ELECTRIC/DIELECTRIC PROPERTIES OF COMPOSITES FILLED WITH ONION-LIKE CARBON AND MULTIWALLED CARBON NANOTUBES

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The dielectric/electric properties of polyurethane composites filled with carbon nanotubes (CNTs), onion-like carbon (OLC) and mixed onion-like carbon/carbon nanotubes are compared across a wide frequency range from hertz to terahertz. The highest value of dielectric permittivity and electrical conductivity is observed in composites with carbon nanotubes. However, the dielectric/electric properties of composites filled with onion-like carbon are also very attractive and can be improved by addition of small amounts of carbon nanotubes due to the strong synergy effect. In composites with inclusions of mixed onion-like carbon/carbon nanotubes, the dielectric permittivity and electrical conductivity increase due to the decreasing of both the potential barrier for carrier tunneling and the average distance between nanocarbon clusters.

Keywords: carbon nanotubes, onion-like carbon, synergy, composites
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1. Introduction

Nowadays, investigations of electrically percolative polymer-based composites with various nanocarbon inclusions are very popular due to their outstanding electric, electromagnetic, mechanical and thermal properties in comparison with the polymer matrix material [1]. Conductive polymer composites find large-scale applications as antistatic materials, in printed electronics, supercapacitors, organic solar cells, biosensors, flexible transparent displays, etc. [2]. In spite of some practical limitations due to their limited processability and their manufacturing cost, DC and AC conductive composites are rapidly gaining attention in new applications such as packaging for electronics and chemical industry, metal replacement, heating elements and fuel cells, for electromagnetic shielding and for radar wave absorbing applications in wide frequency ranges [3]. The major field of applications for electrically conductive composites depends on the magnitude of their volume electrical resistivity. For antistatic applications the range should be at the level of $10^{9} - 10^{14} \ \Omega \text{cm}$, whereas for electrostatic dissipation applications the range is expected to be $10^{5} - 10^{9} \ \Omega \text{cm}$.

Many investigations of such composites were performed within a narrow frequency range and at room temperature in order to find the percolation threshold (the minimum concentration of nanofillers at which composites are conductive) [4]. An important task is to obtain a low percolation threshold to preserve (or reach) optimal mechanical properties of polymers and to use a minimal concentration of expensive fillers. The lowest percolation threshold was observed in carbon nanotube (CNT) composites due to their high aspect ratios [5]. However, CNTs usually exhibit large agglomerates within the polymer matrix because of the high van der Waals force between CNTs, and this leads to an increase of the percolation threshold. Therefore, the percolation threshold in the same polymer matrix and for the same CNTs can vary significantly [6]. Moreover, the percolation threshold in other composites, for example, in carbon black (CB) composites, can also be very low [7]. Thus, investigations of composites with other less expensive inclusions are very promising.

Onion-like carbon (OLC), consisting of stable defected multishell fullerenes, exhibits high conductivity similar to CNTs [8]. The percolation threshold in OLC composites is strictly dependent on the aggregate
primary particles were heated in vacuum (10–4 Torr) at (DND) [8–10]. Aggregates of DNDs consisting of 5 nm delivered vacuum anealing of detonation nanodiamonds from (20 nm diameter, 5–10 micrometre length) purchased urethane. Nanoadditives included multi-walled CNT prepared using Clear Gloss MINW AX® Fast-Drying Polyurethane films with nanoadditives were pre-
itively improved with the addition of CNT. Microstructural properties with OLC inclusions can be substantial-26 K. It was demonstrated that the dielectric and ele-
c. In the frequency range from 1 MHz to 53 GHz, a home-made waveguide spectrometer was used. The method of a thin rod in the waveguide was used [19]. Cylindrically shaped samples where used for these measurements. Dimensions of the samples were with different radius: in 20 Hz – 1 MHz frequency range, the radius of samples was about 3 mm, in the 1 MHz – 3 GHz frequency range it was about 0.5 mm, while in the 8–53 GHz frequency range the radius was about 0.1 mm.

