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Preliminary Study of Synthesis of Polyvinyl Alcohol (PVA) / Hydroxyapatite (HA) Composite Nanofiber with Electrospinning Technique

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ABSTRACT: *Polyvinyl alcohol (PVA)/hydroxyapatite (HAp) composite fiber is obtained using hydroxyapatite made from limestone. Fiber making is done by electrospinning technique using PVA solution with each HAp concentration of 1% and 5%. The polarization images microscope shows that the average diameter of the composite fiber PVA / HAp varies depending on the concentration of HAp in the solution and the voltage applied to electrospinning. At 1% HAp concentration with a voltage of 15kV, the average fiber size was 9.83 µm and with a voltage of 17kV, the average size of the fiber was 14.46 µm. Whereas at a voltage of 20 kV, fiber yield cannot be observed. At the 5% HAp concentration with 5kV the average fiber size was 10.45 µm, with a voltage of 15 kV, the average fiber size was 10.84 µm and with a voltage of 20 kV, the average fiber size was 11.9 µm. It can be concluded that the concentration of HAp and the magnitude of the voltage affect the size of the fiber produced. For this reason, it needs to be investigated further to obtain optimal conditions.*

KEY WORDS: *polyvinyl alcohol, hydroxyapatite, electrospinning, voltage, polarizing microscopes*

I. INTRODUCTION

Nano fibers from a polymer material are made and investigated because they have specific properties such as a broad surface, small pore size and the possibility of forming a three-dimensional structure so that it has the potential to be used as filtration media, optical fibers, protective clothing, delivery systems drug (drug delivery) in the pharmaceutical field [1]. In its application in the biomedical field, nano fiber can be used as a wound dressing [2,3], as a medium for soft tissue formation (tissue scaffold)[4,5] and help in the process of bone regeneration[6].

The technique of making nano fibers can be done in 3 ways, namely drawing, template synthesis, and electrospinning. The drawing technique is the technique of making nano fibers by touching the micropipette on the droplet and pulling it. Template synthesis technique that is making nano fibers by pressing the polymer solution in a small membrane gap to produce nano fibers. Electrospinning is the manufacture of nanoparticles by loading the polymer solution which is then dropped from the pipette in a high-power area [7]. Brown and St Ev Ens (2007) [8] explain that electrospinning is a technique of making nanoparticles by utilizing electrostatic forces as a driver of polymer solutions when the solution is injected from a needle (spinneret) to a collector. The emission of the polymer solution accelerates towards the collector and extends irregularly from the spinneret to the collector. The emission of the solution will thin out and dry out as the solvent evaporates, leaving the nano fibers interconnected with one another to form solid webs. Among several techniques developed in the manufacture of micro and nano fibers, the electrospinning technique is a technique that is considered easier and more effective for making fine fibers from various synthetic and natural polymers [9].

Hydroxyapatite is a crystalline molecule composed essentially of phosphorus and calcium with the molecular formula $Ca_{10}(PO_4)_6(OH)_2$. This molecule occupies 65% of the mineral fraction in human bones. This material is also found in the structure of human teeth, especially in dentine and enamel. Therefore, the role of this material is very important in the world of health [10]. Based on data in Asia, Indonesia is a country with the highest number of fracture sufferers. Among them there are 300-400 cases of bone surgery per month at Dr. Soetomo Surabaya. HA is close to the structure possessed by human bones and teeth, and HA can be bound directly to tissue and can stimulate tissue growth. This causes HA to be applied in the biomedical field, especially for bone and tooth applications. Hydroxyapatite (HA), also known as calcium phosphate, is a bioactive material due to the calcium-phosphate ratio in this material similar to natural bones and teeth. Hydroxyapatite (HA) is one of the main components of bone and teeth. The main constituents of bone are collagen, calcium phosphate and water. Whereas in the teeth there are 2 main parts namely e-mail and dentine.

Email is composed of hydroxyapatite, water and other organic substances. Dentine is composed of hydroxyapatite crystals, collagen fibers, proteins and water [11]. The biocompatible and acceptable properties of hydroxyapatite with body tissues make this material used as a raw material for making biomaterials (materials other than drugs derived from living things / synthetic) that can treat, add or replace organ tissues or functions of the body and are used as supporting material for enzyme immobilization [12]. One of the choices of polymers is PVA which acts as a solution for oil, biodegradable and biocompatible which has been widely used in the biomedical field [13]. According to Jiang, Liu and Feng (2011) [14], PVA is the most important factor in the use of vascular cell culture. Hoffman (2002) [15] has succeeded in using a hydrogel made from PVA for living cell cultivation. PVA is biologically compatible and suitable for natural network simulation. In addition, PVA has good oxygen permeability, is not immunogenic, and has excellent properties in film formation, emulsifying and can be moisturized [16].

