Microstructure of magnetite - polyvinylidene fluoride (Fe₃O₄/PVDF) nanocomposite prepared by spin coating method

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Abstract. Recently, nanomaterials in the world have a very promising potential in the world of technology and industry. One of them is the development of nanocomposite materials. Composite is a combination of two or more different materials, one as a matrix component and the other as a filler component. This study aims to synthesize and characterize Fe₃O₄/PVDF nanocomposite thin film from natural iron sand using the spin coating method. The thin films nanocomposite magnetite - polyvinylidene fluoride (Fe₃O₄-PVDF) was prepared using a sol-gel method and then developed employing a spin coating device with a mirror substrate. The Fe₃O₄/PVDF thin film nanocomposite was characterized using XRD and SEM to determine its microstructure. In this paper, the microstructure of Fe₃O₄/PVDF nanocomposite will be discussed in depth and elaborate the parameters that affect the Fe₃O₄/PVDF microstructure.

1. Introduction
The development of nanostructured materials today has very promising potential, ranging from nanoparticle, nanowire [1], nanotubes, to nanocomposite materials [2]. Composites are a combination of two or more different materials, one as a matrix component and the other as its filler component. While the nanocomposite itself is a solid structure with nanometer-sized dimensions which are arranged repeatedly with the distance between different constituent shapes.

Researchers have done a lot of research on polymer materials to develop nanocomposite materials, which, by using nano-sized fillers, will be dispersed into the polymer matrix system. The mixing of nanoparticles into the constituent matrix is part of the development of the nanotechnology world. After adding a number of nanoparticles into the matrix material, the resulting nanocomposite exhibits superior properties compared to the properties of the prior material[3].

The advantages of this nanocomposite depend on the structure, properties and composition of the material itself. Polymer-based nanocomposites have advantages over other conventional composite materials. This advantage depends on the material properties, structure and composition of the constituent of the nanocomposite material.

A thin film nanocomposite Magnetite - Polyvinylidene fluoride at this time is growing very rapidly because it can be used in various fields, especially in the field of sensor. Magnetite in nano size contained in iron sand has advantages compared to other compounds, because it is superior in response to external magnetic field. So it has a big hope to apply latest various fields like electronics and industry as well as in the manufacture of thin layers of nanocomposite. A thin film of magnetic
nanoparticles inside a polymer matrix is possible to be applied in areas such as electronics, magnetic, optical and mechanical [4, 5].

Polyvinylidene Fluoride or PVDF is a pure thermoplastic fluoropolymer that has a low melting point making it easier to melt [6]. PVDF an actual normally worn applications demanding purity, strength, resistance for solvents, acids, and heat. compared with other fluoropolymers. This PVDF is a noticeable semi-crystalline polymer. So, the use of PVDF as a matrix in making nanocomposite is one of the key parameters for various applications. One application of the PVDF-based thin film polymer is that it can be used as a capacitive biosensor to measure the glucose content of a material [7], as a chemical reaction sensor [8], as piezoelectric materials for liquid viscosity sensor [9]. The microstructure of this nanocomposite depends on several parameters, one of which is the spread of nanoparticles into the polymer matrix.

A thin film is a layer of a thickness of size in a micrometer order to a nanometer made of organic, inorganic, or metallic material having properties such as a conductor, an insulator or a semiconductor, to develop to the incorporation based the atomic equity. There are several methods that can be used to grow thin films such as DC magnetron sputtering method [10, 11], sputtering [12], electrophoresis [13], slip casting [13], as well as pyrolysis spray [14]. However, this technique has the drawback that the cost is very expensive, requires sophisticated instruments and wide area formed on a small layer.

Spinning coating method is the most simple and easy method. Spin coating is a method of growing a thin film through a process of rotation or spin. Where the advantages of this method is that the resulting thin film has a pretty good quality and manufacturing costs are relatively cheap compared with other methods [15]. As for the preparation of a thin film of the best method used is the method of sol-gel because this method has several advantages, one of which is to produce a thin film with high levels of homogeneity [16].

The spin coating process is divided into several stages, namely the penetration stage of the solution on the substrate, the acceleration stage (Spin up), the level of smoothing (Spin off) and the last drying stage. The first step of the spin coating process is the penetration stage of the solution on the substrate. Then in the next stage is the acceleration stage, where the solution will be attracted to the edge of the substrate and spread evenly [17], this is because at this stage there is a centrifugal force that affects. The thin film will then spread evenly on the spin off and then in the last stage the solvent will be absorbed into the atmosphere so that a thin film of thickness is formed.

