Synthesis and microwave characterization of conductive polyaniline prepared by continuous polymerization process

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Abstract. Results of synthesized polyaniline (PANI) prepared by a continuous polymerization process is reported. The purpose of this research is to obtain material absorber which maximum absorption. FTIR spectrum for synthesized PANi showed no double bond absorption peak at 3442 cm⁻¹ which indicates the polymer chain was formed through repetition of single bonds. The results of the electrical conductivity measurement showed the value 17.5 µS/cm for synthesized PANI. The value increased dramatically to 3600, 1520 and 920 µS/cm after the addition of photonic acids of HClO₄, H₂SO₄ and HCl respectively. Those values were obtained through sequences process. Results of particle size distribution confirmed that all synthesized PANi have nanoparticles. In addition, all synthesized PANi have shown electromagnetic wave absorbing properties in the frequency range 12-18 GHz. The best peak Reflection Loss (RL) values -10 dB (~ 68 % absorption) and -25 dB (~ 84 %) at 13 and 16.5 GHz respectively obtained on the PANi Emeraldine base (PANI-EB).

1. Introduction

One of technical requirement for Radar Absorbing Materials (RAM) [1,2] in applications is that beside their high ability to absorb the electromagnetic wave, the RAM should also be made of materials with lighter in weight, chemically stable, possesses suitable mechanical and physical properties. It is not surprising to note that the need to develop lighter and thinner microwave absorbing materials with a high ability for absorbing the electromagnetic wave increased nowadays. Several reports have shown that the best materials for microwave absorbers are made of ions substituted M-type hexaferrites[3-4]. M-type hexaferrite is particularly suitable because it has a high magnetization (Ms = 0.48 T), it is an oxide based compound and hence chemically stable, but its magento crystalline anisotropy constant is a relatively large and hence it possesses a high coercivity (~250 kA.m⁻¹). This is the reason why the M-type hexaferrite is widely used as permanent magnets. However, partially ions substituted for Fe for instance, in BaO.6Fe₂O₃ was able to reduce the coercivity significantly, but with a little sacrificing in the total magnetization making it suitable as a potential candidate for microwave absorbers. It was reported that doped Barium Hexaferrite (BHF) has a larger value of reflection loss in which more than 51 dB was observed in the frequency ~ 16.7 GHz [1]. The report shown that the material has a wider absorbing width in the frequency range 12 - 20 GHz. However, hexaferrite materials have a relatively
larger mass density (~5.8 gr/mL) which is about the third quarter of the mass density of pure iron (~7.8 gr/mL). Therefore, the use of this kind of materials as the microwave absorber shouldn’t be in a large quantity in order to avoid the excessive weight in the applications. One way to achieve this objective is that employing hexaferrites materials as fillers for a composite system. Thus, material selection for matrix is essential to meet therequirement as the lighter microwave absorber. It is considered important to select conducting polymers like conductive polyaniline (PANi) as the alternative for suitable matrix in the composite system. Some reports have also shown the use of PANi as electromagnetic shielding at microwave frequencies [5,6]. PANi which was modified by inorganic filler has shown to improve magnetic and dielectric properties depend on the type of filler. Both properties are essential in the microwave absorber material. Improve electrical permittivity will increase the dielectric constant and hence the capacitance of materials. Whereas, improve magnetic permeability will increase the inductance. The capacitance and inductance together with an electrical conductance are essential for a total impedance of the material. Focus of this research is to explore the properties and characteristics of conductive PANi by additional some strong acids as doping agent to increase the conductivity value then the correlation between electricity property with microwave absorber property will be obtained.

