



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Silver Nanoparticles

In this section, the results of the reduction of silver nitrate salts in the presence of various polyelectrolytes as well as different conditions are reported.

4.1.1 Selection of Polyelectrolytes

There are many ways to reduce silver ions into silver particles such as sodium borohydride, hydrazine, acetone, glucose, sugar and UV light. In this research, UV light was chosen. The occurrence of the silver nanoparticles can be easily seen due to the characteristic colored solution.

Surface plasmons (SPs) are charge–density oscillations of electrons propagating at the interface of plasmon and a dielectric medium. Silver particles show the optical properties as a function of particle density by effect of electromagnetic interactions on plasmon excitations in silver particle. The electromagnetic response of a particle ensemble depends on size and shape of the particles, the surrounding medium, and the particle–particle interactions determined by the mean particle density on the surface. A phenomenon of color-selective absorption at metal/liquid crystal interface with surface plasmons is reported. When a white light is incident at a metal/liquid crystal interface, those photons in surface plasmon resonance frequency range are totally absorbed and the reflected light shows the complementary color. This effect may be made we can be seen the color of silver particle in solution.

The electron charges on metal boundary can perform coherent fluctuations which are called surface plasma oscillations. The fluctuations are confined at the boundary and vanishes both inside and outside of the metal surface. An important property of surface plasmons is the electromagnetic field enhancement at the interface compared with the incoming radiation. Dielectrics have the interesting property of making space seem bigger or smaller than it looks. The dielectric constant value tells you how much smaller or bigger the space gets. Most common dielectric materials (glass, plastics, etc.) have value between 1 and 100. The dielectric constant of a

material affects how electromagnetic signals (light, radio waves, millimetre-waves, etc.) move through the material. A high value of dielectric constant makes the distance inside the material look bigger. This means that light travels more slowly. [21-22]

To be concluded, the formation of silver nanoparticles from the reduction of silver nitrate by photo-induced reduction with polyelectrolyte can be monitored from the changes in color of the solution.

Table 4.1 The color of mixed solution between silver nitrate and polyelectrolyte.

Type of polyelectrolyte with AgNO₃	The Color of solution 1 day after	The Color of solution 2 days after	Charge of the polyelectrolyte
PMA	Light pink	Light brown	-
PDADMAC	Purple unclear	More purple unclear	+
Alginate	Light orange	Dark green	-
Chitosan	No color	No color	+
PSS	No color	Soft green	-
PEI	Soft green	Soft green (precipitate)	+
CoPSS	Light yellow	More light yellow	-
Glucose	No color	No color	N

Visual observation, as reported in Table 4.1, showed that, when the reaction between solutions of PMA, Alginate or CoPSS and silver nitrate proceeded, the color shifted from light pink, light orange and light yellow to light brown, dark green and lighter yellow, respectively, indicating the reduction of Ag cations which consequently coordinated to anions of PMA, Alginate and CoPSS resulting in zero valent Ag. PMA, Alginate and CoPSS were found to react with silver nitrate, led to a clear colored solution without precipitation. Because PMA, Alginate and CoPSS have negative charges, they can react with positive charge of silver, directly. Obviously, in the case of PMA, the color shift from light pink at the initial reaction to dark brown at the end of the reaction. While the color of the solution of CoPSS and alginate shift

from light yellow to olive green through orange. In addition, an aqueous solution of the silver nanoparticles stored for over two months at room temperature remained unchanged.

The color solutions of chitosan, glucose and PSS did not change. For the solutions of PDADMAC and PEI the color shifts from purple, pale light green to more purple and stronger pale light green. However, the solutions precipitated. It indicated that the reduction of Ag cations which consequently coordinated to anions of PDADMAC and PEI resulting in larger size of zero valent Ag. [20]

4.1.2 Effects of Polyelectrolyte Concentration

The stabilization of Ag nanoparticles in aqueous solution by PMA is possible over a wide range of conditions. To control the reduction rate of the particle, one needs to optimize the concentration ratio of the added Ag⁺ ions and PMA, and the reduction time.