2. Experimental

Research here an experiment research. The sample used latest this research is magnetite (Fe₃O₄) prepared from iron sand and polymer used is polyvinylidene fluoride. On this study the device worn are spin coating, HEM-E3D, glasses of chemistry, magnetic stirrer equipped with hot plate, permanent magnet, and digital scales. While other materials needed to make the nanocomposite magnetite - polyvinylidene fluoride (Fe₃O₄ - PVDF) are aquabidest, ethanol, nitric acid, ethylene glycol and oxalic acid.

Before Iron sand is prepared by sol-gel method, iron sand must be purified first. In this research, the process of purification of iron sand is by means of iron sand purified by means of drawn using permanent magnet 30 times, to separate it from impurities (residue). Then the iron sand was washed with aquabidest, and dried. Once dry, the iron sand is pulled employing a permanent magnet. Then pure iron sand act made into nanoparticles using the HEM-E3D tool as long as 30 hour, because on milling 30 hours shows the loss away the hematite phase, such that alone one phase remains, the magnetite phase. Then in the washing to remove dirt or mixture on the iron sand and then dried again [18].

The precursor used to make the magnetite sol gel is Precursor (Fe(NO₃)₃.9H₂O), preceded by reacting 17.4 g of magnetite in 4.5 g oxalic acid (C₂H₃O₄) and 42 mL nitric acid (HNO₃) at 110°C. Then add ethylene glycol to the solution. Stir for 2 hours at 80°C using a magnetic stirrer [19]. The magnetite sol-gel is then mixed into Tetrahydrofuran (THF) and then fed into the ultrasonic cleaner for 2 hours (Solution 1).
Next make polyvinylidene fluoride polymer precursor (PVDF) by dissolving PVDF into Tetrahydrofuran (THF) by comparison (3:70). The mixture is continuously stirred using a magnetic stirrer until homogenously at 75°C (Solution 2).

After that, the nanocomposite was prepared by mixing the solution 1 into solution 2 with a variation of magnetite composition: polyvinylidene fluoride (Fe₃O₄: PVDF) of 5 variations at 10:30, 10:20, 10:10, 20:10 and 30:10.

Then the nanocomposite is grown on a glass substrate using a spin coating tool. The growth of a thin film of nanocomposite magnetite - polyvinylidene fluoride (Fe₃O₄: PVDF) was performed at a rotational speed of 3000 rpm for 60 seconds. Furthermore, a thin film that has been formed in annealing using the furnace for 30 minutes at 60°C[20]. The thin film of Fe₃O₄-PVDF nanocomposite are employing X-Ray Diffraction (XRD) to investigate its microstructure and use Scanning Electron Microscopy (SEM).

3. Results and discussion

The results of characterization using XRD showed that a thin films of nanocomposite magnetite - Polyvinylidene fluoride Fe₃O₄ - PVDF) was developed on the glass substrate, characterized by the presence of magnetite peaks in X-Ray diffraction patterns with variations of Fe₃O₄ and PVDF compositions.

![Figure 1. X-Ray Diffraction Patterning of Nanocomposite Thin Films (Fe₃O₄ : PVDF)](image)

Based at Figure 1 can be seen the influence of the Fe₃O₄ - PVDF composition on nanocomposite thin film crystal structure. Increasing the amount of Fe₃O₄ composition in a thin films of nanocomposite will result in the peak intensity of Fe₃O₄ also becoming higher or more prominent. this is because more of the Fe₃O₄ content in the solution will affect the number of atoms that make up the crystalline plane of the Fe₃O₄ thin film.

In the growth of thin film of nanocomposite, there are several things that will affect the results of characterization so that not all results will be in accordance with the theory. One that affects the
homogeneity of the thin film made, the level of flatness of the thin layer formed, and the difference in gel mass dripped on the substrate [21].

Based on data obtained from the XRD results it can be known the magnitude of the crystal diameter (D) thin layer of nanocomposite. the diameter of the crystal (D) can be calculated using the Scherrer equation.

\[ D = K \frac{\lambda}{B \cos \theta_B} \]  

where \( \lambda \) (lamda) is the wavelength of 1.54 Å, B act like the preferred peak, \( \theta_B \) act the angle of Bragg and K is the actual constant whose price is fewer than one. By using the value of FWHM it can be determined the size of crystallite from a thin films. The magnitude of the crystal size of the Fe\textsubscript{3}O\textsubscript{4} - PVDF nanokomposite thin films can be seen in the Figure 2.

