Romanian Reports in Physics **71**, 508 (2019)

NEW HYBRID MWCNT/Co-Fe-B NANOPARTICLES COMPOSITE MATERIAL FOR APPLICATIONS IN MICROWAVE DOMAIN

A. GHEMES, G. ABABEI, G. STOIAN, N. LUPU, H. CHIRIAC

National Institute of Research and Development for Technical Physics,
47 Mangeron Boulevard, RO-700050 Iasi, Romania
E-mails: *aghemes@phys-iasi.ro; gababei@phys-iasi.ro; gstoian@phys-iasi.ro; nicole@phys-iasi.ro; hchiriac@phys-iasi.ro*

Received August 26, 2019

Abstract. A new hybrid composite material based on multiwalled carbon nanotubes (MWCNTs) and soft magnetic Co-Fe-B nanoparticles for applications in microwave domain is proposed. MWCNTs with length of about 300 μm have been synthesized by chloride mediated chemical vapor deposition method. Co-Fe-B nanoparticles with diameters of about 30 nm were prepared by chemical reduction method. The electromagnetic shielding characteristics of the composite material was investigated by determination of the microwave shielding effectiveness in the 1 GHz to 8 GHz frequency range. The new material showed high shielding effectiveness in broadband frequency range.

Key words: carbon nanotubes, soft magnetic nanoparticles, composite materials.

1. INTRODUCTION

Due to the tremendous development of electronics and telecommunications, electromagnetic interference (EMI) became a major problem nowadays when all modern devices emit radiation which can interfere and impede on the proper use of the devices nearby [1]. Few examples of electromagnetic interferences are disturbance of radio and TV signals from low altitude flying aircrafts, noises in microphones from a cell phone, electronic devices interference with navigation signals during take off and landing of aircrafts. The radiation emitted by GSM mobile phones for example, can be extremely harmful to any implantable electronic device in the human body [2]. On the other hand, radar absorbing materials and coatings are highly required by the military, aircraft and aerospace industry.

To avoid such interferences, a shielding material has to be used. For efficient shielding action, an electromagnetic radiation shielding material should possess either mobile charge carriers (electrons or holes) or electric and/or magnetic dipoles which interact with the electric (E) and magnetic (H) vectors of the incident electromagnetic radiation. Usually, metal-based materials – sheet metal, metal screen or metal foam – are used to fabricate enclosures which are capable to minimize the radiation escape from a certain device. However, the use of metals as shielding materials has certain disadvantages – the increase in the mass of the final device and small corrosion resistance being the major drawbacks.

In the last decade, conductive polymer composites became a better choice due to their lightweight, corrosion resistance, flexibility in fabrication and versatility of the shapes. In general, a conductive filler – carbon black, carbon fibers or powder-like carbon nanotubes (CNT) – is well dispersed into a polymer matrix and then the electromagnetic radiation shielding capability is tested either in reflection or absorption mode. Although this method proved its suitability and some promising results were obtained [3], still their shielding effectiveness (SE) is limited by the conductivity of the filler material, maximum loading capacity and percolation threshold. The percolation threshold strongly depends on the aspect ratio of the conductive filler dispersed into matrix – higher aspect ratio of the filler decrease the percolation threshold. For example, Singh *et al.* [4] used MWCNT with aspect ratio of about 10^4 to prepare reinforced low density polyethylene (LDPE) composites. They obtained average SE values of –22.4 dB for 10% MWCNT-LPDE composites in Ku-band frequency range (12.4–18 GHz). Gupta *et al.* [5] synthesized poly(trimethylene terephthalate)/multiwalled carbon nanotube composites with various amounts of MWCNT. They observed SE values of –36 to –42 dB in Ku band frequency range by using 20 to 30 µm long and 20 to 40 nm in diameter MWCNTs, hence an aspect ratio of about 10^3.

