Structural and Magnetic Behaviours of Magnetite/Polyvinyl Alcohol Composite Nanofibers

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Abstract. This paper reports the nanostructural and magnetic behaviors of nano-sized magnetite/polyvinyl alcohol prepared by electrospinning route. The composition of the magnetite nanoparticles and polyvinyl alcohol were prepared from natural iron sand. The samples were maintained for pure magnetite without fibers, 0.075 g and 0.175 g for the mass compositions of magnetite in the fibers. The experimental data presented that the mass variation of the magnetite decreased the diameter of the fibers. Moreover, the higher composition of the magnetite has led to an increase in the saturation magnetization of the fibers. Such results were confirmed by the increasing content of the Fe atoms originating from magnetite particles. Morphologically, the magnetite/polyvinyl alcohol fibers were formed in continuous fibers with the diameter of 300 nm for optimum voltage of 20 kV.

Keywords: Magnetite, polyvinyl alcohol, nanofiber, electrospinning, structure, magnetization.

1. Introduction
The vast development of nanotechnology in the last couple of decades has contributed to a great influence on the expansion of both various industries and non-industries. One of the materials science disciplines being developed is the nanofiber production. Nanofiber is defined as a fiber with the diameter of 100 – 500 nm [1], with the advantages of having a small diameter, high aspect ratio, and specific surface area [2,3]. In the nanofiber production, many methods can be used. However, in the nanofiber production, the more efficient and effortless method chosen was electrospinning [4,5].

In the nanofiber production, the material component used was originated from natural iron sand. The natural iron sand was chosen as the main component to be used in the nanoparticle synthesis. Besides the effortless synthetic process and the affordable price compared to the commercial component, nanomagnetite particle is an interesting material to be developed due to its potential properties in the application of various fields such as ferrofluid, catalyst, color pigment, medical diagnosis, etc. Specifically, the polymer used to generate nanofiber was polyvinyl alcohol. Polyvinyl alcohol has a forming property, emulsifier, and an excellent adhesive. The coating of the particle surface with
polyvinyl alcohol prevents the incidence of agglomeration. Therefore, monodisperse particles were formed [6].

Specifically, this research was done to follow up the previous research. Magnetite/polyvinyl alcohol becomes crucial to be investigated because magnetite is one of the essential magnetic materials as it is considered to be an ideal material for biologically magnetic application, such as drug delivery for anti-tumor therapy, hyperthermia treatment from cancer, and an intermediary activity for medical diagnostics, due to its preeminent hydrophilic property, biocompatible, non-toxic properties, and high chemical stability [7]. Meanwhile, polyvinyl alcohol is an odorless, non-toxic polymer, soluble in water, able to create a good film plastic, having good mechanical strength and flexibility [8]. Therefore, in this study, the magnetite nanoparticles obtained from natural sand were combined with polyvinyl alcohol using electrospinning route to produce nanofibers. Finally, the magnetization and hierarchical nanostructural characters of the prepared magnetite/polyvinyl alcohol nanofibers were also investigated.

2. Methods
In this experiment, the magnetite particles were prepared by following our previous methods from natural sand [9]. The prepared magnetite particles with mass contents of 0.075 g and 0.175 g were added into tetramethylammonium hydroxide through sonication process to obtain a homogenous solution. Furthermore, the polyvinyl alcohol with the concentration of 10% was reacted with the magnetite/polyvinyl alcohol solutions using a sonication process for 3 hours to obtain the magnetite/polyvinyl alcohol solutions. The solutions were then placed in the injection pipe with a diameter of 0.8 mm. The injection rate of the solution during the electrospinning process was 10 µL/minute. The collector was covered by an aluminum foil with the voltage and flow rate of respective 100 kV and 20 kV/15 cm for 20 minutes. After obtaining fibers, the samples were kept at room temperature for 24 hours. The fibers were then characterized by means of XRD, SEM/EDX, FTIR, and VSM.

