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Preparation and Structural Characterization of Nanosized PVA/Fe$_3$O$_4$ Fibers

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Abstract. Nowadays, nanosized Fe$_3$O$_4$/PVA fibers become promising materials in various advanced applications. Therefore, preparation and characterization become the essential aspects before applying the nanosized Fe$_3$O$_4$/PVA fibers in specific targets. In this work, we reported the preparation of the nanosized Fe$_3$O$_4$/PVA fibers from iron sand using co-precipitation and electrospinning techniques. The data analysis of the XRD data for the Fe$_3$O$_4$ particles presented a single phase of magnetite in cubic structure and crystallized in nanometric scale. The data of the SEM/EDAX characterizations revealed that the Fe$_3$O$_4$ nanoparticles have already been joined into the PVA fibers. In conclusion, the experimental result showed that the higher the Fe$_3$O$_4$ nanoparticles that enter into the PVA, the less the size of the fibers.

Keywords: Fe$_3$O$_4$, nanofiber; PVA, nanoparticles, Indonesian iron sand.

1. Introduction

Studies on magnetic nanomaterials have been exclusively conducted in various aspects, from the synthesis approaches to the functional applications. In particular, magnetic-based nanofibers preparation follows a line of investigation, either in laboratory scale or industrial scale, since they perform excellent characteristics in terms of thermo-mechanical and chemical stabilities [1]. Accordingly, numerous efforts have been completed to produce nanofiber materials with various shapes, sizes, and functions.

Considering the nanofibers-based nanomaterial applications, Fe$_3$O$_4$ nanofiber is one of the magnetic materials that has been extensively developed in the past few years, mainly related to its promising application as a smart magnetic material. The smart magnetic feature of Fe$_3$O$_4$ nanofiber is driven from its ability to be easily controlled under the influence of external magnetic fields and its adjusting superiority to external magnetic fields. At the same time, the selection of smoothly controlled biocompatible matrices is another research interest in producing nanosized Fe$_3$O$_4$ fibers. From many experimental results, polyvinyl alcohol (PVA) is found to meet the criteria as the biocompatible matrix for Fe$_3$O$_4$ nanofibers [2]. The demanding task is to reduce the synthesis expense of nanosized Fe$_3$O$_4$/PVA. Therefore, we introduce the use of Indonesian iron sand to produce highly crystallized magnetite-Fe$_3$O$_4$ as the reinforcement of Fe$_3$O$_4$/PVA nanometer-sized fibers.
There are numerous well-known synthesis approaches of Fe$_3$O$_4$/PVA composites such as template-assisted [3], self-assembly [4], phase separation [5], and electrospinning [6,7]. Above all, electrospinning has extra advantages because it is simple, practical, and efficient [7]. The electrospinning method can produce nanofibers on a large scale, and diameter of the fiber can be controlled in various sizes [8]. Such method is also able to prepare materials directly from a polymer solution especially in the form of nonwoven fibers [9]. In this present study, we describe the electrospinning-based Fe$_3$O$_4$/PVA nanofibers from Indonesian iron sand. To complete our knowledge, fundamental investigation, particularly on their structural characteristics, is also reported.

2. Materials and Methods
The black and shiny Fe$_3$O$_4$ powder extraction from the natural iron sand taken from Pasur Beach Blitar, Indonesia was reported elsewhere [10]. The purified iron sand was initially immersed in HCl at room temperature to obtain a solution containing FeCl$_3$ and FeCl$_2$ prior to NH$_2$OH titration. The pH of the solution was controlled to normal condition to acquire pure Fe$_3$O$_4$ from the drying process for an hour. The pure Fe$_3$O$_4$ powders, with mass variations of 0.100 g (named as sample A), 0.125 g (named as sample B), and 0.150 g (named as sample C), were then homogeneously reacted with tetra-methyl ammonium hydroxide (TMAH) through a sonication process. PVA solution with 10% concentration was mixed with the Fe$_3$O$_4$ powders and sonicated for 3 hours. In the electrospinning method, PVA/Fe$_3$O$_4$ solution was put into an injection of 0.8 mm in diameter with a capacity of 10 mL at an injection rate of 10 µL/min. In this work, the collector was covered with aluminum foil set at an electric field at 20 kV/15 cm for 20 minutes to obtain nanofibers. The formed nanofibers were left for 24 hours to produce homogenous nanosized Fe$_3$O$_4$/PVA fibers. Finally, the samples were characterized by FTIR (Fourier transform infrared) spectrometer, EDX (Energy Dispersive X-Ray) spectroscopy, SEM (Scanning Electron Microscopy), and XRD (X-Ray Diffractometer) to respectively study the functional groups, size, the composition of constituent elements, morphology of particles, and their crystallographic characteristics.

