ISSN (Print) : 2337-9030 ISSN (Online) : 2685-2608

PILLAR OF PHYSICS

Vol. 13 (2), 2020, page. 131-140
DOI : http://dx.doi.org/10.24036/10341171074

MAGNETORESISTANCE CHARACTERIZATION OF NANOCOMPOSITE Fe_3O_4 / PPy THAT SYNTHESIZED WITH SOL-GEL SPIN COATING METHOD

Surya Pertiwi[1], Ramli[1*]

[1] *Department of Physics, Faculty of Mathematics and Sciences, Universitas Negeri Padang, Jalan Prof. Dr. Hamka, Air Tawar Barat, Padang, West Sumatera, 25171, Indonesia*

Corresponding author. Email: ramli@fmipa.unp.ac.id

ABSTRACT

Indonesia is a rich country that has various natural resources, one of which is in the form of mining materials such as iron sand which contains a lot of magnetite (Fe_3O_4). Magnetite (Fe_3O_4) has superior properties compared to others so that magnetite (Fe_3O_4) is a top priority in research activities that are rapidly developing in world research. Polypyrrole (PPy) is a conductive polymer which has several advantages. Fe_3O_4 nanoparticles are a type of magnetic material that has considerable potential in GMR magnetic sensor applications. The aim of this research is to synthesize and characterize the effect of Fe_3O_4 composition on the magnetoresistance properties of Fe_3O_4/PPy nanocomposites synthesized by the Sol Gel spin coating method. In this study, several stages were carried out, namely: the sample preparation stage, the nanocomposite manufacturing stage, the characterization stage and the data analysis. Fe_3O_4/PPy thin layer nanocomposite is made from iron sand that has been purified and milled by previous researchers. Fe_3O_4/PPy nanocomposites were prepared using the sol-gel method with a variation of Fe_3O_4/PPy concentrations of 30%, 40%, 50%, 60% and 70% and then grown using the spin coating method with a rotating speed of 3000 rpm for 60 seconds, the thin layer formed was dried using a furnace at 550^0C for 1 hour. Then the thin layer was characterized using XRF, FTIR, SEM and FPP. Based on all the characterizations that have been obtained, a thin layer of nanocomposite has been successfully grown on glass preparations. Fe_3O_4/PPy nanocomposite thin layer is a thin layer that has good magnetoresistance properties, this is shown in the results of testing the magnetoresistance properties using the Four Point Probe (FPP) method.

Keywords : Fe3O4/PPy, Magnetoresistance, Sol gel - Spin Coating

I. INTRODUCTION

Indonesia is a rich country that has various natural resources, one of which is in the form of mining materials such as coal, silver, nickel, gold, limestone, copper, diamonds, and iron [1]. The distribution of iron sand in Indonesia can be found on various islands, starting from the islands of Sumatra, Kalimantan, Sulawesi, the Nusa Tenggara region, the Maluku islands, and Java [2]. One of the beaches in West Sumatra that contains iron sand is Tiram beach, Padang Pariaman Regency, West Sumatra [3].

Iron sand which contains magnetite material has applicative properties in various fields of science, such as fluids, magnetic gels, biotechnology, bio-medical, catalysts, magnetic resonance imaging (MRI), and data storage. Its strong response to external magnetic fields makes magnetite very useful for research purposes. The wide range of applications makes researchers continue to develop magnetite materials at the nanoscale.

Magnetite (Fe_3O_4) is a form of iron oxide in nature besides maghemite and hematite. Magnetite is mostly contained in iron sand and is a chemical compound in the form of iron oxide. The structure Fe_3O_4 can be written $Fe.Fe_2O_4$ forms the inverse spinel in cubic form. Magnetite contained in iron sand can be processed into a magnet, but it can also be used in various applications. In the last few years magnetite (Fe_3O_4) has become a material of study that has attracted the attention of experts because of its wide application opportunities, especially in industry.

