Magnetic Properties and Electrical Conductivity of NiFe$_2$O$_4$-MWNT/ PVA Nanocomposite Films

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Abstract. Synthesis and characterization of NiFe$_2$O$_4$-MWNT/PVA nanocomposite films have been performed. NiFe$_2$O$_4$-MWNT as a filler of nanocomposite films was gained using a simple mixing method from an aqueous solution containing Fe(NO$_3$)$_3$.9H$_2$O, Ni(NO$_3$)$_2$.6H$_2$O and MWNT. A wet paste-like filler was first characterized by Raman spectroscopy to confirm the presence of NiFe$_2$O$_4$ phase. Referring to the result of Raman spectra, it was known that nanocrystalline nickel ferrite (NiFe$_2$O$_4$) have been successfully synthesized. The morphological investigations using scanning electron microscopy (SEM) and energy dispersive spectroscopic (EDS) revealed that the filler has hair-like structure which correspond to the carbon nanotube with the results of atomic percentage ratio of Fe/Ni correspond to the phase formation of NiFe$_2$O$_4$. Nanocomposite films were made in 4 various concentrations (5, 10, 20, and 50 %vol filler) have been characterized in order to investigate their magnetic properties and electrical conductivity by using vibrating sample magnetometer (VSM) and Inductance-Capacitance-Resistance (LCR) meter. Based on magnetization hysteresis curves, the variation of filler addition has increased the magnetic properties of nanocomposite samples from diamagnetic into paramagnetic. It was also known that the electrical conductivity enhanced align with the increasing concentration of the filler in nanocomposite films.

1. Introduction
Magnetoelectronic polymer composite in which magnetic nanoparticles are insulated from each other in conductive materials are used in a wide array of applications such as electromagnetic interference (EMI) shielding, chemical sensors, sensing components, etc as written by Bartholome et al. and Hudziak et al [1,2]. The conventional method for preparing magnetoelectronic polymer composite is by admixing magnetic nanoparticles and conductive materials as a fillers into the polymer [3]. Carbon nanotubes (CNT) filled by magnetic nanoparticles as fillers in polymer matrix composites have captivated much interest from many research groups due to the magnetic properties and fascinating electrical conductivities. CNT as a filler offering a good conducting network in polymer matrix due to their chain-like aggregate structures. Magnetic nanoparticles especially cubic nanosized spinel ferrites, with the general formula MFe$_2$O$_4$, hold significant potential to the polymer composite because of their unique magnetic, chemical and mechanical properties [4]. One of the most interesting spinel ferrite group is nickel ferrite (NiFe$_2$O$_4$). Based on the formation and particle size, NiFe$_2$O$_4$ shows several magnetic properties from paramagnetic to ferrimagnetic behaviour [5].

In the past few years, many research on fabrication of CNT filled by magnetic nanoparticles/polymer composites have been reported, polymers such as polyacrylonitrile by Nilmoung et al [6], polymethyl methacrylate by Sundaray et al [7], and polyethylene oxide by Naebe
et al [8] have been widely used as matrix. However, the development in polymer/CNT composites has been strongly limited by the problems associated the dispersion of CNT fillers and load transfer across the polymer-CNT interface. In this study, to overcome these barriers and in order to further improve not only the magnetic properties and electrical conductivity but also to prevent the agglomeration of the nanocomposite films, polyvinyl alcohol (PVA) was used as a matrix in nanocomposite films. PVA not only has high solubility in various solvent like water and alcohol but also chemically soft bonding with acid treated MWNT so it can be made to possess an unique capacity to solubilize CNT in aqueous solution. Another advantage of using PVA as matrix is because among the conducting conjugated polymers, PVA is highly stable in air, good electrical conductivity, and easy processibility as written by G.Chakraborty, et al. and Massoti et al [9,10].

A NiFe$_2$O$_4$-MWNT/PVA nanocomposite film is expected to have diverse properties because each component contributes different properties to the nanocomposite films. The aims of this study is to investigate the effect of the filler addition ,which has been made by using simple mixing method, in matrix PVA to the magnetic properties and electrical conductivity of the nanocomposite films. The phase and morphology of the filler was characterized by using Raman spectroscopy and scanning electron microscopy (SEM). Magnetic properties of the nanocomposite films were measured by vibrating sample magnetometer (VSM) and electrical conductivity were measured by Inductance-Capacitance-Resistance (LCR) meter.