3. Results and Discussion

3.1. Functional Groups of Nanosized Fe$_3$O$_4$/PVA Fibers
The characterization of functional groups of nanosized Fe$_3$O$_4$/PVA fibers was carried out using a Fourier transform infrared spectrometer with electromagnetic radiation in the range of 400 – 4000 cm$^{-1}$. The absorption peaks in various wavenumbers representing the functional groups of nanosized Fe$_3$O$_4$/PVA fibers are shown in Figure 1. The Fe$^{3+}$-O$^2-$ and Fe$^{2+}$-O$^2-$ ionic interactions, indicating the Fe$_3$O$_4$ formation, are detected at 424 cm$^{-1}$ and 545 cm$^{-1}$, respectively. The absorption peaks at 934 cm$^{-1}$ and 815 cm$^{-1}$ indicate the O-H and C-C functional groups as reported by Shehap and Akil [11] and Marand et al. [12]. Furthermore, the C-O interaction is found at 1097 cm$^{-1}$ [13]. Infrared absorption peaks at 1255 cm$^{-1}$, 1373 cm$^{-1}$ and 1587 cm$^{-1}$ refer to the mixture of CH and OH bindings. The C=O stretching is depicted by the absorption at 1732 cm$^{-1}$ [11]. Meanwhile, the presence of CH$_2$ and OH molecules are respectively labeled by the absorptions near 2920 cm$^{-1}$ and 3310 cm$^{-1}$ [14].

3.2. Crystallographic Characteristics of Nanosized Fe$_3$O$_4$/PVA Fibers
Figure 2 shows the XRD patterns of the pure Fe$_3$O$_4$ nanoparticles and the composites of Fe$_3$O$_4$/PVA nanofibers. It reveals that for the XRD pattern of the pure Fe$_3$O$_4$ nanoparticles, only the magnetite spinel cubic structure is formed as the crystalline phase. The diffraction peaks of the magnetite refer to the Bragg planes of (220), (311), (400), (422), (511) and (440). The sequence of 2-theta positions and their corresponding intensities is perfectly matched with the Fe$_3$O$_4$ powder diffraction data (JCPDS code: 19-0629). Our Fe$_3$O$_4$-based XRD patterns show broader peaks than that of the JCPDS 19-0629 data, implying that we have a smaller crystalline size [15]. During the composite preparation, PVA plays an essential role in the formation of Fe$_3$O$_4$ by increasing the viscosity system and preventing the reactive species diffusion. Therefore, the decrease of crystallinity of Fe$_3$O$_4$ is reduced originating from PVA.
addition [16]. In this work, the particle size of the Fe₃O₄ powder is 21.54 nm, calculated from the full width at half maximum diffraction peak at (311) using the Scherrer equation [17].

**Figure 1.** IR patterns of nanosized Fe₃O₄/PVA fibers: a) sample A, b) sample B, and c) sample C.

**Figure 2.** XRD patterns of pure Fe₃O₄ nanoparticle and nanosized Fe₃O₄/PVA fibers: a) sample A, b) sample B, and c) sample C.
In addition, PVA is a polymer showing an amorphous structure [18]. In the electrospinning process, polymer solutions are forced through the nozzle under a high electrical charge, and they are oriented towards the nanofiber axis. This leads to better molecular dispersion and consequently increases the molecular crystallization. The composites XRD patterns, in this study, show amorphous phases. There are no Fe$_3$O$_4$ diffraction peaks found in the XRD patterns. It is due to the domination of PVA solutions in the nanosized Fe$_3$O$_4$/PVA composites.