Another approach is to use hybrid combinations of carbon nanotubes and magnetic nanoparticles in order to increase the shielding effectiveness still obtaining lightweight composite materials as compared to bulk metals counterparts. For example, Yu *et al.* [6] used NiO and Fe_3O_4 nanoparticles, Fang *et al.* [7] Ag and $Co_{0.2}Fe_{2.8}O_4$, Chen *et al.* [8] core-shell shaped $Fe@Fe_3O_4$ nanoparticles, while Wang *et al.* [9] used $NiCo_2$ nanoparticles interspersed with carbon nanotubes to enhance the electromagnetic wave absorption properties. Very recently, an innovative technique for the preparation of carbon nanotube based shielding material has been reported [10] and is estimated that the market of electromagnetic radiation blocking solutions will reach 7 billion USD by 2022 [11].

In this paper we propose for the first time to use MWCNT with a high aspect ratio of about 10^4 in combination with soft magnetic Co-Fe-B nanoparticles in order to obtain a new composite material with applications in microwave domain.

2. EXPERIMENTAL PROCEDURE

Multiwalled carbon nanotubes were synthesized by a chloride mediated chemical vapor deposition (CVD) method reported by Inoue in 2008 [12]. Briefly, anhydrous $FeCl_2$ powder 99.5% (Alfa Aesar) was introduced into a quartz tube furnace which was evacuated to a pressure of about 10^{-3} Torr. Then the furnace was heated to a temperature of 850°C and acetylene (C_2H_2) was introduced into the growth area at a flow rate of 200 cm^3/min.

$Co_{74.82}Fe_{14.67}B_{10.51}$ nanoparticles (spectrophotometric composition measured wt.%) with diameters of about 30 nm were prepared by chemical reduction of cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and iron sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) salts in aqueous solution of sodium borohydride ($NaBH_4$) using a Fe/Co ratio of 0.2 as described in our previous paper [13].

For preparation of the hybrid composite material, MWCNTs and Co-Fe-B nanoparticles were mixed by ultra sonication for 1 hour with one component of a 4-component transparent epoxy resin (EPON 812), to assure homogeneity. Then, the other 3 components were added and the mixture was stirred for 10 min. Finally, the material was pressed in a cylindrical Teflon® mold and introduced for 1 hour into an oven at a temperature of 60°C for polymerization of the resin.

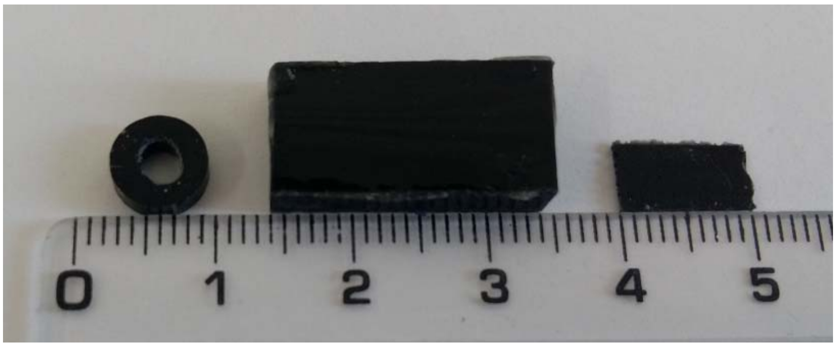


Fig. 1 – MWCNT/Co-Fe-B composite material in different shapes.

We obtained toroidal shaped samples with outer diameter $\Phi_{out} = 7$ mm, inner diameter $\Phi_{in} = 3$ mm and thickness $t = 3$ mm which were used for measurements in the microwave frequency range. For optical microscope observations of the material's structure, we used thin slices of 0.4 mm which were cut from a parallelepiped as shown in Fig 1.