2. Materials and Methods
Aniline monomers was mixed with 1.5 M hydrochloride acid (HCl) at room temperature as monomer solution. Initiator solution was prepared by mixing 10 % of ammonium persulphate (APS) in hydrochloride acid (HCl) 1.5 M. Both solution were introduced into the reactor step by step by controlling flow rate of the feeding. Total duration of reaction time to form Polyaniline emeraldine salt (PANi-ES) was 5 h. The liquid was further treated by subsequence steps starting from filtering, precipitation, washing using ammonia free water and finally drying in the vacuum for 60 h after purging with N₂ gasses. The result of the treatment is a dried PANi-ES. In order to get Polyaniline emeraldine base (PANi-EB), the cleaning of dried PANi-ES were continued using water and methyl alcohol to dissolve residual anilines which formed during the polymerization process. The dry solid, then was dissolved using 0.1 M ammonium hydroxide solution with pH ≥ 8. Mixing for 15 h at room temperature to form a complete (PANi-EB) was required. The subsequent treatment as described above was then repeated to PANi-EB. The pure and dry powder of final Polyaniline as stable PANi-ES, then was dissolved by different acids. There are three types of acid are used with different ionic strength those are HCl 37%, HClO₄ 98% and H₂SO₄ 98%. Each mixture was stirred for 10 h in a separate chamber at room temperature. The precipitant was formed and ready for further characterization. Powders of all synthesized PANi were evaluated by Malvern Particle Size Analyzer.
(PSA) and FTIR for identification studies. Finally, the microwave characteristics of all synthesized PANi were evaluated by vector network Analyzer (VNA) through measurements of transmission and reflection of electromagnetic wave in the 12 - 18 GHz frequency range.

3. Result and Discussion

Figure 1 is a FTIR spectrum for aniline monomer. Aniline monomer has specific bands to Infra-Red transmittance at wave numbers 3442 cm\(^{-1}\) and 3354 cm\(^{-1}\) respectively [7] which are associated with vibration stretching of N-H from primary amine between vibration stretching N-H asymmetric and vibration stretching N-H symmetric. Those bands appear lower than the band of vibration stretching of O-H which appears almost at similar wave number. A shoulder band always appears at 3213 cm\(^{-1}\) especially for aniline. The bending vibration of N-H from primary amine appears at 1600 cm\(^{-1}\) and 1273 cm\(^{-1}\) as stretching vibration of C-N. Another specific band of aniline also are confirmed at 881 cm\(^{-1}\) and 748 cm\(^{-1}\) as bending vibration of C-H and wag vibration of N-H from primary amine.

![Figure 1. FTIR Spectrum of Aniline Monomer](image)

The FTIR spectrum for synthesized PANi are shown in Figure 2 and Figure 3. The PANi was formed which confirmed by the following results of identification. First spectrum interpretation was a band of Infra-Red transmittance at the wave numbers 1564 cm\(^{-1}\) and 1477 cm\(^{-1}\) respectively. These are specific band for stretching vibration of C═C from quinoid ring and benzenoid ring as a backbone of PANi [8]. In addition, a transmittance peak at 1435 cm\(^{-1}\) was identified and it showed stretching vibration of the aromatic group from ammonium. Other specific bands of PANi can also be confirmed in which stretching vibration of C-N from secondary amine were observed at 1305 cm\(^{-1}\) and 1246 cm\(^{-1}\) respectively. The strongest peak appears at 1141 cm\(^{-1}\) which arise from the stretching vibration of C═N from quinoid ring protonated. Finally, the bands at 989 cm\(^{-1}\) and 819 cm\(^{-1}\) respectively ensure that the synthesized PANi has really formed which totally different to that of the monomer.
When NH$_4$OH is added during the polymerization process, proton (H$^+$) was released and Emeraldine Base (PANi-EB) was formed as a neutral based of PANi. When doped (protonated) by strong acid, Emeraldine Salt (PANi-ES) will be formed as highly electrically conducting structure. Thus, there is a difference in structure and properties between PANi-EB and PANi-ES. Pure PANi will be obtained after filtration, cleaning, and drying as silver brown powder. The propagation process will be formed during reversible reaction formation of PANi-ES and PANi-EB. According to the particle size measurement, it didn’t make any effect into particle size of PANi by doping with some different acids. Almost all PANi has particle size below 20 nm, as mentioned by M.A Elita et al., (2016)[9].

