Remarkable microwave absorption efficiency of low loading ratio of Ni_{0.25}Co_{0.25}Ti_{0.5}Fe_{2}O_{4}/SrCoTiFe_{10}O_{19}/Cu composite coated with polypyrrole within polyurethane matrix

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Abstract
NiCoTi spinel ferrite, SrCoTi hexagonal ferrite and copper microparticles were coated with polypyrrole (PPY) using in situ chemical oxidative method. The resulted microwave absorbing material was introduced into polyurethane matrix. XRD patterns indicated the successful preparation of spinel and hexagonal ferrites. SEM micrographs showed the semi-spherical morphology of the prepared composite. The magnetic properties have been investigated using VSM. The microwave absorber with 20\%w/w loading percentage exhibits the best microwave absorption performance (bandwidth under −10 dB of 3 GHz and reflection loss of −24 dB at the matching frequency 9.75 GHz and thickness of 1.8 mm). The measurements of permittivity and permeability reveal that the dielectric loss mechanism is the predominant in the current absorber. The measured reflection loss using free space method also indicates the superior performance of the sample with 20\%w/w loading percentage.

1. Introduction

With the rapid developments of technology and the increased need to establish telecommunications at higher data rate, many new circuits and mobile phones working at higher microwave frequencies have been used. This electronic equipment suffers from electromagnetic interference and cannot work properly under microwave exposure [1]. Also microwaves produced by widespread radar, mobile connecting points and mobile phones affect human health and cause different types of cancers [2]. Therefore, it is important to find solutions to protect human body heath and shield electrical circuits from microwaves.

Ferrites have attracted many researchers due to their inherently magnetic properties which permit them to absorb microwaves due to the possibility of spin changing. Ferrites have spinel and hexagonal ferrites and both are well-known for their complementary microwave absorption properties [3]. Combining the properties of these two types of ferrites may result in better absorption. However, ferrites have high density and narrow absorption band which render the use of ferrite ineffective especially when broad band absorption and light microwave absorbers are needed [1, 2]. Many studies reveal the synergistic effect of incorporating magnetic loss material with dielectric loss material [4]. Polypyrrole is one of the inherently conductive polymers which has a conductivity in the range of semiconductor and it is distinguished by its dielectric loss properties, low density and high conductivity compared to other conducting polymers. Copper metal was also used as a dielectric loss material for low frequency shielding [5]. Incorporating two types of ferrites with polypyrrole and copper have not been studied before to the best of authors knowledge and the resulting composite is expected to be a wide −10 dB bandwidth microwave absorbers.
In the current work, SrCoTi hexagonal ferrite, NiCoTi spinel ferrite and copper microparticles were coated with polypyrrole using the in situ chemical oxidative polymerization of pyrrole monomer in the presence of ferrites and copper particles. The two ferrites were synthesized by sol-gel combustion method. The resulted microwave absorbing material was introduced into polyurethane matrix at different loading percentages. The effect of loading percentage on microwave absorption properties was studied using the waveguide method in the range of X-band (8–12 GHz). The mechanism of microwave absorption was investigated by measuring complex permittivity and permeability of the 20%w/w loaded percentage and the dielectric and magnetic tangent losses were estimated. The impedance of the system (Zin/Z0) along the X-band frequency range was calculated depending on the permittivity and permeability and the correlation with reflection loss measurement was indicated. The absorption by eddy current mechanism was determined depending on the constant eddy current coefficient in the X-band range. The free space method in an anechoic chamber was used to ensure the real behavior of microwave absorber. The absorbing material was structurally characterized using XRD, its morphology was investigated using scanning electron microscope (SEM) and the static magnetic behavior was studied using VSM.

2. Materials and test methods

In the present study, magnetic (Ni0.25Co0.25Ti0.5Fe2O4 and SrFe10CoTiO19) and conductive (Cu, polypyrrole) fillers were used as components for the preparation of microwave absorbing composite samples. Among them, the Cu micro powders are used as purchased (99%, less than 40 μm, spheroidal, CAS Number: 7440–50–8).

