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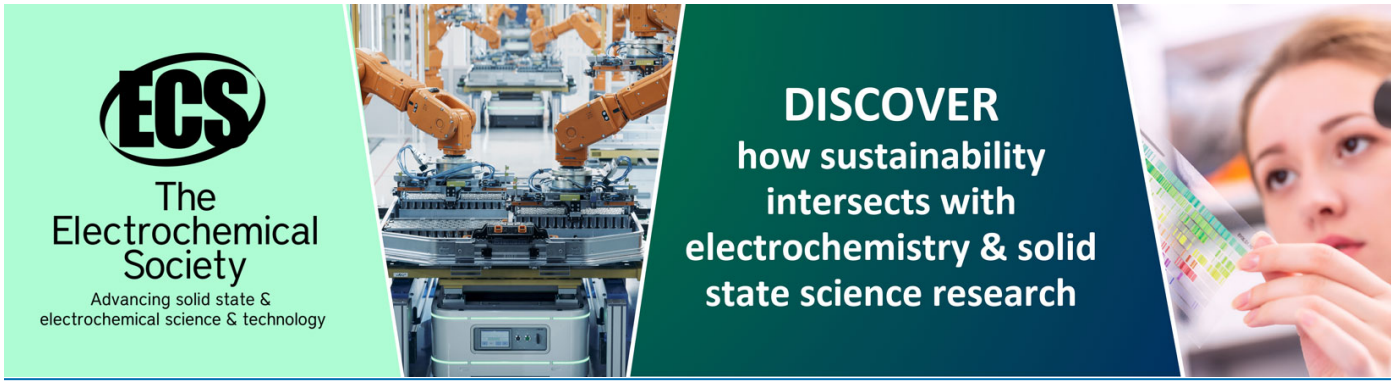

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Synthesis and Characterization of Magnetic Elastomer based PEG-Coated Fe_3O_4 from Natural Iron Sand

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Abstract. Magnetic elastomer nanocomposite based PEG-coated Fe_3O_4 with silicone rubber binder have been prepared from natural iron-sand by using coprecipitation method. The samples were characterized by using X-ray Diffractometer, X-ray Fluorescence, Fourier Transform Infra-Red, tensile strength test, and Vibrating Sample Magnetometer to analyze the physical and magnetic properties. We observed that all samples were formed by single phase cubic spinel magnetite (Fe_3O_4) crystalline structure. The atomic bonding analysis by FTIR showed that the C-O-C and C-H ordering were understood as the PEG – Fe_3O_4 bonding characteristics. We have observed that the Young modulus of elastomer based PEG-coated Fe_3O_4 slightly decreased compared to the natural iron-sand based elastomer. The magnetic properties of PEG-coated Fe_3O_4 were known to be magnetically softer with the lowest coercivity without losing its magnetization saturation value. We propose that the PEG-coated Fe_3O_4 is a promising candidate to be applied as magnetorheological elastomer due to a good mechanical and magnetic characteristic and also promising as microwave absorbing materials.

Keywords: Magnetic elastomer, nanomagnetite, PEG-6000, coprecipitation.

1. Introduction

Natural iron sand is one of the popular minerals which has a ferromagnetic behavior. This case is because the iron sand is mainly composed of hematite (Fe_2O_3) and magnetite (Fe_3O_4) phases. In nanometer size, the magnetite has an interesting property called as superparamagnetic which has a broad range of applications such as biosensor, magnetic hyperthermia, and drug delivery system[1–5]. The superparamagnetic characteristic is achieved if the magnetite particle size approaches its critical value that produces single domain magnetic and zero coercivity field [2].

The surface coating such as PEGylation is one of the standard methods to make the magnetic nanoparticles stable from aggregation. Recent publications stated that number and type of functional groups of PEG as the coated polymer on nanoparticle magnetic surface was affected to the stabilization of the colloidal system especially for biomedical applications [6-7]. Therefore, understanding any route to highly effective synthesis the PEG-coated nano-magnetite became emerged to produce high quality stable magnetic nanoparticles.

However, very little reports have been known for investigating the nanoparticle stabilization effect in the fabrication of magnetic elastomers. The variation of loaded magnetic nanoparticles in a silicone based elastomer has increased the compressive modulus for about 300% [8]. Another research

reported that in the latex based magnetic elastomer, the composition of magnetite was affected by the magnetic properties and also its mechanical properties [9].