![Figure 2. FTIR Spectrum of PANi-ES](image1)

![Figure 3. FTIR Spectrum of PANi-EB](image2)

It is well known that in general aniline has a zero conductivity value. However, when the aniline is polymerized to form PANi, the conductivity value is raised. In Table 1, the electrical conductivity values for all synthesized PANi are summarized. Results as listed in Table 1 suggested that photonic acid has increased the conductivity value of PANi. PANi which doped by HClO$_4$ has the highest conductivity $\sim$ 3600 $\mu$S/cm. The high value for conductivity in PANi-HClO$_4$ could be associated with strongest Brønsted-Lowry acids in which the pKa value is -10 [7]. The conductivity value of PANi is
required to obtain high absorption material when polyaniline is used as a matrix. Conductivity (\(\sigma\)), permittivity (\(\varepsilon\)) and permeability (\(\mu\)) are important parameters could contribute increasing electromagnetic shielding efficiency [10].

Table 1. Conductivity value of PANi

| Material Name | Conductivity Value (\(\mu\)S/cm) |
|---------------|----------------------------------|
| Aniline       | 0                                |
| PANi-EB       | 17.5                             |
| PANi-ES       | 100                              |
| PANi-HCl      | 920                              |
| PANi-H\textsubscript{2}SO\textsubscript{4} | 1520                           |
| PANi-HClO\textsubscript{4} | 3600                           |

According to above result shown that additional perchloric acid (HClO\textsubscript{4}) as doping agent with ratio 1:10 to PANi produced the highest conductivity value of PANi is \(~3600 \mu\)S/cm. It indicates that perchloric acid is able to influence transition phase from amorphous to crystalline phase of polyaniline molecule. It is also confirmed from the observation result was conducted by Zhang et al., (2012) [11], where is due to of this molecule property caused electron easily moves from the back bond chains inducing enhancement conductivity. The additional of dopant plays role as an attractive potential for the charge carriers and as bridge conduction facilitating electron transport inter-chains. Mechanism electron transport inter-chains of conductive polyaniline is used as basic principle for the mechanism of conducted polyaniline property.

Figure 4 describes the Reflection Loss (RL) values were plotted in the frequency range 12-18 GHz from which all conductive PANi have microwave absorber characteristics at least within the range of applied frequency. The absorbing pattern for all PANi looks similar, in which the highest attenuations occurred at about 13 GHz and 16.5 GHz respectively. However, only PANi-EB has the largest attenuation with RL value \(~-10 \text{ dB (}\sim 68 \%)\) and \~-25 \text{ dB (}\sim 84 \%)\) at respective frequencies.

![Figure 4. Microwave Absorption Characteristic of Various Synthesized PANi](image-url)
According to the alternating current basic principle, a part of electrical resistivity and hence the conductivity, a proper matching between dielectric loss and magnetic loss which is the imaginary part of an impedance value determining the losses. When referring to results of Table 1 and Figure 4, the highest conductivity value was obtained in PANi-HClO₄ is 3600 μS/cm but its RL value is the lowest. This is in contrary to that of PANi-EB, which has the lowest conductivity value approximately 17.5 μS/cm, hence the largest resistivity. Overall, PANi-EB has the best microwave absorbing characteristic because a high in its resistivity value and hence the largest impedance among the samples. The largest RL values were due to a high dielectric loss only.

4. Conclusion

The electrical conductivity of pure PANi can be increased from zero to 3600, 1520 and 920 μS/cm after the addition of photonic acids of Perchloric acid (HClO₄), sulfuric acid (H₂SO₄) and hydrochloride acid (HCl) respectively. All conductive PANi have shown electromagnetic wave absorbing properties in the frequency range 12-18 GHz. The best peak Reflection Loss (RL) values -10 dB (~ 68 % absorption) and -25 dB (~ 84 %) at 13 and 16.5 GHz respectively obtained on PANi Emeraldine base (PANI-EB) which correspond to the largest resistivity value. It indicates that additional doping agent by strong acid can increase the electrical conductivity value of PANi also improve the material absorption property until -25 dB.

Acknowledgements

The authors gratefully acknowledge the support of Postgraduate Program of Materials Science Universitas Indonesia for the research facilities. We are also thankful for the financial support provided by the National Higher Education of the republic of Indonesia under program Penelitian Unggulan Perguruan Tinggi Riset Utama contract no. 3447/H2.R12/HKP 05.00/2014.

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