2.1. Synthesis of Ni0.25Co0.25Ti0.5Fe2O4 and SrFe10CoTiO19 magnetic powders

Both of magnetic fillers were synthesized via sol-gel auto combustion method. Briefly, for doped spinel ferrite powder: Stoichiometric amounts of Ni(NO3)2, 6H2O, Co(NO3)2, 6H2O, titanium tetraisopropoxide (TTIP) and Fe(NO3)3, 9H2O are dissolved in distilled water separately. Then mixed together drop-wisely. Afterwards, citric acid (the mole ratio of citric acid/metal ions is considered 1:1) is added onto the above solution. The pH value was adjusted to 7 by adding KOH solution (6 molar). The temperature of the obtained mixture was raised to 300 °C. The solution was evaporated, till formation of a high viscous black gel. After 2 h, the gel automatically ignited and the produced powder washed and dried at 100 °C for 2 h. Finally, the obtained powder was sintered at 700 °C for 1 h. Doped Sr-hexaferrite was synthesized just like the doped spinel ferrite starting from Sr(NO3)2, Co(NO3)2, 6H2O, titanium tetraisopropoxide (TTIP) and Fe(NO3)3, 9H2O as raw materials. The final washed and dried powder is sintered at 950 °C for 30 min.

2.2. Coating composites with polypyrrole polymer

PPY coating, on the magnetodielectric composites powders comprising doped spinel ferrite (55 wt%), doped strontium hexaferrite (35 wt%) and Cu (10 wt%) via in situ polymerization method. Firstly, an appropriate amount of pyrrole (Py) according to weight ratio of PPY to composite weight (2:1) and 1 g of each composite is added into a 50 ml of 0.2 molar HCl solution (Solution A). The solution was mechanically stirred in an ice bath for 30 min. Then, APS was dissolved in 50 cc of 0.2 M HCl solution (Solution B), and was added dropwise into the solution A. Polymerization reaction was allowed to proceed for 1 h at 0 °C–5 °C. The resulting powder is filtered and washed several times with water. Finally, it is dried at 70 °C for 2 h.

2.3. Preparation of composite samples

Microwave characterization of the samples was evaluated with the waveguide and free-space techniques. In this regard, 5, 10, 20 wt% of the coated composite was dispersed in polyurethane resin (Interthane 1021) matrix. An adequate amount of dispersant (DisperBYK-2155), Deloamers (BYK-052N), Desediment (DisperBYK-110) and improve adhesion (BYK-4512) agents were used for preparing single layer microwave absorbers. Samples for the waveguide measurement were molded to the dimensions of 25 × 10 mm with 1.8 mm thickness. Furthermore, the samples for the free-space evaluation were molded to the dimensions of 300 × 300 × 1.8 mm, directly on an aluminum plate with 1 mm thickness.

2.4. Characterization methods

The x-ray diffraction (XRD) patterns of the powder products were obtained by means of an XMD 300 diffractometer (Unisantis S.A, Cu-Kα radiation). Moreover, the microstructure of the prepared samples was investigated by using scanning electron microscopy SEM (VEGA/TESCAN). The static magnetic properties of the coated composite are measured with a vibrating sample magnetometer (VSM, MDK-Meghnatis Daghighe Kavir Co.) up to 15 kOe at room temperature. For the microwave characterization of the composites, the reflection parameter S11 was measured by the single-port waveguide technique with a vector network analyzer.
Agilent, 8510 C in the frequency range of X-band (8–12.4 GHz). In order to simulate the real operating conditions, the rectangular samples in the waveguide were placed on aluminum substrate with 1 mm thickness. Additionally, for the evaluation of the actual absorbing performance of the prepared materials, the free-space characterization of the larger rectangular metal-backed samples was performed at discrete frequency points (8.5, 9.5, 10.5, 11.5 and 12.5 GHz) in the anechoic chamber of the K. N. Toosi University. Particularly, the reflection coefficient of rotating specimens in terms of parameter S11 has been measured, as a function of the azimuth angle. We should note the equivalence of the measured S11 parameter to the overall reflection coefficient $\Gamma$. In the current investigation, the magnitude of reflection coefficient is used. It is expressed in decibels ($RL = 20\log_{10}(|S11|) = 20\log_{10}(|\Gamma|) < 0$) [6].