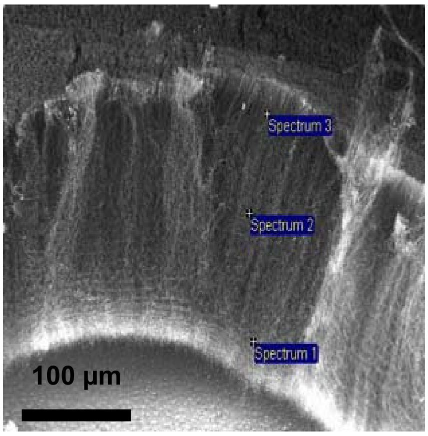
High frequency measurements were done using the 7 mm coaxial transmission line method in the range from 1 GHz to 8 GHz. The coaxial cell was connected between the emission and reception ports, respectively, of a vector network analyzer (Agilent VNA N5203A) [14–16]. To evaluate the microwave absorption characteristics of the proposed material, we determined the shielding effectiveness (SE) at different microwave frequencies as the ratio of output energy to input energy across the shielding material which is defined as:

$$\mathrm{SE} = 10 \log P_{inc}/P_{out}, \tag{1}$$

where, P_{inc} and P_{out} represent the input and the output of the microwave field in the presence of the material.

3. RESULTS AND DISCUSSIONS

Using the chemical vapor deposition method described before, vertically aligned MWCNT arrays were obtained. The height of the array was around 300 µm after 20 min growth time, giving a growth rate of about 15 µm/min. The purity of the as grown MWCNTs was evaluated from energy dispersive X-ray spectroscopy (EDX) analysis and results, shown in Fig. 2, indicated the presence of very small amount of Fe catalyst, less than 0.7 at% into the array.



	C	Fe
Spectrum 1	99.54 at.%	0.46 at.%
Spectrum 2	99.35 at.%	0.65 at.%
Spectrum 3	99.29 at.%	0.71 at.%
Mean	99.39 at.%	0.61 at.%
Std. deviation	0.13 at.%	0.13 at.%

Fig. 2 – EDX analysis in three points along the vertically aligned MWCNT array.

From the HR-TEM image presented in Fig. 3 we can observe that as grown MWCNTs have an outer diameter of about 30 nm and inner diameter of 6 nm.

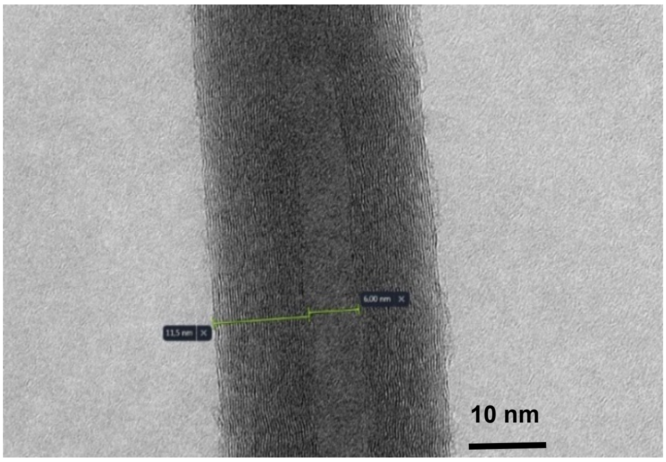


Fig. 3 – HR-TEM image of an individual MWCNT.

As depicted in Fig. 3, if we divide the total width of 11.5 nm of the CNT walls to the inter-walls distance of 0.344 nm we obtain the number of concentric walls which, in this case, was about 33. As we can see, as-grown carbon nanotubes are free of amorphous carbon and only graphitic carbon is present.

In order to check the dispersion and homogeneity of the composite material, thin slices of 0.4 mm thickness were analyzed by optical microscopy. As Fig. 4 shows, Co-Fe-B nanoparticles were distributed uniformly within the polymeric matrix, while MWCNTs show small local agglomerations. It is well known that, the total dispersion of MWCNTs in any media is quite difficult to achieve, often requiring the use of surfactants and/or functionalization [17]. Anyway, the material obtained by combining MWCNTs and Co-Fe-B nanoparticles in a ratio of 1:5 (Fig. 4c) shows a good homogeneity and is suitable to be used as electromagnetic wave absorber.

