Magnetic properties $\alpha$-Fe$_2$O$_3$ Filled MWNT/PolyVinyl Alcohol Composites Film

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Abstract. Magnetic properties of $\alpha$-Fe2O3 partly filled MWNT/Polyvinyl Alcohol (PVA) composites film have been studied by Raman spectroscopy, Fourier Transform InfraRed (FTIR) spectroscopy, Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometer (VSM), Four Point Probe (FPP). The Composite films were prepared by simply mixing between $\alpha$-Fe2O3 – filled Multiwalled Carbon Nanotube(MWNT) dispersed in Sodium Dodecyl Sulphate (SDS) with 10% PVA solution for 4 variation concentrations with a total volume 5 ml. The result of Raman Spectroscopy on precursor sample showing the existence of $\alpha$-Fe2O3 phase and MWNT. From FTIR spectroscopy on the film samples observed the attachment of the PVA with iron oxide and MWNT. The paramagnetic properties of the samples film were investigated by means of Vibrating Sample Magnetometer (VSM). The higher value of magnetoresistance ratio was +40% on the sample with percolation threshold $P_c=0.51$ wt%. The interaction between $\alpha$-Fe2O3 filled MWNT in matrix polymer PVA made shrinkage or decreased the localization length inside the grain of composites film.

1. Introduction
In order to realize the vision of printable magnetoelectronic, polymer nanocomposites containing CNT or MWNT have great attention due to the unique nearly one dimensional (1D) electronic properties. The structure of CNT allows electrons to be transported along the tubes without scattering. It is also interesting to filled CNT/MWNT with some magnetic nanoparticle such as Fe,Ni during the synthesis.[1], even with rare earth metal 4-f. Furthermore to compose with conductive polymer such as PANI [2-3], elastomer, [4-5] and studied its some physical properties included magnetotransport. Since Chakraborty et al.[6] used MWNT-PVA composite film to study the magnetoresistance of the composite film and found MR ratio around +1.2% at RT, with 10% MWNT loading. The aims of this work is to study the effect of $\alpha$-Fe$_2$O$_3$ filled(or trapped) into MWNT in insulator matrix PVA to the magnetic properties and magnetoresistance (MR) of nanocomposite films. It suggesting that to minimize MWNT loading in composite was important,-because high filling in MWNT made intrinsic metallic transport dominant,-therefore the trapped $\alpha$-Fe$_2$O$_3$ nanoparticles magnet in MWNT might be improves the properties of magnetoresistance due to the interaction behavior between iron $\alpha$-Fe$_2$O$_3$-MWNT with matrix insulator polymer PVA.
2. Experimental

2.1. Materials and Methods

Multi-Walled Carbon Nanotube (MWNT) used in this work were produced by catalytic chemical vapor deposition (CCVD) from Nanostructured & Amorphous Materials, Inc. USA. The MWNT have purity of 95%+, inner diameter of 5-10 nm and length of 10 – 30 µm. The polymer matrix polyvinyl alcohol (PVA) with ≥ 99% purity was supplied by Sigma Aldrich. Iron nitrate (Fe(NO$_3$)$_3$.9H$_2$O) in crystal form with purity ≥ 98.5%, surfactant material Sodium Dodecyl Sulfate (SDS) with purity ≥ 98.5%. To open the capping of MWNT an amount of MWNT were heated by furnace at 400 °C for 30 minutes. MWNT/SDS solution, was then transferred to a beaker glass containing over saturated Fe(NO$_3$)$_3$.9H$_2$O. As prepared solution was then stirred for 27 hours at room temperature until the black slurry was developed. The last step, the sample was purified by annealing of 160°C in ambient condition for five hour to decompose Fe(NO$_3$)$_3$.9H$_2$O. The composite films were prepared by simply mixing α-Fe$_2$O$_3$-MWNT dispersed in Sodium Dodecyl Sulphate (SDS) with 10% PVA solution for 4 variation of concentration with a total volume of 5 ml. The solution was then poured into a petry dishes to dry naturally over night.

2.2. Characterization

Observations of nanostructure precursor of iron-filled MWNT was performed by using TEM at GadjahMada University. Characterization of the samples were performed at the Advanced Materials Laboratory of PSBTM – BATAN by using Raman spectroscopy (Senterra Raman Spectroscopy) to determine phase in the precursor sample, FTIR spectroscopy to determine bonding in the composite film. Magnetic properties were performed by means vibrating sample magnetometer (VSM-Oxford 1.2Tesla) for obtained M-H curve. Magnetoresistance ratio was measured by Jandel type Four Point probe(FPP) with attach square 4x4 mm$^2$ film on Si(100) substrate.