Fe_3O_4 nanoparticles are one type of magnetic material that is promising because it has sufficient potential characteristics in the application of Giant Magnetore-system (GMR) magnetic sensors. GMR materials have a very large magnetite-resistance that has the potential to be developed into magnetic field detection devices, as well as the use of GMR materials as magnetic field sensors [4].

Giant Magnetoresistance (GMR) occurs due to the sizeable changes in MR caused by scattering during the transport of electrons. The advantages of using GMR as a magnetic sensor are its small size, relatively low power, and price compared to other magnetic sensors, high sensitivity, and fast response to low magnetic fields [2]. GMR sensors can be used in a variety of applications, such as current measurement sensors, distance measurement, rotational speed measurement, presence, and others.

The properties of magnetic nanoparticles largely depend on the grain size of the magnetic nanoparticles. The relatively small particle size makes the material very reactive with the external magnetic field, but if the external magnetic field is gradually removed its effect will be very similar to the paramagnetic material. The standardization of nanoparticle sizes is expected to be between 20-50 nm, particles smaller than 20 nm will tend to lose their magnetic properties, while those with sizes larger than 50 nm will tend to cling due to the influence of gravitational forces.

Polypyrrole (PPy) is a conductive polymer that has several good advantages such as easy preparation, environmentally friendly, soluble in water, easy to synthesize, and relatively high conductivity compared to other conductive polymers [5]. PPy is used in various potential applications such as electronic devices, biosensors, gas sensors, cables, anti-electric coatings, capacitors, polymer batteries, microactuators, anti-electrostatic coatings, biomedicine, and others [6]. Polypyrrole is a compound with a texture like sponges, decomposes at a temperature of 180 - 237^{0}C and has a glass temperature of 160 - 170^{0}C, and has a conductivity value below 3 S cm-1.

Many methods have been developed to synthesize Fe_3O_4 / PPy nanoparticles such as the coprecipitation method, Sol-Gel method, and hydrothermal method. Sol-Gel method is a method that is relatively simple and can be done in normal environmental conditions [7]. The Sol-Gel method is also one of the most successful methods of preparing nanoscale metal oxide materials. The Sol-Gel method is one of the "wet methods" because the process involves solution as the medium. The Sol-Gel method, as the name implies, undergoes a phase change into Sol (colloid which has suspended solids in the solution) and then becomes Gel (colloid but has a larger solid fraction than Sol) [8].

Magnetoresistance is a property related to electrical resistance when a metal is subjected to an external magnetic field. The nature of magnetoresistance can be defined as the change in resistivity due to an external magnetic field, which can be written in the following equation:

$$MR = \frac{\Delta\rho}{\rho} = \frac{\rho H - \rho H{=}0}{\rho H{=}0} \times 100\% \qquad (1)$$

Where :

$\Delta\rho / \rho$: Magnetoresistance Ratio (MR)

ρH : Resistivity when subjected to a magnetic field

$\rho H = 0$: Resistivity when the magnetic field is zero [8].

Resistivity is the ability of a material to inhibit electric current depending on the magnitude of the electric field and current density. The greater the resistivity of a material, the greater the electric field is used to generate a current density [10]. The basic principle of magnetoresistance (MR) is the change in the resistivity of a material as a result of its response to the presence of an external magnetic field. The four-point probe (4-point probe abbreviated as FPP) is a method that can be used to measure the resistivity value of a conductor or semiconductor and a thin layer of metal.

The GMR effect is a quantum mechanical effect observed in a thin film structure consisting of ferromagnetic layers separated by nonmagnetic layers. This GMR effect is related to the fact that the spin of the electron has two different values (spin up and spin down).

When the spins cross the magnetized material, one of the spins may experience a different resistance than the other spin types. This property indicates the existence of spin-dependent scattering. The physics study of GMR is based on the effect of spin on the conduction properties and the tunneling properties of electrons in ferromagnetic metals. The image below is a schematic of the four point probe.

