

The Microstructure Analysis of Barium M- Hexaferrite Particles Coated by Pani Conducting Material with In Situ Polymerization Process

M. Zainuri and L Amalia

Departement of Physics, Faculty of Mathematics and Natural Sciences, Sepuluh Nopember Institute of Technology Jl.Arief Rahman Hakim, Surabaya 60111 Indonesia.

Email: zainuri@physics.its.ac.id

Abstract, Barium M-Hexaferrite (BaM) was synthesized by coprecipitation method and doped with Zn. Polyaniline (PANI) was synthesized by chemically and doped DBSA. The composite of PANI/BaM was synthesized by in situ polymerization method. The phase identification of the sample was performed by XRD, FTIR and SEM. Based on XRD data, the phase composition of BaM and hematite are 85.52 % and 14.48%. The characteristic peaks of PANI occur at 3435, 1637, 1473, 1298, 1127, 1009, and 799 cm^{-1} . The characteristic metal oxide stretching peaks of BaM occurs at 575 and 437 cm^{-1} . There is no phase changing in PANI/BaM composite. Based on SEM photography, the shape of BaM is hexagonal. The particle size of BaM powder ranges from 400-700 nm. The qualitative interfacial bonding between PANI and BaM particles are conducted very well and the both materials have good wettability.

1. Introduction

Conducting polymer has attracted much attention in recent years because of its properties. The material has high conductivity that can be arranged its dopant concentration level [1]. Among the conducting polymers, polyaniline (PANI) is polymer that mostly using in experiments because it is easy to synthesis and good environmental stability [2]. It has good stability in air, high electrical conductivity, and can be used to the protection of electromagnetic wave [3]. The other applications of PANI are in electrochemical displays, sensors, catalysis, redox capacitors, secondary battery [4]. The present of dopant, such as Dodecyl Benzene Sulphonic Acid (DBSA), it can increase the electrical conductivity of PANI [5]. DBSA plays role as dopant and surfactant [6].

Barium M-Hexaferrite (BaM) is hexagonal molecular structure which use to permanent magnet, magnetic data recording, and microwave absorber. It is because high anisotropic magnetocrystalline, high magnetization, good chemical stability, and good corrosion protection, where is magnetic and electrical properties can be arranged [7]. The magnetization of Barium Hexagonal ferrite can be further improved by ion Zn^{2+} as dopant [8-9]. BaM can be synthesized by iron sand, natural material. The compounds of natural iron oxide (Fe_3O_4 and Fe_2O_3) were found in a great amount in iron sand formed. To increase the technology value of iron sand in Indonesia, it is changed to microwave absorber [10]. The composite of PANI/BaM is a good combination to Radar Absorber Material (RAM) [4].



According [11] the electromagnetic functionalized polyaniline/BaFe₁₂O₁₉ composite was successfully synthesized by in situ polymerization process. In this work, the composite of PANI/BaM was synthesized by in situ polymerization, where BaM was obtained by coprecipitation and PANI as conducting material was prepared by chemical process. The samples were characterized by various experimental measurement such as X-Ray diffraction, FTIR spectroscopy, and SEM. The microstructure of PANI/BaM composite was investigated.

2. Experimental

2.1 Materials

Fe₃O₄ is obtained from iron sand (Tulungagung, Indonesia), Barium Carbonate (BaCO₃) (ACS reagent grade, MP Biomedicals, LLC), Zn powder (pro analys, Merck), Aceton (pro analys, Merck), Hydrochloric Acid (HCl) (pro analys, Merck), Ammonium Persulfate (pro analys, Merck), Dodecyl Benzene Sulfonic Acid (DBSA) (70% wt solution in 2-propanol, pro analys, Aldrich).

2.2 Preparation of Barium M-Hexaferrite

BaM was synthesized by coprecipitation method. Fe₃O₄, Zn and BaCO₃ were dissolved in HCl. That solution was blended by magnetic stirrer for 45 minutes and added NaOH to make precipitate. The precipitate was washed with distilled water and dried at 100°C. Then BaM precursor was calcinated at 1000°C for 5 hours.

2.3 Preparation of Polyaniline

PANI was synthesized by chemical process. Aniline and DBSA were dissolved in distilled water for 30 minutes then slowly added APS solution. The mixture was allowed to react under continous stirring at 0-10°C for 8 hours. PANI was washed and filtered with acetone and distilled water till the filtrate becomes colorless. Then it was dried in room temperature to get PANI powder.

2.4 Preparation of Composite

PANI/BaM composite was synthesized by in situ polymerization. Aniline and DBSA were dissolved in distilled water for 30 minutes then mixed BaM and stirred till homogeneous. APS solution was slowly added dropwise to the above mixture and allowed to react under continous stirring at 0-10°C for 8 hours. The composite was washed and filtered with acetone and distilled water till the filtrate becomes colorless. Then it was dried in room temperature to get composite powder.

