Functionality of Polysiloxane in the Attachment of Silver Nanoparticles on Nylon Fiber Surface

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Abstract—**We have carried out preparation of the composite of nylon fibers with silver nanoparticles and evaluated their antimicrobial properties. Nanoparticle of silver was prepared from reduction of silver nitrate by using ascorbic acid, sodium borohidrate, and trisodium citrate. The obtained nanoparticles showed size of 50-150 nm and maximum wavelength (λ_{maks}) of 418.5 nm. Silver nanoparticles were deposited into nylon fiber with the addition of polysiloxane and polyvinyl alcohol (PVA) as stabilizer. Fourier-Transformed Infra Red (FTIR) spectra of nylon-silver nanoparticle composites showed peaks attributed to nanosilver-amide group, vinyl alcohol, and siloxane. Antibacterial test for composites has been carried out by Colony Forming Units (CFU) methods. Colloidal silver nanoparticles showed antibacterial properties to the bacteria *Staphylococcus aureus* and *Eschericia coli*. From the antibacterial tests showed that the concentration of Polysiloxane 2% and 5 minutes deposition time gave the stability of antibacterial with treatment of several times of washing.**

Keywords– **Nanoparticle, Polysiloxane, Nylon, Silver, Deposition and Antibacterial**

I. INTRODUCTION

In recent years, the situation changed due to the development of the textile world influenced by several things. One is the development of new nanotechnology-related advising new fiber types to add a particular value [1]. Application of nanotechnology in textiles, especially having anti-bacterial properties with respect to an increasing desire to live in a comfortable environment. This is due to higher of pollution levels. Global climate change contributed to the unfavorable environment, such as the growing number and types of pathogenic bacteria that can harm our health [2]. The application of nanotechnology emerging now is the preparation and development of the polymer composites, fibers derived from either natural or artificial as the matrix with substances that have special properties, such as anti-bacterial [3].

The preparation of nanocomposite fiber that has anti-bacterial effect permanently conducted was studied [4]. In that study used polypropylene (PP) chips, PP / Ag master batch, and silver nanoparticles. To test the anti-bacterial activity used *Staphylococus aureus* and *Klebsiela pneumoniae*. The process of adding Ag done when spinning with spinneret temperature was kept at 250 °C and the rotation speed has 1000 m/min. Study on anti-microbial activity of the nanocomposite polyamide 6 (PA6) / silver have been investigate [5]. The process of composites made by melts processing at reduced thermal immersion silver ions. Nanosilver is added to form a composite is at 2% w / w. In this research, an investigation into the release of silver from composites and follows zero-order reaction rate for 100 days of observation. A study on the preparation of nanocomposite nylon / silver as a textile material which has anti-bacterial properties against *S. aureus* has been done [1]. Nanosilver is obtained by the reduction of silver nitrate using trisodium triacetate, and earned silver size 19 nm colloidal forms, the characterization using SEM. Study on the effect of polysiloxane as nano silver binder on polyester fibers as a matrix made [6] which can form hydrogen bonds with polyvinyl alcohol (PVA). The polyvinyl alcohol is a common stabilizer for nanosilver.

Mechanistic Studies on the inhibition process of silver ions against two strains of bacteria, *S. aureus* and *E. coli* have been reported [7]. In this study, both bacteria inoculated on Luria Bertoni medium (LB) and incubated at 37 ° C using a rotary shaker for 16 hours. After the silver nitrate was then added to the cultures and allowed to stand to grow for 4-12 hours. Five milliliters of the culture of the upper separated, centrifuged and biomass contained in the sample was analyzed using TEM to determine changes in morphology and X-ray micro-analysis to determine the changes that occur in *S. aureus* and *E. coli* after treatment the addition of silver ions. The results of TEM showed a large distance between the cytoplasmic membrane and cell wall, and there is a granulation electron around the cell wall. The results of X-ray micro-analysis showed the presence of silver and sulfur assuming silver ions after entering bacterial cells mixed with sulfur as a component of the cell [8].

Studies on the activity of silver zeolite against *E. coli* and compared with the activity of silver nitrate as an anti-bacterial has been reported [9] strain of *E. coli* OW6, CSH7, and UM1 used in this study. Bacterial cells obtained using centrifugation and resuspended back into the suspension of silver zeolite or silver nitrate in the density of 10-100 mg/l. The results clearly indicate that silver zeolite at 100 mg/l reduced the *E. coli* wall OW6 in 20 mM potassium phosphate buffer pH 7.0. Activity of silver zeolite was even more evident at higher temperatures (0 to 42 °C) and higher pH (6.5

to 8.5). As for the strain UM1 CSH7 and look more sensitive to silver zeolite and silver nitrate with the same treatment [7].

