Preparation and characterization of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite and investigation of its microwave absorption properties at x-band by silicone rubber polymeric matrix

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Microwave absorption has attracted a considerable attention in the last decade. Various factors have effect on the microwave attenuation such as permittivity and permeability of absorbers. In this research, these properties were provided by multiwall carbon nanotube (MWCNT) as a conductive polymer and $Zn_{0.25}Co_{0.75}Fe_2O_4$ as a magnetic nanoparticle. MWCNTs were functionalized with carboxylic acid groups through the sonochemical method by the mixture of nitric and sulfuric acid, due to their better dispersion in the medium reaction and enhancing interfacial polarization, and then magnetic nanoparticles were formed base on the functionalized MWCNTs through the sonochemical and solvothermal complementary methods by use of ethylene glycol as a solvent. Finally, MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite was blended in the silicone rubber as a polymeric matrix to investigation of microwave absorption properties. $Zn_{0.25}Co_{0.75}Fe_2O_4$ nanoparticles and MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite were identified by the diffuse reflection spectroscopy (DRS), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), and investigation of microwave absorption properties was performed by vector network analyzer (VNA). Results indicated that magnetic nanoparticles and magnetic and dielectric MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite have been prepared and absorbed more than 47% of microwave at x-band. Moreover, maximum reflection loss of this nanocomposite was 15 dB at 11.96 GHz.

Key words: multiwall carbon nanotube, silicone rubber, microwave absorption, magnetic nanoparticle

Introduction

Due to widespread applications of microwave absorbent nanocomposites in high frequency, various methods have been used to preparation of these nanocomposites. Transmision line theory has indicated that permability and permmitivity are the most important factors effecting on the microwave attenuation[1-3]. Recently, different methods such as sol-gel, solvothermal, and ballmill were used to preparation of the magnetic nanoparticles base on the permittivity and

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insitu polymerization, belending methode, and sonochemical technique were employed to provide of permmitivity of the nanocomposites[1-7]. According to the last researchs, doped hexa ferrite structures and spinel ferrite nanaoparticles have shown intense microwave attenuation because of theire magnetic loss properties[4, 8]. Modified $Ba_{0.2}Sr_{0.2}La_{0.6}MnO_3$ nanoparticles have absorbed 22.36 dB at 14.78 GHz and showed that can be a promissing microwave absorber between the other magnetic nanoparticles[1]. Recently, Polyaniline, polypyrrole, graphene, and carbon nanotube as the conductive polymers were used to dielecteric loss of the microwave absorbent nanocomposite[2, 3, 5, 9-12]. One of the most important factors having effect on the microwave attenuation is the polimeric matrix effect of the microwave absorbent samples. Polyvinylidene fluoride and paraffin wax have been used to preparation of microwave absorbent nanocomposites[2, 4, 6]. In this research, a magnetic and dielecteric nanocomposite were prepared through the sonochemical and solvothermal complementary methods and silicone ruber was used as a polimeric matrix because of reinforcement of interfacial polarization.

Exprimental

Materials and instruments:

All the chemical such as zinc acetate dihydrate, iron(III) nitrate nonahydrate, cobalt(II) nitrate hexahydrate, ammonia solution, and ethylene glycol were purchased from Merck company and silicone rubber ELASTOSIL® M 4503 RTV-2 from WACKER and MWCNT (OD= 10-20 nm) from Neutrino company.

Optical properties of nanostructures were performed with Shimadzu MPC-2200. Functional groups of nanostructures were identified by the Shimadzu 8400 S FT-IR instrument. Magnetic nanoparticles and MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite were prepared by Elma ultrasonic bath at 100 watt and 80 kHz situation. Morphology of the and were investigation by SEM, Tescan vega 2. Finally, microwave absorption characteristics of silicone rubber nanocomposite were carried out by agilent E5071c.