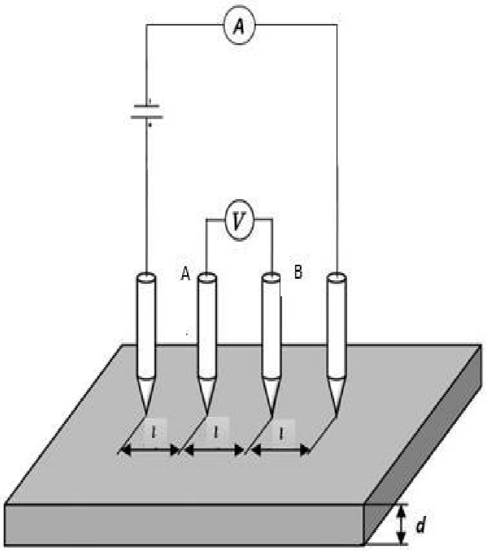

Fig. 1. Four point probe method [10]

From the picture above, it is explained that the four contact points (probes) are lined up in a straight line with the distance between the probes arranged in such a way that each other has the same distance. the working principle of the tool is, before the current flows through the probe, the four probes are lowered so that they touch the surface of the sample.

After that, the current will be flowed constantly along the surface of the sample through the two outermost probes laminar through the sample from one probe to the other probe. Samples that have a resistance value will experience a decrease in voltage when current flows along with the sample. The change in voltage can be seen through the two inner probes.

Some of the phenomena that occur on magnetic sensors include using the Hall effect, flux-gate magnetometer, Superconducting Quantum Interference Device (SQUID) magnetometer, Aniso-tropic Magnetoresistive (AMR), Tunneling Magnetoresistance (TMR), and Gian Magnetoresistive (GMR). GMR sensors can be used in a variety of applications, such as current measurement sensors, distance measurement, rotational speed measurement, presence, and others. So this is what motivates the author to write an article entitled "Characterization of the magnetoresistance properties of Fe_3O_4 / PPy nanocomposites synthesized by the Sol-Gel – Spin Coating method".

II. METHOD

This research is an experimental study. This study examines the magnetoresistance value of Fe_3O_4 / PPy nanocomposites synthesized by the Sol-Gel method. In this research, there are several steps taken, namely: the sample preparation stage, the nanocomposite manufacturing stage, the characterization stage, and the data analysis. with the flow chart shown in Figure 2.

