Modification of carbon fiber by magnetite particles

E V Kornilitsina1,2, E A Lebedeva1, S A Astaf’eva1 and D K Trukhinov1

1 Institute of Technical Chemistry, a branch of the Perm Federal Research Center, Ural Branch of the Russian Academy, Russia, 614013, Perm, Akademika Koroleva, 3
2 The author responsible for correspondence

E-mail: kornilicina.lena@mail.ru

Abstract. In order to expand the application range of carbon reinforced composite materials in shielding field, this paper aimed to modify the chopped carbon fiber (CF) by magnetite particles with ultrasonic treatment. The modification was carried out in three stages and the increasing amount of the cover was proved by TGA analyze. SEM analyze is showed the most part of CF surface was coated by magnetite particles Fe3O4. Also it was noticed some agglomeration on each stages what is possibly connected with high surface energy of these particles. The chemical compound of the coating corresponds to ferrous oxide (II and III) what is confirmed by Raman spectroscopy.

1. Introduction
Nowadays the constant use of electronic devices increases the emission of electromagnetic radiation [1, 2]. In fact, these appliances operate at low voltages, so they can be affected by a lot of unwanted radiated signals, which causes deterioration of the system or equipment characteristics [3-5]. For example, distortion of radio / television signals, interference with conversations on mobile devices, interference with medical or aviation systems, or even the burning of a sensitive device. This electromagnetic interference (EMI) is generated by an external radiation source and affects devices through electromagnetic induction, electrostatic coupling, or conduction.

It’s necessary to provide a protection from EMI for solving these problems. Shielding is a method of reducing the radiation intensity to a set value using conductive or magnetic materials [6, 7]. Shielding could be achieved by minimizing the signal passing through the system, reflecting the wave or absorbing and dissipation of radiation power inside the material [8]. Shielding materials should have high electrical conductivity. To eliminate the disadvantages of traditional shielding materials, researchers are looking for an alternative using conductive polymer composites [9, 10].

It’s well known that electromagnetic shielding consists of electric and magnetic components, which are mutually perpendicular to the direction of wave growth. Thus, for the best shielding effect it’s necessary to reduce the both parts of electromagnetic radiation [11]. For improvement the polymer conductivity and magnetic influence, corresponding materials should be used.

Carbon materials are appropriate conductive component because of their good conductivity and dielectric properties. Due to the high physical and mechanical parameters and conductive characteristics, carbon fibers (CF) are one of the perspective fillers for protection from the electromagnetic radiation [12, 13]. So, X. Luo и D.D.L. Chung suggested that continuous carbon fibers provide greater protection against EMI because of greater conductivity [14]. K.H. Wong и S.J. Pickering found the fiber should be
in contact with each other for the best charge transfer [15]. Thus they provide a conductive net from the short carbon fiber.

For nowadays magnetite particles Fe₃O₄ are used as magnetic material because if ability to absorb electromagnetic waves [16]. It has been established that the combined use of carbon nanofibers and magnetite particles provides synergistic effect in shielding [17]. We suggested that a non-woven veil made of discrete carbon fiber with a magnetic coating will provide high shielding characteristics of the material, due to good conductive and magnetic properties.

In this study, the main objective is to obtain a hybrid composite consisting of short carbon fiber and magnetite. In the future, the resulting composite will be studied as a component of electromagnetic shielding materials.

2. Experimental procedure

2.1. Materials

Raw material is carbon fiber vCF-163 (Germany), used for modification by magnetic particles. Chemical reagents: iron (III) chloride hexahydrate (FeCl₃·6H₂O), iron (II) sulfate heptahydrate (FeSO₄·7H₂O), aqueous ammonia solution (NH₄OH) (JSC Reachim, LLC) were used without further cleaning.

2.2. Synthesis of magnetic fluid

The magnetic fluid was synthesized by chemical condensation. The production of magnetite can be described by the equation:

$$2\text{FeCl}_3 + \text{FeSO}_4 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe(OH)}_2 + 2\text{Fe(OH)}_3 + 6\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{Fe}_3\text{O}_4$$

An aqueous solution of iron salts FeCl₃·6H₂O and FeSO₄·7H₂O was prepared with a concentration 2M and 1 M respectively. To 50 ml of this solution, 60 ml of ammonia with a concentration of 9.4 mol/L was added to form 2 layers. Ammonia must be taken in 20-30 % excess. After mixing, the resulting 2 layers were heated and boiled for 3-4 minutes. After, water was added for a more rapid deposition of sediment. The water layer was drained and this colloid system was washed with water until the neutral reaction.

2.3. Carbon fiber modification

Carbon fibers 3-5 mm long were immersed in the previously obtained magnetic fluid. This system was dispersed by ultrasonic treatment for 1 hour on a Sonopuls HD 3200 device (Bandelin, Germany) at room temperature. Then the sol excess was filtered from the carbon fibers with distilled water. After drying at 100°C for 24 hours, the process was repeated two times for a denser and more uniform coating of carbon fibers with a layer of Fe₃O₄ particles.