In the frequency range from 1 MHz to 53 GHz, the measurement accuracy was ~10%. Silver paste was used for creating the contacts. In the terahertz frequency range (from 100 GHz to 3 THz), a terahertz time domain spectrometer (Ekspla Ltd) based on a femto-
second laser was used for the measurements. The spectrometer is based on the femtosecond laser fiber (wave-
length 1 μm, pulse duration less than 150 fs) and the GaBiAs photoconductive terahertz emitter and detect-
or. The complex effective permittivity was calculated according to the Fresnel equation. For terahertz mea-
surements plate-like thin samples were used (thickness about 0.5 mm). All measurements above 1 MHz were performed only at room temperature. The real part of the complex electrical conductivity was calculated as σ″ = ωε″, where ω is the angular frequency, ε″ is the permittivity of vacuum, and ε″ is the imaginary part of complex effective permittivity.

3. Results and discussion

The scanning electron microscopy images of the composites filled with OLC, CNT and OLC/CNT inclusions are presented in Fig. [3]. The dispersion of
Fig. 1. Scanning electron microscopy image of composites with CNT (top), OLC (middle) and mixed CNT/OLC (bottom).

Fig. 2. Frequency dependence of dielectric permittivity and electrical conductivity for composites with various nanocarbon inclusions at room temperature.

The value of the dielectric permittivity of pure polyurethane is very low (about 2), and it is almost frequency independent for all frequency ranges. At low frequencies, the AC electrical conductivity of pure polyurethane is very low (about 10^{-9} S/m), and no frequency independent conductivity plateau – typical for DC conductivity – is observed. In all composites (with OLC, CNT and CNT/OLC inclusions) the dielectric permittivity is very high (at low frequencies, its value is higher than several hundred). Moreover, at low frequencies the highest value of dielectric permittivity is observed in the CNT based composites (>10^5). At low frequencies, all composites display a frequency independent conductivity plateau; thus, all composites are above the percolation threshold. Nevertheless, we can expect that the lowest percolation threshold value is in the composites with CNT, while the highest value is...
in the composites with OLC inclusions because both the dielectric permittivity and electrical conductivity increase above the percolation threshold in the power law fashion [2]. So, the synergy effect is evident in the system. Thus, even a small part of CNT (30%) in the mixed OLC/CNT composites can substantially increase the value of the dielectric permittivity and electrical conductivity. For the composites with CNT and OLC/CNT inclusions a frequency independent plateau of dielectric permittivity in the frequency range 1 kHz – 1 MHz separates two different dispersions related with the Maxwell–Garnett relaxation (Fig. 2).

At low temperatures, both the dielectric permittivity and the electrical conductivity decrease in the OLC/PU composites (Fig. 3).

However, the most pronounced reduction occurs at temperatures below 100 K. A similar behaviour was observed in the CNT/PU and mixed CNT/OLC/PU composites and is in good agreement with the data presented in literature for composites with nanocarbon inclusions [17, 18]. For the composites with OLC inclusions, not only the DC conductivity changes upon cooling, but the shape of the conductivity spectra is also changed (Fig. 4). Therefore, the conductivity spectra, $\sigma(\nu)$, were fitted with the Almond-West equation [18]:

$$\sigma = \sigma_{dc} + A\omega^\alpha,$$  \hspace{1cm} (1)

where $\sigma_{dc}$ is the DC conductivity and $A\omega^\alpha$ is the AC conductivity. From this fit, it is possible to calculate the critical conductivity frequency ($\omega_{cr}$) at which the value of frequency dependent conductivity becomes higher than DC conductivity. Experimentally, the value for $\omega_{cr}$ has been defined as the frequency at which the value of conductivity is 10% higher than the DC conductivity value.

The critical frequency of the composites with CNT and CNT/OLC inclusions is higher than 1 MHz (Fig. 4) (our upper frequency limit in low temperature measurements); therefore, the critical frequency values were calculated only for the composites with OLC inclusions.

