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Effects of Adding Teos For Upr/*Core-Shell* Fe₃O₄@Sio₂ Composites Nanoparticle from Iron Sand as Microwave Absorption Materials

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Abstract. This study aims for synthesized UPR/Core-Shell $Fe_3O_4@SiO_2$ composites as microwave absorption materials. In this research nanoparticle, Fe_3O_4 was synthesized by using coprecipitation methods from the iron sand with NaOH solution. Core-Shell $Fe_3O_4@SiO_2$ was synthesized by using StÖber methods by using Tetraethylorthosilicate (TEOS) as precursor substances, where nanoparticle Fe_3O_4 as core and SiO_2 the shell. The addition of TEOS was adding in the variation of volume and SEM study indicated that with an increase in TEOS content the particle of core-shell $Fe_3O_4@SiO_2$ become bigger. Composites were synthesized with core-shell $Fe_3O_4@SiO_2$ as the filler and UPR as the matrix. Then, composites were tested for electromagnetic microwave absorption using VNA (Vector Network Analyzer) at 8–12 GHz frequency. The result proved that UPR/Core-Shell $Fe_3O_4@SiO_2$ composites were able to absorb electromagnetic waves at 9 GHz frequency with absorption large range up to -15,8 dB.

INTRODUCTION

Electromagnetic energy can be generated from the excessive use of electronic devices and can cause microwave radiation. Microwave radiation is included in Electromagnetic Interference (EMI) problem that can occur in gadgets if there's any leakage of wave energy [1]. Therefore, a material that can reduce reflections and absorbent microwaves is needed. Microwave absorbent material can reduce reflections and absorb microwave radiation through conversion into heat energy [2 - 5]. The ideal microwave absorbent material must have an electrical permittivity and magnetic permeability. The properties of magnetic permeability, one of is owned by Fe_3O_4 or iron (II), (III) oxide because of its unique magnetic characteristics[6 - 8]. Meanwhile, silica as having an active group such as silanol (-Si-OH) and siloxane (Si-O-Si) has an electric permittivity property that can enhance the absorption ability of microwaves.

Fe_3O_4 nanoparticles are obtained from natural materials, namely iron sand. Iron sand is widely used as the main ingredient in producing magnetite. Magnetite can be extracted from iron sand using the coprecipitation method. Meanwhile, silica is synthesized from Tetraethylorthosilicate precursors (TEOS). Fe_3O_4 nanoparticle material and silica modified into a single material namely core-shell, with Fe_3O_4 nanoparticles as the core (core) will be coated by silica (shell) on the entire surface. This modification is performed to solve some problems of Fe_3O_4 nanoparticles as easily agglomerated because of the large surface area, high surface energy and paramagnetic properties [9].

Fabrication of microwave absorbent material in the form of UPR-based composite filled with core-shell $Fe_3O_4@SiO_2$. The core-shell composition will be made in several comparisons between Fe_3O_4 and TEOS. The making of composite materials is needed as a polymer matrix. The matrix is a constituent with the largest volume that functions as a binder. The matrix used in this study is Unsaturated Polyester Resin (UPR). UPR is a polymer

that has good mechanical and dielectric properties compared to others polymers so it is very good as a support to produce optimal composites [10].

The UPR composite / core-shell $Fe_3O_4@SiO_2$ will be measured for its absorption ability on microwaves using VNA (Vector Network Analyzer). This material will be analyzed in the frequency of X Band type electromagnetic waves (band X) in the range of 8 - 12 GHz. This frequency is used in RADAR, communication and electronic technology applications.

EXPERIMENTAL

Tetraethylorthosilicate (TEOS), HCl, NaOH, Trisodium Citrate, Ethanol, 25% NH_4OH, demineralized water (aqua DM) and Unsaturated Polyester Resin (UPR) polymers.Particle Size Analyzer (PSA) to determine the size distribution of owned by Fe_3O_4 and Core-shell $Fe_3O_4@SiO_2$ nanoparticles, Fourier Transform Infrared Spectroscopy (FTIR) to determine the functional groups in UPR / Core-shell $Fe_3O_4@SiO_2$ composites, X-Ray Diffraction (XRD) to identify crystalline phases of Core-shell $Fe_3O_4@SiO_2$, Scanning Electron Microscopy (SEM) to determine the morphology of Core-shell $Fe_3O_4@SiO_2$ and Vector Network Analyzer (VNA) to measure composites against microwave absorption strength.

