ABSTRACT

Ideal microwave absorber materials (MAM) have maximum reflection loss (RL<sub>m</sub>) ≤ -20 dB, wide range of absorbed frequencies, low density, light, easy to design, cheap and stable in environmental effects. Fe<sub>3</sub>O<sub>4</sub> is one of MAM. Generally Fe<sub>3</sub>O<sub>4</sub> were synthesized from commercially starting materials such as Fe and ferrous feroic solution (FeCl<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>2</sub>·4H<sub>2</sub>O) which are high-priced. An attempt in producing MAM from unexpensive materials have been carried out in this dissertation, i.e. Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> nano particles based on Fe<sub>3</sub>O<sub>4</sub> iron sand. The Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> nano particles were succesfully synthesized by means of coprecipitation route. The absorbed frequency range is extended by forming a microwave absorption structure in term of core-shell and graduall core-shell structures.

The core-shell structure was composed by polyaniline (PANi) nano particles and silver (Ag) powder as a core and a Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> as shell. The core-shell structure of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/PANi and Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/Ag (3:1, 5:1 and 7:1%wt) as well as the absorber with graduall core-shell structures of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/PANi and Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/Ag (3:1, 5:1, 3:1/7:1 and 3:1/5:1/7:1%wt) were prepared by means of wet mixing method using acetone and tetrametil ammonium hydroxide (TMAH) as a surfactant. The PANi was synthesized by polymerization process while the Ag was simply attained from a chemical industry. The MAM in the form of epoxy resins composites with filler of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> (60 and 70 %vol), Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/PANi and Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/Ag [7:1 %wt] (70 %vol) were produced via blend casting method.

The key factors that allow Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> nano particles to be able to absorb microwaves are the size of particles and their magnetic properties. The nano particles size were observed by XRD (X-rays Difractometry) and TEM (Transmission Electron Microscope). The performance of magnetic properties is influenced by temperature. Prior to producing Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> nano particles, the magnetic behaviour of Fe<sub>3</sub>O<sub>4</sub> raw material was characterized by means of VSM (Vibrating Sample Magnetometery) in conditions of with and without heating at 300 – 800 °C for 1 to 3 hours. The characterization of reflection loss of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> nano particles, core-shell and graduall core-shell structures of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/PANi and Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub>/Ag and composite resin epoxy as the indicator of the microwaves absorption was conducted in the frequency range of 8 - 18 GHz using VNA (vector network analyzer) Advantest R 3710 and 3 - 26 GHz using VNA Agilent type E8364C. The measurement of reflection loss was performed using a single layer backed perfect conductor (Naito and Suetake, 1971).

The results showed that the iron sand extracted from Regoyo River of Lumajang East Java comprised of Fe<sub>3</sub>O<sub>4</sub> > 90 % (particles size = 254 ± 0.4 µm and saturation magnetic = 45.06 emu/gr) can be used for a good raw material as a microwave absorber at X-band (f<sub>m</sub> = 8.82 and 10.41 GHz) and Ku-band (f<sub>m</sub> = 12,13 and 16,92 GHz) with the reflection loss in the range of -11.04 to -18.96 dB. The Fe<sub>3</sub>O<sub>4</sub> nano particle which was successfully synthesized from the iron sand exhibits a crystal size of 17.6 ± 0.6 nm and saturation magnetic, M<sub>S</sub> = 45.06 emu/gr. The Fe<sub>3</sub>O<sub>4</sub> nanoparticle pellets that were heated up to temperature of 500 °C for 1 hour revealed an unchanging phase of magnetite, but decreasing saturation magnetic to 32,34 emu/gr. Heat treatment from 600 °C to 800 °C for 1 hour caused a phase transition from magnetite to hematite (anti ferromagnetic) which then followed by the decreasing of the saturation magnetic to 0.67 emu/gr with crystal size = 148.6 nm.

Ni and Zn substitutions to Fe<sub>3</sub>O<sub>4</sub> nanoparticle in the form of Ni<sub>x</sub>Zn<sub>1-x</sub>Fe<sub>3</sub>O<sub>4</sub> (x = 0, 0.25, 0.50, 0.75 and 1.0) have crystal sizes from 19.9 ± 1 to 38.1 ± 4.1 nm and the highest saturation magnetic 66,44 emu/gr was well exhibited by Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>3</sub>O<sub>4</sub> sample. The magnetic properties and the crystal size affect the power of the microwave absorption. The
microwave absorption (with $RL_m \leq -20$ dB) in the frequency range of 8 – 18 GHz of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ nanoparticles was best performed by Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ with the reflection loss $RL_{m1} = -88.46$ dB, matching frequency $f_{m1} = 11.54$ GHz, the range frekwensi ($\Delta f_{m1}$) = 0.95 GHz and $RL_{m2} = -79.64$ dB, $f_{m2} = 13.03$ GHz dan $\Delta f_{m2} = (1.64$ GHz). The core-shell structure, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/Ag (7:1 %wt) and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PANI (7:1 %wt) can widen the frequency bands absorbed on Ku-band than individual Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, with $f_{m1} = 11.62$ GHz, $RL_{m1} = -28.79$ dB, $\Delta f_{m1} = 0.40$ GHz, $f_{m2} = 14.33$ GHz, $RL_{m2} = -70.67$ dB, $\Delta f_{m2} = 1.53$ GHz dan $f_{m3} = 14.73$ GHz, $RL_{m3} = -34.98$ dB, $\Delta f_{m3} = 1.72$ GHz (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/Ag) and $f_{m1} = 11.60$ GHz, $RL_{m1} = -62.91$ dB, $\Delta f_{m1} = 0.75$ GHz, $f_{m2} = 13.81$ GHz, $RL_{m2} = -75.64$ dB, $\Delta f_{m2} = 1.72$ GHz and $f_{m3} = 14.32$ GHz, $RL_{m3} = -24.45$ dB, $\Delta f_{m3} = 0.23$ GHz (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PANI).

The gradual core-shell structure with the composition (3:1/5:1/7:1 %wt) can widen the bands frequency than Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ with the $RL_m = -30.96$ dB, $f_m = 11.92$ GHz, $\Delta f_m = 2.25$ GHz (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/Ag) and $RL_m = -25.48$ dB, $f_m = 14.11$ GHz, $\Delta f_m = 2.14$ GHz (Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PANI). MAM in the form a composite epoxy-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, epoxy-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PANI (7:1 %wt) and epoxy-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/Ag (7:1 %wt) at a concentration of 70 %vol of specification as absorber ($RL_m \leq -20$ dB) in range frequency absorbed 1.32 - 4.35 GHz (X-and Ku-band) and 0.34 - 0.91 GHz (Ka-band).

The described study above has novel findings as follows: (1). the iron sand can be effectively used as raw materials for microwave absorber materials, (2). the information of reflection loss of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x = 0, 0.25, 0.50, 0.75 and 1.0) nanoparticles and the core-shell structure Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PANI and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/Ag in bulk, (3). the absorber with gradual core-shell structure of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PANI and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/Ag (3:1/5:1/7:1 %wt).

**Key words:** nano particles, iron sand, microwave absorber material, coprecipitation, core-shell structure, nano composites.