Preparation of $Zn_{0.25}Co_{0.75}Fe_2O_4$ and MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanostructures

MWCNTs were decorated with the carboxilic acid groups through the our recent recearchs. To preparation of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite at first stoichiometric amounts of Zn, Co, and Fe salts were dissolved in the ethylene glycol by the magnetic stirrer and then functionalized MWCNTs were dispersed in the solution by use of sonochemical method in the ultrasonic Bath for 15 min. Afterward, pH was adjusted about 8 by the ammonia and sonicated for 30 min. Prepared suspension was transferred into the stainless steel autoclave and heated at 180 °C for 12 h to preparation of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite. Feinally, nanocomposite was washed by deionized water several time and dried at the room tempreture.

To preparation of $Zn_{0.25}Co_{0.75}Fe_2O_4$ nanoparticles all the steps were repeated in the absence of functionalized MWCNTs.

Preparation of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$/silicone rubber microwave absorber

MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite (35% w/w) mechanicaly was dispersed in the silicone resine and then hardenere (10% w/w) was added and molded in the rectangular shape to investigation of microwave absorption properties at the x-band.

Results and discusions

Investigation of morphology

Images of $Zn_{0.25}Co_{0.75}Fe_2O_4$ and MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanostructures have been shown in the fig. 1. Results showed that magnetic nanoparticles were synthesized with uniform morphology and have average size of below 50 nm. According to the MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ image, average size of MWCNTs from 10-20 nm to 60-70 nm has been increased due to homogenous coating functionalized MWCNTs by the magnetic nanoparticles through the solvothermal method.

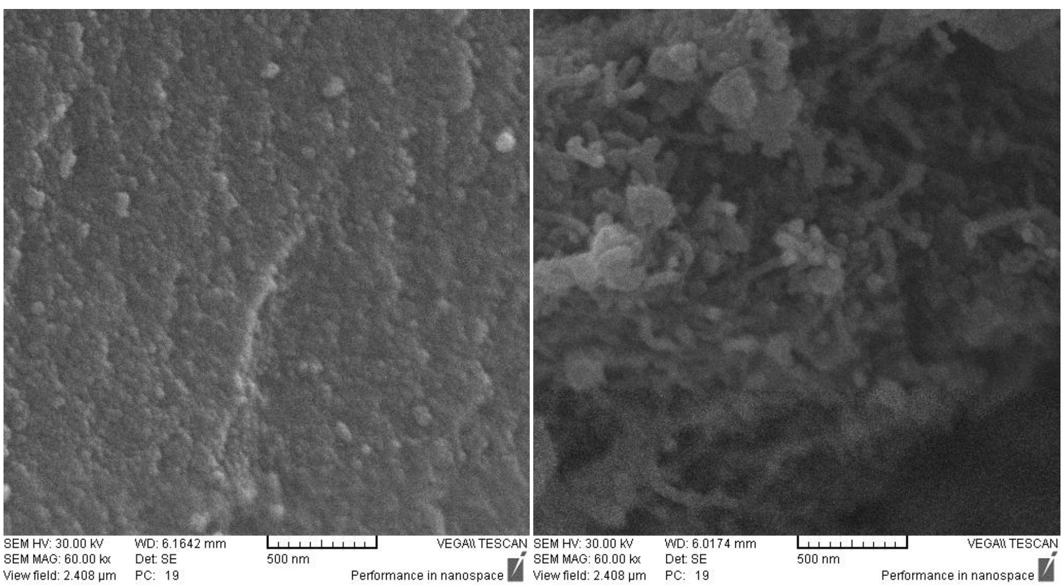

Fig. 1. SEM images of $Zn_{0.25}Co_{0.75}Fe_2O_4$ and MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanostructures

Identification of chemical functional groups

FT-IR curve of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite has been shown in the fig. 2. According to the result, the peak at 3420.09 cm^{-1} is related to the stretching vibration of O-H functional groups, the peak at 1638.14 is assigned to the stretching vibration of C=O groups, and the peak at 1062.68 cm^{-1} is attribiuted to the streching vibration of C-O bonds relating to the carboxilyc acid groups base on the functionalized MWCNTs[2, 3]. Two absorbent peaks at 416.11 and 580.53 cm^{-1} are assigned to vibrations of the metal-oxide bond related to the octahedral and tetrahedral structures of cristal structure of magnetic nanoparticles. Bending vibration of C-H has been shown by the 878.26 cm^{-1} peak and the absorbent band about 1450

cm^{-1} is related to the C-C stretching vibration in aromatic rings. Results indicated that the structures of MWCNT were maintained after solvothermal process, MWCNTs were fuctionalized after acidic treatment, and cationic metals in the solution were reducted to the metal oxides and coated functionalized MWCNTs.

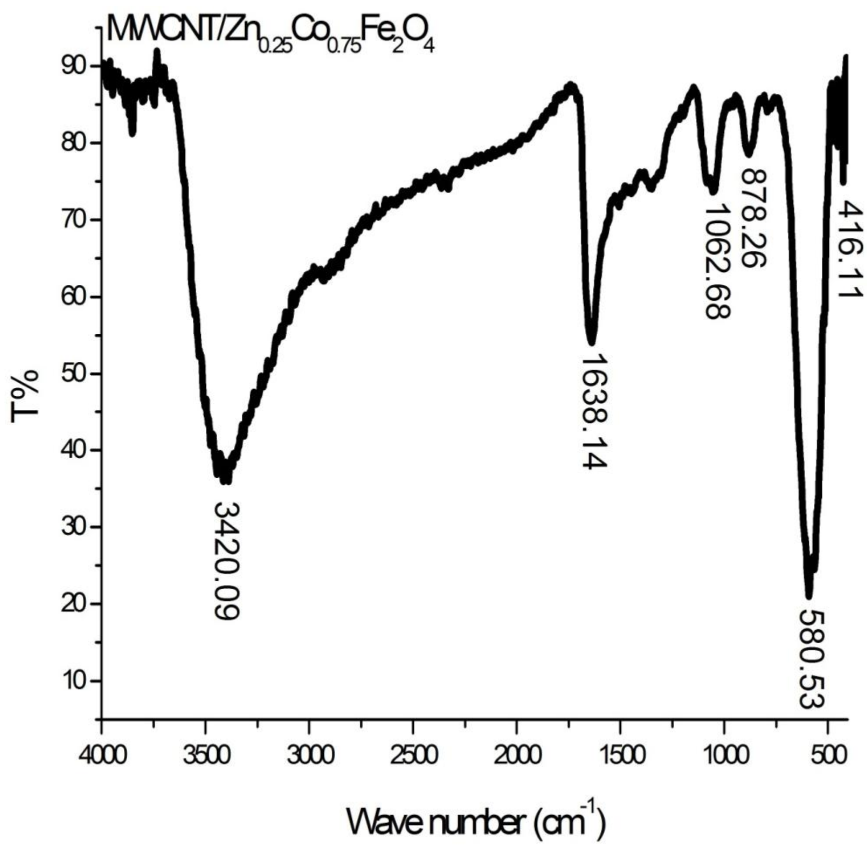

Fig. 2. FT-IR curve of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite

Microwave absorption properties

MWCNTs due to high conductivity and hollow structure are the attractive candidate for microwave attenuation in microwave absorbent composites[2]. Microwave absorbing curve of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$/silicone rubber nanocomposite has been shown in the fig. 3. Maximum reflection loss of nanocomposite was 15 dB at 11.96 GHz. According to the transmission line theory, permeability and permittivity are the most important factors in the microwave absorbing properties that have been provided by magnetic nanoparticles, dielectric silicone rubber, and dielectric MWCNTs. Moreover, because of homogenous coating of nanoparticles base on the functionalized MWCNTs through the sonochemical and solvothermal complementary methods, interfacial polarization and Maxwell–Wagner effect was reinforced that enhanced charges accumulation and microwave absorption of sample[9, 13]. Magnetic loss of the spinel ferrites because of eddy current loss effect and conductive loss of the MWCNTs according to the free electron theory caused the desirable microwave absorption in this nanocomposite[9, 11].