Several studies related to the manufacture of chitosan-based nano fibers have been carried out. Jia et al. (2007) [17] made nano composite fiber of chitosan and PVA (ratio 10:90; 20:80; 25:75; and 30:70 (v / v)) with chitosan deacetylation degree 78%. The results showed that there was an effect of the ratio of chitosan and PVA to the morphology of nano fibers produced. Cai et al. (2010) [2] make nano fiber as a wound dressing material using positive ingredients (Sigma-Aldrich, DD deacetylation 75-85%) and silk fibers. Wahyudi and Sugiyana (2011) [18] made nano fiber using electrospinning methods with chitosan, PVA, and nylon-6 materials. The raw material of chitosan used comes from shrimp shell waste. PVA and nylon-6 materials are capable of producing nano fibers, while the use of chitosan is not able to form nanoparticles. Judawisastra, Winiati and Ramadhianti (2012) [19] have conducted research on making chitosan nano beads without beads through the addition of PVA and hexadecyl amine (HDA). Chitosan used is based on shrimp waste with 65% deacetylation degree. The type of raw material for chitosan influences the characteristics of chitosan produced [20, 21] such as the difference between chitosan from crab shells and shrimp shells, especially viscosity and DD. This difference is thought to affect the characteristics of the nano fibers produced. Composite nano fiber PVA / HAp can be used as an operating thread, it can also be used as a membrane / filter for filtering materials for medical by regulating its porosity according to the use requirements in screening.

II. MATERIALS AND METHODS

Material: Hydroxyapatite material from limestone with a size of 400 mesh, and polyvinyl alcohol (PVA) 96%. The equipment used is beaker glass, electrospinning (syringe, collector, aluminum foil), balance sheet electric, magnetic stirrer.

Electrospinning specification data: The following is the Electrospinning specification data which is in the Center of Technology for Material - BPPT:

Table 1.
Specifications of Electrospinning Machines (Made by BPPT)

Syringe pump	1
Collector	15 cm x 15 cm
Power supply	1
Spinneret	1
Weight	37,8 kg
Dimension	73 cm x 45 cm
Multimeter	1

Machine parts and machine working principles: In general, Electrospinning machines (Figure 1) have important parts that have their respective functions. Starting from the power supply as a source of input to engine power, a control system that regulates the performance of the engine, the collector on the spinneret which functions as a place to manufacture fiber, syringe pump that functions as a solution for electrospinning, a multimeter that functions to find out how much voltage used. In general, the working principle of an electrospinning machine consists of 6 steps. First, start by entering the solution on the syringe pump, then the distance measurement that will be used starts from the tip of the syringe to the collector on the spinneret, the voltage setting will be used, the flowrate meter used, starts the operation and reverses the restart early operation. The length of the presentation for one running (one time making fiber) takes 1.05 minutes for fibers of 5 cm x 5 cm.

Figure 1. Electrospinning Machine

Making PVA / HAp composite nano fibers: Making nano fiber was carried out using electro spinner with 3 replications. Each solution with a mixture ratio as described previously (HAp 1% and HAp 5%) then put into a 10 ml syringe of 3 ml. The diameter size of the outlet syringe is 0.5 mm. The liquid is passed to the media with high voltage electricity (10 kV, 15 kV, 17 kV, 20 kV) to get fiber. On the side of the electrospinner there is a glass preparation attached to aluminum foil (glass) which serves as a sample collector for the fiber produced. The distance between the syringe and the 10 cm collector sample. The time needed in this process is around 1.05 minutes.

Method: Repair the HA solution with a concentration of 1 and 5%, by pouring HAp into the PVA solution. Then the mixture is stirred for ±20 hours at a speed of 800 rpm / minute. Furthermore, it is inserted into the injector (syringe) on the electrospinning machine and ready to run. Furthermore, the engine is regulated with variations in voltage of 15 kV, 17 kV and 20 kV for experiments using 1% HAp. Each fiber yield was observed using a polarizing microscope with magnification (10x and 40x). While for the experiment using 5% HAp, the electrospinning machine is regulated with variations in the voltage of 5 kV, 10 kV, 15 kV and 20 kV.