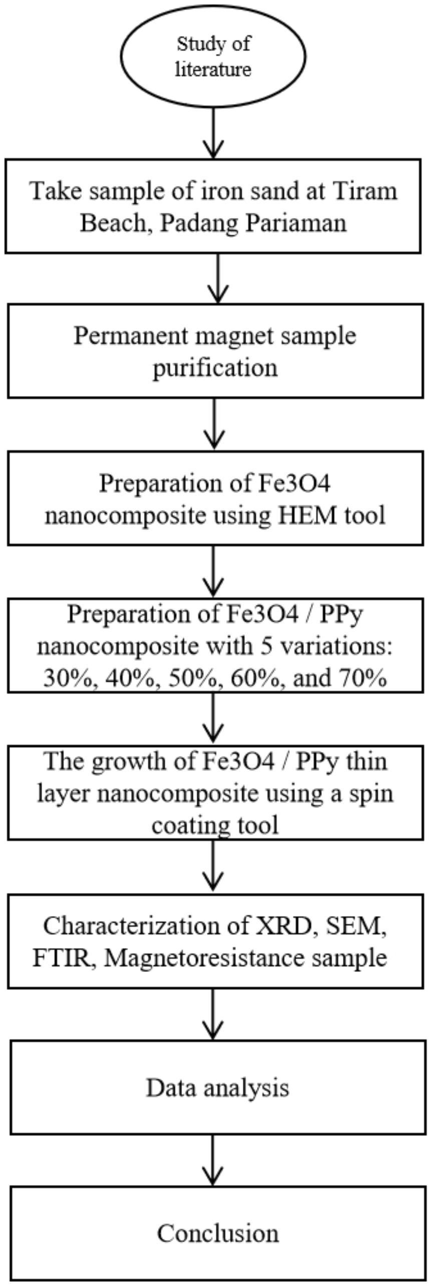

Fig. 2. Research flowchart

In this research, the tools used are High Energy Milling (HEM-E3D), oven, FTIR, magnetic stirrer, furnace, spin coating, permanent magnets, digital scales, glass substrates, lumping and pestle, measuring cups and Erlenmeyer tubes, balls - milling balls, saucers, strainer, and spatula. While the ingredients are iron sand, oxalic acid, ethylene glycol, alcohol, aquabidest, and nitric acid.

Fe_3O_4/PPy thin layer nanocomposite is made from iron sand that has been refined and milled by Nidya and Debi [6, 11]. The milling time used is based on Darvina's [12] research, which is 30 hours [3].

Subsequently, Fe (NO_3) 3.9H_2O precursor was made using the sol-gel method. The process of making Fe_3O_4 precursor was carried out at 110^{0}C by reacting 10.44 grams of Fe_3O_4 and 2.7 grams of oxalic acid ($C_2H_2O_4$) with 25.2 ml of nitric acid (HNO_3).

Then stirred using a magnetic stirrer at a constant speed for 15 minutes, then add 33 ml of ethylene glycol then lower the temperature to 80^{0}C for 2 hours. The gel that is later formed will be used for the thin layer growth process

Then made Fe_3O_4 / PPy Sol-Gel nanocomposite by dissolving 300 ml of Fe_3O_4 in aquabidest and stirring using a magnetic stirrer for 1 hour, then adding pyrrole gradually into the solution with a concentration ratio of Fe_3O_4 / PPy of 30%, 40%, 50%, 60%, and 70%.

Add $FeCl_3$ and stir using a magnetic stirrer at 0-50^{0}C for 8 hours, then wash the solution using aquabidest and ethanol, then dry in the oven at 60^{0}C for 24 hours. Grow a thin layer of Fe_3O_4 / PPy using a spin coating with a rotating speed of 3000 rpm for 60 seconds, the thin layer formed was dried using a furnace at 550^{0}C for 1 hour.

Thin layer samples of Fe_3O_4 / PPy nanocomposites were characterized using an XRF device to determine the concentration of elements contained in it, an FTIR tool to determine the functional groups of the resulting material nanocomposites, the four-point probe method to obtain the magnetoresistance value of Fe_3O_4 / PPy nanocomposites.

III. RESULTS AND DISCUSSION

The results of characterization of the Fe3O4 / PPy nanocom-posite thin layer using the XRF device are shown in Table 1.

Table 1.The Characterization Results of the Fe3O4 / PPy Thin Film Content of Nanocomposite