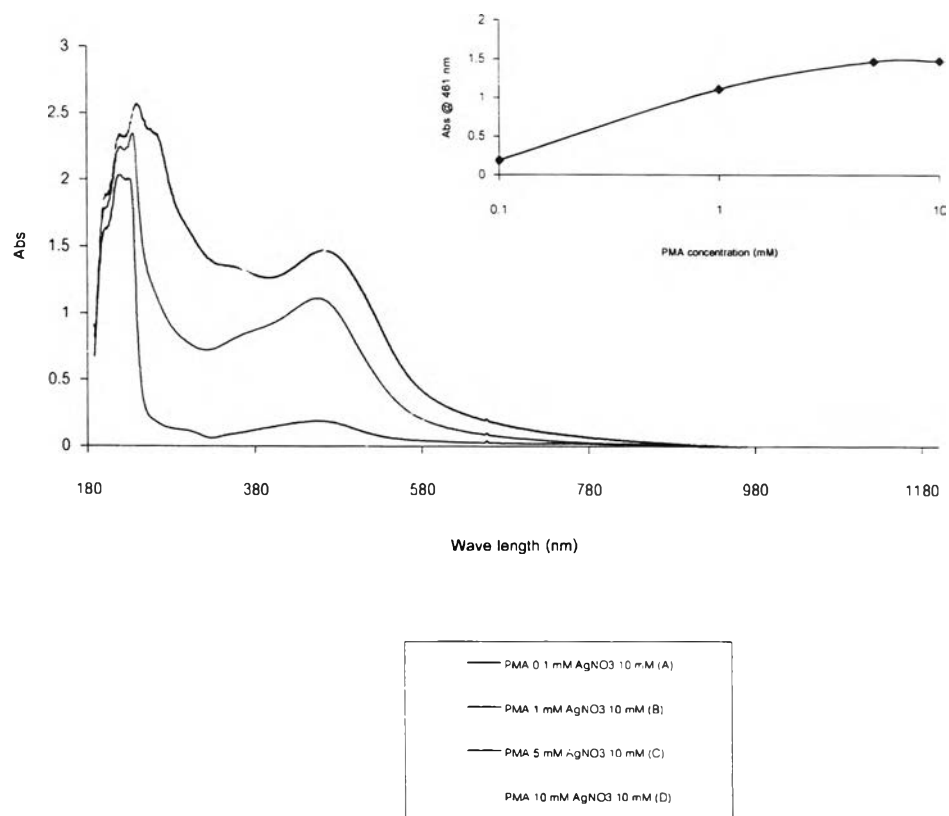


Figure 4.1 UV-Visible absorption spectra of mixed solution between silver nitrate and various PMA concentration. The inset shows the absorbance at λ_{\max} (461nm) vs PMA concentration (See the condition p.47).

The positions of the adsorption peaks, which are attributed to the surface plasmon resonance, are affected by nature of the metal (Ag, Cu, Au), size and shape of the nanoparticles and dielectric of the medium. The shift of maximum absorption wavelength could be explained as formation of the different shape silver nanoparticles. Figure 4.1 shows the UV-Vis spectra of Ag nanoparticles with different concentration ratio of PMA to Ag. The obtained solution showed absorption at λ_{\max} 465 nm(A), 465 nm(B), 470 nm(C) and 480 nm(D) for 0.1, 1, 5 and 10 mM, respectively, which was assigned to the surface plasmon resonance of obtained Ag nanoparticles.

The silver nanoparticle absorbance maximum increased with the increase of the concentration of PMA as shown in Figure 4.1 inset. An increase in an absorbance peak at 461 nm confirmed the growth of silver nanoparticles with PMA concentration. The reason for the λ_{\max} shift is that, at higher PMA concentration, Ag cations can cap with larger amount of anion from PMA. The effect may be explained by the changing of size and morphology or the presence of excess Ag^+ around particle or the well dispersed sphere-like silver nanoparticle.