III. RESULTS AND DISCUSSION

Electrospinning is a machine that functions to print fibers, electrospinning in the center of material technology has 6 working steps. Starting from entering the solution to form fiber. Testing carried out using hydroxyapatite solution is a solution consisting of HAp and PVA, with HAp concentrations used at 1% and 5%. In experiments with a concentration of 1% HAp was carried out 3 times with a voltage of 15 kV, 17 kV, and 20 kV, respectively. In a 1% HAp trial, it was carried out using a distance of 10 cm, flowrate 1.1 mL/hour and a syringe diameter of 0.8 mm. In this test the operating time is 1 time running for 1.05 minutes and by using a 1 cm x 1 cm collector coated with aluminum foil. The test with a 5% HAp concentration was carried out 4 times with a voltage of 5 kV, 10 kV, 15 kV, and 20 kV, respectively. In the 5% HAp test each was carried out with the process conditions as in the process with 1% HAp, but using a glass collector. The results of observations using a polarization microscope, the results of experiments on the manufacture of nanofiber using a concentration of 1% and 2% HAp, can be seen in tables 2 & 3.

Table 2. Observation Results of PVA/HAp Nanofiber
on 1% HAp Concentration using the Polarization Microscope

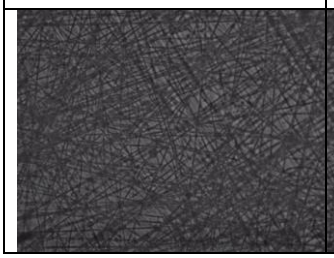
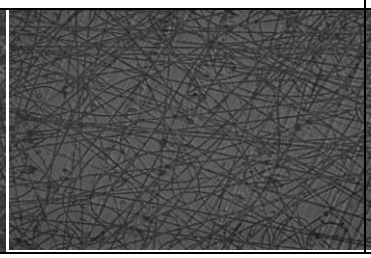
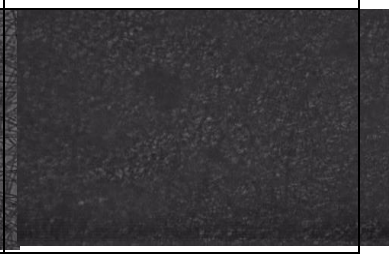
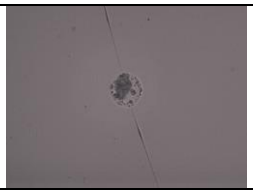
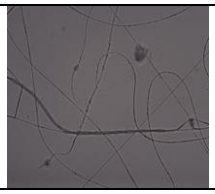
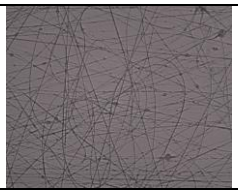
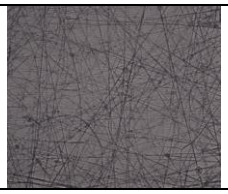
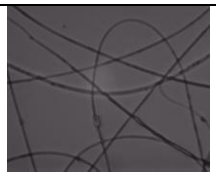
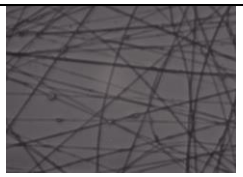
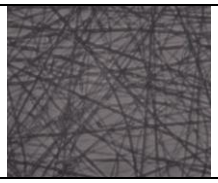
Voltage (kV)				
15		**17**		**20**
				

Table 3. Observation results of PVA / HAp nanofiber
at a 5% HA concentration using a polarization microscope

	Voltage (kV)			
	5	**10**	**15**	**20**
Enlargement 40X				
Enlargement 100X				

Meanwhile to simplify the analysis of the 1% HAp data obtained, it can be seen in table 3. In the 1% HAp solution an experiment was conducted three times using elecrospinning, the first experiment was carried out with a distance of 10 cm injector and collector, 0 syringe diameter , 8 mm, 1.1 mL/hour flowrate, and using a 1x1 cm collector with a duration of 1.05 minutes, and observations using a polarization microscope with 40x magnification.

In Table 4, 1% HAp can be seen that at a voltage of 15 kV, the smallest fiber size obtained is 7.62 µm and the largest is 11.40 µm. And at a voltage of 17 kV the smallest fiber size is 8.94 µm and the largest is 22.80 µm. The difference in the size of fiber can be seen quite clearly, especially in the largest size, the ratio is quite far. This is due to the voltage used, if the greater the voltage used, the size of the fiber will also be greater.

Table 4. Results of Fiber Size Using 1% HAp Concentration

Conc. HAp 1%	15 kV	17 kV	20 kV
The smallest	7,62 µm	8,94 µm	-
The biggest	11,40 µm	22,80 µm	-
Average	9,83 µm	14,46 µm	-

In this third experiment only one coating was carried out and fiber was thick enough, when testing using fiber size polarization microscopes in experiments with a voltage of 20 kV it could not be observed, because the size was too thick and fibers were too close or close together.