![Figure 2. Effect of Fe\textsubscript{3}O\textsubscript{4} - PVDF Composition on crystallite size.](image)

The average crystallite size of the Fe\textsubscript{3}O\textsubscript{4}-PVDF nanocomposite increases with the addition of polyvinylidene fluoride polymer matrix in the nanocomposite, and vice versa the crystallite size decreases with the increasing amount of Fe\textsubscript{3}O\textsubscript{4} composition in the nanocomposite sol-gel. This result corresponds to the results shown in XRD which show that in addition to Fe\textsubscript{3}O\textsubscript{4} the peak crystallinity composition becomes more prominent and narrow. This crystallization peak shows the distribution of crystallite size [22]. So that more concentrations of Fe\textsubscript{3}O\textsubscript{4} in the nanocomposite result in less crystallinity.

The surface morphological structure of Fe\textsubscript{3}O\textsubscript{4}-PVDF nanocomposite thin film using SEM for 5 variations of Fe\textsubscript{3}O\textsubscript{4}-PVDF composition (10:20, 10:30, 10:10, 30:10 and 20:10) at 25.000 times successive magnifications can be seen at Figure 3.

Based on the Figure 3 above can be seen that the morphology of thin films of nanokomposite well distributed throughout the PVDF matrix although there is still formed aglomerisasi on a thin films of nanokomposite. With the increasing concentration of Fe\textsubscript{3}O\textsubscript{4} in the nanocomposite, the agglomerates are also getting bigger. In addition, from this SEM data can also be obtained the size of the grain from the thin films of nanokomposite for variation of Fe\textsubscript{3}O\textsubscript{4} - PVDF composition shown in Figure 4.

Variation of Fe\textsubscript{3}O\textsubscript{4} Composition: PVDF in the Figure 4 shows generally that with the increase of Fe\textsubscript{3}O\textsubscript{4} composition the grain size of nanocomposite will decrease further. enlarged grain size was obtained on the composition ratio (Fe\textsubscript{3}O\textsubscript{4} - PVDF) of 10:20. This grain size depends on the composition of the composite material material. The thickness of the Fe\textsubscript{3}O\textsubscript{4} - PVDF nanokomposite thin films using SEM for 5 variations of Fe\textsubscript{3}O\textsubscript{4} - PVDF composition at magnification 500 times can be seen in the Figure 5.
Figure 3. The surface morphology regarding thin films nanocomposite Fe$_3$O$_4$: PVDF (a) 10:20, (b) 10:30, (c) 10:10, (d) 30:10 and (e) 20:10.

Figure 4. Effect of Fe$_3$O$_4$ - PVDF composition on grains size.

The effect of thickness of the thin layer of nanocomposite on Fe$_3$O$_4$: PVDF composition to be more clearly can also be seen in Figure 6. Based on Figure 6, it can be seen that with the addition of the composition of Fe$_3$O$_4$ in the process of making nanocomposite thin films it results in a decrease in the thickness away the thin films of nanocomposite. This is in accordance with Vegenopal’s research, et al, 2014 [23] which says that the more composition of Fe$_3$O$_4$ we add in a thin film of nanocomposite, the thinner the thickness of the layer. And vice versa, with the addition of a PVDF polymer, the thickness of the thin films will be even greater, we can see the composition ratio Fe$_3$O$_4$: PVDF (10:20). But in the composition away Fe$_3$O$_4$: PVDF as much as 10:30, the thickness of the thin films decreases. The thickness of these different thin layers is influenced by the degree of homogeneity of the nanocomposite thin films made, the level of flatness of the thin film formed, and the difference in gel mass dripped on the substrate [21]. So the results obtained are less significant, due to differences in Fe$_3$O$_4$ and PVDF compositions used in making nanocomposite thin films.
So it can be seen in all test results that the microstructure of the magnetite nanocomposite - PVDF depends on the composition of Fe₃O₄ - PVDF used. Where PVDF as a matrix in making this nanocomposite thin film is one of the important parameters that will influence the spread of magnetite nanoparticles into the polymer matrix.

Figure 5. Cross-Section Imaging Results A thin layer of nanocomposite Fe₃O₄: PVDF (a) 10:20, (b) 10:30, (c) 10:10, (d) 30:10 and (e) 20:10

Figure 6. Effect of Fe₃O₄ - PVDF Composition on Thin Layer Nanocomposite Thickness

4. Conclusion
The results showed that a thin films of Fe₃O₄ - PVDF nanocomposite thin film on a glass substrate with 5 variation of Fe₃O₄ - PVDF composition was performed. One of the parameters that affect the microstructure of the nanocomposite is the spread of magnetite nanoparticles into the polymer matrix. The spread of these magnetite nanoparticles is influenced by the composition of Fe₃O₄ - PVDF compositions used. In addition the Fe₃O₄ composition results in increasingly prominent and narrower
intensity showing the smaller crystal size shown in XRD results. Characterization using SEM indicates that the thin layer of Fe$_3$O$_4$ nanocomposite is well distributed within the PVDF matrix.

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