30%		40%		50%		60%		70%	
MgO	6,903	MgO	5,136	MgO	14,524	MgO	6,187	MgO	18,543
Al2O3	2,228	Al2O3	1,365	Al2O3	6,502	Al2O3	3,072	Al2O3	7,497
SiO2	73,992	SiO2	76,986	SiO2	31,43	SiO2	73,957	SiO2	12,882
P2O5	1,012	P2O5	2,835	P2O5	22,209	P2O5	5,85	P2O5	33,87
SO3	2,685	K2O	0,493	K2O	0,971	K2O	0,283	SO3	20,645
K2O	0,337	CaO	11,418	CaO	8,761	CaO	8,214	K2O	0,137
CaO	9,494	TiO2	0,158	TiO2	0,119	TiO2	0,222	CaO	5,672
TiO2	0,2	V2O5	0	V2O5	0,016	V2O5	0,004	Cr2O3	0,033
V2O5	0,003	MnO	0,008	Cr2O3	0,027	Cr2O3	0,005	Fe2O3	0,39
Cr2O3	0,006	Fe2O3	0,64	MnO	0,039	MnO	0,009	Cl	0,332
MnO	0,009	ZnO	0,04	Fe2O3	13,422	Fe2O3	1,607		
Fe2O3	2,247	Rb2O	0,002	SrO	0,019	NiO	0,004		
ZnO	0,024	SrO	0,01	Ag2O	1,394	CuO	0,006		
SrO	0,019	ZrO2	0,013	Ca2O3	0,059	ZnO	0,003		
ZrO2	0,013	Ag2O	0	Eu2O3	0,04	SrO	0,016		
Ag2O	0,472	In2O3	0,57	Yo2O3	0,026	ZrO2	0,011		
In2O3	0,121	BaO	0,118	Cl	0,443	Ag2O	0,271		
BaO	0,078	Eu2O3	0			In2O3	0,093		
Eu2O3	0,007	Cl	0,207			BaO	0,021		
Cl	0,148					Eu2O3	0,006		
Re	0					Yu2O3	0		
						Cl	0,161		
						Re	0		

Based on the data obtained from the results of characterization using XRF, it can be seen that the percentage content of each thin layer for each variation in composition can be seen.

The XRF characterization results show that the most dominant compound content contained in the thin layer is SiO3 with the highest percentage in the composition of 40%, while the composition of 30%, 50%, 60% and 70% respectively is equal to 73.9%, 31.43%, 73.95% and 12.88%.

In addition, the ferrite content of Fe2O3 in the nanocomposite thin layer that has formed is only slightly, namely 2.247%, 0.64%, 13.442%, 1.67% and 0.39% respectively, as well as other compound contents. contained slightly in the thin nanocompo-site layer.

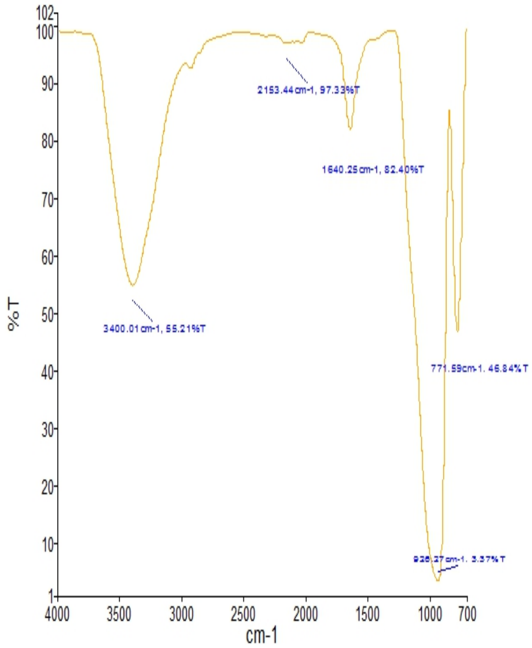

Fig. 3. Graph of FTIR test results with 70% composition variation.

Based on the results of FTIR characterization shown in Figure 3 above, it shows that the Fe3O4 / PPy nanocomposite graph in the area of 928.27 cm-1 shows the types of Fe3O4 / PPy compounds that are already bound. While the results of characterization using SEM are shown in Figure 4 below.