3. Results and Discussion
Figure 1 shows the XRD pattern from magnetite nanoparticles and magnetite/polyvinyl alcohol nanofiber compositied with polyvinyl alcohol. It displays the peak on the hkl plane (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) which represents the main crystal field and the formation of spinel structure on a pure magnetite crystal. The relative position and intensity from all diffraction peaks are compatible with the central cubic phase from standard magnetite powder (JCPDS 19-0629). Based on the data, it is shown that the peak intensity decreases and the peak width increases compared to the standard magnetite powder associated with a low crystallinity and a small crystal size of nanoparticle [10]. This can be dominated by the short aging time or less hygiene during the washing process, thus the solution was almost oxidized and the existence of polyvinyl alcohol affected the crystallinity of the samples. During the synthesis of magnetite, polyvinyl alcohol played an important role in the formation of Fe₃O₄, which increases the system viscosity and prevents the reactive species diffusion. Therefore, the relative magnetite crystallinity decreases due to the effect of polyvinyl alcohol [11]. The average particle size of magnetite nanoparticle was of 17.77 nm, calculated from the width peak (3 1 1) by using a Scherrer equation [12].
Figure 1. XRD patterns of magnetite a) and magnetite/polyvinyl alcohol nanofiber with magnetite mass variation of b) 0.075 g and c) 0.175 g

It is known that polyvinyl alcohol is a polymer which has an amorphous structure, in accordance with another previous work [13]. If the polymer solution is forced through a nozzle under a high electric power distribution, it gets an orientation towards the axis of the nanofiber, which can lead to better molecular dispersion and consequently increase the molecular crystallization. However, in the conducted experiment, after being tested using Cu-Kα radiation, the XRD results showed that magnetite nanoparticles dissolved in the polyvinyl alcohol solution, the crystallinity was invisible. This can be studied in plain sight that there was no formation of crystal peak in magnetite/polyvinyl alcohol nanofiber. This can be possible that the polyvinyl alcohol solution composition was more dominant than the magnetite nanoparticles.

The functional group characterization of magnetite/polyvinyl alcohol fibers was performed using Fourier Transformation Infrared Spectrometer with the electromagnetic radiation focus on the range of 4000 – 400 cm\(^{-1}\). Polyvinyl alcohol has the chemical formula of \([\text{CH}_2\text{CH(OH)}]_n\). Based on the data of Figure 2, the known wavenumber is the functional group of magnetite/polyvinyl alcohol nanofibers. Magnetite has the absorbance on the area of 424 cm\(^{-1}\) which belongs to the functional group of Fe\(^{3+}\) - O\(^2\). The absorbance on the area of 545 cm\(^{-1}\) shows the functional group of Fe\(^{2+}\) - O\(^2\). The wavenumber around 934 cm\(^{-1}\) and 815 cm\(^{-1}\) were the functional groups of O-H and C-C [14]. The result is in accordance with the research results conducted by Zahra [15]. It was also found that the C-O functional group on the wavenumber of 1097 cm\(^{-1}\) is in line with the another work [16]. The wavenumber around 1255 cm\(^{-1}\) belongs to CH functional group. The wavenumbers of 1373 cm\(^{-1}\) and 1587 cm\(^{-1}\) are mixed functional groups (CH and OH) which are related to alcohol. C=O functional group shown on the wavenumber of 1732 cm\(^{-1}\) is in line with previous works [17,18]. The absorbance in the range area of 2910-2940 cm\(^{-1}\) belongs to the CH\(_2\) functional group. The wavenumber of 3307-3342 cm\(^{-1}\) belongs to the OH functional group, according to previous work [19].
From the SEM data, we can identify the morphological form of magnetite/polyvinyl alcohol nanofibers. From the research results as shown in Figure 3.a and 3.b there are still uneven grains on the surface of the fibers because the jet impulse of an unstable electrospinning device resulted in the formation of uneven beads in the fibers. To produce nanofiber sheets with good quality, it is necessary to control morphology with the number of nanofiber granules [20,21]. Based on the EDX data on each mass variation (0.075 g and 0.175 g) magnetite nanoparticles, the Fe content on the red dot indicated the greater amount of the Fe$_3$O$_4$ nanoparticles entering the polyvinyl alcohol matrix, the higher the percentage of Fe compound. Table 1 shows the diameter size of magnetite/polyvinyl alcohol with a mass variation of magnetite. From Table 1, it is known that the more magnetite nanoparticles are mixed with polyvinyl alcohol solution, the smaller is the fiber diameter. This is because fiber binds Fe$_3$O$_4$ nanoparticles. In addition, EDX data as shown in Table 2 also explain the presence of Fe content in fiber, and in accordance with the composition of its mass variations, the mass increases from Fe, the Fe content also increases.

