Deformation of Ferrogel Based on *Carboxyl Methyl Cellulose (CMC)/Polyvinyl Alcohol (PVA)* Hydrogel

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Abstract. Ferrogel is a smart material that combines the elastic properties of hydrogel and magnetic behavior from the filler of magnetic materials. In this work, ferrogel was fabricated through a freezing-thawing process with matrix materials of Carboxyl Methyl Cellulose (CMC)/Polyvinyl Alcohol (PVA) and a filler of magnetite. Magnetite nanoparticles were successfully synthesized by using a coprecipitation method at room temperature. The magnetite filler was investigated via X-ray Diffractometer (XRD) and Transmission Electron Microscopy (TEM), respectively, to analyze the structure and morphology of the magnetite. Based on the XRD analysis, the magnetite nanoparticle was matched by ICSD number of 9013529 and has an average particle size of about ~ 9.67 nm. This result is well confirmed by the TEM characterization that showed an average particle size of 9.32 nm. Furthermore, ferrogel was explored by using a Vibrating Sample Magnetometer (VSM) and an electromagnetic instrument to measure the magnetic properties and deformation of ferrogel, respectively. The VSM analysis showed that CMC/PVA hydrogel-based ferrogel has a superparamagnetic behavior due to its magnetization remanent and field coercivity that is close to zero. Interestingly, the deflection of Fe₂O₄/CMC/PVA ferrogel under the effect of the external magnetic field exhibited a good response. The deformation of ferrogel significantly increased from 4.9 cm to 7.0 cm as the filler of magnetite in the ferrogel was increasing from 14 wt% to 22 wt%. This phenomenon could be improved and explored to change the ferrogel into an artificial muscle by engineering the concentration and magnetite response in the CMC/PVA hydrogel.

Keywords. Carboxyl methyl cellulose (CMC), deformation, ferrogel, hydrogel, magnetite, and polyvinyl alcohol (PVA).
1. Introduction
Ferrogel is a leading material of which compositions offer elastic and magnetic properties. Ferrogel based on polyvinyl alcohol (PVA) polymer is superparamagnetic and non-toxic so that it could be used for biomedical applications, such as artificial muscle and drug delivery [1]. For such applications, the nanomagnetic particles function as fillers that are added to the PVA hydrogel. The nanomagnetic particle is exciting to be developed since it has enormous potential to be used for biomedical, hyperthermia, artificial muscle, bandage, and so forth [2]. A combination of polymer with a magnetic material causes a change in ferrogel morphology when it is a magnetic field [3].

Numerous investigations on ferrogel using various polymer materials and fabrication methods have been reported. Teixeira et al [4] studied the effects of sodium alginate on sodium alginate-based ferrogel material combined with magnetic material as its filler. They have successfully characterized the water absorption in the gel networks. An inclusion of magnetic filler into alginate gel polymer networks can result in a higher level of water absorption and thermal stability than a pure alginate gel.

On previous research, the researchers had also successfully synthesized and characterized polyacrylic acid (PAA)/polyvinyl alcohol (PVA)-based magnetic hydrogel using Fe₃O₄ for the magnetic filler via a freezing-thawing (F-T) method [5]. The F-T process influences the distribution pattern of the magnetite particles inside the PAA/PVA hydrogel. The results of the experiment showed that the F-T process that is repeated for seven times is mostly optimum for the magnetite distribution inside the PAA/PVA hydrogel. However, research on magnetite behavior in Carboxyl Methyl Cellulose (CMC) and Polyvinyl Alcohol (PVA)-based ferrogel has rarely been reported.

Thus, fabrication of CMC/PVA matrix polymer-based ferrogel is challenging to be performed. This research focused on the deformation behavior of the nanomagnetic particles in the CMC/PVA hydrogel matrix to provide additional references regarding its potential application for artificial muscle. The selection of CMC and PVA matrix in this report cannot be separated from their superior characteristics. PVA is a polymer material with a high viscosity, solubility, and translucence. The excellence of CMC is shown by its high viscosity and resistance to low humidity. Also, CMC is stable, even more, stable than metal, though (almost as tough as cast iron), wear resistance, and it has stable chemical elements at high temperature, high strength and resistance, and corrosion resistance.

2. Materials and methods

2.1. Synthesis of Nanomagnetic Particle and Ferrogel
This research used iron sands taken from Wedi Ireng Beach Banyuwangi East Java for the primary material of the magnetic filler. The Fe₃O₄ nanoparticles were synthesized using a coprecipitation method at room temperature. The synthesis result of the magnetite was then prepared to be filler for ferrogel fabrication.

