spectrum for reference and HDPE was 2 THz, while it was about 1.7–1.8 THz for the carbon-filled samples.

The complex transmission coefficient $T(\omega)$ of the sample can be calculated by Eq.(1)^[10].



Fig.1 THz time-domain wave forms (a) and frequencydomain spectra (b) of pure HDPE and composites filled with (V/V) 8.79% MWNTs, 8.36% CB and 9.03% C₆₀.

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

where S is the Fourier transformed amplitude of the output THz wave form; \tilde{n} ($\tilde{n}=n-i\kappa$, n and κ are the refractive index and extinction coefficient, respectively) is the complex refractive index; the subscripts of sam and ref denote the sample and reference, respectively; d is the sample thickness and cis the velocity of light in free space; and $FP(\omega)$ is the Fabry-Pérot factor, which refers to backward and forward reflections from the sample. We note that for thick enough samples of strongly absorption^[10], $FP(\omega)=1$. Absorption coefficient is given by $\alpha(\omega)$ = $2\omega\kappa/c$ with angular frequency $\omega = 2\pi f$.

The refractive index *n* (Fig.2a) of HDPE was about 1.52, and remained almost constant in the whole frequency range, agreeing well with the literature value of 1.52 ± 0.01 at 300 K^[11]. The refractive index of

composites showed an obvious decrease as a function of frequency except the C60-added sample, which changes slowly with frequency. Fig.2 (b) shows the absorption coefficient of pure HDPE and the three kinds of composites as a function of frequency. The pure HDPE is nearly transparent in THz region and the α value is less than 5 cm⁻¹ over the entire frequency range, while α of the composites increased with frequency in quite different magnitudes. The MWNT/HDPE composite had the most prominent absorption, about 2 orders of magnitude higher than C_{60} /HDPE. The absorption of C_{60} /HDPE composite at low frequencies was even lower than that of the pure HDPE. This has been reported in Ref.[12]. The absorption coefficient of the CB/HDPE is much larger than C_{60} /HDPE in the whole frequency range.



Fig.2 Refractive index (a) and absorption coefficient (b) of pure HDPE (**■**) and composites filled with 8.79% MWNT (\blacktriangle), 8.36% CB (\blacklozenge) and 9.03% C₆₀ (\blacktriangleleft). Solid lines are fittings with Cole-Cole model.

The phenomena may be related to special properties of the fillers and their particulate structures, i.e aspect ratio, particle size, and aggregate structure. The π -electrons of MWNT and CB in the same graphene-like layer have overlapping orbits, which

permit the electrons to move easily within the same layer, just like a metal. The high aspect ratio, however, enables MWNT to form percolating structure more easily at low concentration within the matrix, hence the prominent absorption of MWNT. C_{60} is a molecular semiconductor and possess very low conductivity. The weak absorption of C_{60} may be ascribed to the low density of free charge carriers of C_{60} . The localized electronic states and trapped electrons in the conduction band due to the oxygen diffusion would enhance the effect^[13].

The carbon particles in the matrix aggregate easily into clusters in the HDPE. The charge carriers of the isolated clusters are polarized under external electric fields and behave like dipoles. The dispersion and absorption behaviors of this dielectric can be described by Cole-Cole formula^[14] taking into account the dc conductivities σ_0 :

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

where $\varepsilon^*(\omega)$ is the complex permittivity; ε_s and ε_{∞} are static and optical permittivity, respectively; τ is the relaxation time; ε_0 is the permittivity in free space; β is width of the underlying relaxation time distribution,

with the $\beta = 1$ being the broadest distribution, and $\beta = 0$ being the Debye expression. As $1 - \beta < 1$, one sees a considerably broader frequency range of dispersion and absorption.

The real (ε') and imaginary parts (ε'') of the complex dielectric constant are given by

$$\varepsilon' - \varepsilon_{\infty} = \frac{(\varepsilon_{s} - \varepsilon_{\infty})[1 + (\omega\tau)^{1-\beta}\sin\frac{\beta\pi}{2}]}{1 + 2(\omega\tau)^{1-\beta}\sin\frac{\beta\pi}{2} + (\omega\tau)^{2(1-\beta)}}$$
(3a)

$$\varepsilon'' - \frac{\sigma_0}{\varepsilon_0 \omega} = \frac{(\varepsilon_s - \varepsilon_{\infty})(\omega \tau)^{1-\beta} \cos \frac{\beta \pi}{2}}{1 + 2(\omega \tau)^{1-\beta} \sin \frac{\beta \pi}{2} + (\omega \tau)^{2(1-\beta)}}$$
(3b)

The experimental results were analyzed with Eq.(3), and the solid lines in Fig.2 are fittings of refractive index and absorption coefficient. The parameters obtained from the fittings were summarized in Table 1. The experimental results of C₆₀/HDPE can be analyzed using the Cole-Cole formula with a very small distribution parameter of β =0.06, while the MWNT/HDPE and CB/HDPE can be fitted with a much larger value of β ≈0.35, indicating a broader distribution of the relaxation time.