Research on the method of one stage in the synthesis of colloidal silver nanoparticles was reported [8]. In this study, reported the existence of the anti-microbial and anti-bacterial properties of silver nanoparticles high on gram-positive bacteria and gram negative bacteria including the methicillin strains such as *S. aureus* multiresistan. Anti-bacterial activity of silver nanoparticles is known is the influence of the size, and silver nanoparticles having a size 25 nm has anti-bacterial activity better. Nanoparticles are compounds toxic to bacterial cells at low concentrations of about 1.69 g / ml Ag [10].

Silver nanoparticles synthesized using Klebsiella pneumoniae and evaluation of the anti-microbial activity against *S. aureus* and *E. coli*. The result showed that with the addition of antibiotics such as penicillin G, amoxicillin, erythromycin, clindamisin, and vancomisin can enhance the anti-microbial activity after the addition of silver nanoparticles against *S. aureus* and *E. coli*. Higher activity demonstrated synergy in mixtures of erythromycin with silver nanoparticles [10]. While the synthesis of silver nanoparticles in the size of 10-15 nm and dose using a more effective influence on microorganisms gram positive and gram negative bacteria has been reported [11]. From these studies concluded that the dose of silver nanoparticles significant effect against gram-negative microorganisms than gram-positive [12].

In this study, the preparation of composite with a matrix of polyester fibers and nanosilver as the filler has been done using deposition method with polysiloxane compounds as binding agent. The antibacterial activity of the resulting composites was tested against *Staphylococcus aureus* and *Escherichia coli* by colony forming unit (CFU) method.

II. EXPERIMENTAL

The research activities are expected to provide products such as nylon-nanosilver composites that have good stability. The stabilization process is done in two stages: firstly, the process of stabilization nanosilver (NS) preparation results with the addition of polyvinyl alcohol (PVA). The secondly is the stabilization of the nanosilver composite nylon fibers with the addition of polysiloxane (PS). The general scheme is illustrated as well,

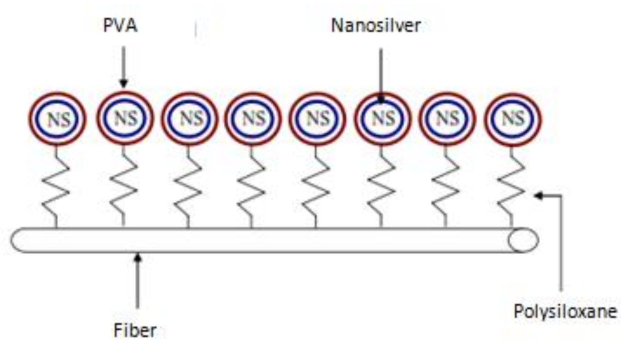

Fig. 1: Schematic diagram of polysiloxane as binding agent

The hypothesis developed in this study is that many PVA compounds containing hydroxyl group (^{-}OH), would include nanosilver particles in order to prevent agglomeration of the particles nanosilver. Polysiloxane compound and nylon fibers have hydrogen atoms in the structure. By doing a particular treatment is expected to form hydrogen bonds among PVA, PS, and nylon fibers. Thus, the composite of polyester-nanosilver will have a stronger antibacterial characteristic. Antibacterial mechanism of nanosilver will occur at the contact with the bacteria. PVA surrounding nanosilver will undergo a process of "swelling" when in a state of moisture. The process of "swelling" would lead to the opening of the pores of the PVA coating. Bacteria that are in a humid environment will go through PVA pores formed by the process of "swelling", and will be in contact with nanosilver.

The Composite of nylon-nanosilver was prepared using deposition method. In this process polysiloxane compound was added as a binding agent between silver nanoparticles and nylon fiber. Polysiloxane was varied in various concentrations. Nylon fibers were immersed at room temperature in an aqueous solution containing silver nitrate at a concentration of about 100 ppm. Furthermore nylon separated from the solution and immersed in a hot solution containing 7.2 g/liter NaOH and sodium persulfate, respectively, and then boiled for 1 minute (95-100 ^{o}C). Nylon removed from the boiling solution, washed with water in a several washing time and then dried.