4.1.3 Effect of AgNO_3 Concentration

Figure 4.2 shows the UV-Vis spectra recording Ag/PMA solutions with different concentrations of AgNO_3 . Figure 4.2 (A) shows that Ag/PMA solutions do not absorb in the visible region, this may be due to the amount of Ag is too low. It is observed from Figure 4.2 (B), (C) and (D) the surface plasmon resonance band occurs at 445 nm, 460 nm and 470 nm with concentration of AgNO_3 of 1, 5 and 10 mM, respectively. Figure 4.2 inset shows the spectra of Ag/PMA solutions with different AgNO_3 concentration, it is clear that, for higher concentrations, the amount of metal nanoparticles increase. The trend is clearly pointed out that the higher concentration of AgNO_3 , the faster the reduction is.[23]

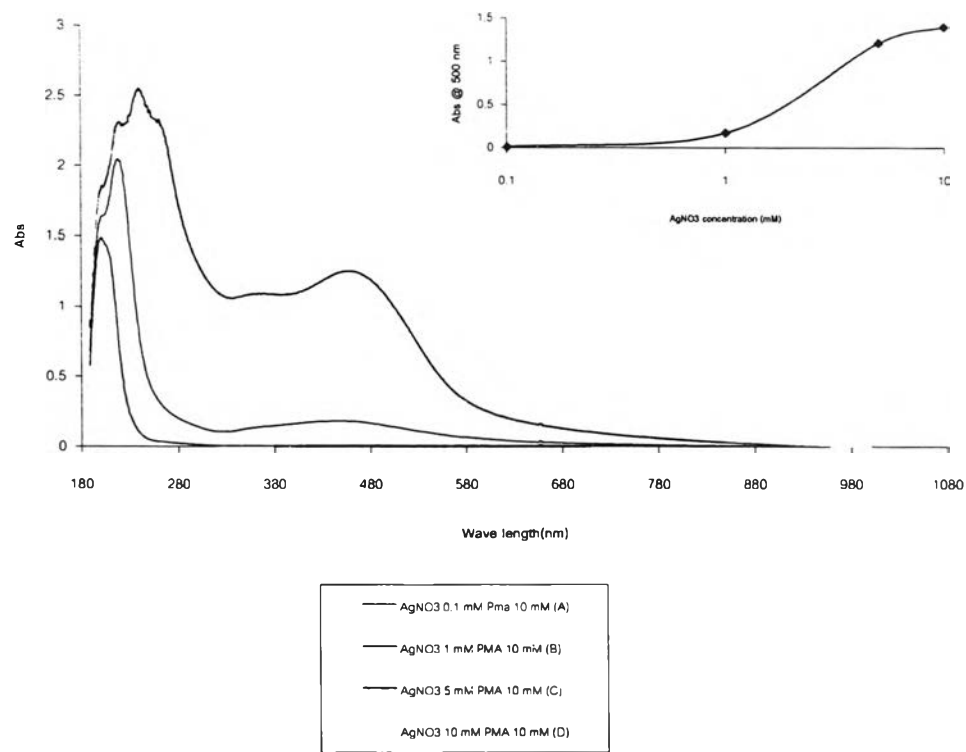


Figure 4.2 UV-Visible absorption spectra of mixed solution between PMA and various silver nitrate concentration. The inset shows the absorbance at λ_{\max} (500 nm) vs silver nitrate concentration (See the condition p.47).

4.1.4 Kinetic of the Formation of Ag Particles in PMA

PMA acts as a capping ligand for the silver particles as well as a photo reducing agent for the silver ions. PMA has one carboxylic group per repeating unit. The carboxylic group will bind to silver. Carboxylate groups from PMA can attract Ag^+ . So Ag^+ ions were separated. After that, Ag^+ ions were reduced by sun light and became silver nanoparticles.