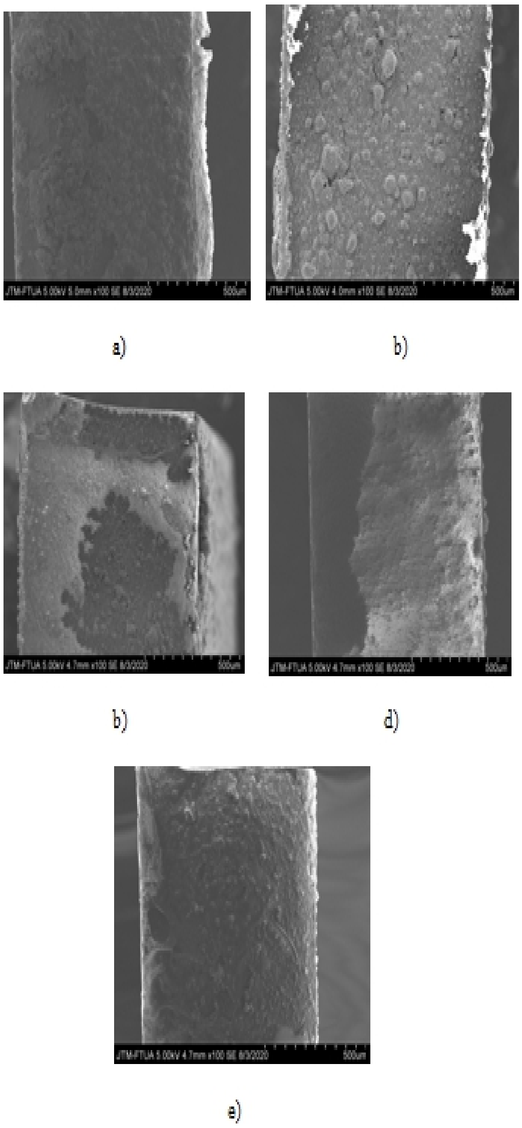

Fig. 4. Graph of SEM test results with the composition of Fe_3O_4 in PPy (a) 30%, (b) 40%, (c) 50%, (d) 60%, (e) 70%.

From Figure 4 above, the thickness value of each thin layer of nanocomposite composition of Fe_3O_4 in PPy is obtained. The thin film thickness value data is shown in Table 2 below.

Table 2. The Value of Thin Film Thickness with The Composition of Fe_3O_4 in PPy

No.	Composition	Thickness
1.	30%	998,3 um
2.	40%	1.062 um
3.	50%	939,7 um
4.	60%	900,4 um
5.	70%	868,8 um

The thickness of the thin films obtained based on testing using a Scanning Electron Microscopy (SEM) tool shows that the thickness of each of the thin films for the variation in the composition of 30%, 40%, 50%, 60% and 70% respectively is 998.3 um , 1,062 um, 939.7 um, 900.4 um and 868.8 um.

Based on these results, we can see that the more Fe_3O_4 composition contained in the thin nanocomposite layer, the greater the thickness of the resulting thin layer. Where the greater the Fe_3O_4 composition used, the smaller the thickness of the resulting thin film. Likewise, the more the PPy matrix composition used, the greater the thickness of the resulting thin layer.

The thin layer with the smallest thickness is obtained at 70% composition variation. While the thin layer with the greatest thickness is obtained at a variation of the composition of 30% and 40%. Where the thickness of this thin layer will affect the magnetorization value of the formed layer.

The graph of data analysis resulting from characterization of magnetorestation properties using the Four Point Probe (FPP) method on Fe_3O_4 / PPy nanocomposites in various composition variations is shown in Figure 5 below.

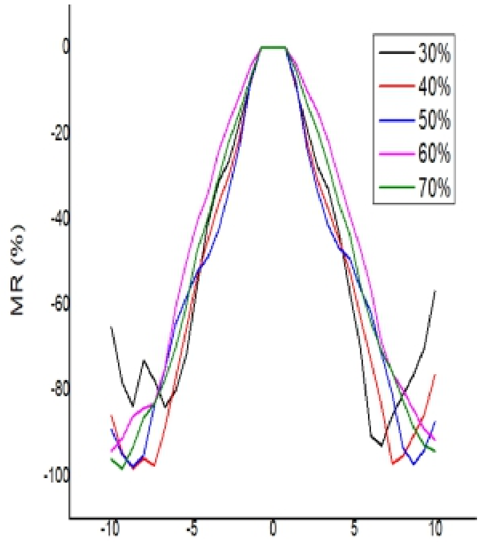

Fig. 5. Graph of Magnetore-resistance test results with the composition of Fe_3O_4 in PPy of 30%, 40%, 50%, 60% and 70%.