In this paper, we have investigated the effect of PEG-coated magnetite nanoparticles by using co-precipitation method from natural iron-sand for magnetic elastomer application. Characterizations performed were XRD, XRF, FTIR, and tensile strength tests to analyze the mechanical and microstructural characteristics. Magnetic properties were studied by hysteresis curve built by vibrating sample magnetometer.

2. Experimental Method

Natural iron-sand from Bingei River, North Sumatera was employed in this experiment. Iron-sand was milled by using planetary ball mill for 15 hours to get the pure powder until passes #200 standard-meshes sieve (≤ 76 μm). From the XRD analysis (Figure 1), we observed that the milled natural iron sand was composed by single phase Fe_3O_4 (magnetite). The co-precipitation method was performed by mixing 16 g of magnetite (from milled iron sand) with HCl (37%, 12M) until 100 mL. The solution was stirred for 90 minutes at a temperature of 70 °C. PEG-6000 crystal from Merck was melted and mixed with magnetite solution (with a ratio of 1:3 v/v) and stirred for 60 minutes at temperature of 70 °C. Ammonia (NH_4OH) was added to the solution with a ratio of 1:5 v/v and stirred again for 90 minutes (70 °C) until the precipitate is settled down driven by a permanent magnet. The sediment of magnetite-PEG was washed with distilled water until reaching the normal pH (~ 7). The sludge was then dried at a temperature of 80 °C for 24 hours. The co-precipitation process reaction is compiled as follow [10,11]:

$$3Fe_3O_{4(s)} + 8HCl_{(l)} \rightarrow 2FeCl_{3(l)} + FeCl_{2(l)} + 3Fe_2O_{3(s)} + 3H_2O_{(l)} + H_{2(g)}$$
$$2FeCl_{3(l)} + FeCl_{2(l)} + H_2O_{(l)} + 8NH_4OH_{(l)} \rightarrow \text{nano-}Fe_3O_{4(s)} + 8NH_4Cl_{(l)} + 5H_2O_{(s)}$$

To make an elastomer, PEG-coated magnetite as a filler blended with silicone rubber RTV-683 with fixed binder composition of 20 wt.%. The elastomer was cast with a thickness of 8.5 mm. For comparison, iron-sand and uncoated Fe_3O_4 based elastomers were also produced by using the same composition of silicone rubber. The natural iron-sand, uncoated and PEG-coated Fe_3O_4 powders were characterized by using Rigaku Smartlab x-ray diffractometer (XRD), Torontech x-ray fluorescence (XRF), Shimadzu Fourier transform infrared spectroscopy (FTIR), and Dexing VSM250 vibrating sample magnetometer (VSM). The tensile strength of elastomer of PEG-coated Fe_3O_4 with silicone rubber binder was characterized by using the universal testing machine.

3. Results and Discussion

The X-ray diffraction pattern of milled iron-sand, uncoated and PEG-coated Fe_3O_4 is displayed in Figure 1. By using the semi-quantitative analysis from Match by Crystal Impact and using COD database, we have analyzed that all samples are composed by single-phase magnetite (Fe_3O_4) with the cubic spinel crystalline structure. The lattice constant of $a = b = c = 8.419$ Å is depicted by (220), (311), (400), (442), (511), and (440) planes. It means that the encapsulation of Fe_3O_4 by PEG using co-precipitation process does not affect the crystalline structure.

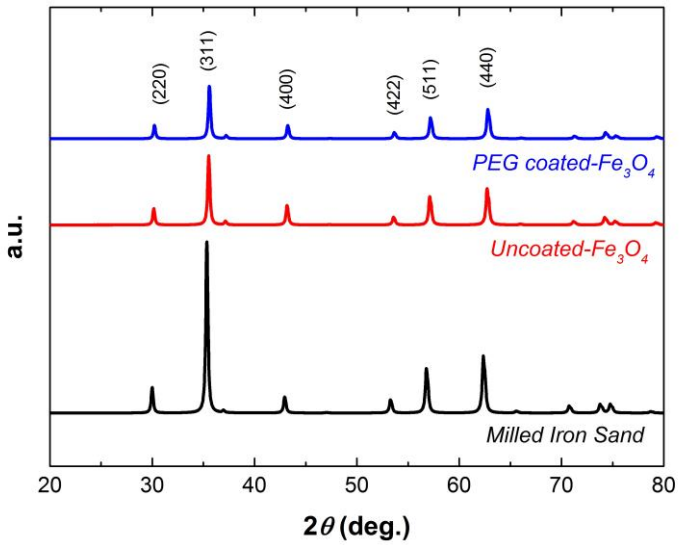

Figure 1. X-ray Diffraction pattern (XRD) of milled iron-sand, uncoated and PEG-coated Fe_3O_4 samples.