3. Results and Discussion

Determination of the precursor phase was performed by using Raman spectroscopy technique with results as shown below. Fig. 1 shows that the peaks at 219, 284, 398, 472, 590 cm$^{-1}$ indicates the presence of α-Fe$_2$O$_3$ phase [7]. Two peaks at 219 and 472 cm$^{-1}$ arise from $A_{1g}$ mode of Fe-O bands. The other peaks was attributed to $E_g$ mode of Fe-O band. While the peaks of the D-band and G-band in 1289 and 1586 cm$^{-1}$ are the peak of MWNT [8]. The more higher ratio of D/G intensity for sample post treatment compare to original MWNT was indicating the presence of defect in the crystal structuresp$^3$ carbons due to the acid treated on MWNT.

![Figure 1. Raman spectrum of sample α-Fe$_2$O$_3$-MWNT post heated at 160°C and original MWNT.](image-url)
The observation of nanostructures on the sample was performed by using Transmission Electron Microscope (TEM) at Gadjah Mada University. The observation condition are 800,000 times for magnification at a voltage of 120kV. Figure 2 shows that the phase of α-Fe₂O₃ (represented by black color) could enter the nanotube with the inner diameter of about 20 nm and the outer diameter of about 50 nm. The phase of α-Fe₂O₃ was impregnated not only through the hollow tube but also through the damaged all of MWNT when interacting with nitric acid [9].

The inclusion of this phase into MWNT through hollow capillary is due to the nature of MWNT during the mixing process took place. The opened cap of MWNT used in this study allowed the entry of α-Fe₂O₃ at 400ºC. This result is slightly different from the techniques developed by Valinejad et al.[10] by heating the MWNT at the temperature of 700ºC and 810ºC, which generate much less the percent loss of material MWNT.

![Figure 2](image)

**Figure 2.** TEM image and SAD from α-Fe₂O₃-MWNT sample at 800.000 x exposure and Voltage = 120kV. Length of bar is 100 nm.

The precursor magnetic properties was performed by using VSM at Advanced Material Laboratory PSTBM. Fig. 3 shows that it precursor sample has ferromagnetic properties with Ms = 0.18 emu/gr, Mr=0.08 emu/g, and Hc=135mT at the external field H=1 Tesla (10kOe).

![Figure 3](image)

**Figure 3.** Magnetization curve M-H from powder precursor α-Fe₂O₃-MWNT post heat treatment 160ºC

This value was comparable with the report by Zilli et al. [11] for iron nanoparticle trapped in MWNT. However, the curve shows the existence of hysteresis indicating the presence of ferromagnetic spin ordering of α-Fe₂O₃ nanoparticles. Kordas et al.[12] reported the presence of Fe nanoparticles trapped in the CNT will bring hysteresis on the measurement results of the M-H curve.
We have developed four variation samples with fraction filler/matrix PVA as follows;

| Sample code | Filler/Matrix (vol./vol%) | Weight% |
|-------------|--------------------------|---------|
| D1          | 1 : 19                   | 0.24    |
| D2          | 1 : 9                    | 0.51    |
| D3          | 1 : 4                    | 1.10    |
| D4          | 1 : 1                    | 4.60    |

The quality of composites film was determined by FTIR spectroscopy as described below.

![FTIR spectra](image)

**Figure 4.** (a) FTIR spectrum of α-Fe2O3/MWNT film at different variation concentration filler/matrix for 600-3100 cm\(^{-1}\); (b) FTIR spectrum for wave number range 3100-4000 cm\(^{-1}\)

The strong signal at 1185 cm\(^{-1}\) and 1225 cm\(^{-1}\) was the proof of C-O bond. These two peaks were clear evidences of successful attachment of PVA on the MWNTs surface. Also, the peak at around 2850-2960 cm\(^{-1}\) on IR curve (Fig.4(a)) was indication of CH/CH\(_2\) bonding of PVA. A shown in Fig. 4(a), the content of iron oxide filled/MWNT increased and the band at 636.5 cm\(^{-1}\) and 1084 cm\(^{-1}\) increased in intensity. These results suggest a strong interaction between iron oxide filled/MWNT and the polymer matrix with the O-H group while the filler fraction increasing. A broad peak as shown in Fig. 4(b) at around 3320 cm\(^{-1}\) verified the presence of a hydroxyl group of –OH, as shown for samples
D1 and D2, also suggesting that broadening the peaks related to existence of uncoated iron oxide/MWNT. Furthermore, these peak become sharper and stonger at around 3400-3500 cm\(^{-1}\) for samples D3 and D4 when fraction filler iron oxide-MWNT with matrix PVA increasing. 

