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RESEARCH PAPER

Improving Radar Absorbing Capability of Polystyrene Nanocomposites: Preparation and Investigation of Microwave Absorbing Properties

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ABSTRACT

Microwave absorbing materials are usually designed to solve protection against electromagnetic interference in wireless communication systems and high frequency circuit mechanisms. In this research polystyrene (PS) nanocomposites containing various nano-fillers were successfully synthesized. The novelty of this work is comparing of three various nanostructures: non-metallic conductive graphene oxide, magnetic Fe_3O_4 and semi-conductor zinc oxide were used as additive. The effect of different fillers loading and homogenizer speed on the reflection loss (RL) amount and electromagnetic wave absorption was investigated. In order to investigate particle size and morphology of the nanostructures the scanning electron microscopy (SEM) was used. The frequency range of 5-8 GHz was employed in the investigation of electromagnetic wave absorption properties of nanocomposites using a vector network analyzer and eventually their absorption properties were analyzed and compared. The results indicate that graphene oxide has substantial effect on absorption in compare with the other nanocomposite samples. Increase of homogenizer speed led to a dispersion improvement of nanostructures and absorption. Therefore, the broadening of the microwave absorption band-width is attributed to the suitable dispersion of nanostructures in polymeric matrix.

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INTRODUCTION

The electromagnetic interference (EMI) has resulted in a new kind of pollution, and electromagnetic radiation also remains a key issue to be solved. Therefore, the microwave absorbing materials, which are used in electromagnetic interference protection, local area network, wireless communication, radar stealth technology and medical applications, have been attracting great attention during the past decades [1-3]. The electromagnetic waves interference caused by these waves should be considered as a serious matter and the demand for discovering and developing new electromagnetic wave absorbing materials has increased [4-5]. Commonly, the intrinsic electromagnetic properties such as frequency, dielectric constant, magnetic permeability, conductivity and thickness determine the materials electromagnetic absorption properties. However, the complexity of electromagnetic waves propagation in materials structure limits the influence analysis of each parameter on the absorption performance.

Structures with Electromagnetic wave absorbing properties are used not only in military but also in industrial applications [6-10]. Absorbers with superior performance, small thickness, lighter weight, anti-wearing, proper heat resistance,

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broader absorption band and low cost are suitable in practical application.

Recently, attention to polymeric nanocomposites has gained a great extent as they present new opportunities to provide superior properties in comparison to pure polymeric materials. Polymer matrix containing magnetic materials or pure dielectric can be a suitable candidate for use in microwave absorbing mediums.

Now, the key point in research on microwave absorption materials is production of small thickness anti-wearing microwave absorbents with high performance in microwave absorption, suitable heat resistance, high band-width and low cost [6]. Transforming the magnetic and electrical energy of reflecting wave into heat can be take place in microwave absorbents. The loss characteristics lead to damping and heat loss when microwaves penetrate into the absorbent [9].

Polymeric matrix containing pure dielectric or magnetic fillers can be used as absorbents with modified electromagnetic properties [11]. Facile preparation and variety of polymeric composites lead to development of electromagnetic absorbents.

Magnetic absorbents and dielectric absorbents are two major groups of electromagnetic absorbing materials based on fillers type and absorption mechanism [2, 12].

Some parameters for express of microwave absorbents properties are as follow: Dielectric loss $\sigma_e = \varepsilon'' / \varepsilon'$, Complex permeability $\mu = \mu' - j\mu''$, Complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$, Magnetic loss $\sigma_m = \mu'' / \mu'$

Suitable absorbent properties can be achieved by higher amounts of complex permeability (μ''), complex permittivity (ε''), σ_m and tan σ_e [12].

Some structures with high permittivity and conductivity, such as aluminum and copper and their composites are suitable candidates as shielding structures unto electromagnetic waves, but some deficiencies such as facile corrosion and high weight restrict their applications as shielding materials.

Recently, composite structures microwave absorbers with high chemical stability and wide bandwidth as shielding materials have been studied intensively.

L. Wang et al. [13] investigated microwave absorption properties of a carbon nanotubes and zinc oxide mixture which were homogeneously distributed in a paraffin matrix and maximum reflection loss (RL) -36/5 dB was at 12.29 GHz. J. Liuet et al. [8] studied the properties of Fe_3O_4 covered hollow glass spheres as an electromagnetic wave absorber in frequency range of 13 GHz and -21.5 dB. A graphene oxide sample which was covered with Ni-Co-Fe-P was studied by W. Yang et al. [14]. In frequency of 6.9 GHz, the maximum reflection loss was -12 dB. X. Tang and K.A. Hu prepared ZnO/barium ferrite-epoxy composite as an electromagnetic wave absorbent. The maximum reflection loss (-17.5 dB) occurs at the frequency of 8.5 GHz [15]. Also, a rubber/Mn Zn ferrite radar was fabricated by A.M. Gaman et al. [16] with radar absorption of -37.2 dB at 11 GHz which is regarded as a high amount. Nanocomposite Fe_3O_4 / flower like ZnO [17] were prepared (W. Fu et al.) and a noticeable loss of -14.95 dB was obtained at 11 GHz. G. Shen et al. reported a microwave absorbent nanocomposite of epoxy/ferrite with an electromagnetic loss of -12.9 dB at 15.45 GHz [18].