The fabrication of ferrogel was started by combining the hydrogel matrix materials, i.e., CMC, PVA, and water in a specific ratio. The hydrogel materials were mixed on a magnetic hot plate using a stirrer at approximately 70 °C to 90 °C. When the hydrogel matrix had been mixed up well, the magnetite filler was then distributed into the hydrogel via a stirring process until it achieved a dark-colored mixture. The last stage of the ferrogel fabrication was putting the mixture of hydrogel and magnetic filler into a mold to be further processed via a freezing-thawing method.

2.2. Nanomagnetic Particles and Ferrogel Characterizations
The magnetite filler obtained by the coprecipitation method was then characterized by using an X-ray Diffractometer (XRD) and Transmission Electron Microscopy (TEM). A magnetite test by XRD was done to identify the structural pattern, lattice parameter, and crystal size. TEM characterization aimed to identify the morphology of the magnetite filler while confirming the results of the XRD test.

CMC/PVA hydrogel-based ferrogel was characterized by using a Vibrating Sample Magnetometer (VSM) and magneto-elasticity test equipment. The VSM test was carried out to identify the pattern of the ferrogel magnetization representing the magnetite filler distributed in the CMC/PVA hydrogel.
The magneto-elasticity test equipment was used to identify the mechanical characteristics of the ferrogel, especially the behavioral deviations of the CMC/PVA-based ferrogel.

3. Results and discussion

3.1. XRD Pattern of Magnetite Filler

Figure 1 presents the profile of the Fe$_3$O$_4$ particles made from iron sand characterized via an XRD. The search-match results showed that all of the sample peaks had been well detected and the formed diffraction patterns were dominated by Fe$_3$O$_4$, which was in accordance with the data of Inorganic Crystal Structure Database (ICSD) model number 9013529. Further, the hkl field position of the Fe$_3$O$_4$ particle has successfully been confirmed by using the OriginPro-8 software.

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

(1)

Figure 1. Position of hkl field for iron sand separation

The analysis of the Fe$_3$O$_4$ particle size based on the XRD results has been conducted successfully (Figure 2) through the Debye Scherer equation below.
Where $K$ is constant, $\lambda$ is X-ray wavelength, and $\beta$ is the full width at half maximum of the peak [6]. The calculation of the average Fe$_3$O$_4$ crystal size through the Scherer equation utilized the principle of the relationship between the crystal size and the $2\theta$ position, the half-width of the peak, and the wavelength of the XRD source. The Fe$_3$O$_4$ particle size obtained from such equation was approximately 9.67 nm. Such result is lower than that of the previous research, i.e., around 12 nm [7]. However, the magnetite particle size in this research almost corresponds to the magnetite particle size reported by Saravanan et al [8] who stated that magnetite particle size of around 7 nm to 9 nm.

Further, Figure 3 shows the synthesized Fe$_3$O$_4$ diffraction pattern after being analyzed by using Rietica software. Based on the results of the refinement, the Fe$_3$O$_4$ particle size was 9.46 nm with an $R_{wp}$ value of around 14.59 and $\chi^2$ of 0.042. Further, the average size of the particle conforms to the Debye Scherer analysis as has been explained beforehand.

3.2. TEM Characterizations
TEM characterization was done to further characterize the magnetite filler morphology and size before being combined with the CMC/PVA hydrogel. The morphology of the magnetite particles that had been successfully characterized (Figure 4) showed a moderately uniform pattern of the particle size. Such results were further analyzed using ImageJ software, and the analysis results presented that the average particle size of the Fe$_3$O$_4$ was 9.32 nm. Such results confirm the average particle size shown by the XRD results either via a refinement by Rietica software showing a 9.46 nm average value or by Scherer equation showing a 9.67 nm average value.
Besides, such average particle size of Fe$_3$O$_4$ is approaching the average value obtained by Shen et al [9], i.e., ~ 8 nm and El Ghador et al [10] of 10.59 nm. They claimed that their research resulted in uniform cube-shaped and monodisperse nanoparticles.

3.3. VSM Data Analysis

The magnetization characterization of the CMC/PVA hydrogel-based ferrogel via VSM had been successfully conducted. The obtained data from such VSM characterization were in the forms of magnetization remanent value ($M_r$), coercivity magnetization value ($H_c$), and saturation magnetization value ($M_s$) as displayed in Table 1.