2. Experimental procedure

2.1. Starting materials
The chemicals were employed in this study as the starting materials included : Iron nitrate (Fe(NO$_3$)$_3$.9H$_2$O) in crystal form with purity $\geq$ 98.5 wt%, Nickel nitrate (Ni(NO$_3$)$_2$.6H$_2$O) in crystal form with purity $\geq$ 98.5 wt%, Sodium Dodecyl Sulfate (SDS) with purity $\geq$ 98.5 wt%, Polyvinyl alcohol with purity $\geq$ 99+ %wt (Sigma Aldrich), and MWNT black powder with outer diameter 13-18 nm and purity 99 wt% (cheaptubes).

2.2. Synthesis of NiFe$_2$O$_4$-MWNT/PVA nanocomposites
Simple mixing method is very suitable for the synthesis of inorganic precursors. It consists of two main process which are dispersion process of the compound materials under vigorous stirring and sonication process using ultrasonicator. NiFe$_2$O$_4$-MWNT as a filler of nanocomposite films were gained using simple mixing method. The filler was synthesized form an aqueous solution containing Fe(NO$_3$)$_3$.9H$_2$O and Ni(NO$_3$)$_2$.6H$_2$O (Fe/Ni = 2:1 mmol) after that MWNT black powder was added and constantly stirred by magnetic stirrer for 20 hours at 100 $^\circ$C then followed by heating treatment at 160 $^\circ$C. This filler was then dispersed in SDS with ratio 9:12 and homogenized by ultrasonicator for 15 minutes at 40 $^\circ$C and 360 rpm. The matrix nanocomposite was synthesized by using 10 gram of PVA in 100 ml aquades and stirred by magnetic stirrer for 15 minutes at 80 $^\circ$C and 360 rpm. In this study, there were 4 different variations filler in nanocomposite films; 5, 10, 20, and 50 %vol. filler. The mixed solution (NiFe$_2$O$_4$-MWNT/PVA) was poured into a petri dish glass and dried overnight in room temperature to evaporate the water.

2.3. Characterization Technique
In order to confirm and examine the functionalization of the NiFe$_2$O$_4$-MWNT as a filler, Raman spectra carried out at room temperature by using Senterra Raman spectroscopy. The Raman spectra were measured in the range 100 – 1700 cm$^{-1}$ with an excitation length of 785 nm. The microstructure micrograph and compound composition of the filler product were observed using Scanning Electron Microscope (SEM) on a JEOL JSM-6510 LA and energy dispersive spectroscopic (EDS) operating at 20kV. The observation of morphologies and 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. The magnetization–magnetic field hysteresis curves of the filler and nanocomposite samples were measured using a vibrating sample magnetometer (Oxford, 1.2 Tesla) at room temperature. The conductivity of the nanocomposite samples were measured by using LCR meter (Hioki 3532-50) varying from 1 to 100 kHz.

3. RESULTS AND DISCUSSION

3.1. NiFe$_2$O$_4$-MWNT phase confirmation and formation

The phase confirmation of the NiFe$_2$O$_4$–MWNT as a filler was determined by Raman spectroscopy. It is a powerful tool for NiFe$_2$O$_4$-MWNT phase identification and further investigation since it provides into their electronic and vibration properties [11]. There are several dominant peaks of NiFe$_2$O$_4$–MWNT Raman spectra at 327, 478, 566, 700, 1043, 1300, and 1595 cm$^{-1}$. A strong peak in the range of 670–710 cm$^{-1}$ is a common feature of the Raman spectra of the inverse spinels otherwise peaks at at 327, 478, 566 cm$^{-1}$ are assigned to the NiFe$_2$O$_4$ crystal phase [12].

A similar Raman spectra pattern of NiFe$_2$O$_4$ phase was also observed by Zhou et al who studied NiFe$_2$O$_4$ nanoparticles in silica matrix made by mechanical activation method with calcination process at 900 °C [13]. The Raman peaks appearing in the 1300, and 1595 cm$^{-1}$ regions correspond to the stretching mode of graphite and poor crystallization of graphite, respectively as reported by Xiong et al. The result of this Raman spectra demonstrated good combination of NiFe$_2$O$_4$ and MWNT as a filler [14].

The SEM micrograph of NiFe$_2$O$_4$-MWNT is shown in Fig. 2.(a). From this figure it can be seen that the surface of the micrograph consists of some hair-like nanostructure which correspond to the well spread MWNT material. Fig. 2.(b) shows the energy-dispersive-spectroscopy (EDS) confirming the presence of the elemental compound of the filler. The result clearly exhibits elemental compound such as C, O, Fe, and Ni. The result of the mass and atomic percentage ratio of Fe/Ni in the filler is more or less correspond to NiFe$_2$O$_4$ phase. This result is equal with the confirmation of NiFe$_2$O$_4$ phase using Raman spectra (Fig. 1).