III. RESULT AND DISCUSSION

Preparation of nano silver was carried out by reducing of $AgNO_3$ using reductor agent. The initial phase is dissolving PVA in warm on triple-neck flask. Colloidal silver was prepared by chemical reduction method by Yang Lee and Meisel. Into this solution was dropping a reductor. The solution was stirred strong during the process. The solution was heated until a clear color change (pale yellow) [13].

To strengthen the deposition of silver nanoparticles on the nylon matrix not only rely on physical interaction, but need to be coupled with chemical interactions. A way to create interaction is to give molecular chemical coatings that are able to interact with the -CONH- in nylon, in this case the polysiloxane used as a binder.

A. FTIR Analysis

FTIR analysis aims to observe the functional group of N - H (amide) derived from nylon fibers, -OH functional groups of PVA compounds and siloxane groups of the polysiloxane compound. Analysis of the functional groups of each compound was conducted to determine that there has been a bond between PVA molecules, molecular polysiloxane and nylon fibers.

Fig. 2 showed a FTIR spectrum analysis for the comparison of composite fibers were added polysiloxane nylon, nylon fiber and nylon fibers were added to the PVA and polysiloxane.

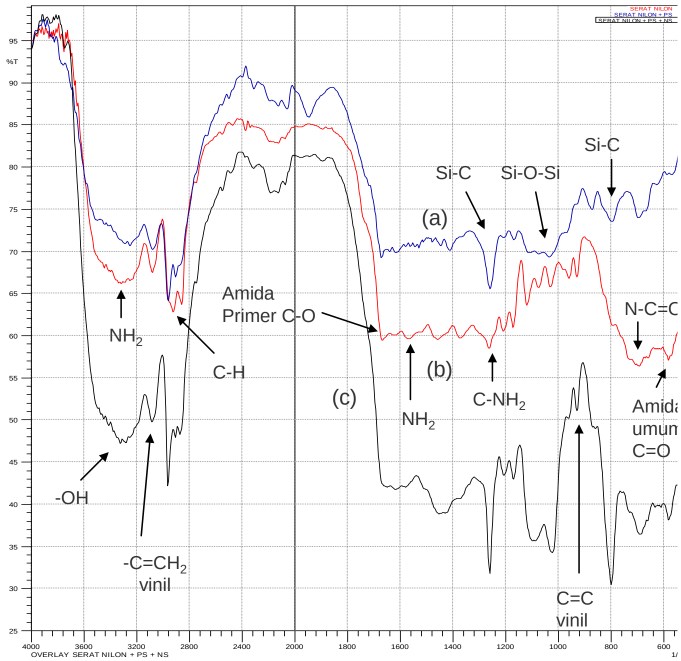

Fig. 2. FTIR spectra for nylon-composite nanosilver as prepared by PVA and polysiloxane, (a) nylon fibers plus polysiloxane, (b) nylon fiber, (c) PVA plus nylon fibers and polysiloxane.

FTIR spectrum analysis for nylon fibers contained absorption peak in the range of wave numbers 570-580 cm^{-1} which shows the C = O of amide in general, peak 660 – 6950 cm^{-1} which shows the bond NC = O. The bond of C - NH$_2$ groups absorption wave numbers shown in the 1170 to 1270 cm^{-1}, whereas the absorption wave numbers 1620 cm^{-1} specifically shows NH groups, absorption wave numbers 1668 cm^{-1} represents a group C = O of a primary amide. While the NH$_2$ group are shown in absorption wave numbers 3248 – 3334 cm^{-1}. From the analysis of the FTIR spectra showed that the Fig. 2 (b) is the FTIR spectra for compound forming amide groups.

Fig. 2 (a) shows the results of the analysis of FTIR spectra of nylon fibers that have been added to the polysiloxane. In the absorption wave number 796 cm^{-1} and 1259 cm^{-1} indicate the presence of Si-C group, whereas the peak 871 cm^{-1} showed absorption wave numbers for the Si-H groups. Cluster Si-O-Si absorption wave numbers shown in the range of 1033 – 1109 cm^{-1}. For the absorption peak wave numbers 2056 – 2125 cm^{-1} represents a group Si-H$_3$, whereas in the range of 2902 – 2960 cm^{-1} represents a group -CH$_3$, and the absorption at wave numbers 3442 – 3512 cm^{-1} represents a group of the C = O amide. From the results of FTIR analysis showed that the compound was present in the polysiloxane nylon fibers.

