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Preparation and Characterization of a Magnetic Paper by Coprecipitation Loading Process

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Abstract: ***Many research of making magnetic paper focus on the substrate as part of the green promotion strategy. For example, research on wood, kenaf, sugarcane bagasse, and other had been successfully used to produce the green magnetic paper. However, in order to achieve better environmental friendly magnetic paper, the production and synthesise method of the magnetic paper also needs to be considered. Previously, there were two famous method in producing magnetic paper namely lumen loading and in-situ coprecipitation method. As a continuity effort to the previous green magnetic wave absorber technology, a new enhanced technique named coprecipitation loading method is introduced; which is better in conserving energy. From this research, the new method had shown average performance in terms of magnetic properties and loading degree of the magnetic particles. However, compared to the previous two methods it save a huge amount of energy in the production process thus leading to better conservation of energy in promoting greener environment.***

Keywords: Lumen loading, in-situ coprecipitation, coprecipitation loading, magnetic paper.

1. Introduction

Magnetic sheet can be used as electromagnetic wave absorbers to encounter electromagnetic interference or to enhance communication signals. Previously, magnetic sheet was produced using pure magnetite or as composite by mixing polymers and magnetic particles. By modern approach, conventional paper can be altered to have additional characteristic such as magnetic properties [1]. The importance of magnetic paper is to encounter the disadvantages of pure magnetic sheet where the magnetic paper has better flexibility, cost efficiency, and disposability.

The research of this magnetic paper was dated back to the 1980s when a group of researcher successfully produced this magnificent paper in laboratory. Green et al. [1] had produced magnetic paper using lumen loading technique. A paper fiber usually has lumen, a hollow cylindrical empty space within the fibers. This method loads the lumen with nano-sized magnetic particles while leaving the exterior surface of the fiber free from magnetic particles. It is important to clear out the outer layer of the fiber from magnetic particles to retain the mechanical properties of the paper.

Next, the other method of making magnetic paper was using in-situ coprecipitation method. This method was first developed by Ricard et al. [2]. The advantage of this process was it allows better control on the size and distribution of the particles inside the lumen. This technique uses the ferric (Fe3+) and ferrous (Fe2+) salts and transform it into magnetite by oxidizing it by the addition of NaOH. The involvement of this nanotechnology give more advantage compared to lumen loading technique in terms of the size and particles distribution but smaller particles lead to lower magnetic saturation value. This is because of nano-sized magnetite shows superparamagnetic behavior [3].

Many previous researches only focus on the substrate and loading technique. Research that focuses on substrate plays between different substrate to promote greener environment. For example, previously, substrate from wood chip paper pulp was changed to kenaf [3] pine softwood [4] and bamboo pulp [5]. On the other hand, research on loading technique usually plays around the method to load the magnetic particles into the lumen. Up to date, there are two major techniques to load magnetic particles in lumen which had been explained before [6]. In this research, the manipulation of the magnetic particles loading techniques had been done by combining both established methods to enhance the energy saving process in order to promote greener environment.

2. Methodology

In the study, the basic material used for making paper was paddy straw pulp. This material was selected as part of the continuing process from the previous work done. The productions of the magnetic papers were done using three different methods. The first method is using lumen loading technique, followed by in-situ coprecipitation method and lastly, the proposed method which is coprecipitation loading method.

2.1 Lumen loading process

Paper pulp weighted at 15g was mix with 1250ml of distilled water and 0.1 g L-1 alum and mechanically stirred at 1000rpm for 30 minutes. 30g of nano magnetite particle at the size of 50 nm produced by Sigma-Aldrich that has

undergone ultrasonic separation later were mix with the colloid for 1hr and rotated at 1000rpm for 60 min. Next, the rotor speed was slowed down at 400rpm and the colloid were mixed with polyethylenimine (PEI, 2%, w/w polymer on pulp) and leave for 4 hr. Afterwards, the suspension were wash in a self designed sieve (45 µm) and later undergone paper making process but placing the washed pulp in a self designed mold and dried for 24 hr.