In this study, polystyrene was used as matrix for preparation of three classes of nanocomposites containing graphene oxide, magnetite and zinc oxide nanostructures. The electromagnetic wave absorption properties of these nanocomposites were investigated to determine the influence of nanoparticles distribution in polymeric matrix on electromagnetic wave absorption and to perform a comparison study with mentioned different nanocomposites.

MATERIALS AND METHODS

The polystyrene (GPPS-1540) as polymer matrix was provided from Tabriz petrochemical company. A vector network analyzer (HP 8410C2) in frequency range of 5-8 GHz was employed for reflection loss measurements. Also, the SEM (SEM, XL30, Philips) was used for study of composites morphology.

Due to the uniform and homogeneous properties of nanostructure materials, they can be used as suitable structures in preparation of the microwave absorbent materials [19]. ZnO, Fe_3O_4 and graphene oxide nanostructures were used in this project.

Synthesis of magnetite and zinc oxide nanostructures

Synthesis of magnetite: 0.004 mol of $Fe(NO_3)_3.9H_2O$ and SDS were dissolved in distilled

Table 1. Prepared nanocomposites with different mixing rates.

Samples	Nanocomposite	Rate (RPM)
1	Ps/Fe_3O_4	2000
2	Ps/Fe_3O_4	6000
3	Ps/Fe_3O_4	10000
4	Ps/ZnO	2000
5	Ps/ZnO	6000
6	Ps/ZnO	10000
7	Ps/Nanographite	2000
8	Ps/Nanographite	6000
9	Ps/Nanographite	10000

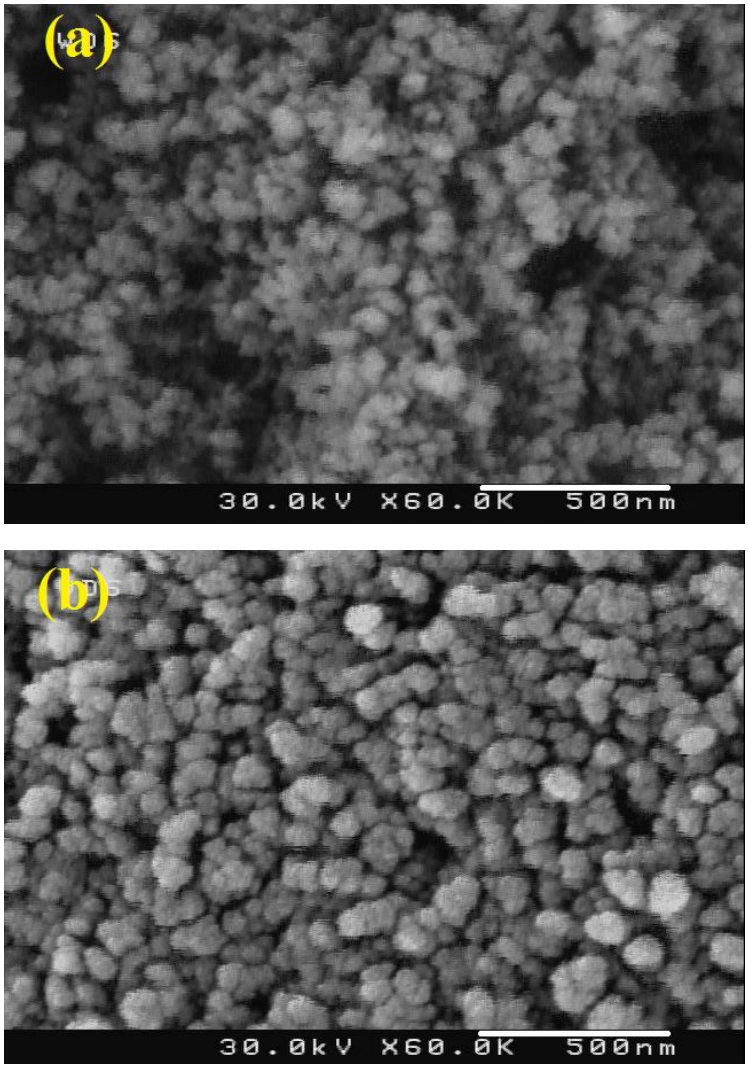

Fig. 1. SEM images of Fe_3O_4 nanoparticles, prepared by (a) NH_3 addition (b) NaOH addition

water. $FeCl_2$ (0.002 mol) was then added to the solution. Next, 50 mL of NaOH (or ammonia) solution 1 M was slowly added to the solution. The formation of Fe_3O_4 was confirmed by a black precipitate in this stage. The precipitate of magnetite is then centrifuged, rinsed with distilled water and dried in 35 °C.