3.3. Morphological and Elemental Characteristics of Nanosized Fe$_3$O$_4$/PVA Fibers

The SEM-captured morphological characteristics of the produced composites are depicted in Figure 3. Although Fe$_3$O$_4$ agglomerations on the surface of the composites, all the SEM images have confirmed the formations of nano-sized Fe$_3$O$_4$/PVA fibers with the fiber sizes of 181.9 nm, 169.6 nm, and 151.1 nm respectively for sample A, B, and C. The nano-sized Fe$_3$O$_4$/PVA fibers produced in this study are relatively smaller than other reports. The electrospinning synthesis of nano-sized Fe$_3$O$_4$/PVA fibers prepared by other methods was reported to have an average diameter around 400 nm [1] and 230 nm [6]. In the electrospinning process, polymer concentration, applied voltage, and plate size are very crucial to prepare fine fibers. In addition, controlling morphology with the number of nanofiber granules is also vital [19, 20].

![SEM images](image1.png)

**Figure 3.** SEM images and selected area (as marked in the circles) for EDX characterization of (a) sample A, (b) sample B, and (c) sample C.

| Sample A | Sample B | Sample C |
|----------|----------|----------|
| Element  | wt%      | at%      | Element  | wt%  | at%  | Element  | wt%  | at%  |
| C        | 13.73    | 21.93    | C        | 27.95  | 42.84  | C        | 22.08  | 33.10 |
| O        | 36.18    | 43.39    | O        | 20.22  | 23.27  | O        | 33.76  | 38.00 |
| Na       | 08.89    | 07.42    | Na       | 06.97  | 05.58  | Na       | 08.70  | 06.82 |
| Mg       | 02.92    | 02.30    | Mg       | 01.93  | 01.46  | Mg       | 02.38  | 01.76 |
| Si       | 32.43    | 22.15    | Si       | 36.36  | 23.83  | Si       | 28.39  | 18.20 |
| Ca       | 05.84    | 02.80    | Ca       | 06.58  | 03.02  | Ca       | 04.70  | 02.11 |

From EDX characterization, it is known that there is no Fe content in the selected SEM images (red circles). However, from the FTIR data, Fe-O functional groups are detected. This “contradiction” is probably because (a) the PVA is too dominating so that Fe$_3$O$_4$ nanoparticles in the red circle area are found to be extremely small or (b) the grain size of Fe$_3$O$_4$ nanoparticles is too small [21]. Based on such result, it becomes a new challenge for developing a new method by employing natural iron sand as the
main precursor in producing the nano-sized Fe₃O₄/PVA fibers with a high homogeneity to be applied in various fields.

4. Conclusion
In conclusion, reducing the synthesis expense of nanosized Fe₃O₄/PVA fibers can be acquired by extracting Fe₃O₄ nanoparticles from Indonesian iron sand, precisely from Pasur Beach Blitar. The particle size of the as-prepared Fe₃O₄ is 21.54 nm. Combining the Fe₃O₄ with PVA by means of electrospinning approach leads to diminishing the crystalline phases in the system, i.e., no diffraction peaks are detected in the nanosized Fe₃O₄/PVA fibers. The existence of Fe₃O₄ nanoparticles, though it was not revealed by the XRD data, was confirmed by the FTIR spectra especially from the Fe³⁺-O²⁻ and Fe²⁺-O²⁻ interactions at the respective wavenumber at 424 cm⁻¹ and 545 cm⁻¹. Finally, the synthesized of nanosized Fe₃O₄/PVA fibers have an average diameter of 167.6 nm.