A mixed solution between AgNO_3 10 mM and PMA 10 mM at volume ratio 1:1 was prepared to investigate the Ag formation, which the process of Ag formation was traced by UV-Vis spectra. In Figure 4.3 shows that the absorption peak at 500 nm increase with the increase of time, indicating silver colloid particles formation. A increasing in an absorbance peak at 500 nm, so UV/Vis spectra confirm the silver nanoparticles growth.[24-25]

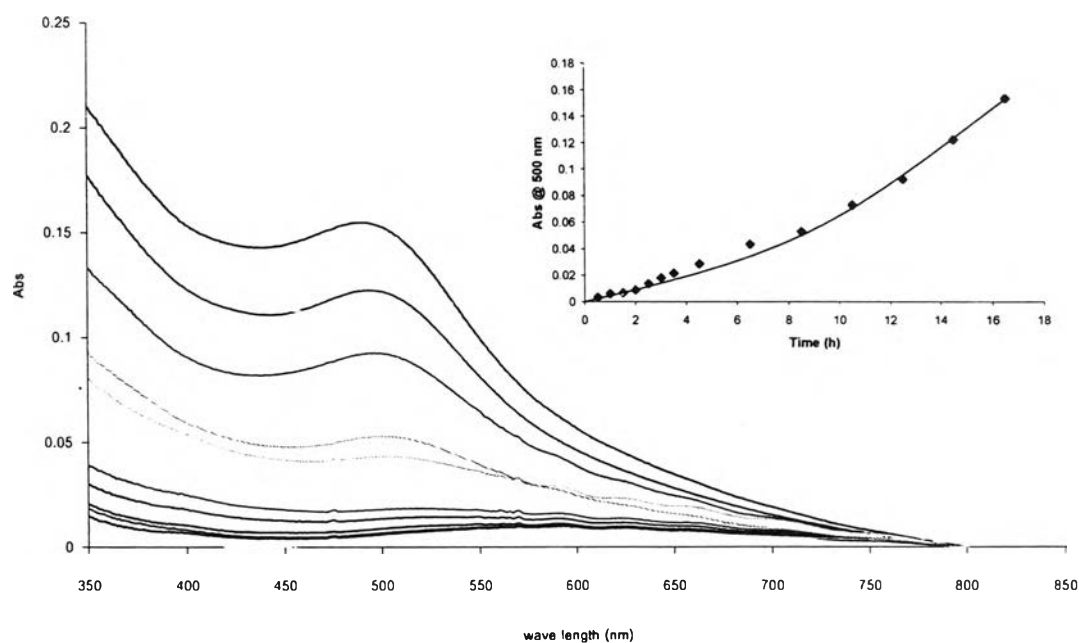


Figure 4.3 Time evolution of the UV-Vis spectra during the formation of Ag particles in PMA. The inset shows the absorbance at λ_{max} (500nm) vs times (See condition p 48)

4.1.4.1 Kinetic of the Formation of Ag Particles in Different Types of Polyelectrolytes

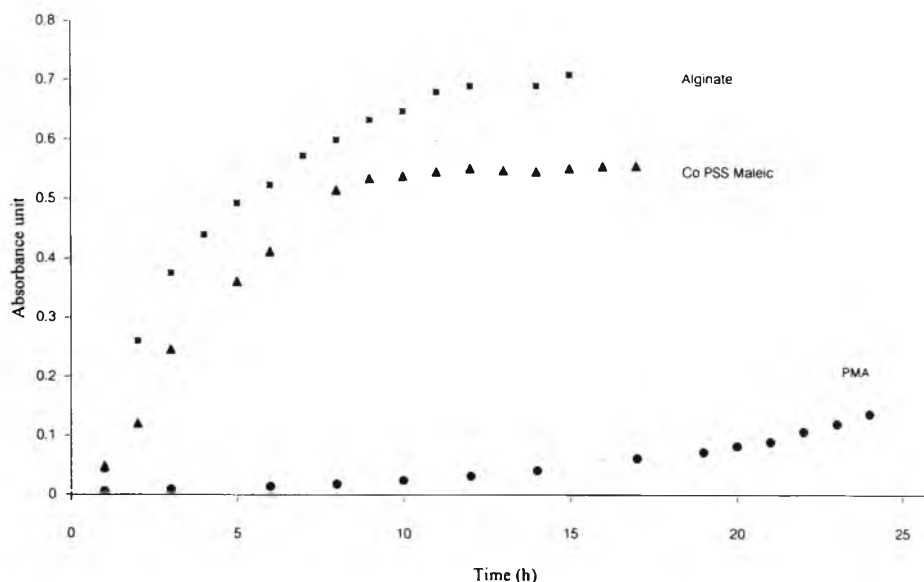


Figure 4.4 Kinetic of Ag nanoparticles absorbance at different type of polyelectrolyte : Alginate (square), CoPSS (diamond) and PMA (circle).