2.2 In-situ coprecipitation process

15g pulp was stirred at 1000rpm in 1500ml distilled water for 30 min. Next, the colloid was heated to approximately 80 ºC. Ferrous chloride (FeCl2.4H2O) and ferric chloride (FeCl3) were mixed in the solution at the ratio of 1:2 respectively and left for 5 min. Later, sodium hydroxide (NaOH) was added into the suspension and left for 15 min. During this process, the suspension will turn into black colour. Then, PEI (2 %, w/w polymer on pulp) was mixed and further stirred for 1hr. Lastly, the suspension was washed, molded, and undergone drying process as the final stage of the magnetic paper making process.

2.3 Coprecipitation loading process

15g of dried pulp was vigorously stirred at 1000rpm for 30minutes in 1250 ml distilled water. Simultaneously, magnetic particles were produced by mixing ferrous chloride (FeCl2.4H2O) and ferric chloride (FeCl3) at the ratio of 1:2 respectively in a 250ml distilled water at 80 ºC. After 5 minutes, the solution was mix with NaOH and black precipitated will form instantaneously and leave for another 15 min before the heat supply can be stop. 15 min of time compensation was needed to ensure that all ferrous and ferric chloride was fully oxidized with the addition of NaOH. Immediately, the black precipitate was mixed with the pulp and stirred for 10 minutes. Then, PEI (2 %, w/w polymer on pulp) was mixed and further stirred for 1hr. Lastly, the suspension was washed, molded, and undergone drying process as the final stage of the magnetic paper making process.

2.4 Morphology Analysis

The lumen structures of the lumen loaded and in-situ coprecipitation pulp were observed using Zeiss EVO-50 ESEM scanning electron microscope machine. Observation of the lumen was made by cross cutting the paper.
Magnetic Measurement: The magnetic properties of the loaded paper were analyzed using Lakeshore 7407 vibrating sample magnetometer machine. The value of magnetization and coercive force of each sample were performed at room temperature only.

2.5 X-ray Diffraction Measurement

The magnetic particles were analyzed using PANanalytical X'PERT PRO MPD X-ray diffraction machine with model number of PW3040/60. This machine was used to identify the particles used for the loading process and to make conformation on the purity of the particles being loaded into the lumen of the pulp.

2.6 Thermogravimetric analyzer

The percentage of the magnetic particles being loaded were determined using thermogravimetric methods. The samples were heated at 900ºC for at least 4 hours and the heating rate was 10 ºC min^{-1}. After the heating process, the weight of the samples at 900 ºC was measured. Next, Calculation of the loading degree was done using this equation.

Loading degree of paper = % Weight of treated paper - % weight of empty paper (1)

Power Consumption: The power needed for each method was calculated. The calculation was based on the mechanical stirring and heating process. The mechanical stirring calculation was based on making assumption that the stirrer was a shaft and the calculation will use the shaft work calculation. The power transmitted through a shaft is as follow:

$$W = 2\square nT \times t \quad (2)$$

where n is the rotational speed, T is the stirrer torque and t is time required for the whole stirring process.

Next, the power consumption calculation also involves the heating process power consumption and the formula was based on maintaining the water temperature at 80□ C for 1 to 4 hours' time interval depending on type of process. The formula for calculating the power required for maintaining water temperature is as follow:

$$Q = mcT \times t \quad (3)$$

where m is the mass of water, c is the specific heat of water, T is the temperature different and t is the time required for the temperature different.

3. Discussion

3.1 XRD measurement

Figure 1 shows the magnetite XRD pattern and the pattern produced after scanning paddy straw samples. In this figure, observation made at the magnetite shows clear reflection peaks at 2θ angles at 18.3°, 30.2°, 35.5°, 43.2°, 53.5°, 57°and 62.5°.This patterns shows that the reflected pattern were the peaks produced by Fe3O4 (Long et al. 2009).
In all pattern in Figure 1, every method shows significant peaks arise from all 2θ angles especially at 35.5°. At this 35.5°, the crystallite size calculation from the 311 reflection (d311) gives values ranging from 10 to 13 nm.
The mean crystallite size of Fe3O4 was determined by using the Scherrer's equation

$$Dhkl = 0.9\,\lambda / \beta \cos\theta, \quad (4)$$

where Dhkl is the mean crystallite size, β is the broadening of full width at half maximum intensity (FWHM) of diffraction peaks (311) in radian, θ is the Bragg angle and λ is the X-ray wavelength (Munawar et al. 2010).