**Table 1.** Average of diameter particles of magnetite/polyvinyl alcohol

| Mass of magnetite | Average of diameter particle |
|-------------------|-----------------------------|
| 0.075 g           | 186.53 nm                   |
| 0.175 g           | 131.36 nm                   |
Figure 3. SEM images and particles size distributions of magnetite/polyvinyl alcohol nanofiber with magnetite mass variation of (a) 0.075 g and (b) 0.175 g

Table 2. EDX elemental content of magnetite/polyvinyl alcohol

| Element | Wt% | Element | Wt% |
|---------|-----|---------|-----|
| C       | 23.97 | C       | 22.5 |
| O       | 27.53 | O       | 28.07 |
| Na      | 8.57  | Na      | 7.56 |
| Mg      | 2.77  | Mg      | 1.71 |
| Al      | 0.82  | Al      | 0.56 |
| Si      | 26.92 | Si      | 26.51 |
| Ca      | 4.41  | Ca      | 4.26 |
| Fe      | 5.01  | Fe      | 8.83 |

The magnetization data of the magnetite/polyvinyl alcohol nanofiber is shown in Figure 4. The vibrating sample magnetometer was performed through a hysteresis curve measured under the influence of the maximum magnetic field of 1 T (tesla) at room temperature. It can be found from the hysteresis curve, the curve shows the coercive field of the magnetite/polyvinyl alcohol nanofibers is almost zero. It indicates that the samples have a superparamagnetic behavior. The detailed magnetization parameters of the samples are presented in Table 3.
Figure 4. The hysteresis curve of magnetite/polyvinyl alcohol nanofiber with magnetite mass variation of a) 0.075 g and b) 0.175 g

Table 3. Magnetization parameters of magnetite/polyvinyl alcohol nanofiber

| Mass of magnetite | Saturation magnetization | Remanent magnetization |
|-------------------|--------------------------|------------------------|
| 0.075 g           | $3.76 \times 10^4$ emu/g | $1.75 \times 10^3$ emu/g |
| 0.175 g           | $14.0 \times 10^4$ emu/g | $2.53 \times 10^3$ emu/g |

Based on Table 3, it is found that the more mass of magnetite added, the more the saturation and remanent magnetizations. The magnetization value is also affected by the level of particle agglomeration so that the saturation magnetization value is higher than the lower level of agglomeration. The decrease in magnetization is likely due to the following reasons: First, the presence of polyvinyl alcohol attached to the surface of magnetite nanoparticles, several studies showed that non-collinear structure is originated from the trapped surface to spin and due to coated by matrix (polyvinyl alcohol) on the surface of iron oxide (magnetite) which effects on the decrement of magnetic moment in the nanoparticle. Second, the effect of the particle size is too small. With the decrease of particle size and the increase of matrix distribution on the surface area, the magnetic molecule on the surface does not have a complete coordination and the magnet spin also encountered some issues [22,23].

4. Conclusion

Based on the conducted study, it was found that the increased in the structure of magnetite/polyvinyl alcohol nanofibers was in line with the increased mass of magnetite. On the contrary, the decreased diameter of nanofiber showed the increased mass of magnetite. This is caused by magnetite which acts as a filler bound by polyvinyl alcohol which acts as a matrix. It is also supported by the magnetization properties, the increased mass of magnetite correlates with the increased magnetization properties. However, the XRD data showed that when magnetite were composited into polyvinyl alcohol, it would lower the crystallinity of magnetite due to the polymer itself having an amorphous structure. Thus, the relative magnetite crystallinity decreases due to the polyvinyl alcohol effect. However, the FTIR data showed there was a magnetite bound in the fiber.
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