Comparison of elemental composition from raw material to uncoated and PEG-coated magnetite nanoparticles is shown in Table 1 which was performed by XRF analysis. The table shows that the co-precipitation process was affected by elemental composition especially for uncoated and PEG-coated nanoparticles. It shows that the Fe composition was slightly increased after the chemical process. On the other side, some impurities such as Ti, Si and Al were decreased. It means that the chemical process was slightly purified and thrown out other elements during co-precipitation process.

Table 1. XRF analysis of milled iron-sand, uncoated Fe_3O_4 and PEG-coated Fe_3O_4 samples.

Element	Iron-sand (at.%)	Nano-Fe_3O_4 (at.%)	PEG-Fe_3O_4 (at. %)
Fe	91.82	93.35	93.58
Ti	4.11	3.83	3.91
Si	1.83	0.61	0.49
Al	1.01	0.95	0.81
Mn	0.78	0.79	0.82
V	0.34	0.36	0.33
Others	0.11	0.11	0.06
Total	100.00	100.00	100.00

The Fourier transform infrared (FTIR) analysis was performed in this experiments to analyze atomic bonding from magnetic nanoparticles and PEG as the coated materials. FTIR curve as shown in Figure 2 shows that the transmittance peak for natural iron sand and uncoated-Fe_3O_4 from co-precipitation did not change for all wavenumber. On the other hand, the PEG-coated Fe_3O_4 transmittance curve shows new peak addition at 1095.5 and 2337.7 cm^{-1}. We believed that this peak contributed from PEG bonding as shown in Table 2. We found that there was a shifting peak at Fe-O bonding region, from 578.6 cm^{-1} to 570.9 cm^{-1} for natural iron-sand and PEG-coated (and uncoated) Fe_3O_4, respectively. This Fe-O shifting peak was suggested that the particle size of Fe_3O_4 had already reduced during the chemical process and this also predicted that the PEG had already coated the Fe_3O_4 particles [12-13]. Another sign that PEG already coated the magnetic nanoparticle is the emerging of C-O-C and C-H bonding with stretch vibration at 1095.5 and 2337.7 cm^{-1}.

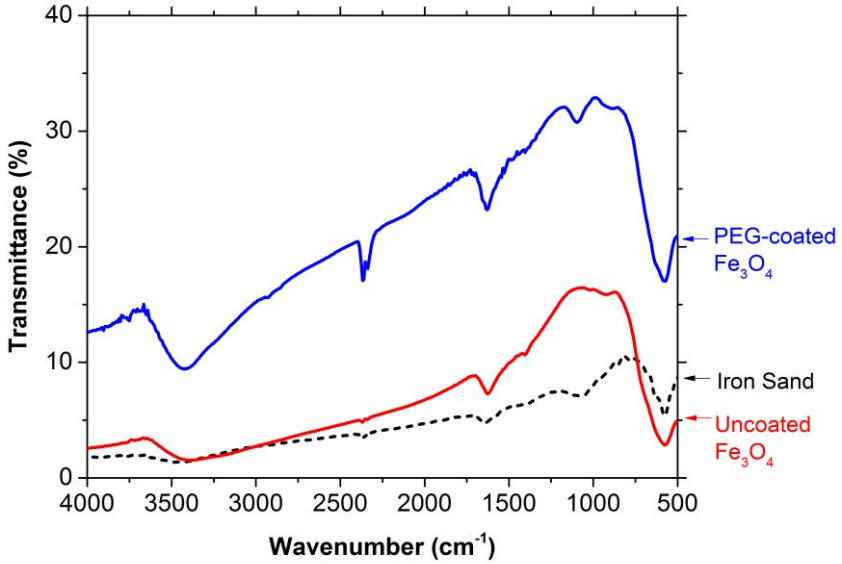

Figure 2. FTIR analysis of the samples: milled iron-sand, uncoated-Fe_3O_4, and PEG-coated Fe_3O_4.