Fig. 2 (c) shows the results of the analysis of FTIR spectra for nylon-nanosilver composites that have been added of polysiloxane and PVA. Polyvinyl alcohol is a compound formed from vinyl groups and alcohol. PVA in this case is the stabilizer of the nanosilver particles. Vinyl group -CH = CH$_2$ is shown in absorption wave number 3084 cm^{-1}, while the alcohol $^-$OH group is indicated by the absorption spectrum of wave numbers 3211 – 3412 cm^{-1}. Comparative analysis of the FTIR spectrum Fig. 2. (a), (b), and (c) show that in Fig 2 (c) is the spectrum of the fiber nylon composite compound that was added to the polysiloxane and PVA.

B. Antibacterial Stability Analysis of Nylon-Nanosilver Fiber Composite

Antibacterial test was performed by the method of Colony Forming Units (CFU), which count the number of colonies of bacteria that forms on composite samples of nylon-nanosilver. At this stage of the research conducted to determine the effect of the addition of polysiloxane at various concentrations and leaching composite samples for antibacterial activity, and to know the effect of deposition time at various concentrations of polysiloxane in the composite of the antibacterial activity. The Antibacterial test performed against two types of bacteria, the gram-positive (*Staphylococcus aureus*) and gram-negative (*Eschericia coli*). Fig. 3 shows photograph of the antibacterial test results with the colony forming unit method. Colonies of bacteria is shown by the dots / white areas in Fig. 3(a).

Fig. 4 and Fig. 5 show the results of antibacterial tests on nylon-nanosilver composite. It can be seen that nylon without added nanosilver gives the number of colony formation around 100, while number of bacterial colonies produced from the nylon-nanosilver composite only about 20, good both for the *S. aureus* or *E. coli* bacteria. Based on these data, it can be concluded that the composite of polyester-nanosilver does have good antibacterial activity.

From both figures, can be seen that the antibacterial activity of the polyester-nanosilver composites against bacteria *S. aureus* or *E. coli* is relatively stable after 3 times washing treatment. At concentration of 1% polysiloxane, looks likely the number of colonies of bacteria is slightly increased. While at concentration of 2% and 3% the number of colonies that formed relatively stable around 20 colonies.

It also can be seen that the nylon-nanosilver composite has slightly better antibacterial activity against *S. aureus* than *E. coli*. This can be caused by the characteristic of *S. aureus* as a gram-negative group that has only single plasma. Gram-positive bacteria such as *Staphylococcus aureus*, common bacterial pathogens in humans, only have a single plasma membrane surrounded by a thick cell wall peptidoglycan form. Approximately 90 percent of the cell wall composed of peptidoglycan, while the rest of the other molecules called teicoic acid. On the other hand, gram-negative bacteria (such as *E. coli*) have a double membrane system in which the membrane pasmanya enveloped by the outer membrane permeable. These bacteria have a thick cell wall in the form of peptidoglycan, which is located between the inner membrane and outer membrane. Thus nanosilver particles more easily perform diffusion on gram-positive bacteria (*S. aureus*) because it has a smaller barrier in which bacterial cells are largely composed by single plasma compared with *E. coli* bacteria.

From Fig. 4 and Fig. 5 it can be seen that the addition of nanosilver particles significantly affect the decrease in both the number of bacterial colonies of *S. aureus* and *E. coli*. Based on the results of previous studies, suggest that nanosilver particles have excellent antibacterial activity against *S. aureus* and *E. coli*. The study shows an increase in antibacterial activity with the increasing concentration of

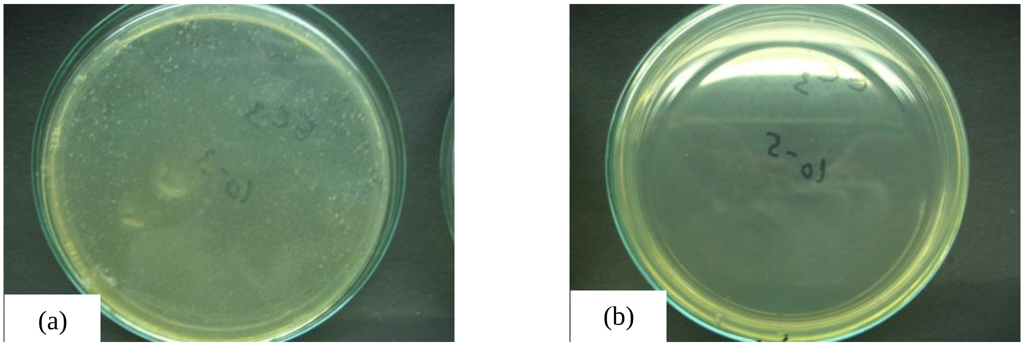

Fig. 3. Visualization of antibacterial test using CFU : (a) nylon fibers without nano-silver, (b) nylon-nanosilver