![Figure 1](image1.png)

**Figure 1.** (a) the Raman spectra, (b) the SEM image, and (c) The EDS pattern of NiFe$_2$O$_4$-MWNT as a filler in the composite.
The EDS results of NiFe$_2$O$_4$-MWNT/PVA nanocomposite films are shown in Table 1. Referring to these results, it can be confirmed that the amount of Fe and Ni are increased with increasing filler in the nanocomposite films. The amount of Ni and Fe (%mass and %atomic) in 10%.vol and 20%.vol filler nanocomposite are increased comparing with the 5%.vol filler nanocomposite. The amount of Ni and Fe in 50%.vol filler nanocomposite is the biggest among of all NiFe$_2$O$_4$-MWNT/PVA nanocomposite samples. The amount of Ni and Fe plays an important role to determine the characteristic of NiFe$_2$O$_4$-MWNT/PVA nanocomposite films such as magnetic properties and electrical conductivity of the nanocomposite films. It also can be seen in Table 1 that along with the increasing volume filler the result of both atomic and mass percentage of Ni and Fe become clearer to confirm the NiFe$_2$O$_4$ phase.

The formation of the NiFe$_2$O$_4$-MWNT as a filler of all nanocomposite films were carried out by using TEM. It is a suitable tool to further study the morphologies and microstructures of nanosized materials. The TEM image is shown that the hollow tube of the MWNT are partially filled with the NiFe$_2$O$_4$ nanoparticles and at the same time it also decorating the outer surface of the MWNT. As shown in Fig. 2.(a), the image indicated the NiFe$_2$O$_4$ phase could partially penetrate into the hollow tube of the nanotube which represented by black arrows, it happened because the ends of some tubular caps were opened as the result of the acid treatment and mixing process. The white arrows in Fig. 2.(a) represented the NiFe$_2$O$_4$ phase which decorating the outer surface of the nanotube, it can be seen that the NiFe$_2$O$_4$ phase attach to each other strongly and form black line into the wall of the nanotube. The SAED pattern of NiFe$_2$O$_4$-MWNT are shown in Fig.2.(b), it can be seen a spotty ring which correspond to the crystal of the NiFe$_2$O$_4$.
Figure 3. (a) Magnetization curves of wet solid paste NiFe$_2$O$_4$-MWNT (b) NiFe$_2$O$_4$-MWNT/PVA nanocomposite films

3.2. Magnetic Properties

The magnetization hysteresis curve of the NiFe$_2$O$_4$-MWNT in wet solid paste form is shown in Fig. 3.(a). The hysteresis curve is typical for a soft magnetic material and demonstrate the superparamagnetic behaviour with specific saturation magnetization (Ms) values of 0.13 emu/g and coercive forces (Hc) 119.5 Oe. The magnetization hysteresis curve shows the existence of hysteresis indicating the presence of magnetic materials which correspond to the attachment of the NiFe$_2$O$_4$ in MWNT reffering to the result of EDS and Raman spectra (Fig. 2.). Superparamagnetic behavior which appeared in this experiment can be a clear evidence that simple mixing method is succeed to synthesize NiFe$_2$O$_4$. Referring to the result of the Ms value, in the process to synthesize the filler still needs a further optimization especially in optimizing heat treatment process so that the NiFe$_2$O$_4$ can be improved to have high ordered structure crystal. The Ms and Hc of the NiFe$_2$O$_4$-MWNT as a filler value was comparable with the report by Nilmoung, et al. (2011) who studied the magnetic properties of the carbon/NiFe$_2$O$_4$ nanofibres stabilized at 280 $^\circ$C for 0.5 hour with polyaclonytrile as the polymer source, he reported the Ms value of 0.36 emu/g and Hc 98.97 Oe.