2.4. Characterization

An analysis of the surface structure of the fibers was carried out using a FEI Quanta 650FEG scanning electron microscope (FEI, USA).

Raman spectra were recorded on a SENTERRA Raman microscope spectrometer (Bruker, Germany) in the range of 100–4000 cm⁻¹ with an emission wavelength of 532 nm.

The thermogravimetric method was used to determine the magnetite content on the carbon fiber surface using a TGA / DSC 1 instrument (Mettler Toledo) in the temperature range 25–1000 °C at a heating rate of 10 °C / min in air. The sample holder is a 70 µl alumina crucible. All samples weigh 4 mg.
3. Result and discussion

3.1. SEM

Figure 1 shows SEM images of pure CF and CF/Fe$_3$O$_4$ composite after each modification stage. The diameter of the initial CF is about 6-9 µm. The fibers have a fibrillar structure with a diameter of 150-250 nm.

![Figure 1. SEM of initial CF(a), CF with Fe$_3$O$_4$: first stage (b), second stage (c), third stage(d).](image)

Ultrasonic dispersion of CF in a magnetic fluid resulted in the formation of magnetite particles on their surface (figure 1b). It is obvious that after each subsequent modification stage, the amount of magnetite on the fiber surface increases, which is confirmed by SEM (figure 1c and 1d).

From figure 1d, it is noticeable that most of the CF is covered with magnetite particles, sometimes with a small aggregation, which may be due to the relatively high surface energy of Fe$_3$O$_4$ particles.

3.2. Raman-spectra

Raman spectroscopy was performed for synthesized magnetite particles and carbon fibers modified with magnetite for each stage to investigate the presence of magnetite particles on the surface and the influence of deposited particles on the fiber structure. Figure 2 shows the Raman spectra of magnetite and CF modified by magnetite.
Figure 2. Raman spectra of magnetite and modified CF.

For all Raman spectra, a peak 664 cm\(^{-1}\) corresponding to magnetite is usually observed and represents a symmetrical section of oxygen atoms along Fe-O bonds corresponding to the A\(_{1g}\) mode. The peaks at 369 and 504 cm\(^{-1}\) correspond to the peaks of partial oxidation of magnetite to maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)) [18].

The degree of graphitization of carbon fibers is judged by typical bands of Raman spectra [19]. In the Raman spectra, two characteristic bands of D (defects) at 1343–1356 cm\(^{-1}\) and G (graphite) at 1586–1594 cm\(^{-1}\) are usually observed [20-22]. The G band is determined by vibrations of carbon atoms in the plane of graphene layers and is associated with carbon atoms in the state of sp\(^2\) hybridization. The D band is induced by disordered carbon atoms and is associated with carbon atoms in both sp\(^2\) and sp\(^3\) hybridization states localized in the region of defects and the periphery of graphene layers [20, 21]. The obtained spectra show a shift of the D band, which can be explained by the overlap with the 1393 cm\(^{-1}\) band, which refers to the second-order peak of pure magnetite-like materials at \(\sim\)1400 cm\(^{-1}\), which is associated with the resonant behavior of the Raman spectrum when excited by green light [23].

The TGA method was used to make a preliminary estimate of the amount of deposited magnetite on the surface of carbon fibers, which was 17, 23 and 34 % for stages 1, 2 and 3, respectively.

Thus, a hybrid CFS/Fe\(_3\)O\(_4\) composite was obtained by ultrasonic deposition. The fiber surface is characterized by SEM and Raman spectroscopy. The content of magnetite on their surface is determined. The CFs/Fe\(_3\)O\(_4\) material is a potential material that absorbs microwave radiation. The magnetic properties will be considered in our future work.

Acknowledgement
The reported study was funded by RFBR and Perm Territory as part of a scientific project no. 19-43-590024 p_a.

References
[1] Wan Y J, Zhu P L, Yu S H, Sun R, Wong C P and Liao W H. 2017 Graphene paper for exceptional EMI shielding performance using large-sized graphene oxide sheets and doping strategy Carb. 122 74-81 doi.org/10.1016/j.carbon.2017.06.042
[2] Yan D-X, Pang H, Li B, Vajtai R, Xu L, Ren P-G, Wang J-H and Li Z-M. 2014 Structured reduced graphene oxide/polymer composites for ultra-efficient electromagnetic interference shielding Adv. Func. Mat. 25(4) 559-66 DOI: 10.1002/adfm.201403809
[3] Kubík Z and Skála J. 2016 Shielding effectiveness simulation of small perforated shielding enclosures using FEM Energ. 9(3) 129-40 doi.org/10.3390/en9030129
[4] Saini P and Arora M. 2012 Microwave absorption and EMI shielding behavior of nanocomposites
based on intrinsically conducting polymers, graphene and carbon nanotubes. New polym. for spec. applic. InTech 71-112 doi.org/10.5772/48779

[5] Naeem S, Baheti V, Tunakova V, Militky J, Karthik D and Tomkova B. 2017 Development of porous and electrically conductive activated carbon web for effective EMI shielding applications. Carlb. 111 439-47 doi.org/10.1016/j.carbon.2016.10.026