Magnetite (Fe_3O_4) is extracted from iron sand by dissolving in 6M HCl and stirred with a magnetic stirrer for 30 minutes. After that, the precipitating agent NaOH is slowly added. The resulting reaction results are then washed repeatedly with aqua DM until neutral and free of impurities. Permanent magnets are placed in the bottom of the glass with the aim of being able to pull Fe_3O_4 so that it precipitates faster than Fe_2O_3. A synthesis of Fe_3O_4 nanoparticles is ball-milling for 20 hours.

Fe_3O_4 nanoparticles that have been made are modified with silica from TEOS to be made into core-shell to increase the absorption capability of Fe_3O_4. First, Fe_3O_4 nanoparticles will be produced by coprecipitation method. Second, the silica coating process on the surface of Fe_3O_4 forms a core-shell with the stÖber method or hydrolysis of TEOS. Synthesis of core-shell Fe_3O_4 nanoparticles begins by dissolving Fe_3O_4 nanoparticles in trisodium citrate 0.3 M and ultrasound for 1 hour. The results of Fe_3O_4 nanoparticle deposits were dissolved in ethanol and water in a ratio of 4: 1 and then ultrasonic for 1 hour. The solution was then added with 25% NH_4OH and tetraethylorthosilicate (TEOS) slowly in a distorted state. The addition of TEOS is done in several variations, namely 2 ml; 2.5 ml and 3 ml. Then the solution is maintained in a stirrer condition for ± 24 hours and repeated washing is done using water and ethanol to neutral.

RESULTS AND DISCUSSION

Synthesis Fe_3O_4 Nanoparticles

Fe_3O_4 nanoparticles were successfully synthesized through coprecipitation method and ball-milling. Figure 1 shows the size distribution the Fe_3O_4 Nanoparticles located at 48.66 nm with the value of Polydispersity Index (PDI) of 0.598. This shows that magnetite is already on a nanometer scale with high homogeneity [6].
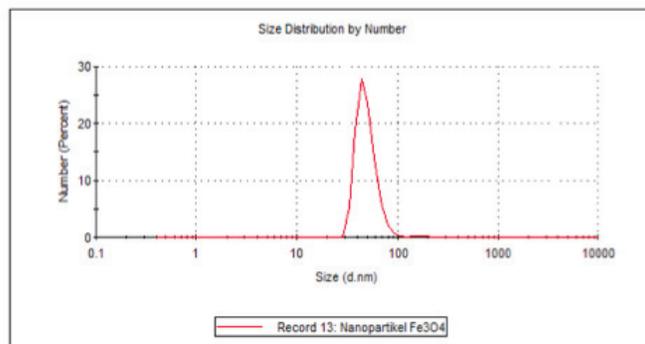

FIGURE 1. Size distribution of Fe_3O_4 Nanoparticles

The IR spectrum of the Fe_3O_4 nanoparticle is shown in Fig 2. The IR spectrum of Fe_3O_4 nanoparticles showed a strong typical peak at wave numbers 582.50 cm^{-1} which were suspected of stretching Fe-O bonds. Whereas, at wave number 3388.93 cm^{-1} there is a widening typical peak which is thought to be the vibration of water (H_2O) in the sample. The results of the Fe_3O_4 nanoparticle patternXRD are shown in Figure 3. the suitability of the diffraction pattern shows the crystallinity of magnetite compound. The suitability of the data results with the database is indicated by the magnetite database source number 99-101-2444. The highest peak was at 2 thetas 35.32 in the area of 311, followed by peaks at 2 thetas 62.75 in the field of 440; 30.00 in the 220 fields; 57.00 in the field of 511; 43.06 in the fields of 400 and 18.25 in the 111 field.
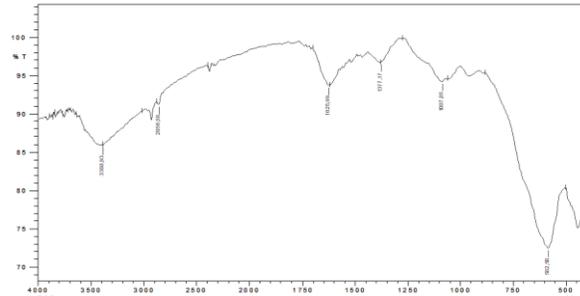

