In situ polymerization technique for the production of novel composite materials based on polyethylene and multi-walled carbon nanotubes modified by Co nanoparticles for EMI applications.

M.A. Kazakova,[a,b,*] N.V. Semikolenova,[b] E.Yu. Korovin,[c] A.V. Ischenko,[b] V.L. Kuznetsov,[a,c] V.I. Suslyaev,[c] M.A. Matsko,[b] V.A. Zakharov[b]

[a]*Novosibirsk State University, Pirogova 2, Novosibirsk, 630090, Russia*
[b]*Boreskov Institute of Catalysis, SB RAS, Lavrentieva 5, Novosibirsk 630090, Russia*
[c]*National Tomsk State University, Lenina Ave. 36, Tomsk 634050, Russia*
**Corresponding author: mas@catalysis.ru*

Abstract: Herein, the possibility of obtaining new triple composite materials based on polyethylene and MWCNT modified by Co nanoparticles has been studied. A new approach for the synthesis of these materials based on *in situ* polymerization of ethylene using Ti-containing catalysts previously adsorbed on the surface of Co/MWCNTs has been developed and utilized. Co/MWCNT-PE composites with different ratios of the components Co:MWCNT:PE have been obtained. The study of electromagnetic response has shown that the Co/MWCNT-PE composites can be used as a promising material for the development of broadband shielding to be used for effective reflecting the electromagnetic radiation (10-16 GHz).
Keywords: *In situ* polymerization, Multi-walled carbon nanotubes, Co/MWCNT-PE composites.

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) have been widely regarded as an attractive candidate to be used as fillers in composite materials due to their unique mechanical properties, large surface area, high electrical and thermal conductivity, and chemical stability. The development of new composite materials based on widely used polymers and MWCNTs is one of the promising fields of modern material science. The addition of a small amount of the MWCNT to the composite materials based on polyolefins provides significant improvement of their mechanical and electrical properties. The addition of the third component such as metal magnetic nanoparticles to the composite material at the preparation stage potentially allows the adjustment of the electromagnetical properties of the material by varying not only the dielectric properties of MWCNT, but also magnetic properties of metals. Moreover, the resulting "triple" composite materials are able to acquire completely new properties, for instance, electromagnetic shielding. In this work, the special attention has been paid to the issue of how the uniformity of the Co/MWCNT distribution in the polyethylene (PE) matrix influences the electrophysical properties of the triple composite materials.

2. Experimental

MWCNTs were synthesized by CVD of ethylene decomposition over the bimetallic Fe-Co catalysts at 680°C. We have used functionalized MWCNTs containing surface carboxylic groups (2.6 groups per 1 nm^{-2}) produced via boiling in concentrated nitric acid (denoted as MWNT-Ox-NA). Co-containing samples were prepared by the impregnation of MWCNTs (surface area of 305 m^2/g, average particle diameter of 9.4 nm) with the aqueous solutions of Co (II) salts followed by calcination under an inert atmosphere and reduction in a stream of hydrogen at the temperature of 350°C. The samples with Co concentrations of 3.5, 7.3, 11.7 and 14.1 wt. % were thus obtained.

3. Results and discussion

The structure and morphology of pure and Co-containing MWCNTs and obtained composites were monitored by TEM. The sample of 3.5% Co/MWCNT-Ox-NA mainly contains Co-oxide particles within the channels of MWCNTs of 3-5 nm in the size. The increase of Co content (within the range from 3.5 up to 14.5 wt. %) leads to the growth of Co^0 particle with the sizes from 5–10 nm to 50–80 nm (Fig. 1). The studied samples show both types of Co metal particles as inside of the MWCNTs with the diameter of 5 nm as maximum and various lengths, and Co metal particles located on the surface.