Figure 5 shows the results of the VSM characterization refinement of the ferrogel through two treatments that employed a different number of F-T process repetitions, namely 5 and 6 times. Based on Figure 5, the ferrogel with 5 repetitions of the F-T process has the highest saturation magnetization value of 22.16 emu·g$^{-1}$. Meanwhile, the ferrogel with 6 repetitions of the F-T process has a saturation magnetization value of 21.27 emu·g$^{-1}$. Furthermore, the remanent and coercivity magnetization of the two ferrogel samples obtained its minimum value, and it tended to have a relatively low value that is close to zero. In accordance with the report [11], such results indicated that CMC/PVA hydrogel-based ferrogel has a superparamagnetic behavior.

The superparamagnetic behavior indicated that the magnetite filler is used for controlling ferrogel magnetization. Also, the CMC/PVA-based ferrogel has a relatively high value of saturation magnetization, namely around 21.27 emu·g$^{-1}$ (with 6 times F-T) and 22.16 emu·g$^{-1}$ (with 5 time F-T) when compared with the saturation magnetization of PVA-based ferrogel of 6.52 emu/g [7] and Polyacrylamide-based ferrogel of below 0.5 emu/g with a magnetite percentage range of around 0.75 % from its weight [12]. A high level of saturation magnetization of CMC/PVA-based ferrogel is influenced by, among others, the magnetite behavior of the CMC/PVA hydrogel. The magnetite filler tends to experience aggregation caused by its polymeric property. CMC polymer has a high viscosity level that is not affected by low humidity. Such fact requires the magnetite particles to consume high energy to be fairly distributed inside the semi-crystalline networks of the CMC/PVA hydrogel. Therefore, it prevents the particle distribution that results in aggregation causing an increase in the saturation magnetization level.

Figure 4. Fe$_3$O$_4$ morphology shown by TEM characterization
Figure 5. VSM Profile of Fe$_3$O$_4$/CMC/PVA Ferrogel based on the number of freezing-thawing cycles repetition, i.e., 5 (a) and 6 times (b). The red line is experimental data fitting by the Langevin function (L).

Table 1. Magnetization value of Fe$_3$O$_4$/CMC/PVA Ferrogel by a LangevinMod model (LM)

| Sample | $M_r$ (emu·g$^{-1}$) | $M_s$ (emu·g$^{-1}$) | $H_c$ (T) | $\mu$ (10$^{-19}$ J/T) | $D$ (nm) |
|--------|------------------|------------------|----------|------------------|--------|
| FT 5x  | 0.064            | 22.162           | 0.016    | 8.9              | 6.72   |
| FT 6x  | 0.007            | 21.273           | 0.081    | 9.2              | 6.89   |

The results of VSM characterization and refinement on the average size of the magnetite particle have also been successfully obtained. Table 1 shows the average size of the magnetite particles contained in CMC/PVA hydrogel.

$$D = \left(\frac{18k_B T}{\pi \rho M_s} \chi_i\right)^{1/3}$$ (2)

Where $\chi_i$ is the initial susceptibility of the sample, $\rho$ is the mass of the magnetite filler, i.e., 5670 kg m$^{-3}$ (based on the Rietica analysis), and saturation magnetization (emu·g$^{-1}$).

The refinement showed a smaller average particle size compared with those taken from the data of XRD and TEM characterizations. It is due to two factors. First, the powder sample morphology used in the XRD and TEM characterizations while the VSM characterization employed gel sample morphology after inclusion into the CMC/PVA polymer networks. Second, the use of a dark-field mode on VSM [14] caused construction of a slightly smaller particle dimension than that caused by the bright-field mode for sample morphology observation. The results of the VSM refinement also resulted in the value of magnetic moment shown in Table 1. Based on such data, the filler magnetic moment value of Fe$_3$O$_4$ conforms to the filler magnetic moment value of Fe$_3$O$_4$ nanoparticles that was reported by Prajapat et al [15 – 17]. According to the theoretical review, the average particle size is already proportional to the particle magnetic moment on a single domain area. A magnetic nanoparticle size can be classified to be in a single domain area if it is below a critical size [18]. Also, according to a report by Tong et al [19], a critical size of a particle is around 25 nm. With such value, the magnetite filler used in this research is categorized into a single domain. Hence, the bigger the particle size, the more the magnetic moment that could be obtained. It is in excellent agreement with the data obtained from the samples with 5x FT and 6x FT. However, a correction was performed on
the data of the 6x FT sample saturation magnetization, where the sample showed a reduction when its magnetic moment increased.

