Synthesis and Characterization of BaFe$_{12}$O$_{19}$/Poly(aniline, pyrrole, ethylene terephthalate) Composites Coatings as Radar Absorbing Material (RAM)

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Abstract. Barium hexaferrite (BaM) was prepared by sol gel method with Ni-Zn doping; mole fraction of 0.4 at 950 °C to obtain soft magnetic material. BaM/Poly(aniline, pyrrole) (BaM/(PAni,PPy)) composites were synthesized by in-situ polymerization method with polymerization time of 8 hours at ~0 °C. BaM/Poly(ethylene terephthalate) (BaM/PET) composite was produced by melt compounding above 200 °C. The composites were coated on A-grade AH36 steel vessel using Dallenbach Layer, Salisbury Screen and Jaumann Layer methods with thickness of 2, 4, and 6 mm. The structure, morphology, functional groups, magnetic, electrical conductivity and microwave absorbtion properties were characterized by instruments; XRD, SEM, FTIR, VSM, LCM-meter and VNA. Results showed that both of non-doped and doped BaM were single-phase BaFe$_{12}$O$_{19}$. BaM and BaM/(PAni,PPy,PET) composites possessed globular morphology with M–O and C–H bonds. BaM (BaNi$_x$Zn$_x$Fe$_{12-2x}$O$_{19}$) exhibited the value of Ms and Hc, 56.6 emu/g and 60 Oe respectively. A high electrical conductivity of 1.77744 x 10^{-5} S/cm was achieved of BaM/PAni composite. The maximum reflection loss (R$_L$) reached to -48.720 dB at 8.1 GHz of BaM/PAni coating with 6 mm thickness at Jaumann Layer. These results indicated that BaM/PAni composite was a soft magnetic material with a high R$_L$ value that was suitable for radar absorbing material.

1. Introduction

Radar absorbing material (RAM) is a material used in stealth technology to camouflage structure of vehicle from radar detection. RAM can absorb the electromagnetic wave by two ways, absorbs the magnetic field by magnetic materials and reduce the incident/reflected wave energy by dielectric materials [1]. Therefore, in RAM application it will need two main materials, magnetic and dielectric materials. Barium hexaferrite (BaM) is utilized as magnetic material. Hexaferrite has large anisotropic crystal and resonance location which can be modified in wide frequency range using ion substitution in hexaferrite. Besides, it is a soft magnetic material with relatively large permeability. Therefore, it is potential for RAM. Barium Heksaferit (BaFe$_{12}$O$_{19}$) possesses high saturation magnetization (Ms = 72 emu/g), high coercive force (Hc = 6700 Oe) and high Curie temperature (720 K) [2]. While, RAM has high magnetization with low coercivity. Therefore, metal ion substitution in BaM is required to RAM application. Ion substitution of Fe with Ni, Zn, Cu, Mn, Cu and others. The substitution causes intrinsic coercivity to decrease and magnetic saturation also decreases considerably at the same time [3]. Agustianto reported that substitution of Ni^{2+} and Zn^{2+} ions in BaM achieved minimum coersivity

and magnetic saturation was 1200 Oe and 84.89 emu/g for $X_{Ni-Zn} = 0.6$ sample in temperature sintered 950 °C [4]. Conducting polymers as dielectric materials, polypyrrole (PPy) and polyaniline (PAni) have been regarded as a new class of materials in the last few years due to their high electrical conductivity, easy preparation, and excellent environment stability [5]. Wang reported that BaM/PPy composite has a reflection loss of -21,5 dB at 10,7 GHz with the thickness of 3 mm [5].

RAM effectiveness can be increased by the variations of thickness layer and coating method. The thicker the layer of RAM will increase the absorbtion. The coating methods are Dallenbach Layer, Salisbury Screen and Jaumann Layer. The three of those methods have layer constructions which differents so it will affect the absorbtion. Castro reported that PET(PU-PAni/DBSA) with Salisbury Screen method obtained optimum reflection loss of -23 dB at 9 GHz when the thickness of PET was 0.25 cm [6].

In this research, BaM and BaM/(PAni,PET,PPy) composites were produced by sol gel, in-situ polymerization and melt compounding method, respectively. These methods have several advantages such as shorter processing time and more general chemical reagents. The variations that were used in this research were the polymer type, coating method and coating thickness.