3. Results and discussion

3.1. Morphological characterization-x-ray diffraction - static magnetic properties

SEM micrographs of the coated composite (figure 1) show homogenous semi-spherical particles with a uniform polypyrrole layers deposited on them. The average particle size of the composite is 189 ± 56 nm. In the XRD patterns, there is a broad peak around $2\theta$ of 25° which is assigned to the amorphous phase of polypyrrole [4]. Also, spinel ferrite shows four peaks at $2\theta$ of 35, 43, 57 and 62° which correspond to (hkl) planes (311), (400), (511) and (440) respectively [1]. The peaks at $2\theta$ of 30, 32, 35, 40, 43, 57, and 62° indicate the presence of hexagonal crystal structure of Sr hard ferrite [7]. Copper has two peaks around $2\theta$ of 43 and 51°. These peaks suggest the successful preparation of the composite with its different components. The peaks of ferrite have broad peaks with lower intensity compared with a conventional ferrite which can be explained by the chemical method of ferrite preparation and the presence of amorphous polypyrrole [4]. The magnetization of the prepared sample as a function of applied magnetic field is shown in figure 1. The magnetic hysteresis loop of coated composite is a bit narrow and exhibits a coercivity lower than Sr hexagonal ferrite and higher than CoNi spinel ferrite which is due to the presence of two types of ferrites (spinel, hexagonal). Saturation magnetization of the coated composite is also lower than those of the two constituent ferrites. This can be explained by the fact that copper and PPY are dielectric materials and they dilute magnetic phases and this results into lower saturation magnetization. Also the presence of copper particles and PPY increases the magnetic anisotropy, anisotropy constant (K) can be estimated from the magnetic properties derived from hysteresis loop and it can be expressed as: $K = \mu_0 H_M M_s / 2$ ($\mu_0$ is the free space permeability which equals $4\pi \times 10^{-7}$ H m$^{-1}$) and this constant is related to the magnetocrystalline anisotropy energy ($E_A$) of a single domain nanocrystalline material by Stoner-Wohlfarth theory which is presented in equation (1):

![Figure 1. SEM micrographs, x-ray diffraction pattern and VSM hysteresis loop of the prepared absorber.](image-url)
Where \( V \) is the volume of nanocrystal and \( \theta \) is the angle between easy direction and magnetization induced direction by applied field \([8]\). The calculated value of \( K \) is 2.76 HA² kg⁻¹ which is a lower than calculated magnetic constant for Sr (96 HA² kg⁻¹) or CoNi (25 HA² kg⁻¹) ferrite and this supports the idea of anisotropy increase. From other side of view, the saturation magnetization decreases in core/shell structure due to the interparticle interaction at the surface between core and shell and the non-collinearity of the magnetic moments at the interface \([9]\). Finally, also the presence of copper particles in the composite can hinder the domain wall motions \([8]\).

### 3.2. Microwave absorption characteristics

The reflection loss (RL) of the composite was measured using the waveguide method. The composite was loaded in polyurethane at different percentages (5, 10 and 20%w/w) at a thickness of 1.8 mm. Figure 2 shows the homogenization of the composite on the left, molding it in the middle and the resulted sample on the right. Figure 2 also depicts the RL of the composite. The minimum reflection loss increases when the loading percentage increases. This is due to the increase of the amount of the absorbing material which can absorb microwaves in PU. So, the sample with 20%w/w loading percentage has the maximum reflection loss of \( -24 \) dB with a broad \(-10\) dB bandwidth equals to 3 GHz from 8.7 to 11.7 GHz, and the matching frequency is about 9.75 GHz. Also, the matching frequency shifts to higher frequencies while the loading percentage increases. In fact, loading percentage affects the density of the composite material and there is a critical density where the reflection of the wave on an absorbing particle results in absorption process by another particle and so on. This
consequent absorption promotes the microwave absorption properties of the PU-absorbing material composite. The enhanced microwave absorption performance of the composite material can be attributed to the combination of two types of ferrite (spinel that absorbs at low frequencies and hard that absorbs at higher frequencies) to obtain better absorption in this desired range of frequency. Also, adding copper particles enhances the loss by eddy current. Finally, the dielectric loss material PPY was added to enhance dielectric loss mechanism due to its conductivity from one side, and due to the interfacial polarization between PPY and the other components of the composite from another side. The interfacial interaction modifies the band gap structure in both of PPY and ferritic crystals by adding more energy levels and this permits the dissipation of incident microwaves power through additional electronic transitions [4]. The synergistic effect in combining different materials with different attenuation mechanisms of the microwaves has been proved and reported in the specialized literature [4].

The complex permittivity and complex permeability of the 20%w/w loaded sample were measured. Also, the dielectric and magnetic loss tangents were estimated as shown in figure 3 in the X-band to investigate the absorption mechanism of the prepared composite. From figure 3, it is clear that the dielectric absorption is the major mechanism of microwave absorption and this is clear from the higher values of dielectric loss tangent compared to the magnetic loss tangent of the prepared absorbing material [10]. The dielectric loss tangent increases in the range between 9.5 and 11 GHz which indicates the high microwave absorption in this range as obtained from RL measurements.