The objective of this experiment was to compare the reduction rate of different polyelectrolyte types. The PMA, Alginate, CoPSS and AgNO_3 were dissolved in deionized water to form aqueous solution $10 \times 10^{-3} \text{M}$. The aqueous solution of each polyelectrolytes were mixed with AgNO_3 solution as same volume and exposed under the sun light. Then the mixed solutions were measured with UV-Vis spectrophotometer. Figure 4.4 shows that the spectral absorbance at 480 nm with PMA 460 nm Alginate and CoPSS which indicated the silver nanoparticle formation. It can be seen that, for PMA, absorbance value was lower when compared with absorbance value for alginate and CoPSS. This mean alginate and CoPSS had faster reduction rate than PMA. CoPSS stabilized after several hours and faster than alginate and PMA. This indicated that the high yield reaction was occurred in the case of CoPSS.

4.1.4.2 Optical-absorption Properties

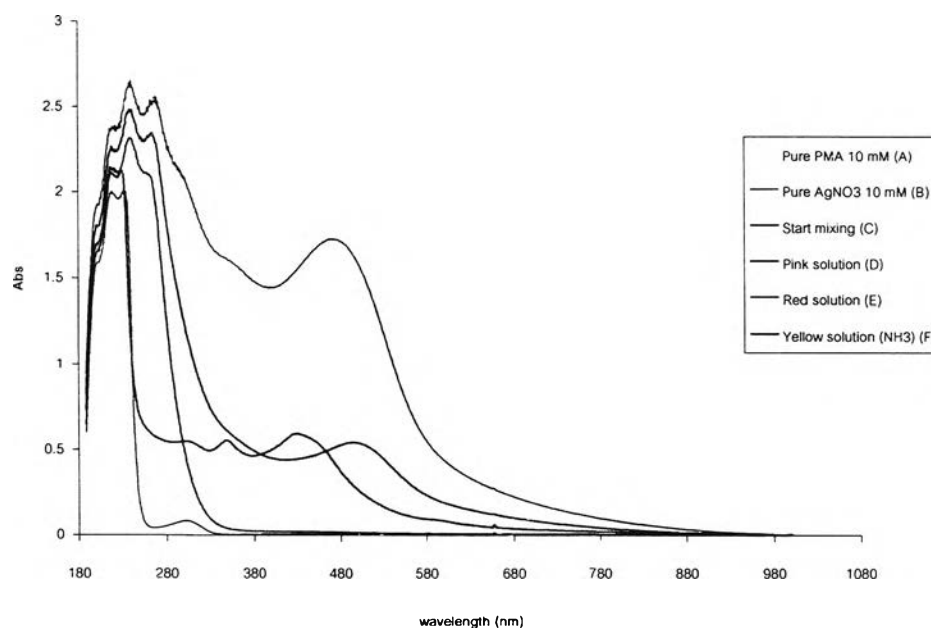


Figure 4.5 Schematic of surface plasmon band

Figure 4.5 shows the optical absorption spectra of the Ag solution in the range 200 to 1000 nm.