2. Experimental analysis

2.1. Materials
All chemicals used to prepare the BaM/(PAni,PPy,PET) composites were reagent grade and used without further purifications. Barium nitrate ($Ba(NO_3)_2$), ferric nitrate ($Fe(NO_3)_3.9H_2O$), zinc nitrate ($Zn(NO_3)_2.4H_2O$), nickel nitrate ($Ni(NO_3)_2.6H_2O$), citric acid ($C_6H_8O_7.H_2O$), ammonium hydroxide (NH_4OH), and aniline ($C_6H_5NH_2$) poly(ethylene terephthalate) (PET), pyrrole (C_4H_4NH), dodecyl benzene sulfonic acid (DBSA), ammonium persulfate (($NH_4)_2S_2O_8$), polyol, isocyanate, acetone were supplied by Merck. The paint used in this research was Epoxy type from Jotun. Demineralized water was used during all synthesis and treatment process.

2.2. Preparation of Ni-Zn dopped Barium hexaferrite (BaM)
Barium hexaferrite (BaM) was produced by mixing $Ba(NO_3)_2$ and $(Fe(NO_3)_3.9H_2O$ solutions with constant stirring for 15 minutes. Afterwards, $Ni(NO_3)_2.6H_2O$ and $Zn(NO_3)_2.4H_2O$ solutions were added with mol fraction of 0.4 as doping materials followed by citric acid as reducing agent and then continued stirring for 15 minutes. After that, ammonia was added to obtain pH~7 and stirred for 1 hour. The mixture was then stirred at 80 °C for 3 hours to produce wet BaM gel and heated to 250 °C for 3 hours to dry it. To optimize its polymerization process, dry BaM gel was crushed into fine powder and sintered at 950 °C for 3 hours.

2.3. Preparation of BaM/(PAni,PPy,PET) composites
BaM/(PAni,PPy) composites (30:70 wt%) were prepared by in-situ polymerization method. The monomers were added with BaM and DBSA as oxidator. After that, ammonium persulfate (APS) aqueous solution was added and polymerized for 8 hours. It was then filtrated and washed using ethanol and aquades. The composites were dried at room temperature for 12 hours. While, BaM/PET composite (30:70 wt%) was produced by melt compounding above 200 °C.

The composites were mixed with epoxy paint (10:90 wt%) and painted (in accordance to ASTM 5068) on A-grade AH36 steel vessel using Dallenbach Layer, Salisbury Screen and Jaumann Layer methods with thickness of 2, 4, and 6 mm. Polyurethane (PU) foams was used as band gap replacement in the layer constructions of Salisbury Screen and Jaumann Layer methods. PU was produced by reacting polyol and isocyanate (30:70 wt%) at room temperature. The coated steels were then dried at room temperature for two days to obtain the final product.

2.4. Characterization

Phase characteristic and crystal structure were determined using X-ray diffraction (XRD) X'Pert PRO PANalytical. Scanning electron microscope (SEM) FEI S50 with maximum magnification up to 20000 times and energy dispersion X-ray (EDX) were used to analyze the morphology and chemical composition of the samples. Functional groups of the composites were observed using fourier transform infrared (FTIR) Thermo Scientific. Magnetic properties (magnetic saturation and coercivity) of non-doped and doped BaM were measured using vibrating sample magnetometer (VSM) OXFORD 1.2H. Electrical conductivity properties of the samples were obtained using inductance capasitance resistance (LCM-meter) HIOKI. While, microwave absorbing properties of the coated steels were analyzed using vector network analyzer (VNA) ADVANTEST R3770 300 kHz – 20 GHz.