Synthesis of zinc oxide: 1 gr Cetyl

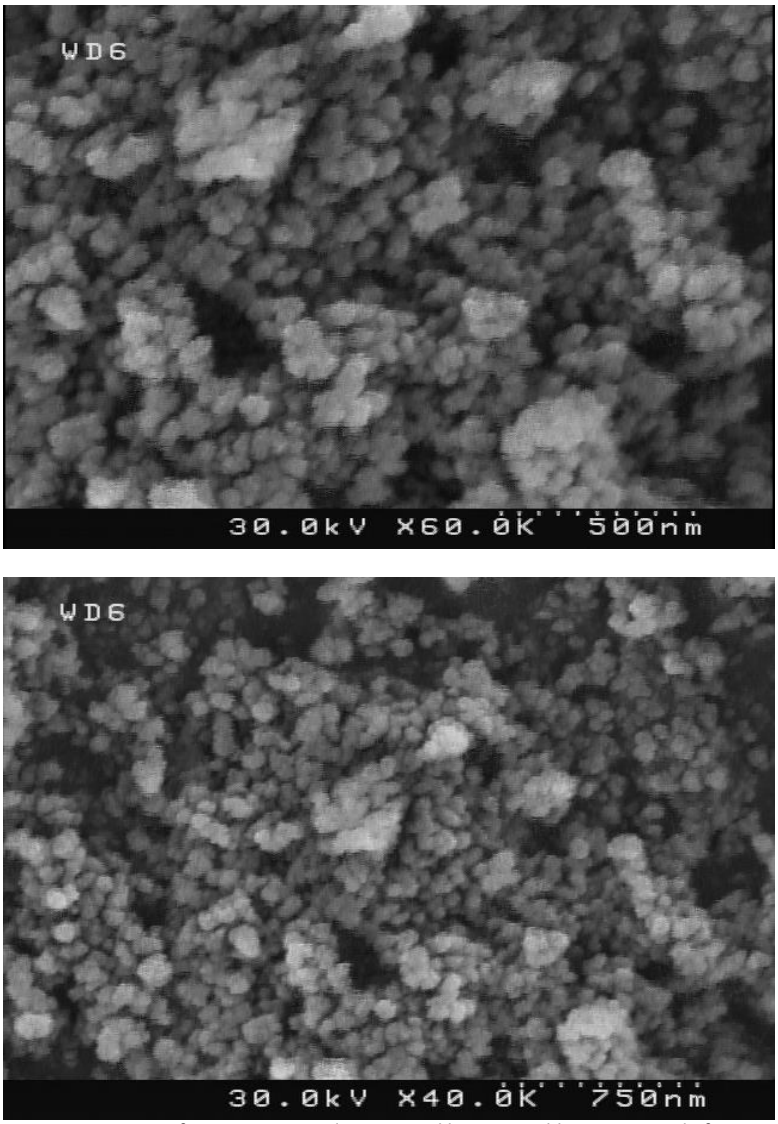

Fig. 2. SEM images of Fe_3O_4 nanoparticles prepared by NaOH addition at 250 ml of water

trimethylammonium bromide (CTAB) and 2.5 gr $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in H_2O. Then, with vigorous stirring the ammonia (or ethylene diamine) solution (0.5 M) was slowly added into the above solution for 17 min. The obtained product was heated (55 ˚C) for 1hour and was centrifuged and washed with deionized water, and dried (for 20 hours) at 75˚C in a vacuum dryer.

Preparation of nanocomposites

A solution of 18 wt% polystyrene was prepared in toluene. Then, each nanostructure (graphene oxide, magnetite and zinc oxide) with the weight amount of 8 percent was dispersed in a container via a mixer. Afterward, the dispersed nanostructures were added to polymeric solution and it was placed in a stirrer under mixing rates of 10000, 6000 and 2000 rpm for 90 minutes (in order to achieve different levels of dispersion).

Eventually the obtained solutions of nanocomposites were placed in a glassy plate and dried in a bath at 105 ˚C for 35 min up to the point where the polystyrene films were obtained. The prepared films were grinded and poured in to screw extruder at 180 ˚C with a speed of 45 rpm until complete removal of toluene was achieved. A manual hot-press (with a pressure of 5 tons) was used to compact the materials of extruder output. The obtained dimensions of nanocomposite samples were 2×15×30 mm^3. Table 1 represents

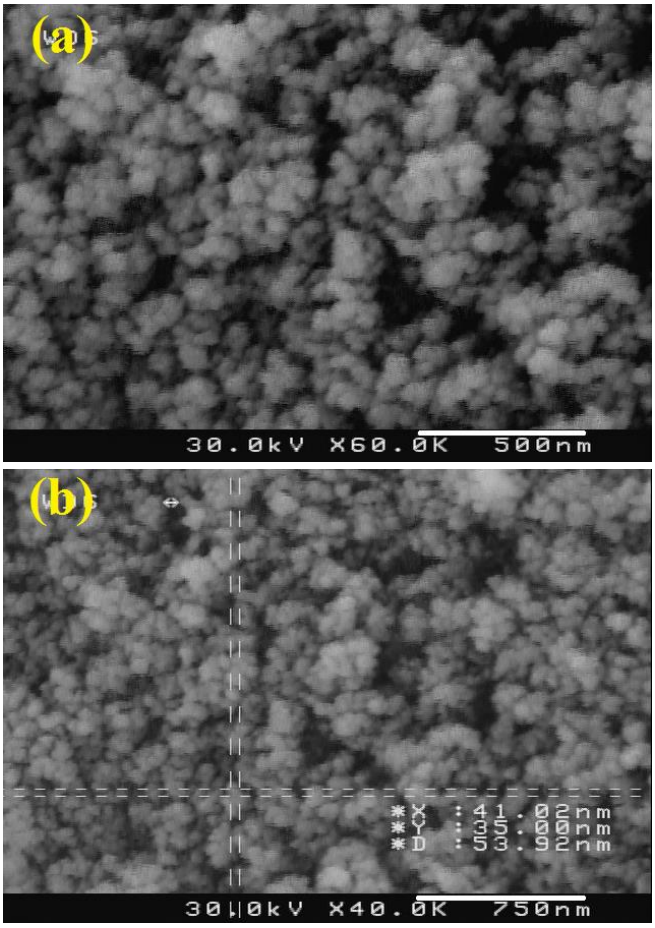

Fig. 3. SEM images of ZnO nanoparticles prepared by (a,b) NH_3 addition

the mixing conditions for preparation of each nanocomposite samples.