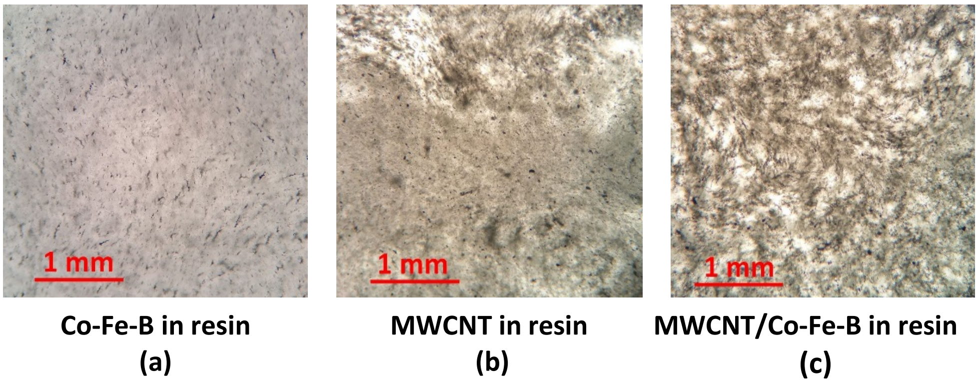


Fig. 4 – Optical microscope images of: a) Co-Fe-B nanoparticles, b) MWCNTs, and c) MWCNTs/Co-Fe-B nanoparticles dispersed in epoxy resin.

For high frequency measurements we prepared toroidal test samples using mixtures of MWCNTs and Co-Fe-B nanoparticles in ratios of 1:5, 2:5 and 3:5 corresponding to a MWCNTs loading into epoxy resin of 0.2 wt.%, 0.4 wt.% and 0.6 wt.%, respectively. This was the maximum amount of MWCNTs which could be incorporated and dispersed into the epoxy resin used for this study.

The microwave spectra presented in Fig. 5 indicated that the prepared composite materials attenuate the microwave radiation and absorb its energy in a frequency range from about 1 GHz to 8 GHz. By using the combination of MWCNTs with Co-Fe-B nanoparticles, we obtained a composite material with two absorption bands: one around 4 GHz given by the presence of Co-Fe-B nanoparticles and another one above 5 GHz due to MWCNTs. Increasing the MWCNTs loading from 0.2 wt.% to 0.6 wt.%, the absorption of the composite materials rose by almost 8 dB. This improvement of the SE can be attributed to the higher electrical conductivity of the composite material with higher MWCNTs loading [18]. Anyway, such small carbon nanotubes loading (lees than 1%) is very useful, reducing the weight and cost of the prepared electromagnetic shield. This behavior of our composite material might be given by the higher aspect ratio of the MWCNTs used in this study.

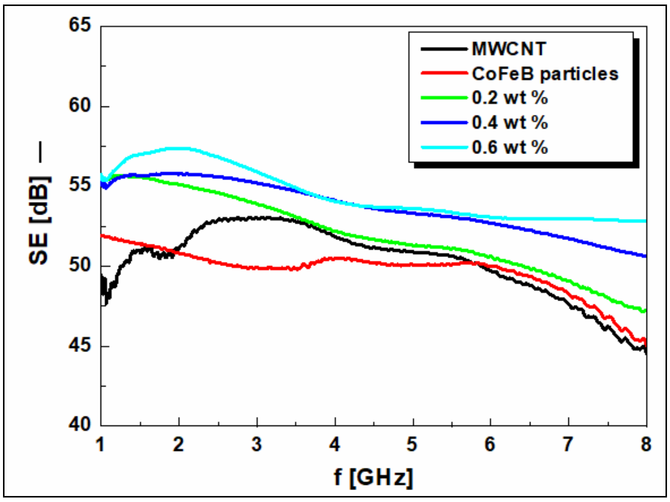


Fig. 5 – Shielding effectiveness (SE) *versus* radiation frequency for different MWCNTs loadings.