From the graph above, the magnitude of the value of the magnetoresistance properties of each Fe_3O_4 composition in PPy. The magnetoresistance value data are shown in Table 3 below.

Table 3. Data on Thin Film Magnetoresistance Values Data on Magnetoresistance Values

No	Composition of Fe_3O_4 in PPy	MR (%)
1.	30%	92,8 %
2.	40%	98,2 %
3.	50%	97,8 %
4.	60%	94,2 %
5.	70%	98,2 %

This magnetoresistance value shows the magnitude of the decrease in resistivity experienced by the sample (thin layer of Fe_3O_4 / PPy nanocomposite) as a result of the influence of the external magnetic field (H). Based on the Graph and Table above, we can see that a thin layer of Fe_3O_4 / PPy nanocomite in a 30% composition produces a magnetoresistance value of 92.8%, at a composition of 40% produces an MR value of 98.2%, at a composition of 50% it produces The magnetoresistance value was 97.8%, the 60% composition resulted in a magnetoresistance value of 94.2% and the 70% composition produced a magnetoresistance value of 98.2%.

The magnitude of this magnetoresistance value is influenced by the composition of the magnetic material used in the thin layer, where with different compositions used, the resulting thin film thickness will also be different. This is in accordance with the theory which states that the smaller the thickness of the thin layer, the greater the resulting magnetoresistance value will be and this is also in accordance with the research conducted by Ramli [8,9].

So this shows that the difference in the composition of Fe_3O_4 in PPy will affect the thickness of the resulting thin film and the resulting Magnetore-resistance value in each thin layer of nanocomposite. The largest or maximum magnetoresistance value was obtained in a thin layer of Fe_3O_4 /PPy nanocomposite with a composition of Fe_3O_4 in PPy of 40% and 80%, with the magnitude of the obtained magnetoresistance value of 98.2%.

The difference in the composition of Fe_3O_4 in PPy resulted in an increase in the magnetore resistance value in the Fe_3O_4 / PPy nanocom-posite thin layer. This is due to the emergence of an inactive area in the Fe_3O_4 layer which reduces the ratio value

GMR due to the occurrence of shunting current (shunting current) on the effect of GMR [13]. When the GMR ratio value is maximum, it shows that the location of the center of the scattering depends on the spin in the ferromagnetic layer. Where in the ferromagnetic layer, there are 2 parts, namely the active part and the inactive part. Apart from the thickness of the thin film, the value of the MR ratio is also influenced by other factors such as the type of material used as the constituent layer [14].

IV. CONCLUSION

Based on the research that has been done, it is concluded that a thin layer of Fe_3O_4 / PPy nanocomposite has been successfully grown with a composition of Fe_3O_4 that varies in PPy, namely 30%, 40%, 50%, 60% and 70%. This thin layer was made using the sol-gel method grown on glass preparations using the spin coating method for a rotating speed of 3000 rpm.

Based on all the characterizations that have been carried out, namely by using XRF, FTIR, SEM, and testing the magnetoresistance properties using the Four Point Probe (FPP) method, it was found that a thin layer of nanocomposite was successfully grown on the glass preparation, this is shown from the characterization results. using XRF and FTIR.

Fe_3O_4 / PPy nanocomposite thin layer is a thin layer that has good magnetoresistance properties, this is shown in the results of testing the magnetoresistance properties using the Four Point Probe (FPP) method with the maximum resistance value obtained in the Fe_3O_4 / PPy nanocomposite thin layer with the composition of Fe_3O_4 in PPy of 40% and 80% with a magnetoresistance value of 98.2%.

Where the magnetoresistance value is influenced by the composition of the thin layer that is grown which results in a different thickness for each layer.