Samples	β	\mathcal{E}_{∞}	\mathcal{E}_{s}	Δε	au / ps	$\sigma_0 / \text{S·cm}^{-1}$	A	t
MWNT	0.34	2.55	15.21	12.66	0.65	0.002	1.50	0.70
CB	0.35	2.76	5.63	2.87	0.087	0	0.41	1.18
C ₆₀	0.06	2.41	2.48	0.07	0.041	0	0.01	2.00

 Table 1
 Parameters obtained by fitting experiment data to Cole-Cole formula and power-law

This phenomenon can be related to different particulate properties and aggregate structures of MWNT/HDPE and CB/HDPE. The morphology of the composites observed using atomic force microscopy (not shown) suggested that the fillers might agglomerate easily to form conductive clusters due to attractions among the particles^[15-17]. It was found^[17] that the distribution of the CB aggregates have a wide range of about 20–150 nm in size. The MWNT^[15] tend to aggregate even in the presence of surfactant, and the size is much larger than that of CB clusters^[17]. Furthermore, shapes of the conductive clusters are different from each other. So the observed distribution

of relaxation times can be interpreted in terms of the shape and size distribution of the clusters^[18]. C_{60} particles can only be electrically touched with their neighbor particles through tunneling. So the relaxation time is influenced to a much less extent by the shape and size distribution of C_{60} aggregates. As a result, C_{60} /HDPE can be analyzed using the Cole-Cole formula with a nearly single relaxation time.

Optical permittivity (ε_{∞}) of the three kinds of composites has similar value. The static permittivity values ε_s , consequently the relaxation strength $\Delta \varepsilon = \varepsilon_s - \varepsilon_{\infty}$ differ greatly, which can be attributed to the influence of dipole polarization at THz frequencies.

MWNT and CB have a much larger number of free electrons than C_{60} do, so the relaxation strength of MWNT and CB filled composites is larger than that of C_{60} in similar concentrations. The relaxation strength is also influenced by the size of the conductive clusters^[19]. It increases with the cluster size. The length-to-diameter ratio of MWNT is larger than CB. It makes MWNT entangle and aggregate to form larger clusters in HDPE, hence larger $\Delta \varepsilon$ and ε_s of the composite^[13, 17].

The real part of ac conductivity $\sigma'(\omega)$ of the composites can be evaluated from the imaginary part of dielectric constant ε'' through $\sigma'(\omega) = \varepsilon_0 \varepsilon'' \omega$. Fig.3 is a log-log plot of the real conductivity of the composites as a function of frequency. It is found that $\sigma'(\omega)$ follows a power law dependence on frequency. The exponent value can be determined by the following the equation:

$$\sigma'(\omega) = \sigma_0 + A\omega^t \tag{4}$$

where $\sigma'(\omega)$ is the total ac conductivity, *A* is a constant dependent on temperature and *t* is an exponent dependent on both temperature and frequency. *A* and *t* determined by fitting the calculated results of $\sigma'(\omega)$ to Eq.(4) are summarized in Table 1. The exponents for the composites of MWNT, CB and C₆₀ are 0.7, 1.2 and 2, respectively.

The exponent value of 0.7 for MWNT filled composite is close to the theoretical value (0.72) of intercluster polarization^[20]. The polarization effects can be explained by making an analogy between the samples and an equivalent circuit that has capacitance between different clusters. As the frequency increases, the current passing through each capacitor increases, hence the increase of conductivity. The conductivity for both CB and C₆₀ filled composites shows frequency-dependent behaviors with $1 \le t \le 2$. Such a frequency dependence of the conductivity is often found in some semiconductor systems^[21,22]. It was suggested that the quadratic frequency dependence of the real conductivity might be attributed to the artificial contact effects on the electrodes^[23]. In our THz-TDS measurements, however, no direct contact between the samples and the electrodes are needed and the 2-power frequency dependence of the conductivity is an essential property of the sample, resulting from

perhaps the phononless tunneling, for which a quadratic dependence of the conductivity on frequency is expected^[24]. For the C₆₀/HDPE, as the absence of metallic contact within the individual clusters, inter-particle transport has to proceed by means of tunneling. In case of the CB composites, the exponent value 1.2 is larger than the suggested value of 0.5-0.6contributed by anomalous diffusion at low frequencies^[25,26]. The superlinear dependence of the real conductivity on the frequency can be interpreted in terms of the tunneling conduction among different aggregates and the metallic contact of the CB particles. The metallic diffusion can take place within the aggregates formed by the primary CB particles. But between different aggregates, charges tunneling under THz field contribute to the conductivity which leads to the higher value of the exponent.



Fig.3 Real conductivity of the composites filled with 8.79% MWNT (\blacktriangle), 8.36% CB (\blacklozenge) and 9.03% C₆₀ (\blacktriangleleft). Dashed lines are fittings with Cole-Cole formula and solid lines are the power-law fittings.

In conclusion, the frequency dependence of optical constants of the composites, filled with MWNT, CB and C_{60} , respectively, were measured at the frequency range between 0.3 and 1.6 THz using a THz-TDS setup. It is found that the MWNT filled composite possesses the largest absorption coefficient and refractive index at the similar concentration. The C_{60} /HDPE composite, however, shows very little changes in refractive index and absorption coefficient compared with pure HDPE. The experimental results are fitted by using the Cole-Cole model assuming that the isolated clusters in insulating matrix behave like dipoles. The fitting results indicate that MWNT and CB filled composites possess larger distributions in relaxation time compared with C_{60} which can be

analyzed with a nearly single relaxation time. The phenomenon is related to their distribution of the shapes and sizes of the conductive clusters. Compared to CB and C_{60} , the MWNT filled composites has larger relaxation strength which can be attributed to its larger conductive clusters as well as larger density of free carriers. The real conductivities for three kinds of composites all follow power law behavior with respect to frequency but the exponents are quite different for the different conducting mechanisms.

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