Multi-Wall Carbon Nanotubes in Microwaves

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Abstract: - The electromagnetic (EM) response of multi-wall carbon nanotubes (MWCNT) prepared by chemical vapor decomposition (CVD) method has been analyzed in the microwave frequency range. EM absorption properties of MWCNT depend on their medium diameter related to their conductivity, concentration of highly dispersed Fe-Co metal particles localized inside and in the tips of nanotube. MWCNT display high EM absorption in microwaves and can be used as fillers for the design of the effective EM coatings.

Key-Words: - carbon nanotube, microwave, electromagnetic absorption, coating

1 Introduction

Nanocarbon plays an important role in the development of coatings absorbing and reflecting EM fields [1-3]. Graphite powder, various kinds of soot, and carbon fibers are widely used. However, it is difficult to provide a structure and size control of such materials even at the level of several tens of nm. Variation of one parameter causes an uncontrollable change of other parameters. That is why carbon nanotubes (CNT), whose length and diameter, purification degree and therefore electromagnetics are well controlled, can be the most promised filler for producing effective EM coatings. In the present communication we report study of the EM response of MWCNT powders, either high-purity or with some amount of metallic impurities, in order to clarify their usage as absorbing elements in Ka-band (26-37GHz).

2 Experimental

Two sets of MWCNT samples were produced for the study of the influence of CNT diameter and metal particle content on their EM response (see Table 1). MWCNT with different mean diameters (8.8 -24.5 nm) were produced by CVD method via catalytic decomposition of ethylene at 950K on FeCo-based catalysts supported on CaCO\textsubscript{3}, MgO and Al\textsubscript{2}O\textsubscript{3}. MWCNT produced with Fe-Co/CaCO\textsubscript{3} and Fe-Co/MgO (NT1 and NT2 respectively) were purified from the catalyst’s residue by refluxion with HCl (1:1) for 2 hours, washed with distilled water until neutral pH and dried in air. NT3 sample produced with Fe-Co/Al2O3 was not purified and used “as is”. According to TEM data (JEM-2010 transmission electron microscope with resolution 1.4 Å and accelerating voltage 200 kV) samples NT1-NT3 produced with a fixed time (15 min) show narrow distributions of mean outer diameter – 24.5, 13.4 and 8.8 nm respectively. To get MWCNT with different content of metal particles consisting of ferromagnetic Fe and Co we have used Fe-Co/Al\textsubscript{2}O\textsubscript{3} catalyst and varied the time of CNT growth. Thus samples NT3-NT5 were produced with carbon/metal ratio 30:1, 20:1 and 10:1 respectively. According to TEM data, MWCNT in these samples have almost the same mean outer diameter, ~ 8.8 nm, that corresponds to the invariability of number of nucleation centers in the catalysts with variation of CNT growth time. One can propose that the ratio of CNT length in NT3-NT5 samples is close to 3:2:1. In this case metal particles are localized mainly at the CNT tips and inside internal channels (see Fig.1). The acid treatment removes only oxide support with traces of unreduced active component but leaves dispersed prolonged metal particles (3-8 nm in diameter) inside tubes almost intact. According to Energy dispersive X-ray spectroscopy (EDX) analysis metal particles located inside CNT channels consist mainly of Fe-Co alloy. Content of metal inside purified MWCNTs varies within 1-1.5 wt.% and was close to that in pristine sample NT3.

For conductivity measurements the MWCNT powder was pressed in glass ampoule with electrical contacts made by 0.1 mm silver wires. The temperature dependences of the conductivity \(\sigma(T)\) were measured by four-point-probe technique in the temperature range 4.2–300 K [4].
The complex elements of the scattering matrix, $s_{11}$ and $s_{21}$, have been measured with high accuracy within 26-37 GHz frequency range (Ka-band) by free space technique. Samples were placed into microwave-transparent polymethylmethacrylate cell (21x21 mm, the sample workspace thickness was 0.8 mm). Attenuation of the signal transmitted through the sample ($s_{21}$) was calibrated to empty cell. Standard procedure of the calibration on reflecting plate has been used for EM reflection measurements ($s_{11}$). Powder density was measured for each sample and is presented in Table 1.

![Figure 1. TEM images of MWCNT produced with Fe-Co catalysts. A) – low magnification general view, B) – low defect MWCNT, C) – Fe-Co particle inside MWCNT, D) – Fe-Co particle on the MWCNT tip.](image)

### 3 Results and discussion

The influence of the MWCNT mean diameter on the EM response has been investigated. Reflectance, transmittance and absorbance were measured for MWCNT samples with different mean diameter (see Fig. 2). It has been shown that the increase of the mean diameter of MWCNT leads to corresponding decrease of the reflectance with the increase of the EM absorbance. At the same time, the transmission coefficient for all samples changes slightly. Electrical conductivity of NT1-NT3 samples (see Table 1) demonstrates non-monotonous behavior. Comparing conductivity data and reflectance/absorbance ratio one can see that NT1 sample shows lower conductivity with lower reflectance and higher absorbance in Ka-band despite of lower package density. NT2 and NT3 samples with close mean CNT diameter and conductivity (which is higher than for NT1), possess higher reflectance and lower absorbance of EM radiation. Thus, one can see a correlation between conductivity and EM response properties of MWCNT – lowering of the conductivity leads to corresponding decrease of the reflectance and increase of the EM absorption in Ka-band.