RESULTS AND DISCUSSION

Nanostructures characterization

Fig. 1a and 1b show the SEM images of Fe_3O_4 nanoparticles prepared by NaOH and NH_3 addition. The images indicate that in both case the magnetite nanostructures with average diameter size less than 100 nm were obtained.

The effect of concentration on the size and shape of Fe_3O_4 was also studied and the obtained results (Fig. 2a and 2b) confirmed that by dilution of solvent from 150 to 250 ml the nanoparticles size of 73 nm can be achieved.

Fig. 3a and 3b illustrate the scanning electron microscopy images of ZnO nanoparticles prepared by ammonia addition. The average size of 52 nm was obtained for prepared nanostructures.

The influence of concentration on ZnO particle size was investigated by varying the H_2O volume from 120 to 220 and the SEM images of ZnO nanoparticles (at different magnifications) are shown in Fig. 4a and 4b.

Also, the ZnO nanostructures were fabricated by ethylene diamine addition and the SEM images of mentioned nanoparticles is shown in Fig. 4c and the images approve average particle size is less than 73 nm.

The scanning electron microscopy images of nanocomposites are shown in Fig. 5. The SEM image of PS/ZnO/ Graphene oxide/ Fe_3O_4 nanocomposite is presented in Fig. 5a that confirms the presence of all three additives and as expected a little agglomeration in the polymeric matrix can be seen. Fig. 5b shows the pure graphene oxide with thickness in the range of 45 nanometers and plate morphology. The PS/Fe_3O_4-ZnO nanocomposites sample is shown in Fig. 5c that approves dispersion of spherical nanoparticles in the PS matrix.

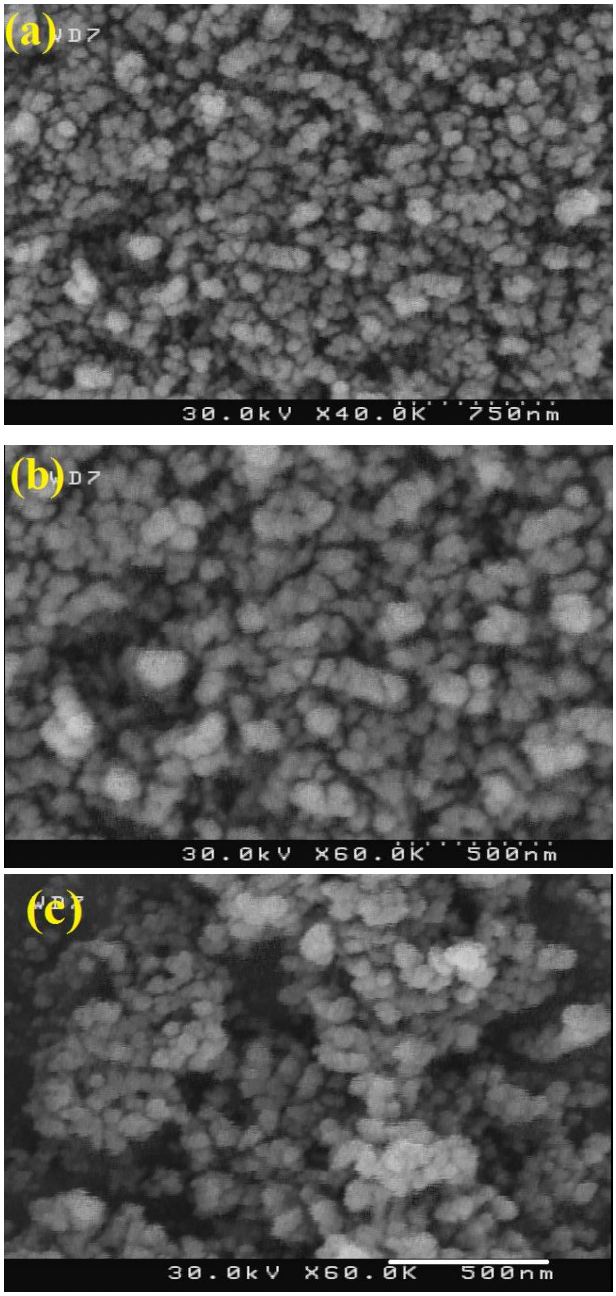

Fig. 4. SEM images of ZnO nanoparticles prepared (a,b) at 250ml of water (effect of concentration) (c) by ethylene diamine addition (as precipitating reagent)

The results indicate that in all conditions nanostructures with mediocre size less than 100 nm were obtained. In addition, diluted solutions at 250 ml of H_2O show smaller nanoparticles in comparison to concentrated solutions at 150 ml of toluene.