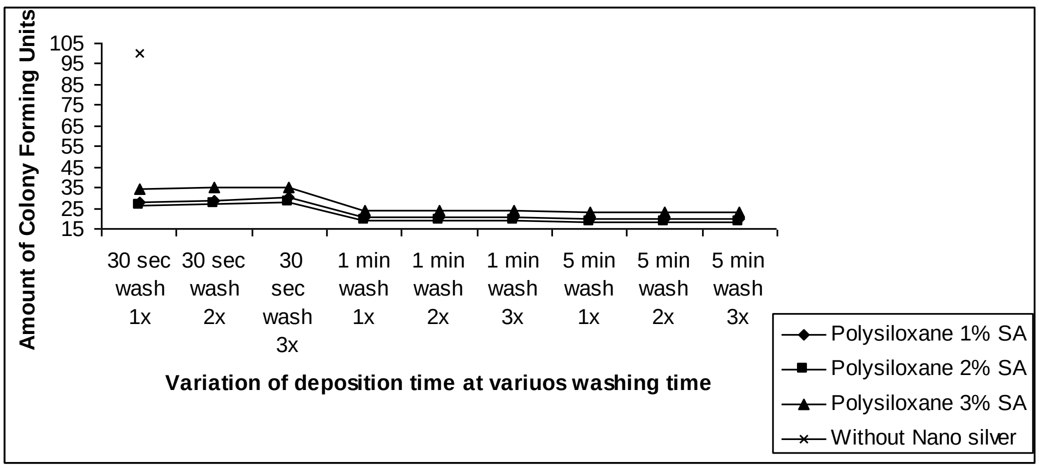

Fig. 4. Antibacterial test results of nylon-nanosilver composite against *S. aureus*

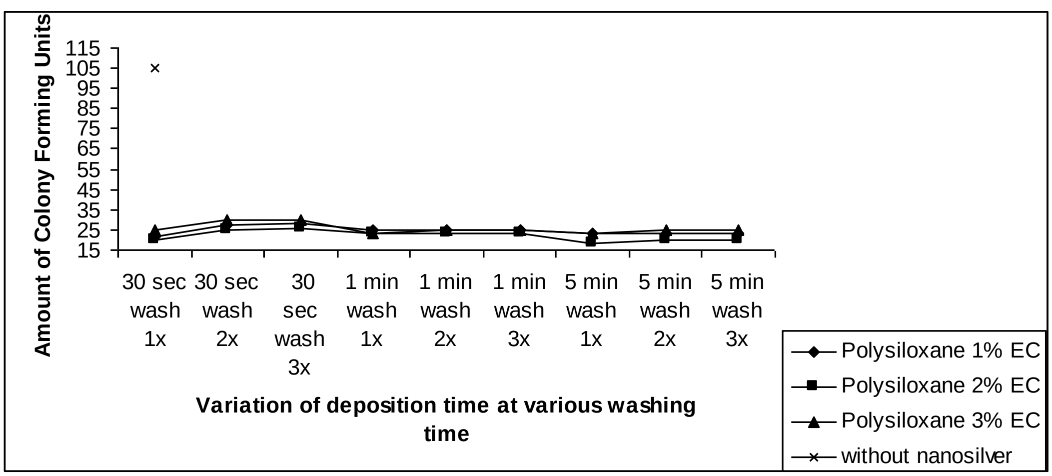

Fig. 5. Antibacterial test results of nylon-nanosilver composite against *E. coli*.

$AgNO_3$ as precursors of making colloidal nanosilver. Nanosilver particles are known to have good antibacterial activity because it has a high surface area that allows for excellent contact with microorganisms. During the diffusion process is running, nanosilver closer to the bacterial cell membrane and penetrate into the bacteria. Bacterial cell membranes contain sulfur as its main component. Nanosilver interacts with this protein, and then through interacts with phosphorus-containing compounds such as DNA. At the time of nanosilver into the bacterial cell, it causes the formation of regions with low molecular weight in the middle of bacteria region, which serves to protect the bacterial DNA. Furthermore nanosilver performs diffusion and attack bacterial respiratory chain, and eventually it becomes dead bacterial cells [15].