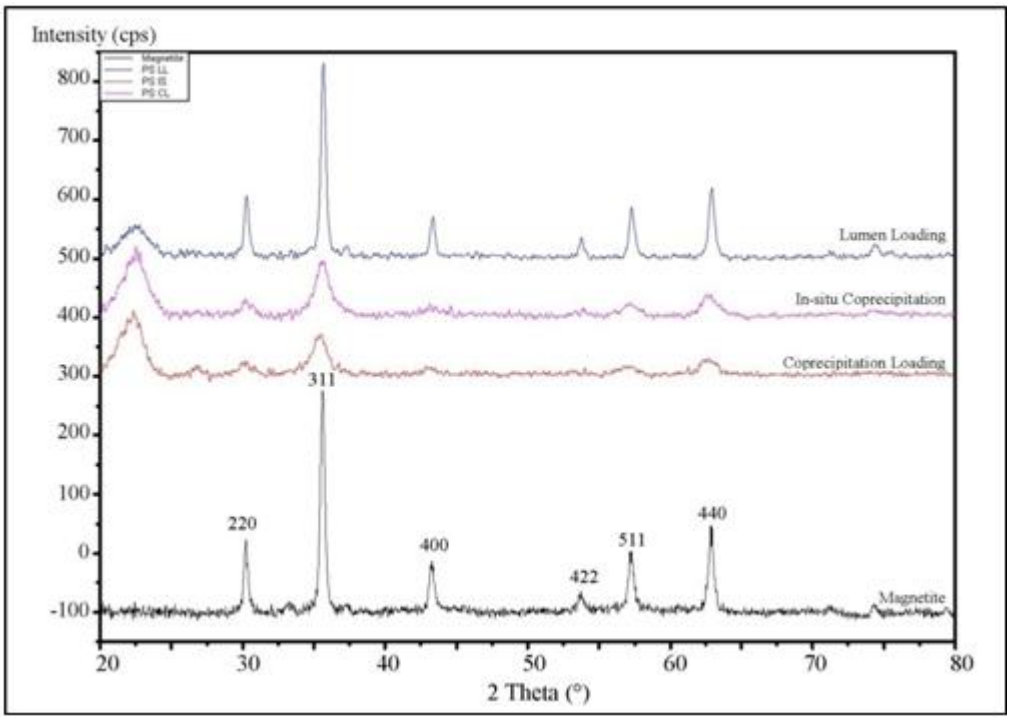

Figure 1: XRD graph for magnetite and magnetic papers from paddy straw

In Figure 1, every pattern shows clear peak at several important points and these points indicates the presence of magnetite and its purity in the sample being examined. Since no other unwanted or foreign peaks, it can be interpreted that the commercially and synthesized particles used in all techniques had high purity and homogeneity of magnetite (Fe3O4).

3.2 Morphology Analysis

Figure 2 shows the morphology images of the samples. Figure 2 (a) is the image of samples without magnetic particles and it shows the image of lumen, a hollow part that exists inside of fiber. Lumen is important because it act as a chamber to be filled with magnetic particles.

Figure 2 (b) shows the image for lumen loading samples. Here, most of the parts in the lumen are fully filled with magnetic particles while the exterior surfaces of the samples are cleaned from any foreign particles. The outer surface needs to be cleaned so that it will not interfere with the inter-fiber bonding. This situation will help to maintain the mechanical properties of the magnetic paper while still giving the paper significant magnetic properties.

In lumen loading method, during the impregnation stage, the fluid flow was very fast and in turbulence manner. This allows the magnetic particles to enter the lumens through pit. While most of the particles will remain inside, residue of the particles at the outer surface of the fiber were washed out leaving the outer surface free from fillers. However, investigation by Zakaria et al. [6] showed that it was difficult to clean out the magnetic particles from the exterior fiber surface thus reducing the fiber mechanical strength.

In-situ technique gives a new perspective in producing magnetic paper. In this method, the particles were produced chemically through in-situ method. This means that during the vigorous stirring of pulp, chemical synthesis of magnetite particles took place. After certain time interval or so called as aging time, particles grew in size and deposited on the surface of the fibres [7]. Particles in the lumen remain while most of the excess particles were washed out during the washing process.