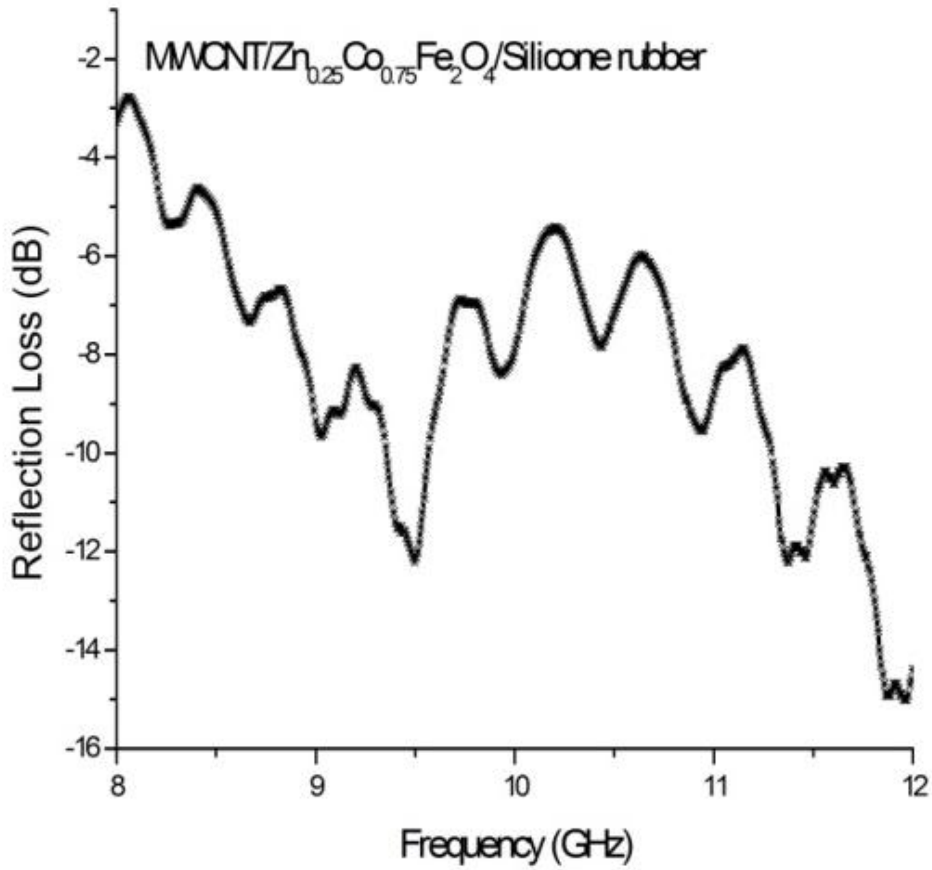

Fig. 3. Microwave absorbing curve of MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$/silicone rubber nanocomposite

Conclusion

Results indicated that MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$ nanocomposite was prepared through the sonochemical and solvorthermal complementary methods by use of ethylene glycol as a solvent. FT-IR spectroscopy showed MWCNTs were fuctionalized by the acidic treatment and metal oxides formed base on the MWCNTs and MWCNTs structure was maintained after sonochemical and solvorthermal treatments. Uniform structure of magnetic nanoparticles and homogenous coat of MWCNTs by nanoparticles was confirmed by SEM images. Finally, VNA result showed that MWCNT/$Zn_{0.25}Co_{0.75}Fe_2O_4$/silicone rubber nanocomposite have a substantial microwave absortion properties. This research introduced a promising complementary method to preparation of nanocomposites and microwave absorbing nanomaterials.

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