FIGURE 2. IR Spectrum of Fe_3O_4 Nanoparticles

The XRD pattern is processing with the Highscore software obtained crystallinity measurements of Fe_3O_4 nanoparticles, namely 232.2 Å or 23.2 nm. This shows that the crystal size of Fe_3O_4 nanoparticles is on the nanoscale and this data is in accordance with Particle Size Analyzer (PSA) measurements using Dynamic Light Scattering (DLS) analysis techniques.
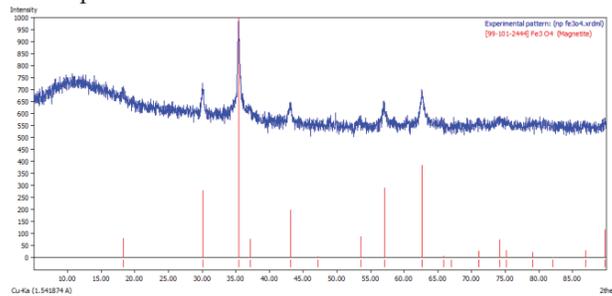

FIGURE 3. XRD Pattern of Fe3O4 nanoparticles

Figure 4 shows the particle shape of Fe3O4 is round and quite uniform. However, there was a high agglomeration so that the morphology on the surface of Fe3O4 nanoparticles was not smooth enough. Aggregation can reduce the surface energy that occurs in Fe3O4 nanoparticles, this can occur because a materials nanoparticle has very high surface energy [7]. Then, the measurement (scaler) in the image is done on several spot particles that are round in shape with an average diameter of 37 nm.
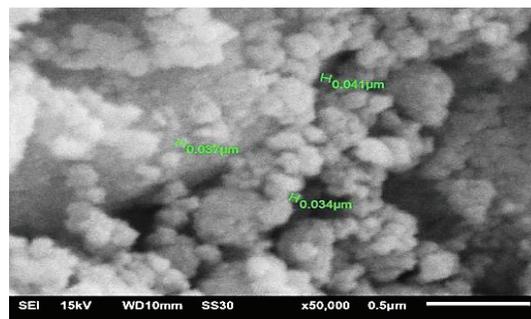

FIGURE 4. SEM morphology of Fe_3O_4 Nanoparticles

Synthesis *Core-shell* Fe₃O₄@SiO₂

Based on Figure 5, there are absorption peaks in wave numbers 3207.62 cm^{-1}, 1089.78 cm^{-1} and 580.57 cm^{-1} indicating the vibration between elements of O-H, Si-O and Fe-O [8]. The wide absorption peak at wave number 3207.62cm^{-1} is the O-H strain and bending vibration of H-O-H and adsorption by water. The characteristics of the three absorption peaks in the wave number indicate the characteristic between magnetite and silica so that it can be said that the core-shell Fe₃O₄@SiO2 has been formed.

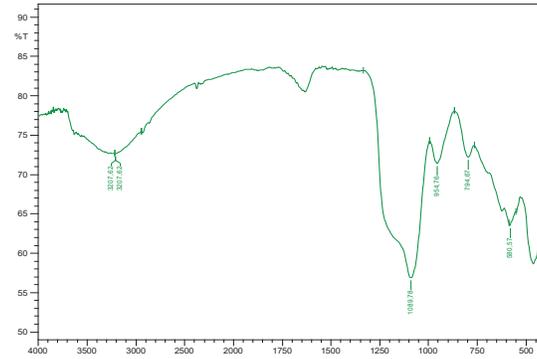**FIGURE 5**. IR Spectrum of Fe₃O₄@SiO2 Nanoparticles

The synthesized core-shell Fe₃O₄@SiO₂ is then tested with an XRD device to determine the phase formed. In Figure 6 is a diffraction pattern of core-shell Fe₃O₄@SiO₂ with a ratio of silica thickness. Tests were carried out on 2 thetas 20°-80° and all three core-shell samples Fe₃O₄@SiO₂ produced six characteristic magnetite peaks (Fe₃O₄) [9].
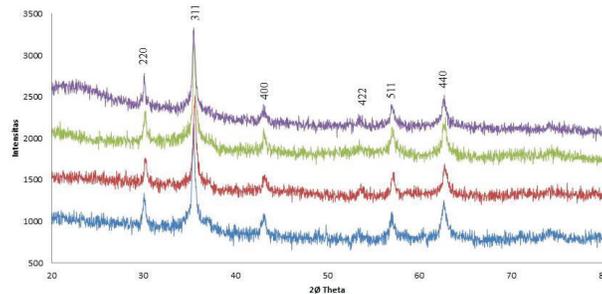