This method produces particles around 60-80 nm [3] and can be observed as slurry image as in Figure 2 (c). On the other hand, lumen loading that was using purchased magnetite was around 50 nm. However, due to time factor, the particles tend to agglomerates. This fact make the image of particles is more pronounce in lumen loading as in Figure 2 (b) compared to in-situ technique as in Figure 2 (c) respectively.
In this project, one of the novelties was the introduction of coprecipitation loading method. This method was the combination of lumen loading and in-situ coprecipitation method. Magnetite particles were first produced chemically and after a moment, it was mixed with the pulp suspension. The dispersion of particles and behavior was almost for both in-situ and the proposed method. This can be proved by Figure 2 (d) where coprecipitation loading shows a slurry image that indicates the magnetic particles presence which was almost similar to the image obtained from in-situ method as in Figure 2 (c).

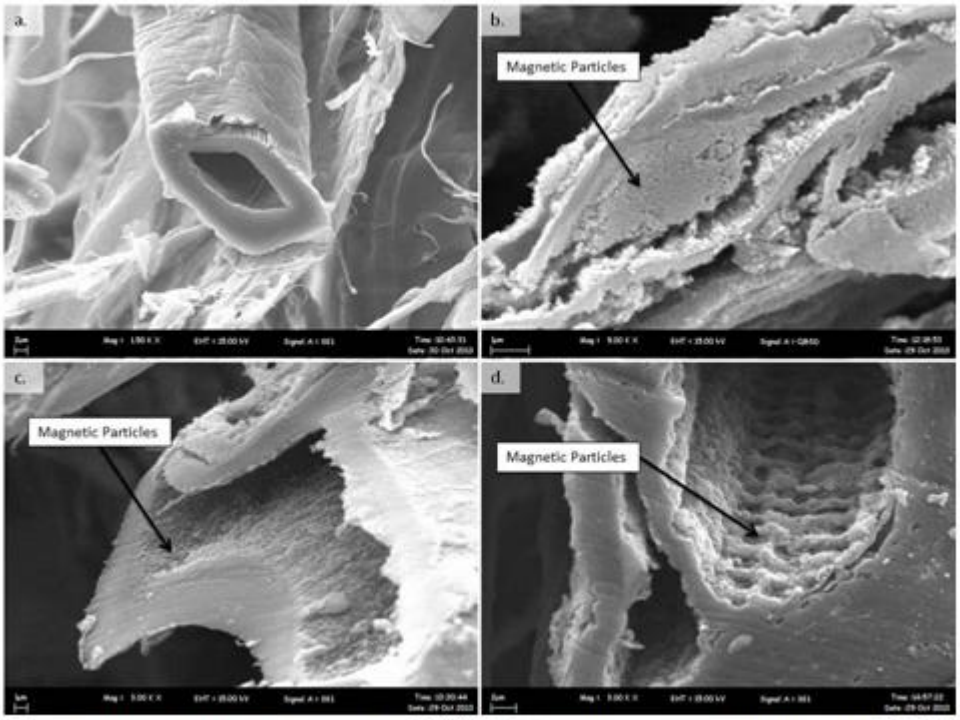

Figure 2: Image of fiber and lumen of magnetic samples: (a) unloaded paper, (b) lumen loading paper, (c) in-situ coprecipitation paper, and (d) coprecipitation loading paper.

3.3 Degree of Loading

Degree of loading gives an idea on the percentage of particles being loaded into the fiber. From Figure 3, observation shows a trend where lumen loading has the highest degree of loading with 34.4% followed by in-situ method having average value at 24.4% and the lowest degree of loading was coming from coprecipitation loading technique with 20.4%.

One of the reasons that leads to this trend was because in lumen loading technique, different sizes of particles were enforced to settle down inside the lumen and fill most of the empty spaces. This can be proved by Figure 2 (b) where the lumens are almost fully filled by the magnetic particles. However, both in-situ and coprecipitation loading had lower degree of loading because the magnetic particles that were chemically produced only laminates the surface of the lumens and the exterior surface of the fibers as shown in Figure 2 (c) and (d). Since much of the voids of the lumens were not fully filled, it leads to less degree of loading readings.