Table 2. FTIR bond analysis of the materials.

Bond	Wave number, cm^{-1}			Vibration
	Milled iron sand	Uncoated Fe_3O_4	PEG-coated Fe_3O_4	
(Fe-O)	401.19	401.19	401.19	Stretch
(Fe-O)	578.64	570.93	570.93	Stretch
(C-O-C)	-	-	1095.57	Stretch
(O-H)	1635.64	1627.92	1627.92	Bend
(C-H)	-	-	2337.72	Stretch
(O-H)	3425.58	3387.00	3425.58	Stretch

All powder samples were embedded in a silicone rubber (20 wt.%) to make magnetorheological elastomers. To analyze the mechanical properties of the elastomers, we have performed a tensile test for all samples according to ASTM D3039. The tensile test result is displayed in Figure 3. The Young modulus was calculated from the stress-strain graph which produced the values of 0.47, 0.53, and 0.32 MPa for natural iron-sand, uncoated nano-Fe_3O_4, and PEG-coated Fe_3O_4 composites, respectively. We observed that the chemical process which produced a refined particle of Fe_3O_4 did not change the mechanical properties of the elastomers significantly. As shown in Figure 3, the Young modulus of iron sand and uncoated Fe_3O_4 elastomers did not relatively change. On the other hand, the PEG-coating to Fe_3O_4 particles was affected to slightly decrease the Young modulus. This effect is expected to be caused by the densification of the PEG-coated magnetic nanoparticles. The decrease of particle size was known to reduce the pore and strengthen the bonding between filler and matrix in nanocomposite materials [14]. In this case, the increase of bonding strength is related to the increase of the elastomer stiffness.

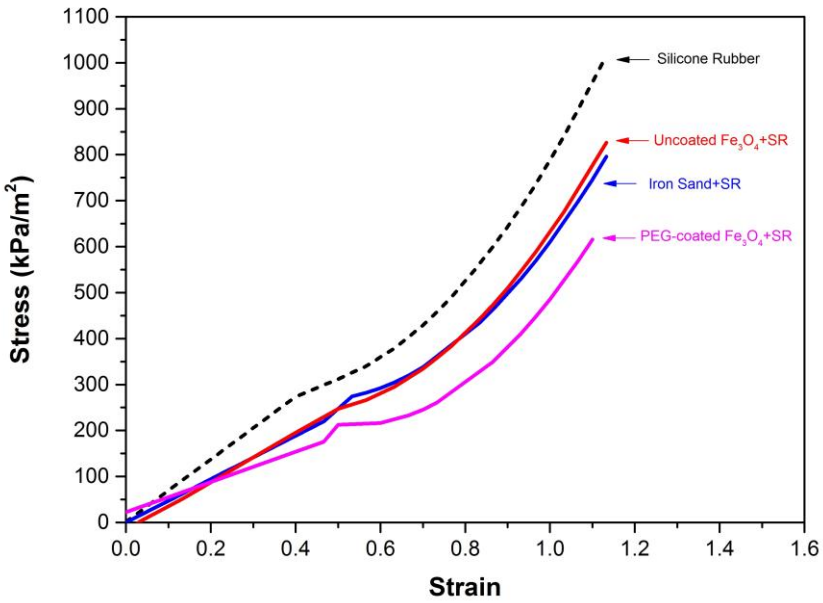

Figure 3. Stress-Strain analysis of elastomer material made of 100% silicone rubber (SR), 20% SR + uncoated Fe_3O_4, 20% SR + PEG-coated Fe_3O_4, and 20% SR + Milled iron-sand