FIGURE 6. XRD diffraction pattern (a) NPs Fe₃O₄, *coreshell* Fe₃O₄@SiO₂with TEOS (b) 2 ml, (c) 2,5 ml and (d) 3 ml

Figure 6 shows that the three core-shell samples Fe₃O₄@SiO₂ do not change the characteristic peak position of Fe₃O₄ nanoparticles. There is also a widening peak at 2 thetas 20 ° - 30 ° which indicates the presence of (SiO₂) silica with an amorphous phase. In the diffraction pattern (c) it can be seen that the silica formed is quite high compared to diffraction patterns (a) and (b). It can be concluded that the procedure of coating or modification of core-shell Fe₃O₄@SiO₂ does not change the crystalline structure of Fe₃O₄ nanoparticles.
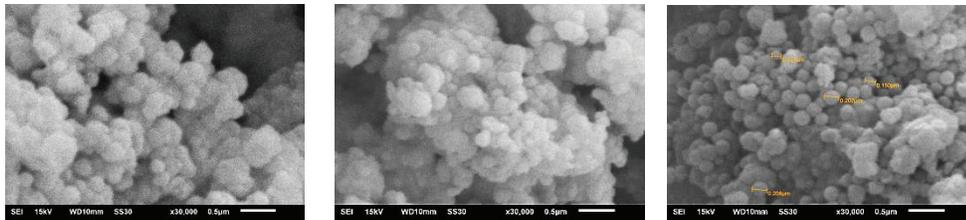

FIGURE 7. SEM morphology of *core-shell* Fe₃O₄@SiO₂

In Figure 7 (a) is a core-shell $Fe_3O_4@SiO2$ by TEOS addition of 2 ml, round-shaped surface morphology. The characteristics of spherical particle shape are characteristic of magnetite (Fe_3O_4) [10]. High agglomeration is possible because the silica coating is not enough to prevent reactivity of Fe_3O_4 nanoparticles. Meanwhile, in Figure 7 (b) the core-shell surface is $Fe_3O_4@SiO2$ with the addition of TEOS 2.5 ml round shape which is quite uniform and smooth. The average core-shell $Fe_3O_4@SiO2$ particle size is 150 nm. Also, in Figure 7 (c), the core-shell surface of $Fe_3O_4@SiO2$ round particles is larger but the surface is not smooth enough compared to figure 7 (b).

Analysis with SEM continued with mapping in Figure 8 which was carried out at 3000 times magnification. In Figure 8 (a) there are several elemental signals consisting of elements of Fe, Si, and O. The appearance of the Fe signal in figure 8 (c) is seen to be distributed throughout the sample with a low intensity of red contrast. Then, the signal element with green contrast is the Si element shown in figure 8 (d) also distributed thoroughly on the surface of Fe. The intensity of the Si element signal is higher than Fe due to the position of silica as a shell or located on the surface of Fe (core). In Figure 8 (e) is a signal display representing the O element that is seen as a whole O element distribution. This is because the element of oxygen (O) also binds to elements of Fe and Si. Based on the analysis of testing and mapping of SEM on $Fe_3O_4@SiO_2$ core-shell it can be concluded that silica successfully coated the entire surface of Fe_3O_4 nanoparticles.
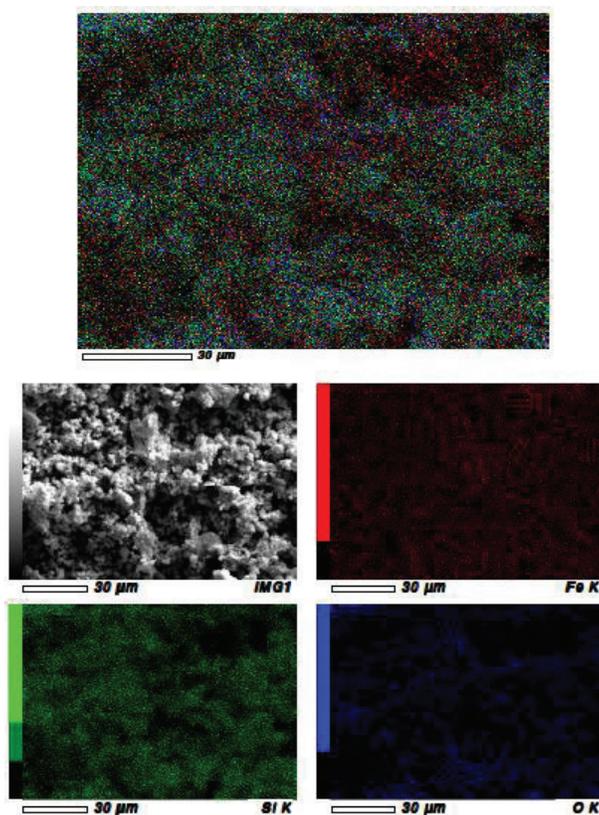