3. Result and discussion

3.1. Structural characterization

BaM can be prepared using sol gel method with Ni-Zn doping. From XRD pattern of non-doped ($BaFe_{12}O_{19}$) and doped BaM ($BaNi_xZn_xFe_{12-2x}O_{19}$) on Figure 1, both samples have the barium hexaferrite single-phase with no intermediate phase. It was perfectly indexed to the crystal plane of hexagonal $BaFe_{12}O_{19}$ (JCPDS Card No. 01-074-1121 and 00-043-0002). The line profile, as described by Jiang et al. [7], Kanagesan et al. [8], Xie et al [9] and Sharma et al. [10], was shown in Figure 2. It was fitted for the observed 14 peaks with the following miller indices: (1 1 0), (1 0 7), (1 1 4), (1 0 8), (2 0 0), (2 0 3), (2 0 5), (2 0 6), (3 0 0), (2 1 7), (2 0 1 1), (2 2 0), (2 0 1 4) and (3 1 7).
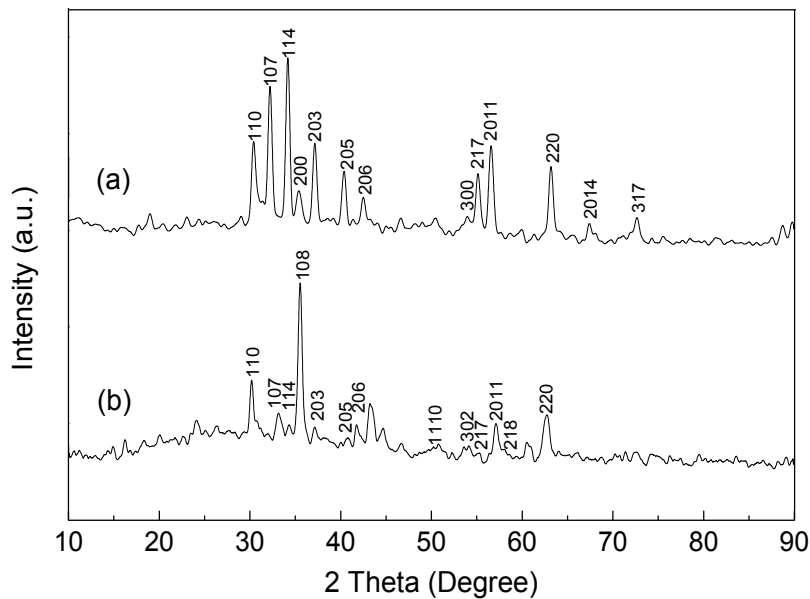

Figure 1. XRD at (a) Non-doped BaM, (b) Doped BaM

Table 1. Crystal size of Barium hexaferrite (BaM)

Materials	Height [cts]	B	θ	Crystal Size [nm]	Unit Cell Volume [A^3]
Non-doped BaM	318.30	0.0669	17.056	61.228	696.99
Doped BaM	232.58	0.0669	17.089	61.238	697.56

The average crystallite size and unit cell volume of both samples have value as seen in Table 1. Furthermore, it indicated that Ni^{2+} and Zn^{2+} ions have entered $BaFe_{12}O_{19}$ lattice and become $BaNi_xZn_xFe_{12-2x}O_{19}$ particles. Subtitution of Ni^{2+} and Zn^{2+} ions caused the intensity of $BaFe_{12}O_{19}$

diffraction peaks declined and BaM peak phase shift to right as seen in Figure 1b. It showed that Ni^{2+} and Zn^{2+} ions have influenced to the phase growth of $BaFe_{12}O_{19}$, in which the radius of Ni^{2+} and Zn^{2+} ions were larger than Fe^{3+}. So that, Ni^{2+} and Zn^{2+} ions substituted Fe^{3+} ion caused the crystal size was greater because the radius size of Ni-Zn ions were larger than Fe^{2+} ion that was substituted.
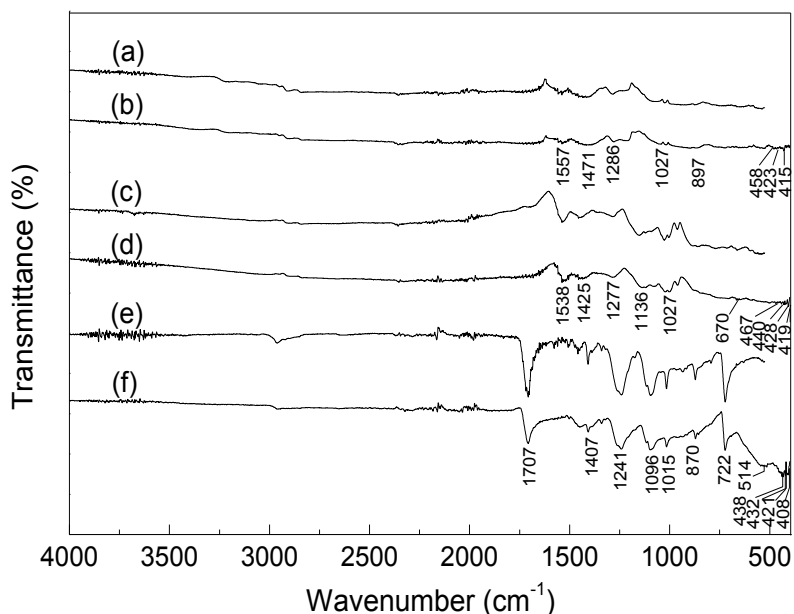