3.4 Magnetic properties

From Figure 4, observation from the hysteresis loop shows highest magnetisation is coming from lumen loading samples with the value of 34.40 emu/g. On the other hand, magnetisation from recycled paper from both in-situ and coprecipitation loading techniques shows the value of 11.18 emu/g and 8.96 emu/g respectively and a bit lower compared to the lumen loading technique. Despite of lumen loading had higher value, all magnetisation value is significantly smaller than the standard value of magnetite crystals which is 92 emu/g. Lower than this value, the samples exhibit good superparamagnetic behaviour [8].

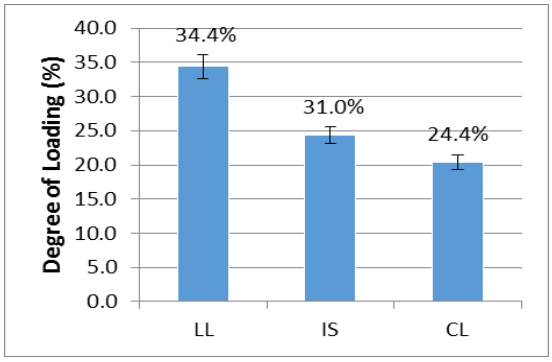

Figure 3: Degree of magnetite loading in the magnetic papers. (LL is for lumen loading, IS is for in-situ coprecipitation and CL is for coprecipitation loading methods

The low value of magnetic saturation was basically due to the size of the magnetite particles. According to Garcia et al. [9] nano-sized magnetic particles show very low of magnetic saturation (Ms) and coercivity (Hc). The smaller the nano-sized particles, the smaller the Ms and Hc will be thus leading the sample to show superparamagnetic behaviour.
From the trend, it can be interpreted that when the loading degree increase, the Ms and Hc also increases. Despite of the trend, lower loading will increase paper strength. This is due to the loss of fibre–fibre bonding sites as a result of the deposit of the magnetic particles on the fibre surface ([10]