FIGURE 8. SEM Mapping of *core-shell* $Fe_3O_4@SiO_2$

The synthesized core-shell $Fe_3O_4@SiO_2$ is then used as filler in a composite with UPR (Unsaturated Polyester Resin) matrix with a weight/ weight ratio (w / w%) between UPR and core-shell is 85%: 15% of the total mass of the composite 2 grams.

FTIR spectrum of composites can be seen in Figure 9, showing typical absorption peaks of functional groups found in UPR compounds. Typical absorption peaks in benzene, polyester, and esters are each wave numbered 744.52 cm^{-1}, 1128.36 cm^{-1}, and 1278.81 cm^{-1}. Strain C-H bonds are also found in wave numbers 1728.22 cm^{-1} and 2926.01 cm^{-1}. At wave numbers 3400.50 cm^{-1} there is a widened absorption peak which shows the vibration

characteristics of O-H bonds from Si-OH and H_2O in magnetite compounds. Whereas, at wave numbers 1070.49 cm^{-1} and 518.85 cm^{-1} there is a typical absorption peak that shows the strain characteristics of Si-O and Fe-O. This result can prove the synthesis of UPR / core-shell $Fe_3O_4@SiO_2$ composites has been successfully made
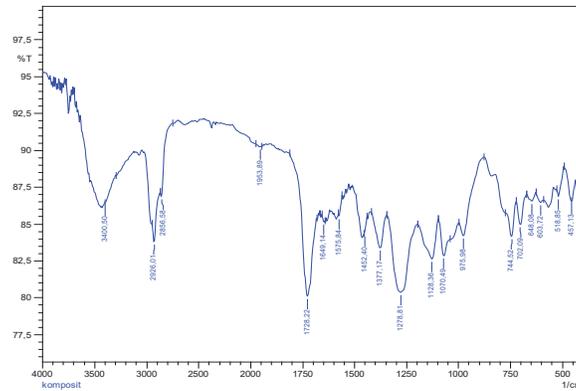

FIGURE 9. IR spectrum of UPR/*Core-shell* $Fe_3O_4@SiO_2$ composites

The optimum composition of the material for the absorption of electromagnetic waves is the addition of silica or as a magnetite coating in the core-shell $Fe_3O_4@SiO_2$ of 3 ml. The optimum absorption of UPR/core shell $Fe_3O_4@SiO_2$ composite to microwaves at 9 GHz wave frequency is -15.8 dB. The test results of core-shell composite material $Fe_3O_4@SiO_2$ for microwave absorption can be seen in Figure 10.
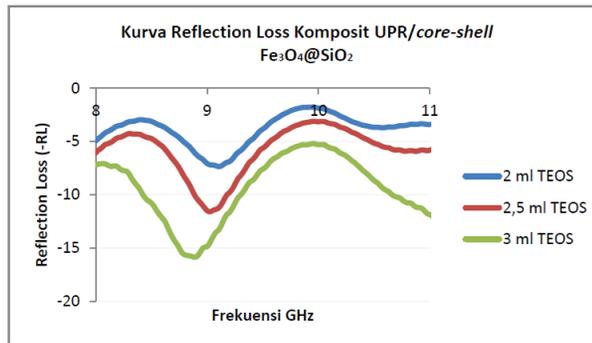

FIGURE 10. *Reflection Loss* from UPR/*core-shell* $Fe_3O_4@SiO_2$ composites

CONCLUSIONS

Based on the discussion of the results of the UPR / core-shell $Fe_3O_4@SiO_2$ composite research on microwave absorption capability, the following conclusions can be drawn:
1. $Fe_3O_4@SiO_2$ nanoparticle core-shell material was successfully synthesized
2. The composition of silica in the UPR / core-shell composite $Fe_3O_4@SiO_2$ which has the maximum absorption is the addition of TEOS 3ml
3. The maximum absorption of microwaves occurs at a frequency of 9 GHz with the greatest absorption capability of -15.8 dB.

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