The magnetic properties measurement was performed by using VSM for the square film with sizes 4x4 mm\(^2\) and magnetic external field perpendicular to film surface up to 10 kOe. All the film sample has paramagnetic properties, except the sample D1 (filler/matrix weight ratio 0.24\%) as shown in Figure. Magnetic saturation of D1 sample is around -0.01 emu/g which representing diamagnetic properties from MWNT-PVA film [13]. The other hand, saturated magnetization Ms at H=10 kOe for samples D2, D3 and D4 were 0.04, 0.05 and 0.11 emu/g, respectively. This paramagnetic properties curve shows indicating the presence and degree of random spin interaction between $\alpha$-Fe\(_2\)O\(_3\) nanoparticles trapped inside MWNT where induced by the coated of PVA film matrix.

**Figure 5.** Magnetization curve M-H for composite films with variation volume fraction filler (iron oxide-MWNT)/matrix (PVA)

Magnetoresistance (MR) is defined as the difference between the value of resistance of materials in zero magnetic and maximum magnetic field. MR ratio measurement was conducted by using the Four Point probe (FPP) at magnetic external up to H=8kOe. The MR ratio of $\alpha$-Fe\(_2\)O\(_3\)-MWNT/PVA thin film on the top of Si (100) were 16\%, 40\%, 13.6\% and 6.2\% for positive magnetic field direction with variation volume ratio filler/matrix as shown in Table 2. But this MR behavior were not reversible relatively at low loading filler samples D1 and D2 while the external magnetic field applied in the opposite direction. In the other hand, the MR ratio was reversible for higher volume fraction filler at sample D3 and D4. As shown in Fig.5. The reasonable explanation might be this phenomenon related to the loading volume fraction of $\alpha$-Fe\(_2\)O\(_3\)-MWNT in matrix polymer PVA. The filler $\alpha$-Fe\(_2\)O\(_3\)-MWNT were well dispersed with more strongly bonding condition with insulator polymer PVA as explained from FTIR spectrum in Fig.4(b). Furthermore, the highest result of MR ratio at 0.51wt% filler/matrix might be related to percolation threshold of carbon nanotube in polymer PVA as predicted by Bauhofer et al.(2009). This result is higher than the phenomenon of magnetoresistance (MR) in MWNT / PVA composite film[6], where MR ratio only +1.2\% in the field H = 10kOe with 10 wt% MWNT loading. Thus, the phenomenon of linear positive magnetoresistance (MR) in the above system were coincident with the model for Variable Hopping Transport (VRH) by Nguyen et al.[15]. In this model, a positive MR linear with external field at low magnetic field due to the effect of shrinkage wave function between localization lengths of a grain of filler/matrix. Yosida and Oguro[16] also reported about the phenomenon VRH conduction in bulk samples composed by CNT. Recently, similar phenomenon also evidence in magnetite-Polypyrrole meta composites as reported by Guo et al. [17] and in advanced polyaniline composites [17].
Table 2. The ratio of magneto resistance for α-Fe₂O₃-MWNT/PVA film.

| Sample code | Volume ratio Filler/matrix (v/v %) | Weight ratio (wt%) | MR ratio (%) at H=+8 kOe (positive direction) | MR ratio (%) at H=–8 kOe (negative direction) |
|-------------|---------------------------------|-------------------|-----------------------------------------------|-----------------------------------------------|
| D1          | 1 : 19                          | 0.24              | +16                                           | +9.8                                          |
| D2          | 1 : 9                           | 0.51              | +40                                           | +9.8                                          |
| D3          | 1 : 4                           | 1.15              | +13.6                                         | +8.6                                          |
| D4          | 1 : 1                           | 4.61              | +6.2                                          | +7.4                                          |

Figure 6. Magnetoresistance ratio in film composite of Fe₂O₃-MWNT/PVA with variation concentration

4. Conclusions
Nanocomposite film α-Fe₂O₃ filled (trapped) into MWNT/Polyvinyl Alcohol (PVA) were successfully synthesized by simple mixing method. TEM images show that iron oxide filled or trapped in MWNT hollows/walls. The filling nanoparticles into MWNT shows α-Fe₂O₃ phase as revealed by Raman spectroscopy. The bonding between filler iron oxide-MWNT with matrix polymer PVA were clearly appear with dependency on the fraction volume filler with matrix as determined by FTIR spectroscopy. This bonding or a coated iron oxide-MWNT by PVA made all film have a paramagnetic properties, except a diamagnetic character at sample D1 with the lowest fraction 0.24wt% filler to matrix PVA. The highest MR ratio obtained in composite film materials are approximately +40% at Ha = 8kOe with a fraction volume filler/matrix 1:9 or 0.51 wt% (sample D2). The linear positive of the MR ratio was interpreted by the wave function shrinkage model between α-Fe₂O₃/MWNT as filler and PVA as the matrix. This behavior strongly related to the trapped or filled some iron oxide filling MWNT in matrix polymer insulator PVA. The interaction between iron-oxide filled MWNT in matrix polymer PVA made shrinkage or decreased the localization length inside the grain of composites.

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