Meanwhile to simplify the analysis of the 5% HAp data obtained, can be seen in Table 5. The settings on the Electrospinning machine used are the distance between the injector to the 10 cm collector, 1.1 flowrate, the syringe diameter of 0.8 mm, and using a collector glass type with a duration of 1.05 minutes, and observations using a polarization microscope with 40x and 100x magnification.

Table 5. Results of Fiber Size Using a 5% HAp Concentration

Conc. HAp 5%	5 kV	10 kV	15 kV	20 kV
The smallest	9,49 µm	14,42 µm	9,22 µm	8,06 µm
The biggest	15,23 µm	37,00 µm	13,00 µm	17,12 µm
Average	10,45 µm	20,48 µm	10,84 µm	11,9 µm

In this 5% HA experiment using different voltages. In the first try the 5% HAp uses a voltage of 5 kV, the second is 10 kV, the third is 15 kV, and the fourth uses a voltage of 20 kV. In Table 4, a 5% HAp can be seen at a voltage of 5 kV and the smallest fiber size is 9.49 µm and the largest fiber size is 15.23 µm. At a voltage of 10 kV the smallest fiber size is 14.42 µm and the largest is 37.00 µm. At a voltage of 15 kV the smallest fiber size

is 9.22 µm and the largest is 13.00 µm. And at a voltage of 20 kV the smallest fiber size is 8.06 µm and the largest is 17.12 µm. By looking at these results we know that many factors affect the quality of the fiber, and one of them is internal factors. Internal factors are factors that originate from the device, namely electrospinning and from the solution itself, namely hydroxyapatite. The most influential factor is the magnitude of the voltage, the distance of the syringe from the collector, flowrite and how much hydroxyapatite is used. Of the four factors that are most influential are the amount of voltage and the amount of hydroxyapatite used. Voltage is the most important factor because it determines the size of the fiber, while the hydroxyapatite impurity affects the number of beads on the formed fiber. The distance of the colector and flowrite will affect the size of the fiber, the farther the distance and the smaller the flowrite, the smaller the size of the fiber as well as the closer the distance and the greater the flowrite given, the greater the size of the fiber formed.

In hydroxyapatite, the solution used will also affect the width of the fiber, if the HAp used is a concentration of 1% with a voltage of 20 kV compared to a 5% HAp and at the same voltage of 20 kV, then the fiber size is measured by a polarizing microscope with an increase of 40 times then a 5% HAp will produce greater fiber. This is probably due to the fact that the 5% HAp has a higher viscosity compared to the 1% HAp, where during the electrospinning process, viscosity can affect the process of fiber formation. If HAp which has too low viscosity then the electrospinning process does not occur in the formation of fibers, on the contrary if the thickness is too high then the solution will not easily reach the collector, so that fiber is not formed. For this reason, it is necessary to examine the amount of solution and voltage concentration that is suitable for fiber formation. This also affects the bits formed on hydroxyapatite, in this bit if the higher the amount of hydroxyapatite used, the more and more the number of bits contained in the fiber.

Besides internal factors there are also external factors. External factors that affect fiber yield are factors that originate from outside the engine and hydroxyapatite itself as from the influence of the room. Not only does hydroxyapatite and electrospinning affect fiber yield, many other factors such as wind factors can affect the fiber during the process of making fibers, such as breaking fiber during the process. Another factor is the purity of the solution and syringe used must also be free from contamination, such as dirt, dust, or even insects. Likewise, the syringe must be ensured that there is only a solution, to avoid the presence of air and gas in the syringe (injector). Due to the presence of air and gas in the syringe, the fiber syringe pump will be cut off during the process. So, in broad outline the things that can affect the results of a manufacture of hydroxyapatite fiber with electrospinning are hydroxyapatite and electrospinning itself and the large voltage electrospinning (internal factor). Then the purity of the solution and the conditions in the room during the process of making fiber can also affect fiber yield (external factor).

IV. CONCLUSION

Making polyvinyl alcohol/hydroxyapatite nanocomposites fibers has been successfully carried out by the electrospinning method. The hydroxyapatite concentration and voltage of the electrospinning machine greatly influence the size of the composite fiber produced. Hydroxyapatite concentration does not significantly affect the size of the nanocomposite fibers produced, but the higher the voltage applied will increase the size of the fiber even though the addition is not significant. Further research is needed to obtain optimum conditions, HAp concentration, concentration of PVA solution and the amount of voltage required. It is also necessary to characterize the produced nano fibers. In general, the electrospinning machine produced from the development of the Center of Technology for Material (PTM) - BPPT with one spinneret is already quite good, it has been able to produce nano fiber. However, paying attention to the performance of the electrospinning machine designed and developed by PTM - BPPT, it is necessary to increase the ability of the electrospinning, especially the development of systems to produce a longer range of voltage variations.

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