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References
[1] Beachley V and Wen X 2009 Effect of electrospinning parameters on the nanofiber diameter and length Mater. Sci. Eng. C 29 663–668
[2] Wang S, Sun Z, Yan E, Yuan J, Gao Y, Bai Y, Chen Y, Wang C, Zheng Y and Jing T 2014 Magnetic composite nanofibers fabricated by electrospinning of Fe₃O₄/gelatin aqueous solutions Mater. Sci. Eng. B 190 126–132
[3] Rambo C R, Recouvreux D O S, Carmiatti C A, Pitlovanciv A K, Antônio R V and Porto L M 2008 Template assisted synthesis of porous nanofibrous cellulose membranes for tissue engineering Mater. Sci. Eng. C 28 549–554
[4] Chang G, Zhu X, Li A, Kan W, Warren R, Zhao R, Wang X, Xue G, Shen J and Lin L 2016 Formation and self-assembly of 3D nanofibrous networks based on oppositely charged jets Mater. Des. 97 126–130
[5] Zhang H, Liu X, Yang M and Zhu L 2015 Silk fibroin/sodium alginate composite nano-fibrous scaffold prepared through thermally induced phase-separation (TIPS) method for biomedical applications Mater. Sci. Eng. C 55 8–13
[6] Wang S, Wang C, Zhang B, Sun Z, Li Z, Jiang X and Bai X 2010 Preparation of Fe₃O₄/PVA nanofibers via combining in-situ composite with electrospinning Mater. Lett. 64 9–11
[7] Xingxing C, Xuebin Z, Hao S and Yi F 2014 Fabrication of Magnetic Fe₃O₄ Nanotubes by Electrospinning Rare Met. Mater. Eng. 43 2330–2334
[8] Fang J, Wang X and Lin T 2011 Functional applications of electrospun nanofibers (InTech–Open Access Publisher)
[9] Tunáň M, Antoch J, Kula J and Chvojka J 2014 Estimation of fiber system orientation for nonwoven and nanofibrous layers: local approach based on image analysis Text. Res. J. 84 989–1006
[10] Taufiq A, Rachman Putra E G, Pratapa S and others 2015 Nano-structural studies on Fe₃O₄ particles dispersing in a magnetic fluid using X-ray diffractometry and small-angle neutron scattering Materials Science Forum vol 827 (Trans Tech Publ) pp 213–218
[11] Shehap A M and Akil D S 2016 Structural and optical properties of TiO₂ nanoparticles/PVA for different composites thin films Int. J. Nanoelectronics and Materials 9 17-36
[12] Marand Z R, Farimani M H R and Shahtahmasebi N 2014 Study of magnetic and structural and properties of Zn doped Fe₃O₄ nanoparticles synthesized by co-precipitation method for biomedical application Akash. Ginekol. (Sofija) 15 238–47
[13] Zucechiati P, Mitri E, Kenig S, Billé F, Kourousias G, Bedolla D E and Vaccari L 2016 Contribution of Ribonucleic Acid (RNA) to the Fourier Transform Infrared (FTIR) Spectrum of Eukaryotic Cells Anal. Chem. 88 12090–8
[14] Khandanlou R, Ahmad M, Shameli K and Kalantari K 2013 Synthesis and Characterization of Rice Straw/ Fe₃O₄ Nanocomposites by a Quick Precipitation Method *Molecules* **18** 6597–607

[15] Yee W A, Nguyen A C, Lee P S, Kotaki M, Liu Y, Tan B T, Mhaisalkar S and Lu X 2008 Stress-induced structural changes in electrospun polyvinylidene difluoride nanofibers collected using a modified rotating disk *Polymer* **49** 4196–203

[16] Jayakrishnan P and Ramesan M T 2017 Synthesis, Characterization, Electrical Conductivity and Material Properties of Magnetite/Polyindole/Poly(vinyl alcohol) Blend Nanocomposites *J. Inorg. Organomet. Polym. Mater.* **27** 323–33

[17] Zhang P, Wang B, Williams G R, Branford-White C, Quan J, Nie H and Zhu L 2013 Self-assembled core-shell Fe₃O₄@SiO₂ nanoparticles from electrospun fibers *Mater. Res. Bull.* **48** 3058–64

[18] Fattah A A A, Elfadly A M, Naggar A Y, Ebiad M A and A. Mandor M 2013 Physicochemical characterization of poly (ethylene glycol) with molecular weights (8000, 12000) by inverse gas chromatography *Int. J. Acad. Res.* **5** 226–31

[19] Nuryantini A Y, Ekaputra M P, Munir M M, Suciati T and others 2014 Sintesis nanoserat poli (vinil alkohol) dalam bentuk lembaran dengan pemintal elektrik multi nozel dan kolektor drum *J. Pendidik. Fis. Indones.* **10** 186–193

[20] Zheng J-Y, Zhuang M-F, Yu Z-J, Zheng G-F, Zhao Y, Wang H and Sun D-H 2014 The Effect of Surfactants on the Diameter and Morphology of Electrospun Ultrafine Nanofiber *J. Nanomater.* **2014** 1–9

[21] Singh G, Jalandhara D and Yadav K 2016 Effect of grain size on optical properties of iron oxide nanoparticles p 020409