Figure 2. FTIR at (a) PAni, (b) BaM/PAni, (c) PPy, (d) BaM/PPy, (e) PET, (f) BaM/PET

Figure 2 shows that all composites have M–O and C–H bonds, wavenumbers of 514-408 cm^{-1} corresponding to M-O bond. It indicated interaction between metals (Fe, Ba, Ni, Zn) and oxygen. The peaks at 897-670 cm^{-1} were the out-of-plane deformation of C–H bonds in benzenoid ring which can be attributed to the presence of polymer. The vibrational mode of N=Q=N (Q is quinoid ring) bonds and C=C (pyrrole ring) in the doped PAni and PPy chain was also found at 1557 and 1538 cm^{-1} as described by Quillard et al. to be "electronic-like band" because their electronic structure is based on the overlap of alternating nitrogen and C_6 rings [11], as seen in Figure 2a-d. This electronic structure produced conductive properties in polymers. Therefore, it can be utilized as dielectric material to absorb energy of electromagnetic wave, known as radar absorbing material (RAM). The peaks at 1241 and 1407 cm^{-1} (Figure 2e and f), showed the stretched CH_3COOR and C-H ester bond in BaM/PET composite.

3.2. Morphology

Figure 3a shows SEM images of non-doped BaM. It exhibits pores and shape like sponge. Moreover, doped BaM showed polygonal morphology with increased pore size as seen in Figure 3b. Substitution of Ni-Zn ions caused the pore size was greater because the radius size of Ni-Zn ions were larger than Fe^{2+} ion that was substituted, this result also accord with XRD test results in Table 1. While, SEM images of BAM/(PAni,PPy,PET) composites on Figure 3c, d, and e, indicated same globular morphology. It was observed that BaM particles in BaM/(PAni,PPy) composites exhibits hexagonal and polygonal shape. Some aglomerates were found at surface of BaM/PAni composite (Figure 3c) which was caused by residual product of polymerized solution as concluded by Jiang et al. [12]. Figure 4a shows the presence of Ni-Zn elements inside BaM, while C, N, O, S, Ba, Fe, Ni and Zn were found on BaM/(PAni,PPy,PET) composites as seen in Figure 4b. It showed that BaM/(PAni,PPy,PET) composites have been succesfully synthesized, supported by FTIR spectra of polymers and composites on Figure 2.
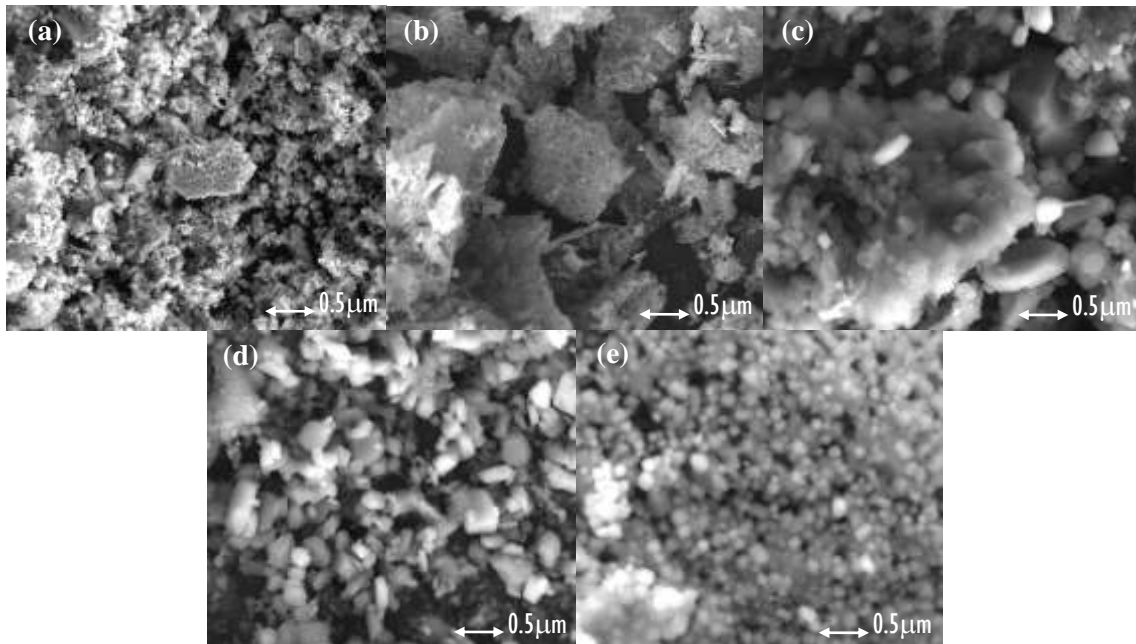
Figure 3. SEM at (a) Non-doped BaM 2000x (b) Doped BaM 2000x (c) BaM/PAni 5000x (d) BaM/PPy 5000x (e) BaM/PET 20000x
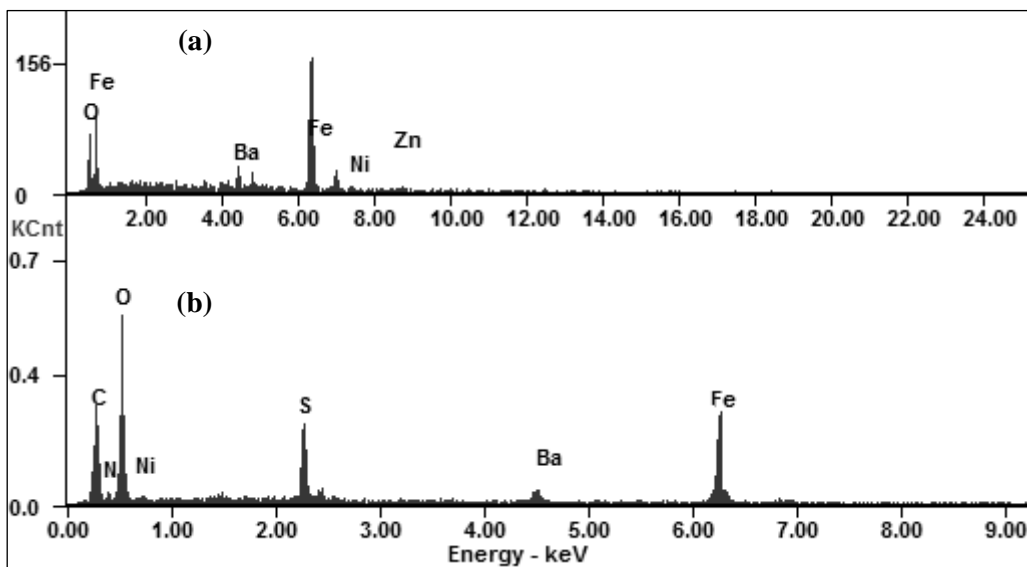