2.5 Characterization

The phase identification of the sample was performed with XRD using Philips X'Pert MPD with Cu K α ($\lambda=1.54056$ Å). The XRD data was analyzed by using Rietica, a Rietveld-based refinement software to determine phase composition. The diffraction was recorded from 15° to 75°. FTIR measurement of the sample was recorded on PerkinElmer spectroscopy at 400-4000 cm⁻¹ to analyze the bonding formed. The morphology of sample was performed by SEM EVO MA 10 at an accelerating voltage of 20kV.

3. Result and Discussion

3.1 In situ polymerization

PANI/BaM composite was synthesized by in situ polymerization of aniline in the presence of BaM particles. During the polymerization process, color changing occurs [12]. The color changing shows that chemical reaction between initiator and aniline monomer is happened. The polymerization in the acidic environment causes the surface of the BaM is positively charged. Therefore, the adsorption of amount anions may happen and compensate the positive charges on BaM surface. The while, the specific adsorption of these anions on BaM may also occur [11]. It happens when aniline monomers are changed to cationic anilinium ions in acidic environment. The interaction between anions adsorbed on BaM surface and the ions of cationic anilinium appear. The interaction is electrostatic forces between BaM particles and PANI chains [13]. The aniline monomers are electrostatic attracted to BaM surface then polymerized. It shows that polyaniline is formed and precipitated in mixture which change into dark green. The color of emeraldine salt is dark green. Emeraldine salt is a form of conducting polyaniline.

3.2 Phase analysis

XRD patterns of the prepared PANI, BaM and PANI/BaM composite have shown in Figure 1. It is confirmed that polyaniline which contains the characteristics of PANI at $2\theta = 20.5^\circ$ and 25.5° . It is similar to other experiment result [11] that PANi peaks at $2\theta = 20.4^\circ$ and 25.4° . PANi is amorphous polymer material. For BaM, it is confirmed that $\text{BaFe}_{12}\text{O}_{19}$ (identified by collection number 00-039-1433) and $\alpha\text{-Fe}_2\text{O}_3$ (identified by collection number 00-033-0664). $\text{BaFe}_{11.7}\text{Z}_{0.3}\text{O}_{19}$ is identified as the major phase with a small amount of residual $\alpha\text{-Fe}_2\text{O}_3$. The phase composition of $\text{BaFe}_{11.7}\text{Z}_{0.3}\text{O}_{19}$ and $\alpha\text{-Fe}_2\text{O}_3$ is determined by Rietica software with Rietveld refinement. The weight percentage of phase composition are 85.52 % $\text{BaFe}_{11.7}\text{Z}_{0.3}\text{O}_{19}$ and 14.48% $\alpha\text{-Fe}_2\text{O}_3$. The value of the GoF (goodness-of-fit) is 1.68. It shows the refinement is accepted. In BaM case, the input of parameters for refinement is hexagonal structure, $a=b= 5.8932 \text{ \AA}$ and $c= 23.1877 \text{ \AA}$. The PANI/BaM composite presents the characteristics BaM peaks and amorphous PANI. The main peaks of BaM still stand in PANI/BaM composite and the amorphous phase of PANI also take places. The peaks of BaM in composite are weaker than the peaks in BaM. It is showed on the decreasing of intensity of BaM peaks.