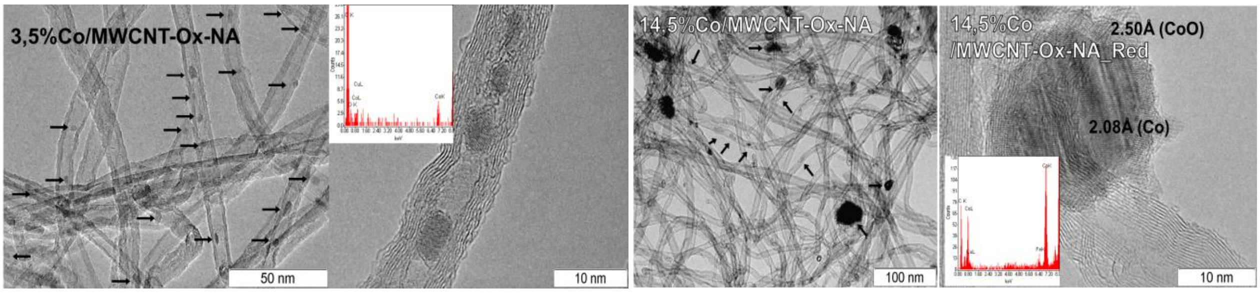

Figure 1. TEM images of 3.5 and 14.5 wt.% Co/MWCNT-Ox-NA, correspondingly. Arrows show Co particles inside and outside nanotube channels.

For the preparation of “triple” composite materials, (3,5 - 14,5)% Co/MWCNT-Ox-NA samples were used as a support for the Ti-containing polymerization catalyst. Ethylene slurry polymerization was performed in heptane, TIBA was used as the cocatalyst of $TiCl_4$ polymerization catalyst. During the polymerization, the ethylene pressure and temperature were maintained constant with the automatic computer-controlled system. The reaction was carried out until the desired amount of PE was obtained. We obtained composite materials Co/MWCNT-PE containing about 10 wt. % of additives (3.5 - 14.5 wt% Co/MWCNT) with a maximum cobalt content of 1.74 wt. %. For investigation of the structure of Co/MWCNT-PE composites TEM, IF ^{59}Co NMR, DSC were used.

The high resolution electron micrographs shows the dispersed Co particles of 3–5 nm, uniformly distributed in the channels of the nanotubes. In addition, we observed the formation of polymer films on the surface of the tubes without clearly defined droplets. Hence, MWCNTs are uniformly wet by PE molecules (contact angles cannot be registered this corresponds to a high value of the adhesion work of the polymer on the surface of the tubes). The formation of PE films on the surface of MWCNT leads to the preservation of Co nanoparticles from oxidation that was confirmed by IF ^{59}Co NMR method. So, we obtained “triple” composite materials combining the initial properties of three different components Co-MWCNT-PE.

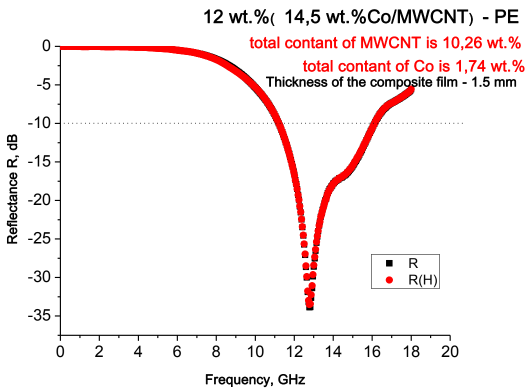

Figure 2. The frequency dependence of the reflection coefficient for the composite material 12% (14.5% Co/MWCNT) - PE.

According to the study of electromagnetic response the composite material 12% (14.5% Co/MWCNT)-PE (with a thickness of 1.5 mm) has a minimum reflection coefficient in the frequency of 13 GHz and its value is - 34 dB. The frequency band by the level of -10 dB is 5 GHz (Fig. 2). Thus, these composites demonstrate the effect of broadband shielding of electromagnetic radiation (10-16 GHz) at the location on the metal surface.

4. Conclusions

The results provide promising ways for Co/MWNT-PE composites preparation via the catalyst distribution on the surface of MWCNTs followed by polymerization of ethylene. The homogeneous coverage of nanotubes surface with PE molecules has been observed. Co/MWNT-PE composites with high concentration of homogeneously distributed nanotubes and Co nanoparticles are perspective as a material for the development of broadband shielding to be used for effective reflecting the electromagnetic radiation (10-16 GHz).

Acknowledgements The reported study was funded by RFBR, according to the research project No. 16-32-60046 mol_a_dk.