The reflection loss is given by equation (2), where $Z_{in}$ input impedance and the $Z_0$ free space impedance. Equation (3) expresses the dependency of $Z_{in}$ on $\mu_r$ and $\varepsilon_r$, the complex permeability and permittivity of the absorbing material respectively, $f$ the frequency, $d$ the thickness and $c$ the light velocity in the free space. It is clear that the reflection loss is higher when $Z_{in}$ is very close to the $Z_0$ which means that microwave can enter into the deep layers of absorbing material rather than reflect on the surface [11].

$$RL(\text{dB}) = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (2)$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tan h \left( \frac{2\pi f d}{c} \sqrt{\mu_r\varepsilon_r} \right) \quad (3)$$

$Z_{in}/Z_0$ is also plotted as function of frequency in figure 4. This parameter is usually taken as an indicator to assess the attenuation of the reflection at the interface air-absorbing material. The high values of $Z_{in}/Z_0$ mean that the wave can penetrate the absorber instead of being reflected at the interface. From figure 4, it can be seen
that the calculated curve of $Z_{in}/Z_0$ (depending on measured permittivity and permeability) is in good match with the measured RL.

The magnetic loss can be related to the natural resonance, eddy current, hysteresis loop or domain wall displacement. The domain wall displacements loss always occur at lower frequencies. Also the hysteresis loop loss is negligible when a conductive material and a nonmagnetic material are incorporated so the magnetic loss in this case is mainly due to the eddy current or natural resonance. When eddy current is the only cause of magnetic loss, the eddy current coefficient $C_0$ is almost constant [1,2,12]. $C_0$ can be calculated using equation (4)

$$C_0 = \mu''(\mu')^{-2} f^{-1}$$  

Figure 5 shows $C_0$ along the X-band frequency range. $C_0$ decreases drastically from 0.7 ns at 8 GHz to 0.3 ns at 10 GHz. Therefore, the magnetic loss is due to the natural resonance in the range from 8 to 10 GHz. At higher frequencies from 10 to 12 GHz, $C_0$ becomes almost constant and eddy current is the main cause of magnetic loss [1,2].

As for the origin of dielectric losses, there are mainly two types which are polarization losses and conduction loss. Polarization losses are mainly classified into electronic, ionic, orientational and space charge polarizations. $\varepsilon'$ and $\varepsilon''$ can be expressed by equations (5) and (6) according to Debye theory that describes the dielectric relaxation response of an ideal, non-interacting population of dipoles to an alternating external electric field, with one relaxation time. Also, the equation of Cole-Cole plot can be written as equation (7) [2,13].

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$  

**Figure 4.** Simulated $|Z_{in}/Z_0|$ as function of frequency for sample with 20 wt% filler loading.

**Figure 5.** Simulated $\mu''\mu'/f^{-1}$ as function of frequency for sample with 20 wt% filler loading.
\[ \varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau + \frac{\sigma}{\omega \varepsilon_0} \]  
\[ \left( \varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right)^2 - (\varepsilon'')^2 = \left( \frac{\varepsilon_s - \varepsilon_\infty}{2} \right)^2 \]  

Where \( \varepsilon_\infty \) is the relative dielectric constant at high frequency limit, \( \varepsilon_s \) is the static dielectric constant, \( \omega \) is the angular frequency, \( \tau \) (function of frequency and temperature) is the polarization relaxation time, \( \sigma \) is the dc conductivity. Figure 6 depicts the Cole-Cole plot of the current absorber and it allows to predict the dielectric loss mechanism. From figure 6, one can easily observe that there is no semi-circle shape. The multi--semicircles
in the present system indicate the presence of multiple dielectric relaxation losses, which can effectively enhance the microwave absorption [13, 14]. This multi-relaxation system consumes more electromagnetic power which means higher microwave absorption performance. The multi-relaxation is mainly related to interfacial interactions between PPY shell and different particles in the composite material.
A large tile of the absorber was prepared as shown in figure 7 to conduct the free space measurements. H-plane radiation patterns (radar cross section) of the prepared material at different loading percentage as a function of the azimuth angle for discrete frequencies in the range 8–12 GHz are presented in figure 7. Figure 8 summarizes the H-plane results (S11 parameter) and shows similar microwave absorption behavior as resulted by waveguide method regarding the superior absorption of the sample of 20 wt% filler loading. But the discrepancy of the results between the two techniques is related to the finite tile dimensions in the waveguide method. In fact, the free space technique is more suitable than waveguide method for thin flat faced materials [15]. For the line technique, the sample is deformed into a particular shape, depending on the transmission line used, either waveguide or coaxial type. Moreover, the measurements in a waveguide take place with the propagation of TE10 mode, whereas those in free-space tests are performed with a TEM wave [16]. This indicates that using a small sample for waveguide measurements is sufficient for obtaining a good idea of microwave absorption behavior of sample, but the real behavior of the sample is obtained by using bigger sample in the case of H-plane measurements.