Figure 4. EDX at (a) Doped BaM (b) BaM/PAni

3.3. Magnetic property

VSM graphs on Figure 5 exhibits broad and narrow curve which indicated hysteresis loop of non-doped ($BaFe_{12}O_{19}$) and doped BaM ($BaNi_xZn_xFe_{12-2x}O_{19}$). Based on this curve and Table 2, it showed that non-doped BaM had magnetic saturation (Ms) and coercivity (Hc) value of 53.5 emu/gr and 13160 Oe. Whereas, doped BaM had Ms and Hc value of 56.6 emu/gr and 60 Oe. It can be concluded that doped BaM possessed soft magnetic properties based on its higher Ms and lower Hc value than non-doped one. This characteristic was caused by doping addition which reduced high energy loss in demagnetization process [13]. Therefore, it could be more efficient in absorbing the energy of electromagnetic wave or radar.
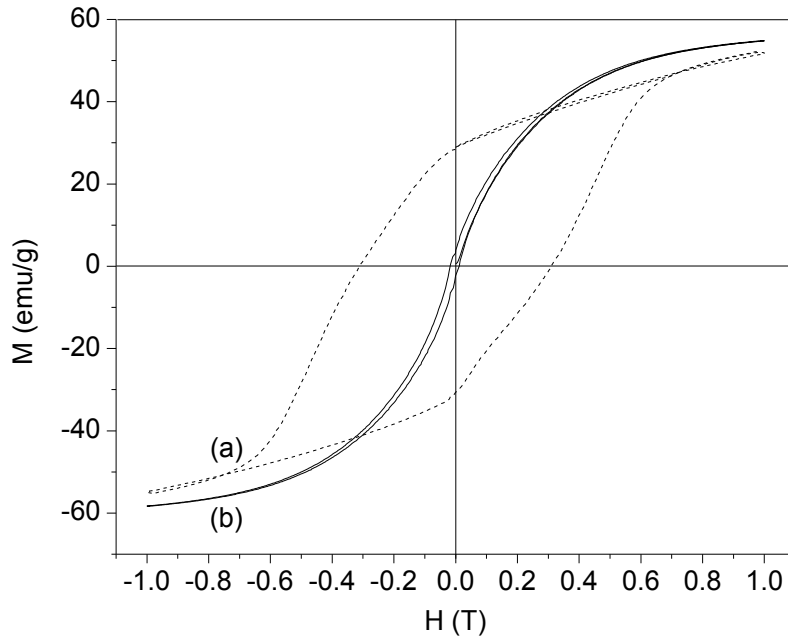
Figure 5. VSM at (a) Non-doped BaM, (b) Doped BaM

Table 2. Magnetic properties of Barium hexaferrite (BaM)

Materials	Ms (emu/g)	Hc (T)	Hc (Oe)
Non-doped BaM	53.5	0.329	13160
Doped BaM	56.6	0.0015	60

### 3.4. Electrical conductivity

The samples for the conductivity measurement were made by pressing the polymer and composites into a slice with 10 mm diameter and about 0.5 mm thickness. The results of LCR-meter analysis are shown in Table 3, that a high electrical conductivity of 1.77744×10^{-5} S/cm was achieved by BaM/PAni composite. Whereas, BaM/(PPy,PET) had a smaller electrical conductivity than BaM/PAni, which is adequate to reduce the reflected wave energy. It indicates that the DBSA dopant has an important influence on conductivity. This may be attributed to the fact that the acid concentration has an important effect on the oxidative polymerization [14]. It is known that the presence of the acid is needed in the polymerization step and also the acid protonates the polymer [5]. Conducting polymers are inherently conducting due to the presence of a conjugated π electron system in their structure [9]. The appearance of these conjugated π electron caused by the effect of the acid that protonates the polymer.

Table 3. The electrical conductivity of polymers and composites

Materials	Conductivity (S/cm)
PAni	8.79809×10^{-8}
BaM/PAni	1.77744×10^{-5}
PPy	1.5007×10^{-7}
BaM/PPy	8.68413×10^{-6}
PET	1.47397×10^{-9}
BaM/PET	1.0354×10^{-5}