Also, the results show that nanoparticles prepared by ammonia addition are smaller compare to nanoparticles prepared by ethylene diamine and NaOH (as precipitating reagents).

XRD pattern of magnetite is shown in Fig. 6. The ferrite with cubic phase (JCPDS No. 88-0315) and space group of Fd-3m can be identified in mentioned pattern.

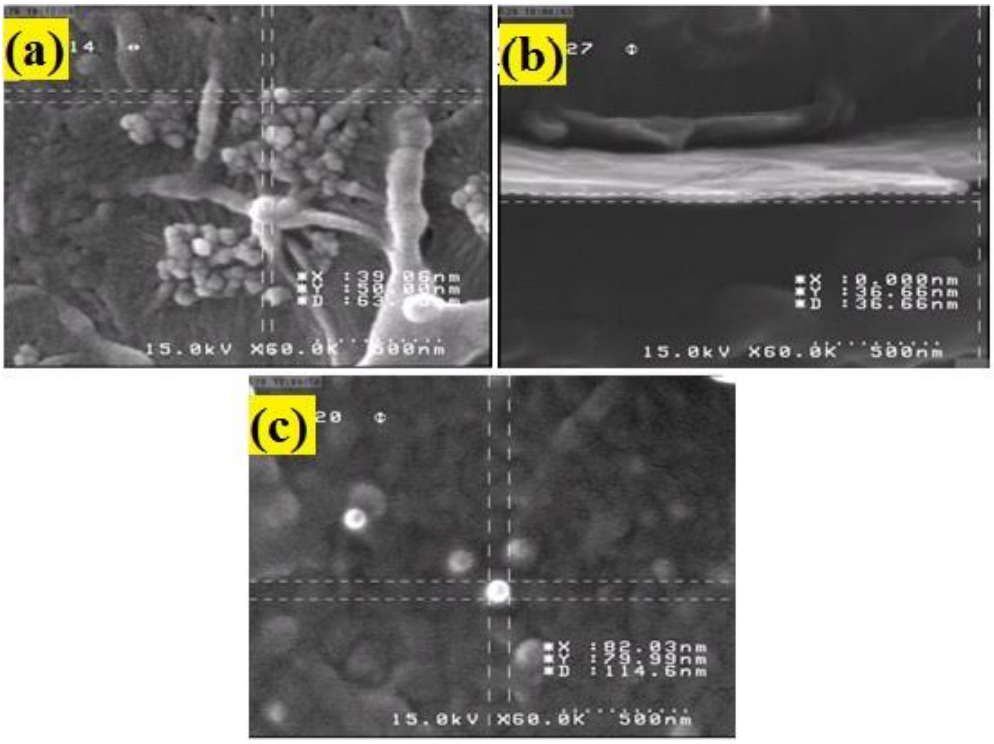

Fig. 5. SEM images of prepared nanocomposites (a) PS/ZnO+Fe_3O_4+Graphene oxide, (b) Graphene oxide, (c) PS/Fe_3O_4+ ZnO

Also, XRD pattern of zinc oxide nanostructures is illustrated in Fig. 7. ZnO with Hexagonal phase (JCPDS No. 72-0208) and space group of P63mc can be approved in mentioned pattern.

Microwave absorption properties of prepared nanocomposites

Equations 1 and 2 are used to calculate the absorption properties of single layer absorbers (Fig. 8) with various thicknesses and a metal surface at the back of each sample (based on transmission line theory):

$$RL(db) = 20\ log\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \quad (1)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tan h\ [\,j\left(\frac{2\,\pi\,f\,d}{c}\right)\sqrt{\mu_r\,.\,\varepsilon_r}\ ] \quad (2)$$

Which, $\mu_r = \mu' - j\mu''$ and $\varepsilon_r = \varepsilon' - j\varepsilon''$ are the complex permeability and complex permittivity of samples, Z_{in} is the normalized input impedance relative to the free space impedance, c is the speed of light, d is the thickness of absorber and f is the frequency of electromagnetic wave in free space. The perfect results of absorption properties is achieved at Z_{in}= 1 (impedance matching reservation). The parameters including: ε´, ε˝, μ´, μ˝, f and d determine the impedance matching reservation. In a certain thickness and frequency the amount of RL can be easily determined using ε_r and μ_r [20-22].

For example, at RL equal to -20 dB, 99% of the wave is absorbed by the absorber and if this amount decreases to -10 dB, the absorbent amount will be 90% [23].

RL (Reflection loss) of polystyrene/zinc oxide nanocomposite is shown in Fig. 9. It can be seen that in this case homogenizer speed doesn't have noticeable effect on reflection loss. This unexpected phenomenon can be justified based on polarity of used materials. In fact zinc oxide is a polar nanostructure and PS has a non-polar polymeric network and it should be mentioned that polar structures can be suitable dispersed in polar matrix and vice versa. Therefore non-polar and polar materials usually are immiscible and ZnO nanoparticles do not disperse well in the polystyrene matrix.

