Terahertz Dielectric Properties of MWCNT/PE Composites

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Abstract—**The terahertz dielectric properties of MWCNT/PE composites prepared in different ways and with various contents of carbon nanotubes have been measured by terahertz time-domain spectroscopy. The experimental dielectric susceptibilities were modeled within effective medium approximation.**

I. INTRODUCTION AND BACKGROUND

ONE of the potential applications of nanocomposites is associated with creation of materials with desired dielectric response in selected frequency range. Particularly, new nanocomposites are topical for the terahertz frequency range, where the set of materials with known and tunable properties is very limited. In the present work, the composites formed by multiwall carbon nanotubes (MWCNT) embedded into the polyethylene (PE) matrix using different procedures were obtained. Their dielectric susceptibility spectra in terahertz range have been studied. To model the recorded experimental spectra, the effective medium approximation (EMA) was employed.

II. EXPERIMENTAL DETAILS AND RESULTS

To obtain the composites MWCNT with average diameter of 9 nm were used. The composites with MWCNT contents of 4 wt. % (type 1) and 29 wt. % (type 2) were obtained by ethylene polymerization on the MWCNT powder.[1] Two other types of the composites were obtained by mechanical mixing of MWCNT and polyethylene powders in knife mill followed by extruding (type 3) or without extruding (type 4). Finally MWCNT/PE samples (Fig. 1) of all types were formed by pressing powder at 190°C and P=5 kg/cm^2.

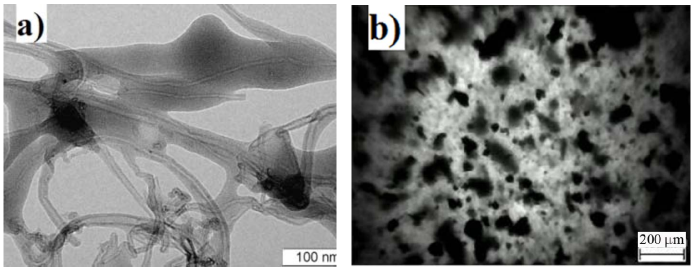

Fig. 1. TEM image of type 1 MWCNT/PE composite with 4 wt. % of MWCNTs (a) and optical microscope image of MWCNT/PE composite (type 2) with 1wt. % MWCNT content (b).

The dielectric properties of MWCNT/PE composites were measured using THz-TDS setup.[2] The THz pulses were produced via eee-type optical rectification of femtosecond pulses from MaiTai SP (Spectra-Physics, USA) laser ($\tau \approx 100$ fs, $\lambda = 780$ nm) in a 1 mm thick GaSe crystal.[3] The detection was performed in a 1 mm thick ZnTe crystal. The sample area illuminated by the THz waves was about 1 cm in diameter. This large terahertz spot was believed to be helpful in measuring the inhomogeneous MWCNT/PE samples (Fig. 1).

Since the polyethylene matrix was used for the MWCNT embedding, at first, the terahertz dielectric susceptibilities of pure polyethylene were measured. The obtained spectra of real and imaginary dielectric susceptibility components are shown in Fig. 2. The dispersion of the measured values is comparatively low over the frequency range of 0.3-2.7 THz.

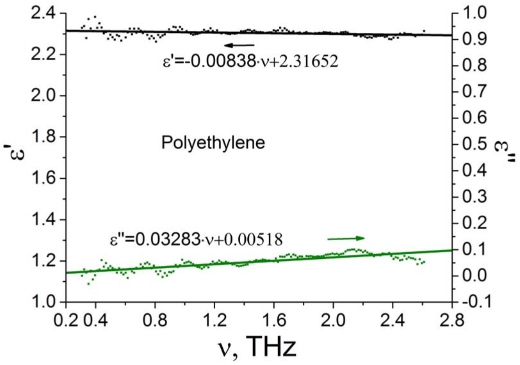

Fig. 2. Real and imaginary dielectric susceptibilities of the PE matrix: solid lines – linear fitting; symbols – THz-TDS experimental data.