Where the greater the Fe3O4 composition used, the smaller the resulting thickness, and vice versa, the greater the composition of the PPy matrix used, the greater the thickness of the layer formed. The smaller the thickness of the thin layer, the greater the resulting magnetoresistance value

REFERENCES

[1] Muflihatun, Siti Sofiah, Edi Suharyadi. *Sintesis Nanopartikel Nickel Ferrite (Nife2o4) Dengan Metode Kopresipitasi Dan Karakterisasi Sifat Kemagnetannya.* Jurnal Fisika Indonesia *Ugm,* 2015.

[2] Djamal, M And Ramli. *Development Of Sensor Based On Giant-Magnetoresistance Material. Proseeding Enginering,* No 32, Pp:60-68. 2012.

[2] Darvina, Yenni dkk. *Struktur Nano Partikel Oksida Besi Dari Pasir Besi Pantai Tiram Sumatera Barat*. Universitas Negeri Padang: Padang. 2017.

[3] Wang, Lin-Xia., Xin-Gui Li, Yu-Liang Yang. *Preparation, Properties And Applications Of Pollypirolles.* 2001.

[3] Ramli. Penumbuhan Lapisan Tipis Giant Magnetoresistance Cofe$_2$o$_4$ Dan Karakterisasinya. Disertasi. Bandung. Pascasarjana Institut Teknologi Bandung. 2014.

[4] Rianto, Debi. *Analisis Struktur Kristal dan Morfologi Lapisan Tipis Magnetit (Fe_3O_4) Berbahan Dasar Pasir Besi Alam yang Ditumbuhkan Menggunakan Metode Spin Coating*. FMIPA: UNP. 2017.

[5] Qomariyah, S.N. Pengembangan Sensor Alkohol Dari Bahan Polipirol Konduktif Dengan Variasi Konsentrasi Dopan Fluoroborat, Skripsi, Universitas Jember. 2011.

[7] Phumying. S. *Nanocrystalline Spinel Ferrite (Mfe$_2$o$_4$, M=Ni, Co, Mn, Mg, Zn) Powders Prepared By A Sample Aloe Vera Plant-Extracted Solution Hydrotermal Route*. Departement Of Physics. Fakulty Of Science.Khon Kaen University. Khon Kaen 4002. Thailand. Material Research Bulletin. 48. 2060-2065. 2010.

[8] Xue Qz. The Influence Of Particle Shape And Size On Electric Conductivity Of Metal-Polymer Composite. *Eur Polyn J*; 40(2):323-7. 2004.

[9] Mufahir, Iim Abdul. Pengaruh Suhu Substrat Terhadap Sifat-Sifat Listrik Bahan Semikonduktor Lapisan Tipis Pbs, Pbse, Pbte Hasil Preparasi Dengan Teknik Vakum Evaporasi. Skripsi. Yogyakarta: Universitas Negeri Yogyakarta. 2015.

[10] Yulfriska, Nidya. *Analisis Sifat Optik dari Lapisan Tipis Fe_3O_4 yang Dipreparasi dari Pasir Besi Pantai Tiram Kabupaten Padang Pariaman Sumatera Barat dengan Metoda Sol-Gel Spin Coating*. FMIPA: UNP. 2017.

[4] Jahidin. *Analisis Suseptibilitas Magnetik Pasir Besi Desa Laea Kabupaten Buton Utara Sulawesi Tenggara. Jurnal* Aplikasi Fisika, Universitas Haluoleo, 2012, Vol 8.

[12] Ramli, Sustini, E., Rauf, N., Djamal, M. Giant Magnetoresistance In Femn/Nicofe/Cu/Nicofe Spin Valve Prepared By Opposed Target Magnetron Sputtering, *Advanced Materials Research*, 979, Pp. 85-89. 2014.
[13] Djamal, M Dan Yulkifli. *Penumbuhan Lapisan Tipis Nicofe/Si Sebagai Material Pembuatan Sensor Giant Magnetoresistance (Gmr)*, Jurnal Fisika Himpunan fisika Indonesia, 2009, Vol 9.