The results of reflection loss investigation for polystyrene /magnetite nanocomposites

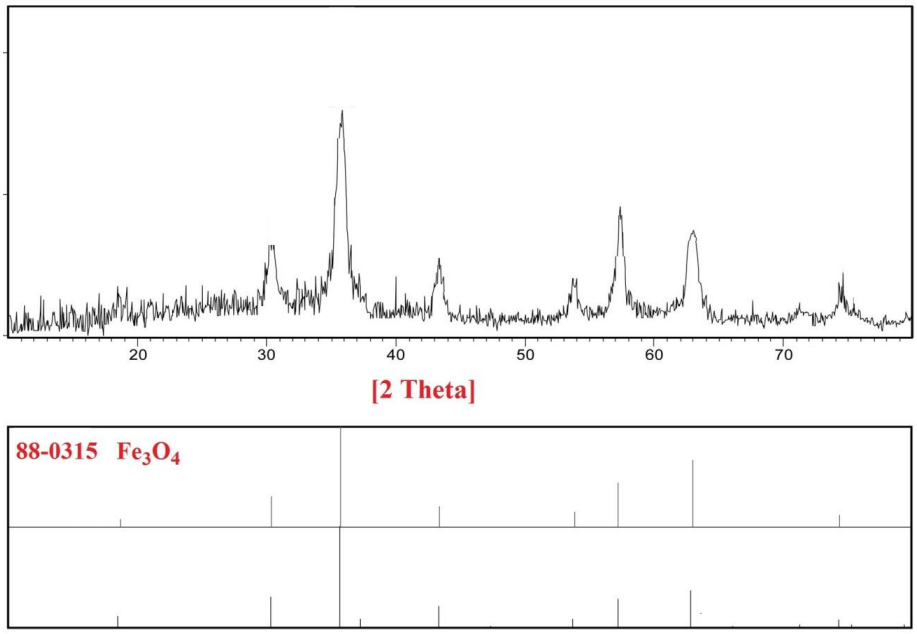

Fig. 6. XRD pattern of magnetite nanoparticles

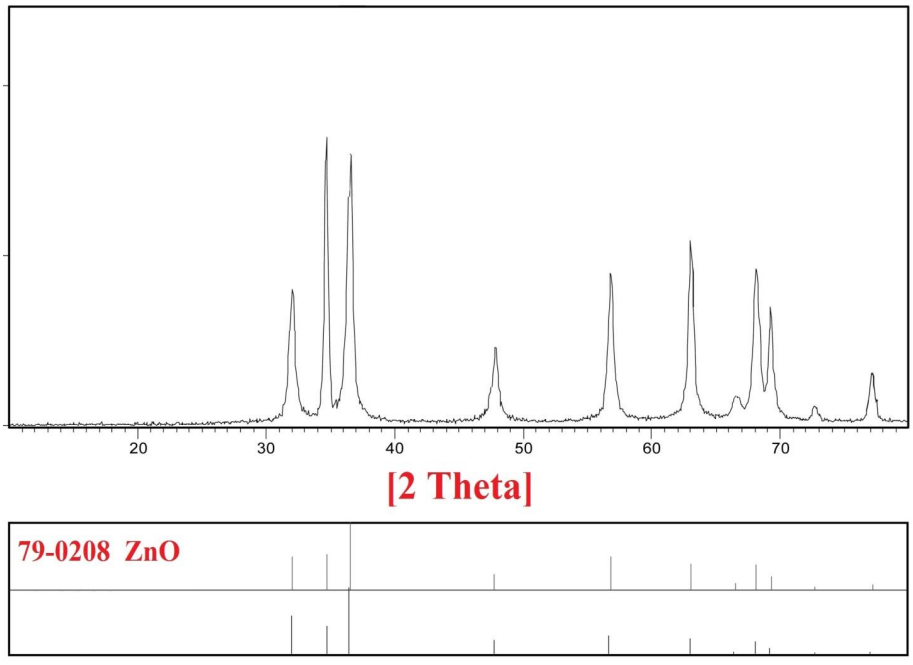

Fig. 7. XRD pattern of zinc oxide nanoparticles

are presented in Fig. 10. The results show that homogenizer speed has a positive effect on this section of experiments. Increment in homogenizer speed from 2000 to 10000 led to reflection loss increase and band width expanding. The Absorption bands widths (with more than 50 % absorption) are equal to 1.25 GHz for sample 1, 1.38 GHz for sample 2 and 1.67 for sample 3. Therefore, the improvement of nanostructures dispersion led to increase in reflection loss

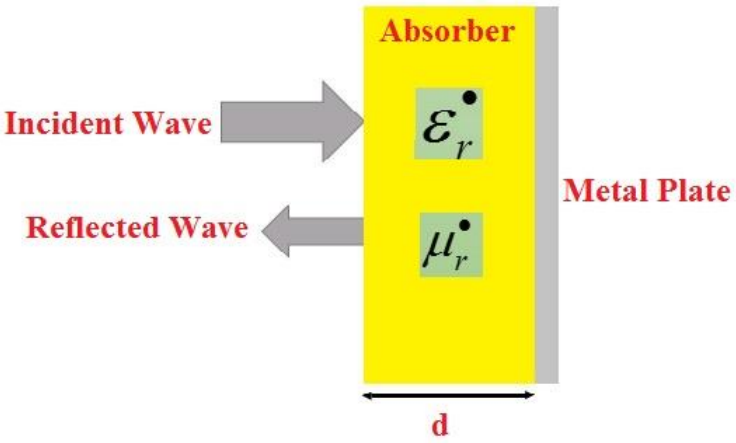

Fig. 8. Single layer absorbent [23].