Thus, the experimental curves were fitted by linear functions: $\varepsilon' = -0.00838\cdot\nu + 2.31652$ and $\varepsilon'' = 0.03283\cdot\nu + 0.00518$. Here, ε' and ε'' are real and imaginary parts of dielectric susceptibility, and ν is a terahertz frequency. In the following these functions were used in approximation of the MWCNT/PE dielectric susceptibilities. To model MWCNT/PE dielectric permittivity we used Maxwell-Garnett effective medium approximation (EMA)[4]:

$$\varepsilon_{eff} = \varepsilon_{PE}\frac{(N+f(1-N))\varepsilon_{CNT}+(1-N)(1-f)\varepsilon_{PE}}{N(1-f)\varepsilon_{CNT}+(fN+1-N)\varepsilon_{PE}}.$$

Here, ε_{PE} is the PE dielectric constant, ε_{CNT} is the dielectric constant of MWCNT ensemble, N and f are geometric and filling factors, respectively. In THz-TDS measurements, narrow phonon-like peaks in the MWCNT/PE dielectric permittivity absorption spectra were not observed. Thus, a simple Drude approximation for the dielectric susceptibilities of MWCNTs can be used $\varepsilon_{CNT} = \varepsilon_{CNT}^{\infty} - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}$. Here ω_p is plasma frequency, Γ – damping constant.

Complex dielectric permittivity components for MWCNT/PE composites were approximated using numerical fitting (Fig. 3, Table 1). The fitting parameters were kept the same for all the samples of the same composite type; only geometric and filling factors (N and f) were fitted to simulate different content of MWCNTs.

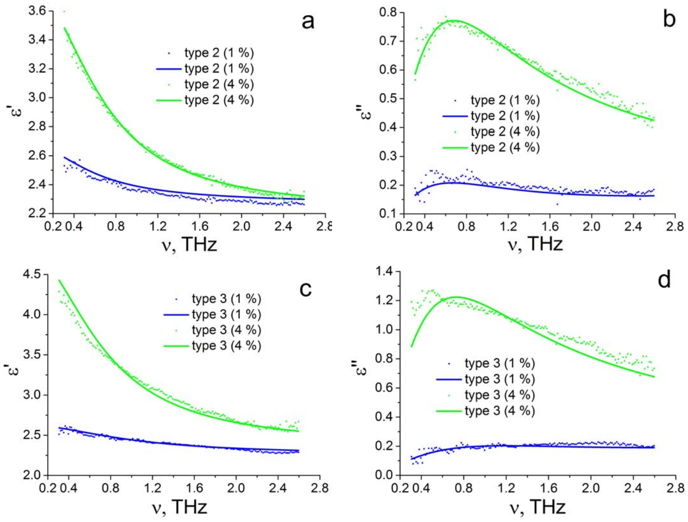

Fig. 3. Real and imaginary dielectric susceptibilities of MWCNT/PE composites (type 2 a and b; type 3 c and d): solid lines – model with fitting parameters given in Table 1; symbols – experimental data. MWCNTs contents are given in the legends.

The spectra for some samples were fitted better. To obtain the adequate description, for several samples the fitting parameters were constrained near the fitting parameters obtained for the samples with less spread data points. From Table 1 it is seen that the filling factors expectedly increase on the MWCNT content increase. The plasma frequencies of the samples $\omega_p/2\pi$ are close to 10-12 THz.

Table 1. Fitting parameters of EMA-Drude model for type 1-4 MWCNT/PE composites.

Sample	$\varepsilon_{CNT}^{\infty}$	N	f	$\omega_p/2\pi$, THz	$\Gamma/2\pi$, THz
type 1 (0.5 %)	2.57	0.5	0.08	12.2	33.49
type 1 (1 %)	2.83	0.5	0.1	13.83	24.13
type 2 (1 %)	2.23	0.5	0.07	9.83	33.49
type 2 (4 %)	2.23	0.5	0.24	9.83	24.67
type 3 (1 %)	2.23	0.5	0.06	9.83	21.55
type 3 (4 %)	2.76	0.5	0.35	13.43	33.49
type 4 (1 %)	2.23	0.5	0.06	9.83	33.49
type 4 (4 %)	2.82	0.5	0.28	13.68	33.49

The measured experimental data and their analysis showed that for the MWCNT/PE composites with low MWCNT content (0.1 and 0.5 %) the dielectric properties are rather close to those of pure PE. Therefore, at fitting, the modeled filling factors f tended to minimal values. Also, the type 1 composite is characterized by more dense distribution of MWCNTs. The terahertz transmission measurement of type 1 sample with 4 % MWCNT content was impossible because of its high absorption. For this composite type, the 0.5 % MWCNT content results in noticeable change of dielectric properties with respect to the PE matrix.

III. SUMMARY

Possibility to gradually vary dielectric properties of MWCNT/PE composites changing MWCNT content was verified. It was found that dielectric response of the MWCNT/PE composites can be satisfactory modeled within effective medium approximation.

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