The DC conductivity data fit well to the fluctuation induced tunneling model, as can be seen in Fig. 5 [19]:

$$\sigma_{dc} = \sigma_0 \exp[-T_1/k(T+T_0)],$$  \hspace{1cm} (2)

where $T_1$ represents the energy required for an electron to cross the insulator gap between the conductive particle aggregates, and $T_0$ is the temperature above which thermally activated conduction over the barriers begins to occur. The tunneling model is represented by Eqs. (3) and (4) [19]:

$$T_1 = wA\beta_\alpha/8\pi k,$$  \hspace{1cm} (3)

$$T_0 = 2T_1/\pi\chi w,$$  \hspace{1cm} (4)
where $\chi = (2 m V_0^{0.5}) / h$ and $\beta_0 = 4 V_0 / \epsilon w$, $m$ and $\epsilon$ are the electron mass and charge, respectively, $V_0$ is the potential barrier height, $w$ is the interparticle distance (gap width), and $A$ is the area of capacitance formed by the junction. The obtained parameters are listed in Table 1. From Eqs. (3) and (4) it follows that $T_1 / T_0$ is proportional to the gap width $w$ and the potential barrier $V_0$. Thus, they both decrease in the composites filled with mixed CNT/OLC inclusions. The critical frequency ($\omega_{cr}$) is related with DC conductivity according to the Barton–Nakajima–Namikawa relation:

$$\sigma_{DC} = \Delta \epsilon \epsilon_0 \omega_{cr}, \quad (5)$$

where $\Delta \epsilon$ is the dielectric strength and $\epsilon_0$ is the dielectric permittivity of vacuum.

Table 1. Tunneling model fit parameters.

<table>
<thead>
<tr>
<th></th>
<th>$\ln \sigma_{0, S/m}$</th>
<th>$T_1, K$</th>
<th>$T_0, K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLC, 12 wt%</td>
<td>–2.8</td>
<td>134</td>
<td>12</td>
</tr>
<tr>
<td>OLC/CNT, 12 wt%</td>
<td>–2.5</td>
<td>92.9</td>
<td>37</td>
</tr>
<tr>
<td>CNT, 12 wt%</td>
<td>–0.6</td>
<td>33.2</td>
<td>32.8</td>
</tr>
</tbody>
</table>

Thus, for the critical frequency, we have assumed similar temperature dependence as for DC conductivity:

$$\omega_{cr} = \omega_{cr\infty} \exp[-(T_1/(T + T_0))]. \quad (6)$$

For the composites with OLC inclusions, the best fit was obtained with the same values of parameters $T_1$ and $T_0$ as for DC conductivity and $\omega_{cr\infty} = 729$ kHz (Fig. 5).

4. Conclusions

The dielectric/electric properties of carbon nanotube (CNT), onion-like carbon (OLC), and mixed onion-like carbon/carbon nanotube (OLC/CNT) polyurethane composites are presented across a wide frequency range from hertz to terahertz. Although the highest dielectric permittivity value is observed in the composites with CNT inclusions, the dielectric properties of composites with OLC inclusions are also very attractive and can be improved by addition of small amounts of CNTs due to the strong synergy effect. In the composites with mixed OLC/CNT inclusions, the dielectric permittivity and electrical conductivity increase due to the reduction of both the potential barrier for carrier tunneling and the average distance between nanocarbon clusters.

Acknowledgements

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References


KOMPOZITŲ SU SVOGŪNINĖS ANGLIES IR DAUGIASIENIŲ ANGLIES NANOVAMZDELIŲ UŽPILDU ELEKTRINĖS IR DIELEKTRINĖS SAVYBĖS

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Santrauka

Straipsnyje aptariamos kompozitu su anglies nanovamzdelių, svogūninės anglies, mišrių nanovamzdelių ir svogūninės anglies užpildų elektrinės ir dielektrinės savybės.

Kompotuose su anglies nanovamzdelaiais yra stebimos didesnės dielektrinės skvarbos ir laidumo vertės nei kompozituose su svogūninės anglies užpildu. Kompozitu su svogūninės anglies užpildu elektrinės savybės gali būti pagerintos įterpiant nedidelį kiekį kiek anglies nanovamzdelių. Mišriuoju kompozitūs dėl sumažėjusio atstumo tarp anglies intarpų mažėja potencinis barjeras elektronams tuneliuoti, todėl padidėja kompozitu dielektrinė skvarba ir elektrinis laidumas.