4. CONCLUSIONS

A new hybrid composite material based on MWCNTs with aspect ratio of 10^4 and soft magnetic Co-Fe-B nanoparticles with diameter of 30 nm has been prepared. We found that composite materials with MWCNTs loadings from 0.2 wt.% to 0.6 wt.% absorb microwave radiation in a frequency range from 1 to 8 GHz. Shielding effectiveness of 57 dB has been achieved for the composite with highest MWCNTs loading of 0.6 wt.% used in this study. These results indicate the potential use of the hybrid MWCNT/Co-Fe-B nanoparticles composites for electromagnetic interference shielding applications.

Acknowledgments. The authors gratefully acknowledge the financial support from Project PN 18 06 01 01.

REFERENCES

1. S. Geetha, K. K. Satheesh Kumar, R. K. Rao Chepuri, M. Vijayan, and D. C. Trivedi, *EMI Shielding: Methods and Materials – A Review*, J. Appl. Polym. Sci. **112**, 2073 (2009).
2. W. Kainz, F. Alesch and D. D. Chan, *Electromagnetic interference of GSM mobile phones with the implantable deep brain stimulator, ITREL-III*, Biomed Eng. Online, 2:11 (2003).
3. http://www.materialenkennis.nl/dico/UserFiles/File/PolyCond.pdf

4. B. P. Singh, Prabha, P. Saini, T. K. Gupta, P. Garg, G. Kumar, I. Pande, S. Pande, R. K. Seth, S. K. Dhawan, and R. B. Mathur, J. Nanoparticle Res. **13**, 7065 (2011).
5. A. Gupta, and V. Choudhary, Compos. Sci. Technol. **71**, 1563 (2011).
6. L. Yu, X. Lan, C. Wei, X. Li, X. Qi, T. Xu, C. Li, C. Li, and Z. Wang, J. Alloy Compd. **748**, 111 (2018).
7. J. Fang, Y. Wang, W. Wei, Z. Chen, Y. Li, Z. Liu, X. Yue, and Z. Jiang, RSC Adv. **6**, 8364695 (2016).
8. C. Chen, S. Bao, B. Zhang, Y. Chen, W. Chen, and C. Wang, Appl. Surf. Sci., **467–468** (2019).
9. B. Wang, C. Zhang, C. Mu, R. Yang, J. Xiang, J. Song, F. Wen, and Z. Liu, J. Magn. Magn. Mater. **471**, 185 (2019).
10. G. M. Weng, J. Li, M. Alhabeb, C. Karpovich, H. Wang, J. Lipton, K. Maleski, J. Kong, E. Shaulsky, M. Elimelech, Y. Gogotsi, and A. D. Taylor, Adv. Funct. Mater. **28**, 1803360 (2018).
11. https://phys.org/news/2018-11-tech-high-tech-blocks-electromagnetic.html
12. Y. Inoue, K. Kakihata, Y. Hirono, T. Horie, A. Ishida, and H. Mimura, Appl. Phys. Lett. **92**, 213113 (2008).
13. G. Ababei, M. Gaburici, L.-C. Budeanu, M. Grigoras, M. Porcescu, N. Lupu, H. Chiriac, J. Magn. Magn. Mater. **451**, 565 (2018).
14. P. Savi, M. Miscuglio, M. Giorcelli, and A. Tagliaferro, PIER Lett. **44**, 63 (2014).
15. Lakshmi, Honey John, K.T. Mathew, R. Joseph, and K.E. George, Acta Mater. **57**, 371.
16. A. Munir, Adv. Polym. Tech. **36**, 21617-1 (2015).
17. O. V. Kharissova, B. I. Kharisov, and E. G. de Casas Ortiz, RSC Adv. **3**, 24812 (2013).
18. J. I. Ejembi, I. H. Nwigboji, Z. Wang, D. Bagayoko, and G.-L. Zhao, Physical Science, 2015.