The magnetization hysteresis curve of all NiFe$_2$O$_4$-MWNT/PVA nanocomposite films are given in Fig. 3.(b), It exhibits a lower Ms value than the Ms of NiFe$_2$O$_4$-MWNT as a filler. It can be explained due to the existence of diamagnetic phase of PVA in the nanocomposites; Interaction between NiFe$_2$O$_4$-MWNT and PVA as matrix in nanocomposite samples may affect the uniformity of magnetization by extinguishing the surface magnetic moment [15]. The improvement of magnetic properties of the nanocomposite films because the presence of the filler in the matrix is expected. From the shape of the magnetization hysteresis curves in Fig.3.(b) is known that the addition of NiFe$_2$O$_4$-MWNT as a filler can improve the magnetic properties of the nanocomposite film. The 5, 10, and 20% vol filler nanocomposite films exhibit diamagnetic behavior which indicated that the role of the PVA as the matrix is too strong but there is a clear improvement of the magnetic properties from 5% vol to 20% vol filler nanocomposite film, respectively. Unlike the magnetic properties of other nanocomposite films, the 50% vol filler nanocomposite film exhibits paramagnetic behavior which indicating a random spin interaction of the NiFe$_2$O$_4$ magnetic nanoparticle inside the nanocomposite films. The analysis results of the magnetic properties showed that the magnetic properties of nanocomposite materials are dependent on the content of NiFe$_2$O$_4$ as a compound of the filler. It can be confirmed from the result of the atomic and mass percentage of Ni and Fe (table 1), the 50% vol filler nanocomposite film exhibited the biggest amount of Ni and Fe which also had the highest Ms value of 0.04 emu/g whereas the lowest value of the Ms was obtained in 5% vol filler nanocomposite film which also has least amount of Ni and Fe among all nanocomposite films.
3.3. Electrical Conductivity

Fig. 4. shows the effect of NiFe$_2$O$_4$-MWNT loading as a filler to the conductivity values of the nanocomposite films, varying from 5%.vol to 50%.vol filler nanocomposite film, respectively [16]. The NiFe$_2$O$_4$-MWNT/PVA nanocomposite samples were characterized by using LCR meter to define the relation of the volume filler to the electrical conductivity values. A universal relationship between the addition of the filler and the electrical conductivity values can be described using the equation as follows;

$$\sigma \propto (V - V_p)^t$$  \hspace{1cm} (1)

The conductivity behavior can be described by using the equation (1) when the volume fractions greater than the percolation threshold. $V$ is the volume fraction of the filler, $V_p$ is the percolation threshold, and $\sigma$ and $t$ are the conductivity and a critical exponent respectively, Oskouyi et al. (2014). Referring to the quantum mechanical tunneling theory known that electrical current can flow through the insulator matrix based, so it can be assumed that the filler as a conductive materials are connected by resistor formed of the matrix which allowed the electrons to interact with the neighbor electrons [17]. Referring to the equation and the explanation above, it can be noticed that the conductivity values are equal to the volume filler contain in nanocomposite films.

In accordance with those theory the results of all nanocomposite films are increased gradually along with the increasing filler. The electrical conductivity of 5, 10, and 20%.vol filler nanocomposite films were $9.87 \times 10^{-8}$ S/cm, $4.60 \times 10^{-7}$ S/cm, and $7.38 \times 10^{-7}$ S/cm, respectively. The low conductivity value of the 5%.vol filler nanocomposite film was because the role of PVA as the insulator matrix still dominant rather than the filler materials. Along with the increasing volume filler composition, it can be seen from 10% and 20%.vol filler nanocomposite films that the influence of PVA to the conductivity of the films were being replaced by the filler. The 50%.vol filler nanocomposite film has the highest conductivity among all nanocomposite films with the value of $1.92 \times 10^{-6}$ S/cm. As shown in fig.4 the conductivity value was increased sharply in the low range frequency (less than 5kHz), it happened because a greater conductive materials in the nanocomposite films could increase the contact of the filler to filler junction to create some electron tunneling which allowed for the electron hopping under the insulator condition. The results of our research to investigate the relationship between volume filler concentration and the conductivity values is in accordance with the research that has been done by Mohd Faiz Muaz, et al. (2011) who reported that...
the addition of the filler of MnO₂-MWNT/PVA could enhance the electrical conductivity of polymer composites in the range of 10⁻⁶ S/cm from its neat conductivity.

4. CONCLUSION
Referring to the result of the Raman spectra and the EDS results NiFe₂O₄-MWNT were successfully synthesized by using simple mixing method from the starting compound of Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, and MWNT black powder. NiFe₂O₄-MWNT/PVA nanocomposite samples were successfully prepared by using a simple casting method. Magnetic measurement by using VSM revealed that magnetic properties of nanocomposite samples were improved with the increasing of filler content. The synergistic effect of the filler volume to the nanocomposite films was observed, where the electrical conductivity gradually increased with the increasing filler content. If this progress continues apace, we can expect a continuing bright future in this fascinating and potentially very useful area in some new applications as electronic material for energy and nanodevices.

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