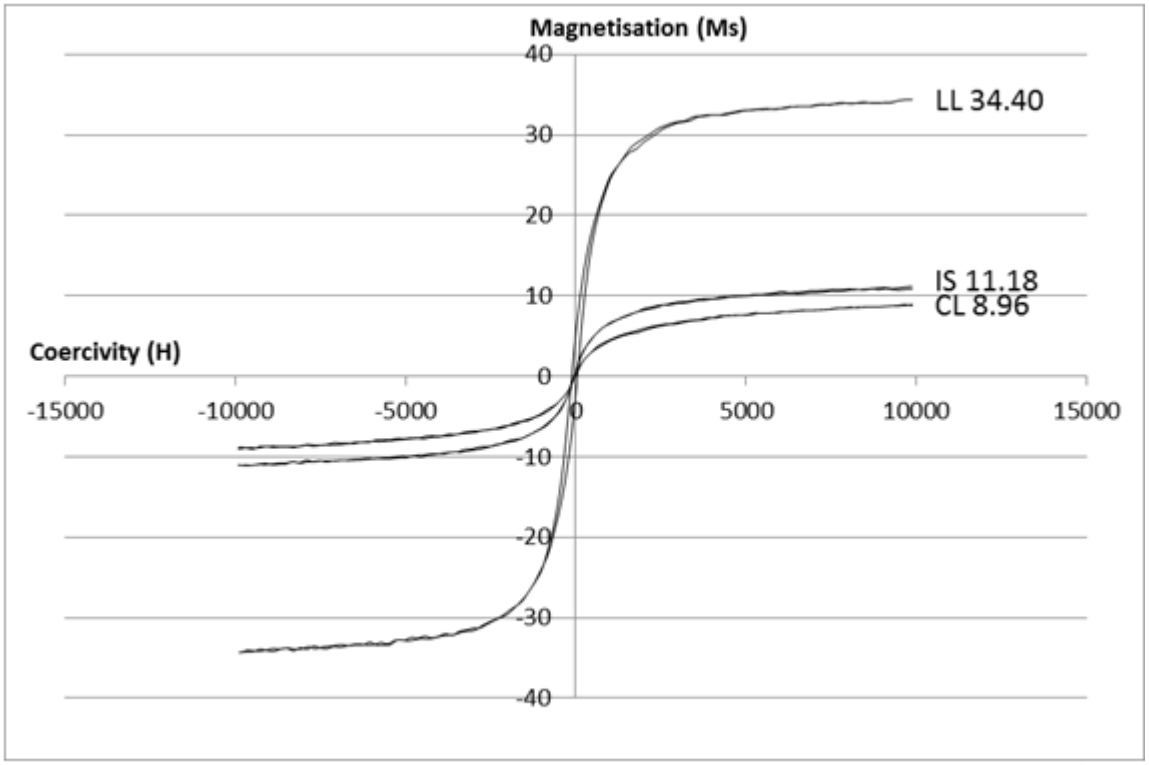

Figure 4: Hysteresis loop for magnetic samples. (LL is for lumen loading, IS is for in-situ coprecipitation and CL is for coprecipitation loading methods)

3.5 Power Consumption

The power consumption calculation was only base on the level of energy used in mechanical stirring process and heating of water during chemical synthesis. Although the calculation only shows energy needed to produce 3 g of magnetic paper, it gives general idea on how much energy needed to produce the magnetic paper.

In mechanical stirring, work done calculation was based on work done in rotating shaft. This calculation gives the value of how much work was needed in the impregnation stage of all methods. On the other hand, the heating calculation was based on inversion of how much energy was dissipated to the surrounding during the heating process. From the calculation, in-situ method used the most energy at 185.22 kW, followed by lumen loading technique at 94.48kW and lastly coprecipitation loading at 56.81 kW as portrayed in Figure 5.

In in-situ and coprecipitation loading methods, water was needed as the chemical synthesis medium and heat was for the chemical synthesis to initiate. Coprecipitation loading used six times less water than in-situ method and only for the purpose of producing the magnetic particles. However, in-situ method needs more water for the pulp to be fully immersed while the chemical synthesis took placed. More water means more heat was needed to start the chemical synthesis and needed to be maintained at elevated temperature until the synthesis complete thus making in-situ consume more energy compared to coprecipitation loading.

Lumen loading on the other hand consumes less energy than in-situ method because it only involves mechanical stirring process. Despite of this situation, it needs more work than coprecipitation loading because total stirring time was 4 hr while coprecipitation loading only need 1 hr of stirring time. During the first hour, vigorous stirring makes the total work consumption spikes high. However, during the 4 hr stirring, this stage was done at slower stirring rate at 400rpm. This makes the total work for the later 4 hours used less energy compared to the first hour.

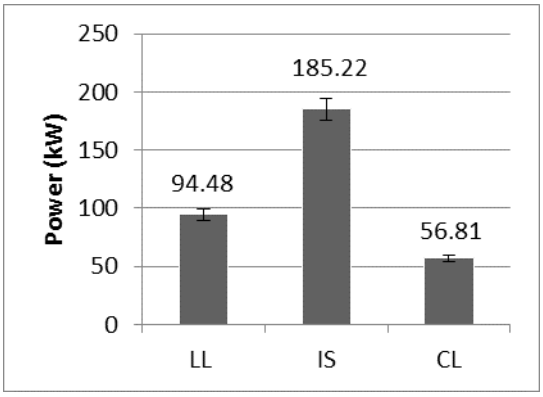

Figure 5: Power consumption of different methods to produce magnetic papers. (LL is for lumen loading, IS is for in-situ coprecipitation and CL is for coprecipitation loading methods)

4. Conclusion

From the experiment, all data shows that lumen loading had better magnetic properties compared to the in-situ coprecipitation method and coprecipitation loading. Besides that, lumen loading method also gives better filling in the lumen compared the other two method. Despite of the advantages, the proposed method had better power saving during the production with slight significant performance in

terms of magnetic and loading degree. As a conclusion, objective of the study had been achieved by introducing this new simple, cost efficient and energy saving method. Future effort should be done to enhance this new developed method in terms of magnetism and mechanical properties of the magnetic paper produced thus taking this new method to another level.

5. Acknowledgement

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