To understand the magnetic characteristics in the form of powders and as magnetic elastomer of PEG-coated Fe_3O_4, we have performed hysteresis analysis by vibrating sample magnetometer as shown in Figure 4. We observed that the co-precipitation products which are uncoated and PEG-coated Fe_3O_4 showed a decrease of magnetic remanence and coercivity field compared to the milled iron-sand. This effect was closely looked to the superparamagnetic phenomena. PEG-coated Fe_3O_4 sample depicted the lowest coercivity both in the form of powder and a magnetic elastomer with the value of 85.9 and 78.4 Oe, respectively. The magnetic characteristics summary of milled iron-sand, uncoated and PEG-coated Fe_3O_4 is displayed in Table 3. It shows that the PEG-coated Fe_3O_4 behaves differently compared to the natural iron-sand and uncoated Fe_3O_4 in the form of powder and elastomer. The coercivity of PEG-coated Fe_3O_4 decreases while increasing trend is observed for milled iron-sand and uncoated Fe_3O_4. It means that the polymeric coated nanoparticle was stabilized by the nanoparticle distribution in the form of elastomer materials and prevents it to be aggregated during elastomer fabrication. Therefore PEG-coated Fe_3O_4 elastomer is a promising candidate to be a good magnetorheological elastomer due to the good mechanical and magnetic characteristics.

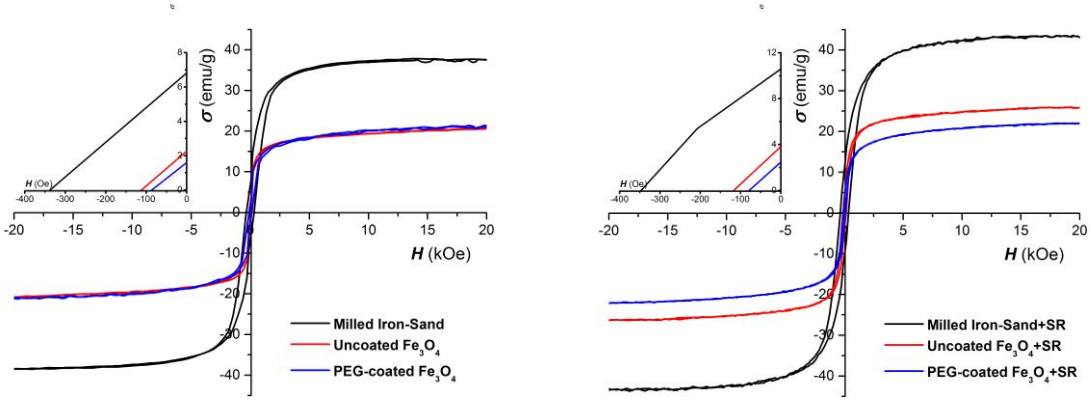

Figure 4. Hysteresis Curve of milled iron-sand, nano-Fe_3O_4 and PEG-coated Fe_3O_4 at powder condition (a) and as a magnetic elastomer (b).

Table 3. Magnetic characteristics of the milled iron-sand, uncoated and PEG-coated Fe_3O_4 materials in the form of powder and magnetic elastomer.

Sample Form	Sample Type	σ_s (emu/g)	σ_r (emu/g)	H_{ci} (Oe)
Pow□er	Milled Iron-Sand	37.5	6.8	340.7
	Uncoated Fe_3O_4	20.6	2.2	113.1
	PEG-Coated Fe_3O_4	21.2	1.6	85.9
Elastomer	Milled Iron-Sand + SR	43.2	13.4	353.6
	Uncoated Fe_3O_4 + SR	25.7	3.8	119.3
	PEG-Coated Fe_3O_4 + SR	21.8	2.4	78.4

4. Conclusion

Magnetic elastomer based on PEG-coated Fe_3O_4 has been prepared by co-precipitation method from natural iron sand. The milled natural iron-sand and uncoated nano-Fe_3O_4 were also prepared as the compared materials. The XRD analysis showed that all samples were composed by single phase magnetite, Fe_3O_4. The co-precipitation process contributed to the reduction of particle size to the nanometer scale (< 100 nm) and vanishing impurity from the natural iron-sand. The addition of PEG to the chemical process was to prevent aggregation of the nanoparticles by coating the particle surfaces. The atomic bonding analysis by FTIR showed that the C-O-C and C-H ordering in the PEG-coated which is known as the PEG – Fe_3O_4 bonding characteristics. We have observed that the elastomer based PEG-coated Fe_3O_4 has decreased the Young modulus compared to the natural iron-sand based elastomer. The magnetic characteristic of PEG-coated Fe_3O_4 was known to be magnetically softer with the lowest coercivity without losing its magnetization saturation value. We propose that the PEG-coated Fe_3O_4 elastomer is a promising candidate to be a good magnetorheological elastomer due to the good mechanical and magnetic characteristics and also promising to be microwave absorber materials.

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