4. Conclusion

In this work, a new multicomponent composite material was successfully synthesized. The composite consists from spinel and hard ferrits with copper microparticles covered with polypyrrole. A −10 dB bandwidth of −3 GHz was obtained with only 20% w/w loading percentage in polyurethane. The estimated dielectric and magnetic loss tangents indicated the prevalence of the dielectric loss mechanism of microwave absorption. The eddy current constant showed the eddy current loss mechanism is the predominant in the high frequency range, whereas the natural resonance is predominant at the lower frequencies. The cole-cole plot showed multiple dielectric relaxation processes which enhance the microwave absorption.
[5] Ohno M, Numamoto S, Shinagawa M, Tanaka K, Imamura H, Sato K and Ono T 2018 Low-frequency shielding effectiveness of multi-layered device using Cu and PET film TENCON 2018–2018 IEEE Region 10 Conf. pp 0342–5 (Piscataway, NJ)

[6] Vinoy K J and Jha R M 1996 Radar Absorbing Materials, From Theory to Design and Characterization (Massachusetts: Kluwer Academic Publishers)

[7] Afghahi S S S, Peymanfar R, Javanshir S, Atassi Y and Jafarian M 2017 Synthesis, characterization and microwave characteristics of ternary nanocomposite of MWCNTs/doped Sr-hexaferrite/PANI J. Magn. Magn. Mater. 423 152–7

[8] Mohammed J, Carol T T T, Hafeez H Y, Basandrai D, Bhandu G R, Godara S K and Srivastava A K 2019 Electromagnetic interference (EMI) shielding, microwave absorption, and optical sensing properties of BaM/CCTO composites in Ku-band Results in Physics 13 102307

[9] Xia J, Shen Y, Xiao C, Chen W, Wu X, Wu W and Li J 2018 Structural and magnetic properties of soft/hard Mn 0.6 Zn 0.4 Fe2O4@Sr 0.85Ba0.15Fe12O19 core/shell composite synthesized by the ball-milling-assisted ceramic process J. Electron. Mater. 47 6811–20

[10] Choudhary H K, Kumar R, Pawar S P, Bose S and Sahoo B 2019 Effect of microstructure and magnetic properties of Ba-Pb-hexaferrite particles on EMI shielding behavior of Ba-Pb-hexaferrite-polyaniline-wax nanocomposites J. Electron. Mater. 30 1–12

[11] Hu K, Wang S, Zhang M, Huang F, Kong X and Liu Q 2019 Enhanced microwave absorption properties of La doping BaSnO3 ceramic powder J. Mater. Sci., Mater. Electron. 30 1–9

[12] Ribbenfjärd D 2010 Electromagnetic transformer modelling including the ferromagnetic core Doctoral dissertation (KTH)

[13] Qiao Y, Xiao J, Jia Q, Lu L and Fan H 2019 Preparation and microwave absorption properties of ZnFe2O4/polyaniline/graphene oxide composite Results in Physics 13 102221

[14] Jafarian M, Afghahi S and Atassi Y 2019 New insights on microwave absorption characteristics of magnetodielectric powders: effect of matrix chemical nature and loading percentage J. Magn. Magn. Mater. 462 153–9

[15] Wee H, Soh P J, Atassi Y and Suhaital A H M 2009 Free space measurement technique on dielectric properties of agricultural residues at microwave frequencies IEEE Xplore, Conf.: Microwave and Optoelectronics Conf. (IMOC), 2009 SBMO/IEEE MTT-S Int. (https://doi.org/10.1109/IMOC.2009.5427603)

[16] Rahman A, Islam M, Samuuzzaman M, Singh M and Akhtaruzzaman M 2016 Preparation and characterization of flexible substrate material from phenyl-thiophene-2-carbaldehyde compound Materials 9 358