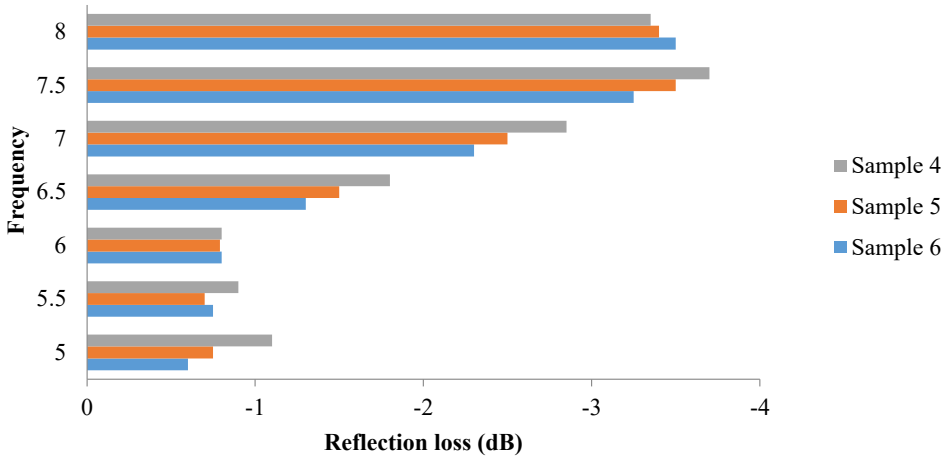

Fig. 9. Reflection of PS/zinc oxide nanocomposites in the C-band frequency range.

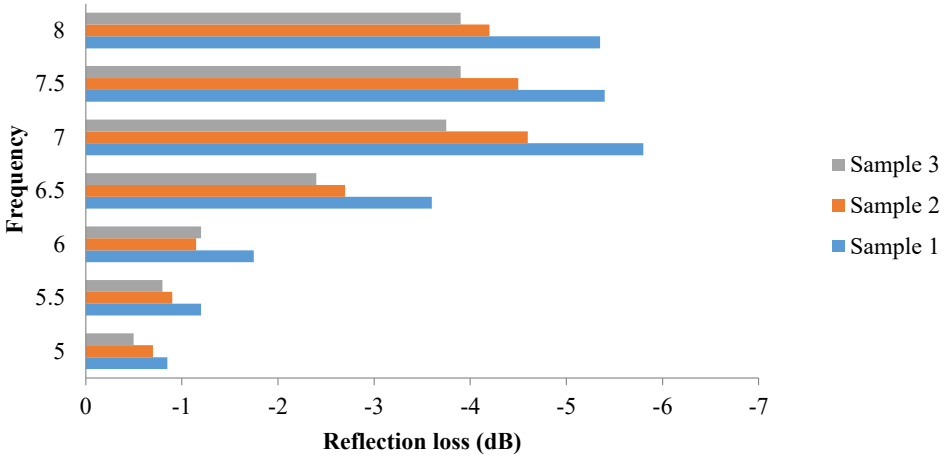

Fig. 10. Reflection of PS/magnetite nanocomposites in the C-band frequency range.

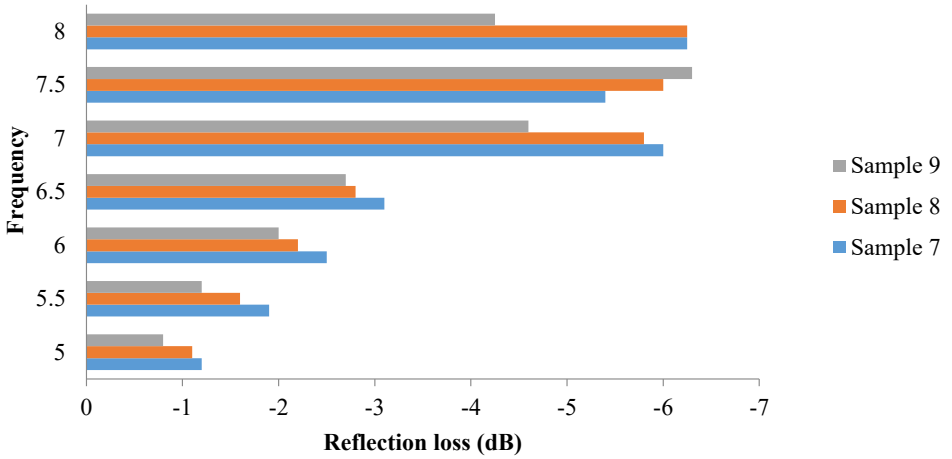

Fig. 11. Reflection of PS/graphene oxide nanocomposites in the C-band frequency range.