The influence of the content of metal particles on EM response properties of MWCNT has also been investigated. Reflectance, transmittance and absorbance for EM radiation (Fig. 3), and electrical conductivity (Table 1) were determined for MWCNT samples with different metal loading. The lower content of the metallic impurities the more pronounced absorption peak of EM attenuation (lower transmission) is characteristic for the MWCNT samples. The existence of frequency ranges with pronounced nonuniformity of EM response provided by CNT-based composites has been reported in many publications [5-6].

Note that increase of metal loading leads to decrease of its electrical conductivity (Table 1) with simultaneous decrease of reflectance and increase of absorbance of EM radiation (Fig. 3). The monotonous decrease of the conductivity in NT3-NT5 series corresponds to similar decrease of EM reflectance. Note that some changes in EM interaction with MWCNT are probably caused by changes of the CNT length due to different synthesis conditions. The detailed analysis within the wide frequency range is required to study the problem of the interaction between nanocarbon and EM radiation, that will be investigated in the future and reported elsewhere.

It is reasonable to propose that metal nanoparticles situated mainly inside nanotube channels are shielded from interaction with electrical part of EM radiation due to conductive upper layers of the nanotube. In this case ferromagnetic nanoparticles would interact mainly with magnetic part of EM wave, which may lead to attenuation of incident radiation.

However, detailed mechanism of interaction of EM radiation with wavelength much higher than the characteristic size of nanoparticles is still not clear. Attenuation due to absorption of EM radiation may be caused by (i) complex impedance of carbon nanomaterials [7], (ii) excitation of mechanical oscillation at eigenfrequency [8, 9], (iii) manifestation of far replica of antenna resonance inherent to multi-wall CNTs in THz frequency range [10, 11], that, in its turn, is supposed to be associated with the excitation of plasmon-polariton modes (surface waves) [12].
Table 1. Samples generic characteristics, packed densities, and electrical conductivity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total content of CNT by weight : content of metallic impurities</th>
<th>Catalyst</th>
<th>Mean diameter, nm</th>
<th>Surface area, m²/g</th>
<th>Conductivity, Sm/cm</th>
<th>packed density</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT1</td>
<td>purified 30%FeCo/CaCO₃</td>
<td></td>
<td>24.5 ± 11.1</td>
<td>135</td>
<td>22</td>
<td>0.107</td>
</tr>
<tr>
<td>NT2</td>
<td>purified 60%FeCo/MgO</td>
<td></td>
<td>13.4</td>
<td>339</td>
<td>40</td>
<td>0.163</td>
</tr>
<tr>
<td>NT3</td>
<td>30:1 60%FeCo/Al₂O₃</td>
<td></td>
<td>8.7 ± 2.4</td>
<td>404</td>
<td>38</td>
<td>0.152</td>
</tr>
<tr>
<td>NT4</td>
<td>20:1 60%FeCo/Al₂O₃</td>
<td></td>
<td>8.7 ± 2.4</td>
<td>401</td>
<td>29</td>
<td>0.122</td>
</tr>
<tr>
<td>NT5</td>
<td>10:1 60%FeCo/Al₂O₃</td>
<td></td>
<td>8.8 ± 2.5</td>
<td>354</td>
<td>27</td>
<td>0.091</td>
</tr>
</tbody>
</table>

4 Conclusion

We have reported the experimental study of the EM response of MWCNT powders obtained by CVD method with the different content of the metallic impurities (from 0 to 10 wt%). It has been demonstrated that the increase of the metal concentration leads to the decrease of the EM attenuation ability of the nanocarbon fillers. The evident non-monotonous frequency behavior of all types of investigated CNTs correlate well with the theoretical data on the antennas resonance predicted to be observed for single-wall CNTs [10] and CNT bundles [11] in the THz frequency range. EM response of MWCNT powders is found to be sensitive to the CNT type and purification degree in 26-37GHz frequency range. All samples demonstrate high level of absorption ability (up to 50-85% on average). Thus, MWCNT is found to be perspective candidate for applications in the microwave frequency range: having high resistivity to environmental erosion, high mechanical strength, good adhesion to the metallic substrate, being thin and light, MWCNT-based coatings can possess effective EM absorption in Ka-band.

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