3.5. Microwave absorbtion properties

Figure 6 shows the R_L value of BaM/(PAni,PPy,PET) composites in the X-Band frequency of 8–12 GHz. All of samples have excellent absorbing performances for electromagnetic wave (EMW), which are related to the coating thickness of the absorber.
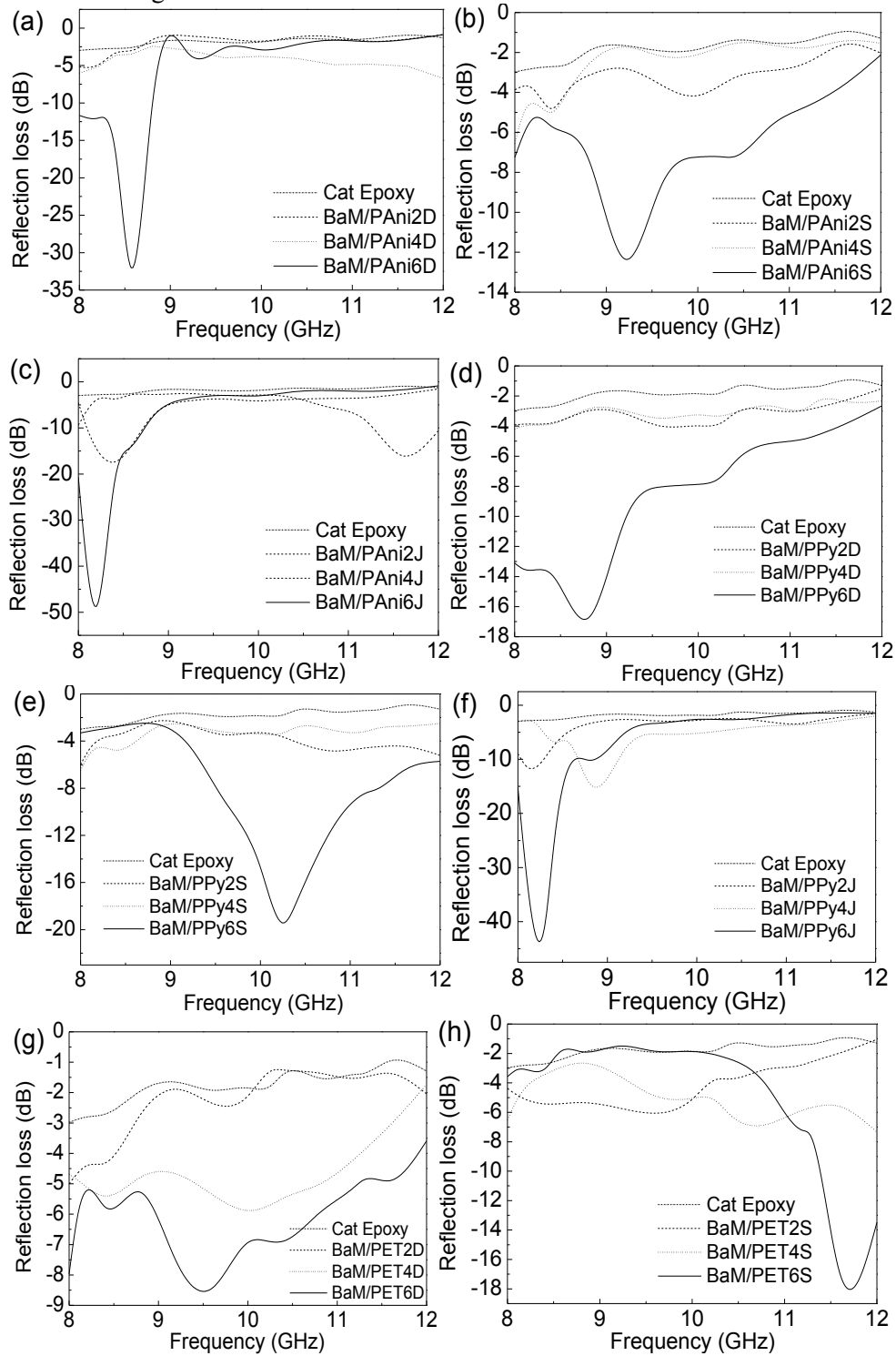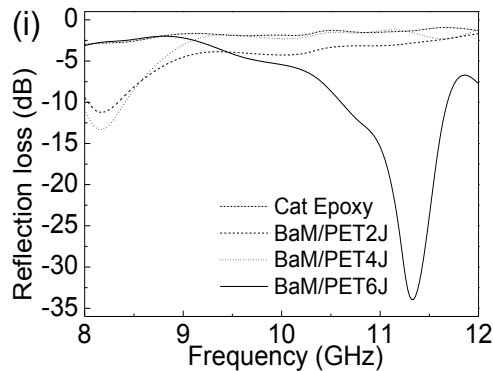
Figure 6. VNA at (a) BaM/PAni Dallenbach Layer, (b) BaM/PAni Salisbury Screen, (c) BaM/PAni Jaumann Layer, (d) BaM/PPy Dallenbach Layer, (e) BaM/PPy Salisbury Screen, (f) BaM/PPy Jaumann Layer, (g) BaM/PET Dallenbach Layer, (h) BaM/PET Salisbury Screen, (i) BaM/PET Jaumann Layer