3.4. Data Analysis of Mechanical Properties

The potential application for artificial muscle of CMC-PVA-based ferrogel could be observed from its magnetic field threshold mechanical response under the influence of an external magnetic field. The deflection of the magnetic field threshold investigation on ferrogel is illustrated in Figure 6. The ferrogel was made static on its upper point, and it experienced a position changing as its reaction against an external magnetic field from its lower point.

Figure 6. Deformation of Fe₃O₄/CMC/PVA ferrogel; a). Before; b). After an external magnetic field was given

The observation results of ferrogel responses to an external magnetic field are presented in Figure 7 and Table 2 by showing the threshold value of the magnetic field. Such values represent the minimum force of the magnetic field that is necessary to move the deviation to its maximum position. The ferrogel deflection will suddenly increase a moment after it goes beyond the threshold value of the magnetic field. Based on the results of the experiment, the threshold value of the magnetic field experienced a decrease along with the increasing magnetite filler concentration contained in the ferrogel. Such results conform to the results reported in previous studies conducted by Sunaryono et al [20] and Ramanujan et al [21]. Table 2 shows a 14 wt% filler concentration, with up to 26.2 mT magnetic field threshold value of the ferrogel. Such results are slightly higher than those previously reported in which the magnetic field threshold of the PVA polymer-based ferrogel was recorded as around 12.6 mT for 15 wt% magnetite filler concentration (Sunaryono et al) [20] and 15.2 mT for 10 wt% concentration as reported by Ramanujan et al [21].

A higher amount of the magnetic field threshold in a 14 wt% concentration than the previous report (Sunaryono et al) [20] showed that the magnetic response of the CMC/PVA-based ferrogel is much weaker than PVA-based ferrogel. It is possible under the influence of a CMC polymer that functions as a matrix in the ferrogel. A high viscosity level of CMC polymer will increase the ferrogel density, which results in a compact semi-crystalline space of the CMC/PVA polymer in ferrogel. Such condition will result in a lower magnetic response of the CMC-PVA-based ferrogel compared with the PVA-based ferrogel.

Besides the magnetic field threshold report, an analysis of the ferrogel mechanical response has also been confirmed through the ferrogel deformation test via an electromagnetic instrument. Table 2
presents the characterization results of the CMC/PVA-based ferrogel deformation with a variation of magnetite filler concentrations. The deviation pattern of ferrogel increased along with the increasing content of magnetite filler in the ferrogel. Therefore, the higher the Fe$_3$O$_4$ filler concentration, the more sensitive the ferrogel to any changes from the external magnetic field. It is in good agreement with the report stating that the concentration of Fe$_3$O$_4$ nanoparticles significantly affects the resultant changes in the composite material [22].

![Figure 7. The magnetic field threshold value versus the Fe$_3$O$_4$ filler concentration in CMC/PVA-based ferrogel.](image)

Ferrogel sensitivity is a crucial variable in the application of artificial muscle. In this research, the mechanical properties of the ferrogel could result in deformation from 4.9 cm to 7 cm from the average magnetite fillers of 14 wt% until 22 wt%. Such results were the maximum deformation of ferrogel as its response to the influence of an external magnetic field. Thus, the CMC/PVA-based ferrogel is a leading material with a high density and sensitivity that is potential for several technology engineering applications.

| Deflection (cm) | Magnetic Threshold (mT) | Filler Concentration (wt%) |
|-----------------|-------------------------|--------------------------|
| 4.9             | 26.2                    | 14                       |
| 5.2             | 22.4                    | 16                       |
| 5.5             | 17.5                    | 18                       |
| 6.0             | 13.2                    | 20                       |
| 7.0             | 11.1                    | 22                       |

4. Conclusions
The characterization of a magnetite nanoparticle that is used as filler in the CMC/PVA-based ferrogel composite has successfully been conducted, and it shows a moderately uniform pattern of the particle size with an average particle size of 9.32 nm. Such results are well confirmed by the results of the XRD analysis. The mechanical characteristic showed a declining magnetic threshold of the ferrogel
from 26.2 mT to 11.1 mT along with an increasing filler concentration of 14 wt% to 22 wt%. Furthermore, the deformation of ferrogel also resulted in an optimum deviation pattern from 4.9 cm to 7 cm from the average magnetic filler of 14 wt% to 22 wt%. Such results showed the effectiveness of magnetite filler in carrying an inclusion of the magnetic property in the CMC/PVA polymer networks. Besides, the matrix characteristics of the CMC/PVA materials also affect the level of the ferrogel density that is potential for artificial muscle application.

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