PVA compounds have semi-crystalline and hydrophilic properties. While the polysiloxane compounds tend to have hydrophobic properties (Reis et al., 2006). Therefore, based on this study, the concentration of 3% of polysiloxane is considered optimum to the process of nanosilver particles attachment on nylon fibers. After 3 times washing treatment, the number of visible colonies are relatively stable. From this study it can be concluded that the addition of polysiloxane compounds affect the stability of the antibacterial activity of nylon fiber-nanosilver composite.

C. SEM Analysis

SEM analysis was performed in order to determine the morphology of polyester fibers after being given treatment of nanosilver deposition and washing treatment several times. Fig. 6 and Fig. 7 shows the morphology of composite and silver nanoparticles distribution.

From Fig. 6 and Fig. 7, we can see the structure of the morphological distribution of nanosilver particles on nylon fibers appear uniformly showed no aggregation, but the dispersion of nanosilver particles on nylon fiber is uneven, and the particle size is not the same. This occurred because of the PVA polymer is added to the colloidal nanosilver. PVA nanosilver particles' surrounding the well has not been agitated.

Based on those figures, the nanosilver particles remain attached to the fiber, although nylon has been given washing treatment. This is appropriate with the results of antibacterial tests on nylon fibers-nanosilver composite which showed good antibacterial stability, because the composite still contained with silver nanoparticles although has been washed in several times.

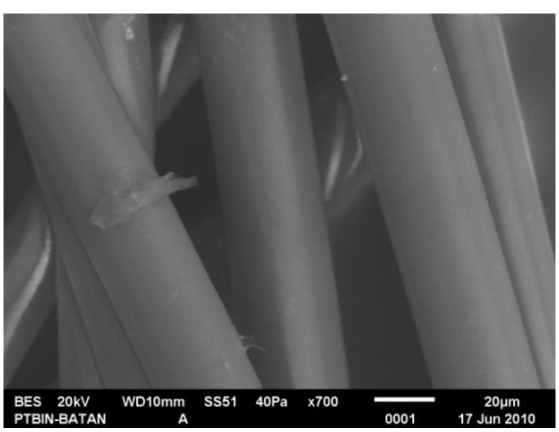

Fig. 6. SEM analysis result of nylon - nanosilver fiber composite

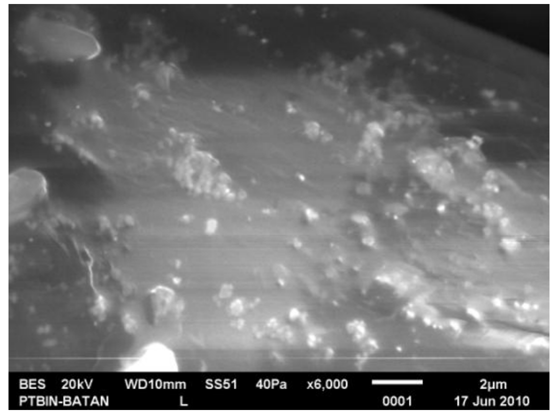

Fig. 7. SEM analysis result of nylon - nanosilver composite

IV. CONCLUSION

Nylon-nanosilver preparation is successfully carried out by 5 minute deposition with the addition of polysiloxane compound as the binding agent. The results of FTIR analysis identifies the group of amide from nylon fiber, $^{-}$OH functional group of PVA compound, and siloxane on the composite. A comparison of spectra wave number absorption of nylon-nanosilver composite with polysiloxane and PVA compounds indicates the crosslinking between the fibers, PVA and polysiloxane in the composite.

Antibacterial test results on composite of polyester-nanosilver using colony forming units (CFU) showed that the addition of polysiloxane gives good results to antibacterial stability after three washing treatments. The results of SEM analysis of nylon-nanosilver composite also showed that silver nanoparticles are still deposited on the fibers after three times washing treatment.

V. ACKNOWLEDGMENT

Authors would like to say thanks to Research Center for Chemistry – Indonesia Institute of Sciences and Department of Chemical Engineering, University of Indonesia for the laboratory facilities and also to Dr. Arbi from PTBIN BATAN for his effort and fruitful discussion on SEM analysis.

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