[6] Sharma S, Singh B P, Chauhan S S, Jyoti J, Arya A K, Dhakate S R, Kumar V and Yokozeki T 2018 Enhanced thermomechanical and electrical properties of multivalled carbon nanotube paper reinforced epoxy laminar composites. Comp. Part A: Appl. Scie. and Manuf. 104 129-38 doi.org/10.1016/j.compositesa.2017.10.023

[7] Joshi A and Datar S 2015 Carbon nanostructure composite for electromagnetic interference shielding. Pram. 84(6) 1099-116 DOI: 10.1007/s12043-015-1005-9

[8] Chung D D L 2001 Electromagnetic interference shielding effectiveness of carbon materials. Carlb. 39(2) 279-85 doi.org/10.1016/S0008-6223(00)00184-6

[9] Ameli A, Jung P U and Park C B. 2013 Electrical properties and electromagnetic interference shielding effectiveness of polypropylene/carbon fiber composite foam. Carlb. 60 379-91 doi.org/10.1016/j.carbon.2013.04.050

[10] Kuang T R, Ju J J, Yang Z Y, Geng L H and Peng X F 2018 A facile approach towards fabrication of lightweight biodegradable poly (butylene succinate)/carbon fiber composite foams with high electrical conductivity and strength. Comp. Scie. and Tech. 159 171-9 doi.org/10.1016/j.compscitech.2018.02.021

[11] Biswas S, Arief I, Panja S S and Bose S 2016 Absorption-dominated electromagnetic wave suppressor derived from ferrite-doped cross-linked graphene framework and conducting carbon. ACS App. Mat. and Inter. 9(3) 3030-9 DOI: 10.1021/acsami.6b14853

[12] Gao S-L, Mäder E and Zhandarov S F 2004 Carbon fibers and composites with epoxy resins: Topography, fractography and interphases. Carlb. 42(3) 515-29 doi.org/10.1016/j.carbon.2003.12.085

[13] Cao M S, Song W L, Hou Z L, Wen B and Yuan J 2010 The effects of temperature and frequency on the dielectric properties, electromagnetic interference shielding and microwave-absorption of short carbon fiber/silica composites. Carlb. 48 788-96 doi.org/10.1016/j.carbon.2009.10.028

[14] Luo X and Chung D D L 1999 Electromagnetic interference shielding using continuous carbon-fiber carbon-matrix and polymer-matrix composites. Comp. Part B: Engin. 30(3) 227-31 doi.org/10.1016/S1359-8368(98)00065-1

[15] Liang J, Gu Y, Bai M, Wang S, Li M and Zhang Z. 2019 Electromagnetic shielding property of carbon fiber felt made of different types of short-chopped carbon fibers. Comp. Part A: App. Scie. and Manuf. 121 289-98 doi.org/10.1016/j.compositesa.2019.03.037

[16] Zhang H M, Zhang G C, Li J T, Fan X, Jing Z X and Shi X T. 2017 Lightweight, multifunctional microcellular PMMA/Fe3O4@MWCNTs nanocomposite foams with efficient electromagnetic interference shielding. Comp. Part A 100 128-38 doi.org/10.1016/j.compositesa.2017.05.009

[17] Crespo M, Méndez N, González M, Baselga J and Pozuelo J 2014 Synergistic effect of magnetite nanoparticles and carbon nanofibres in electromagnetic absorbing composites. Carlb. 74 63-72 doi.org/10.1016/j.carbon.2014.02.082

[18] Jacintho G V M, Brolo A G, Corio P, Suarez P A Z and Rubim J C. 2009 Structural investigation of MFe2O4 (M = Fe, Co) magnetic fluids. J. Phys. Chem. 113(18) 7684-91 doi.org/10.1021/jp9013477

[19] Washer G and Blum F J. 2008 Raman spectrscopy for the nondestructive testing of carbon fiber. Res. Let. Article ID 693207 doi.org/10.1155/2008/693207

[20] Ferrari A C and Roberson J. 2000 Interpretation of Raman spectra of disordered and amorphous carbon. Phys. Rev. B 61 14095 doi.org/10.1103/PhysRevB.61.14095

[21] Tuinstra F and Koenig J L. 1970 Raman spectrum of graphite. J. Chem. Phys. 53 1126 doi.org/10.1063/1.1674108

[22] Pimenta M A, Dresselhaus G, Dresselhaus M S, Cancado L G, Jorio A and Saito R. 2007 Studying
disorder in graphite-based systems by Raman spectroscopy *Phys. Chem. Chem. Phys.* **9** 1276-90 doi.org/10.1039/B613962K

[23] Cvejic Z, Rakic S, Kremenovic A, Antic B, Jovalekic C and Colomban P 2006 Nanosize ferrites obtained by ball milling: Crystal structure, cation distribution, size-strain analysis and Raman investigations *Sol. Sta. Scie.* **8**(8) 908-15 doi.org/10.1016/j.solidstatesciences.2006.02.041