Tabel 4. Reflection loss BaM/Polymer composites with 6 mm thickness

Coating Materials	Coating Method	Thickness (mm)	Frequency (GHz)	Reflection Loss (dB)
BaM/PAni	Dallenbach Layer	6	8,57	-32,029
	Salisbury Screen	6	9,2	-12,333
	Jaumann Layer	6	8,1	-48,720
BaM/PPy	Dallenbach Layer	6	8,8	-16,768
	Salisbury Screen	6	10,25	-19,435
	Jaumann Layer	6	8,312	-40,808
BaM/PET	Dallenbach Layer	6	9,6	-8,438
	Salisbury Screen	6	11,6	-16,959
	Jaumann Layer	6	11,28	-32,717

When the thickness is equal to 2 mm, the R_L value was lower than 4 mm but the maximum R_l value was reached at 6 mm thickness of BaM/PAni composite at Jaumann Layer of -48.720 dB at 8.1 GHz, as seen in Table 4. Whereas, BaM/PPy and BaM/PET composite at Jaumann Layer with 6 mm thickness have the R_l value of -40.808 dB 8.312 GHz and -32.717 dB 11.28 GHz, respectively. It can be concluded that absorption increase with increase in thickness of material [15]. It is caused when the layers of material are getting thicker, the absorber particles in the coating will also increase. As a result, the absorbtion process will increase. Park reported that -10 dB absorbing bandwidth means the frequency bandwidth having over 90% reflection loss characteristics [16].

There are many kinds of electromagnetic absorbers. Salisbury screens and the Dallenbach layer are resonant absorbers in the narrow band frequency. There are also Jaumann absorbers of multilayer structures with reflection film as broadband absorbers in the broadband frequency [16]. It was caused the maximum R_L value was obtained BaM/PAni composite at Jaumann Layer. This result also in accordance with the conductivity test results in Table 3, that BaM/PAni has highest conductivity value of 1,77744 x 10^{-5} S/m. The reflection loss of sample is related to dielectric loss and magnetic loss besides the coating thickness of the absorber [17]. It is well known that conducting polymers can effectively shield or absorb EMW generated from an electric source, whereas EMW from a magnetic source can be effectively shielded or absorbed only by magnetic material that was BaM material which has soft magnetic properties based on test results in Table 2. Thus, incorporation of magnetic constituents and conducting polymeric materials opens new possibilities for the achievement of good shielding or absorbing effectiveness for various electromagnetic sources [7]. Furthermore, the coming

EMW are reflected to the receiver radar and become weaker, which means there has been an absorption of EMW by RAM composites.

Conclusions

Barium hexaferrite (BaM) was doped with Ni-Zn ion. Both of non-doped and doped BaM were single-phase $BaFe_{12}O_{19}$. BaM/Poly(aniline, pyrrole, ethylene terephthalate) (BaM/(PAni,PPy,PET)) composites were successfully synthesized. BaM and BaM/(PAni,PPy,PET) composites possessed globular morphology with M–O and C–H bonds. BaM ($BaNi_xZn_xFe_{12-2x}O_{19}$) showed the highest value of Ms and Hc, 56.6 emu/g and 60 Oe respectively. While, non-doped BaM had Ms and Hc value of 53.5 emu/gr and 13160 Oe. It can be concluded that doped BaM possessed soft magnetic properties. A high electrical conductivity of 1.77744×10^{-5} S/cm was achieved of BaM/PAni composite, which is adequate for reduce the reflected wave energy. The maximum reflection loss (R_L) reached to -48.720 dB at 8.1 GHz of BaM/PAni coating with 6 mm thickness at Jaumann Layer. These results indicated that BaM/PAni composite was a soft magnetic material with a high R_L value that was suitable for radar absorbing material (RAM).

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