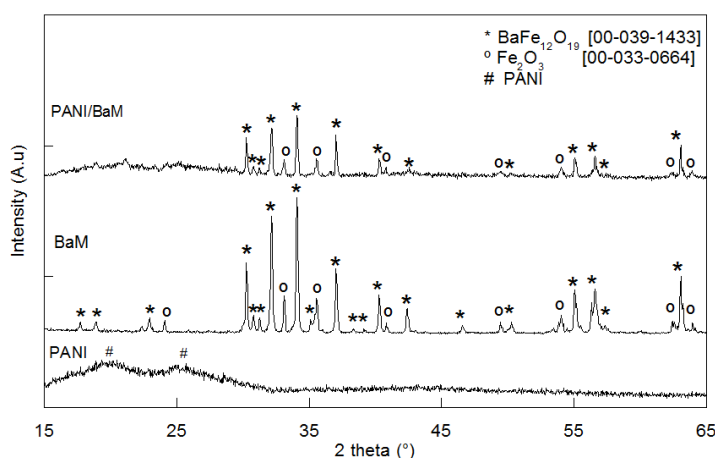


Figure 1. XRD patterns of PANI, BaM, and PANI/BaM composite

3.3 Spectroscopy FTIR

The FTIR spectroscopy of PANI, BaM and PANI/BaM composite have shown in Figure 2. The characteristic peaks of PANI occur at 3435, 1637, 1473, 1298, 1127, 1009, and 799 cm^{-1} . The peaks at 3435, 1637, 1473, and 1298 cm^{-1} are attributed to the characteristic N-H stretching, C=N stretching, C=C stretching of quinoid and C-N stretching. The peak at 1127 cm^{-1} is assigned N=Q=N vibration mode. The peaks at 1009 and 799 cm^{-1} show S=O stretching of DBSA and benzenoid rings. The characteristic metal oxide stretching peaks of BaM occur at 575 and 437 cm^{-1} . The metal oxide stretching peaks in [14] occur at 600 and 460 cm^{-1} . PANI/BaM composite presents the characteristics PANI peaks and metal oxide peak of BaM. The main peaks of PANI present in PANI/BaM composite and the metal oxide peak of BaM may also be seen. This FTIR measurement completely supports XRD data that composite material does not occur the phase changing. The interactions between conducting material and BaM particles happen because of secondary bonding such as electrostatic bonding and the polarity of both materials.

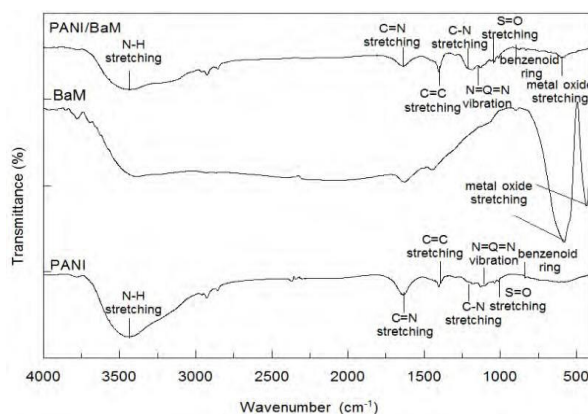


Figure 2. FTIR spectroscopy of PANI, BaM, and PANI/BaM composite

3.4 SEM Morphology

SEM images of BaM and PANI/BaM composite have shown in Figure 3. It can be seen that the shape of BaM is hexagonal. The particle size of BaM powder ranges from 400-700 nm. In Figure 3a the particles are polydisperse, and some of them form multi particle aggregates because of the magneto-dipole interparticle interactions. The distribution of BaM particles is dispersed homogenously. After coating with PANI (Figure 3b), BaM particles stamped in conducting material, PANI. The BaM particles are attracted to PANI each other so making composite formed by in situ polymerization method. From the composite microstructure in Figure 3b, the qualitative interfacial bonding between PANI and BaM particles are conducted very well. Based on the microstructure of PANI/BaM composite, the both materials have good wettability because PANI coated BaM particles.

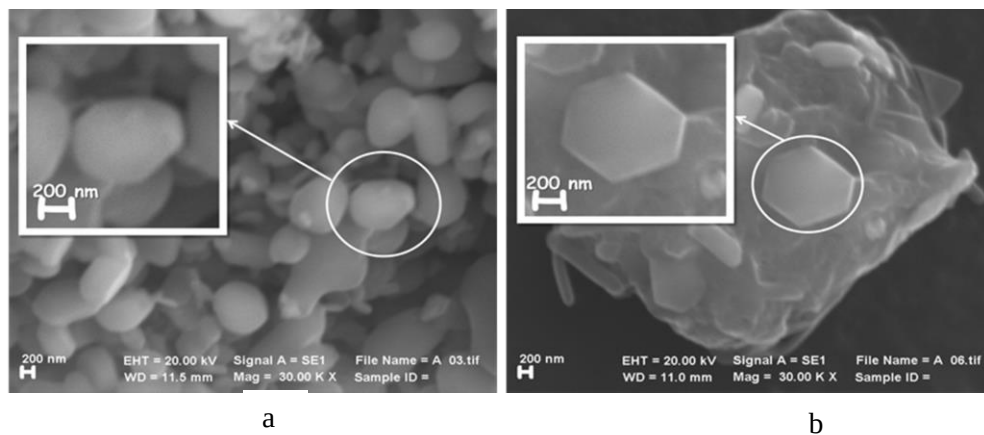


Figure 3. The SEM images of (a) BaM particles, and (b) PANI/BaM composite

4. Conclusion

PANI/BaM composite was successfully synthesized by in situ polymerization of aniline in the presence of BaM particles. From the XRD data and FTIR measurement, it can be conclude that there is no the phase changing in composite PANI/BaM. It is secondary bonding between PANI and BaM particles. Based on SEM photograph, the shape of BaM is hexagonal. The particle size of BaM powder ranges from 400-700 nm.. The qualitative interfacial bonding between PANI and BaM particles are conducted very well. The PANI and BAM particles have good wettability

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