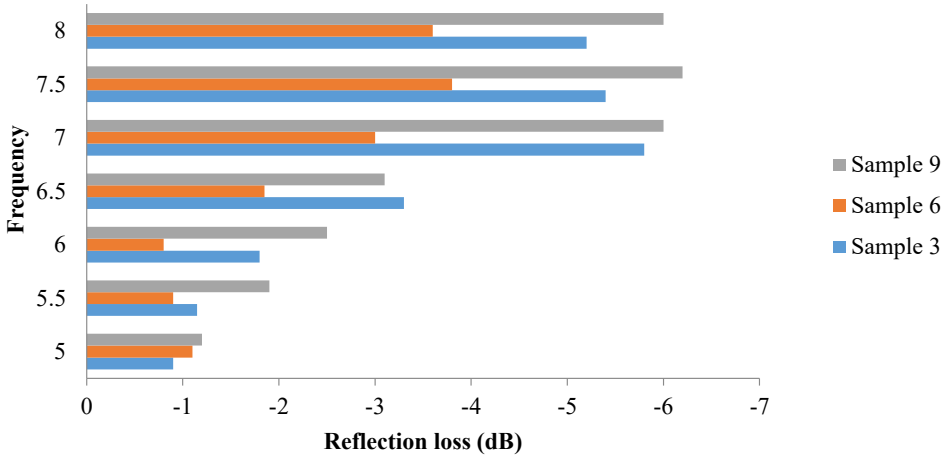

Fig. 12. Reflection loss in frequency range 5 to 8 GHz for the produced nanocomposites with homogenizer speed of 10000 rpm.

and absorption. Considering the SEM images, improved dispersion of magnetite nanostructures in polymeric matrix is due to increase of shear stress provided by homogenizer speed which leads to decrease in aggregation of nanoparticles.

Graphene oxide as a type of carbon nanostructures has several advantages such as resistance against corrosion and low cost [23]. Graphene oxide can be found in most environments and due to its large specific surface area and high electrical conductivity is regarded as a suitable shielding material with high performance [21-23]. Fig. 11 shows the reflection loss of polystyrene/graphene oxide nanocomposites and frequency range of 5 to 8 GHz was selected for RL investigations. The obtained results indicate that by increase of homogenizer speed from 2000 to 10000 and improvement of graphene oxide dispersion the absorbent band width and reflection loss were increased.

Absorption band widths (with more than 50% absorption) are equal to 1.45 GHz (from 6.55 to 8 GHz), 1.5 GHz (from 6.5 to 8 GHz) and 1.6 GHz (from 6.4 to 8 GHz) for sample 7, 8 and 9, respectively. Fig. 12 shows the RL of prepared nanocomposites at frequency range of 5 to 8 GHz and homogenizer speed of 10000 rpm. It can be found that at the same preparation conditions the polystyrene/graphene oxide nanocomposites have higher absorption compared with the PS/ZnO and PS/Fe_3O_4 nanocomposites. The inherent high reflection loss and surface structure of graphene

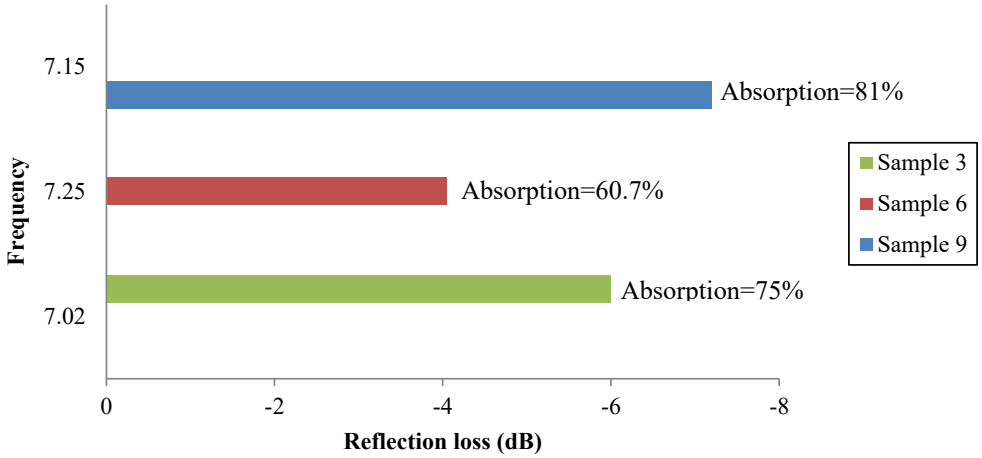

Fig. 13. Maximum reflection loss and absorption percentage of the produced samples.

oxide nanostructure are the logical reasons for these obtained results.

The maximum reflection loss and absorption amounts of prepared samples are presented in Fig. 13.

CONCLUSIONS

In this study for investigation of zinc oxide nanoparticles as a traditional semi-conductor and synergism of three different nanostructures (Fe_3O_4, ZnO and graphene oxide), some nanocomposites were prepared and their reflection loss were studied. The prepared nanocomposite samples in this study were able to absorb the certain amounts of electromagnetic waves and it is worth noting that various nanocomposites have different absorption intensity. The obtained results reveal that all nanocomposites samples showed reflection loss decreasing by increase in homogenizer speed. In addition, the absorption band widths were increased as a result of suitable dispersion of nanostructures in polymeric matrix at higher homogenizer speed.

Polystyrene/graphene oxide nanocomposites have higher absorption compared with the PS/ZnO and PS/Fe_3O_4 nanocomposites. The inherent high reflection loss and surface structure of graphene oxide nanostructure are the logical reasons for these obtained results. The suitable amount of reflection loss equal to -7.2 dB at 7.15 GHz was obtained for nanocomposites sample containing 7 wt% graphene oxide at homogenizer speed of 10000 rpm. In the mentioned conditions a considerable amount (about 81%) of wave energy is absorbed by sample.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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