Figure 4.5 curve A and Figure 4.5 curve B show that the pure PMA and the pure AgNO_3 do not absorb in the visible region. It is noted that pure PMA has no absorption peak in the visible spectra. The exhibit of solution containing AgNO_3 at 323 nm resulted from the coordinative bonds of $\text{H}_2\text{O}:\text{Ag}:\text{OH}_2$. Figure 4.5 curve C shows the mixing solution between PMA and AgNO_3 were combined by pure PMA and pure AgNO_3 . It is observed from Figure 4.5 curve D that the surface plasmon resonance band occurs at 500 nm with photo-reduction of mixed solutions between PMA and AgNO_3 under the sun light about six hour. If the reduction time is increased until pink solution became red solution, Figure 4.5 curve E shows that the intensity of plasmon peak changes and a new peak appears at 470 nm. A plausible explanation for this effect is that initially the particle surface is positively charged due to the adsorption of unreacted Ag^+ . As the reaction proceeded, the ion concentration decreased and change the particle surface which a neutral charge. [26]

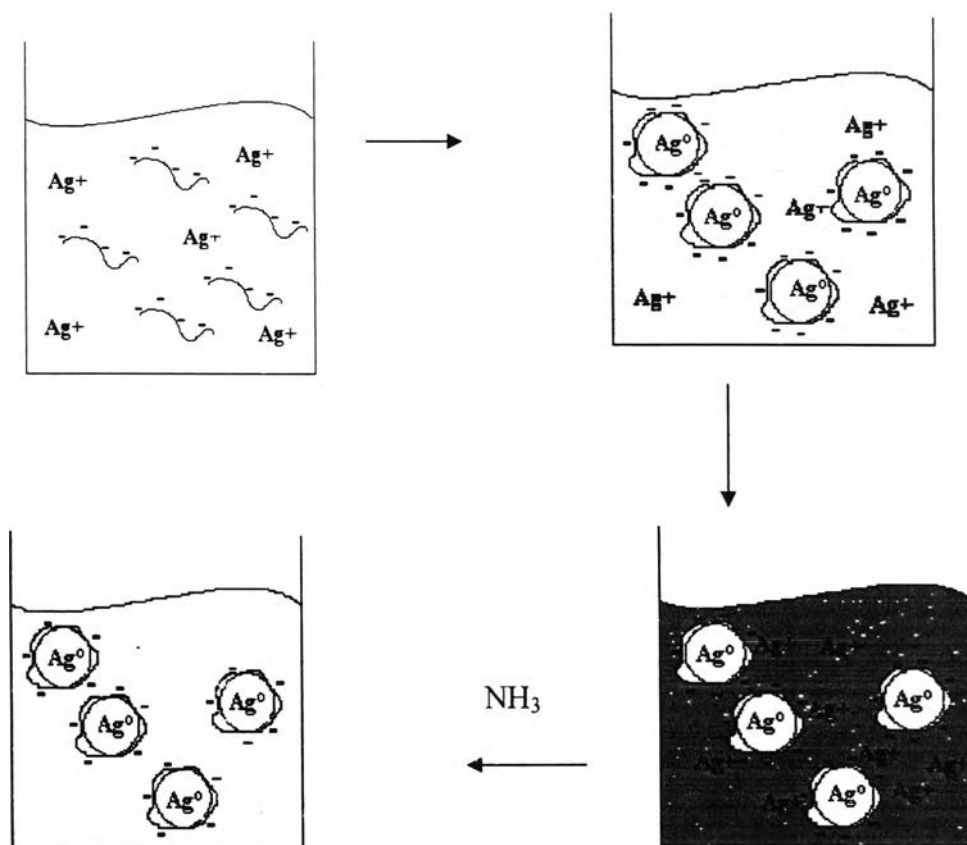


Figure 4.6 Schematic of silver in solution

In Figure 4.5 curve F, the 1% w/w of ammonia was added into red solutions which became yellow solutions appearing at different wavelengths. This was because of the excess silver ions were attracted by ammonia. So the yellow solutions showed the intensity of surface plasmon at 430 from metal colloid. The electromagnetic response of a particle ensemble depends on size and shape of the particles, the surrounding medium, and the particle–particle interactions determined by the mean particle density on the surface. Presumably, ammonia can removed excess ion around silver particle. The effect of surrounding medium resulted in the absorption shift to 430 nm from 500 nm. [27-28]

Transmission electron micrographs in Figure 4.7 show that silver particles are in nano-size and well dispersed.

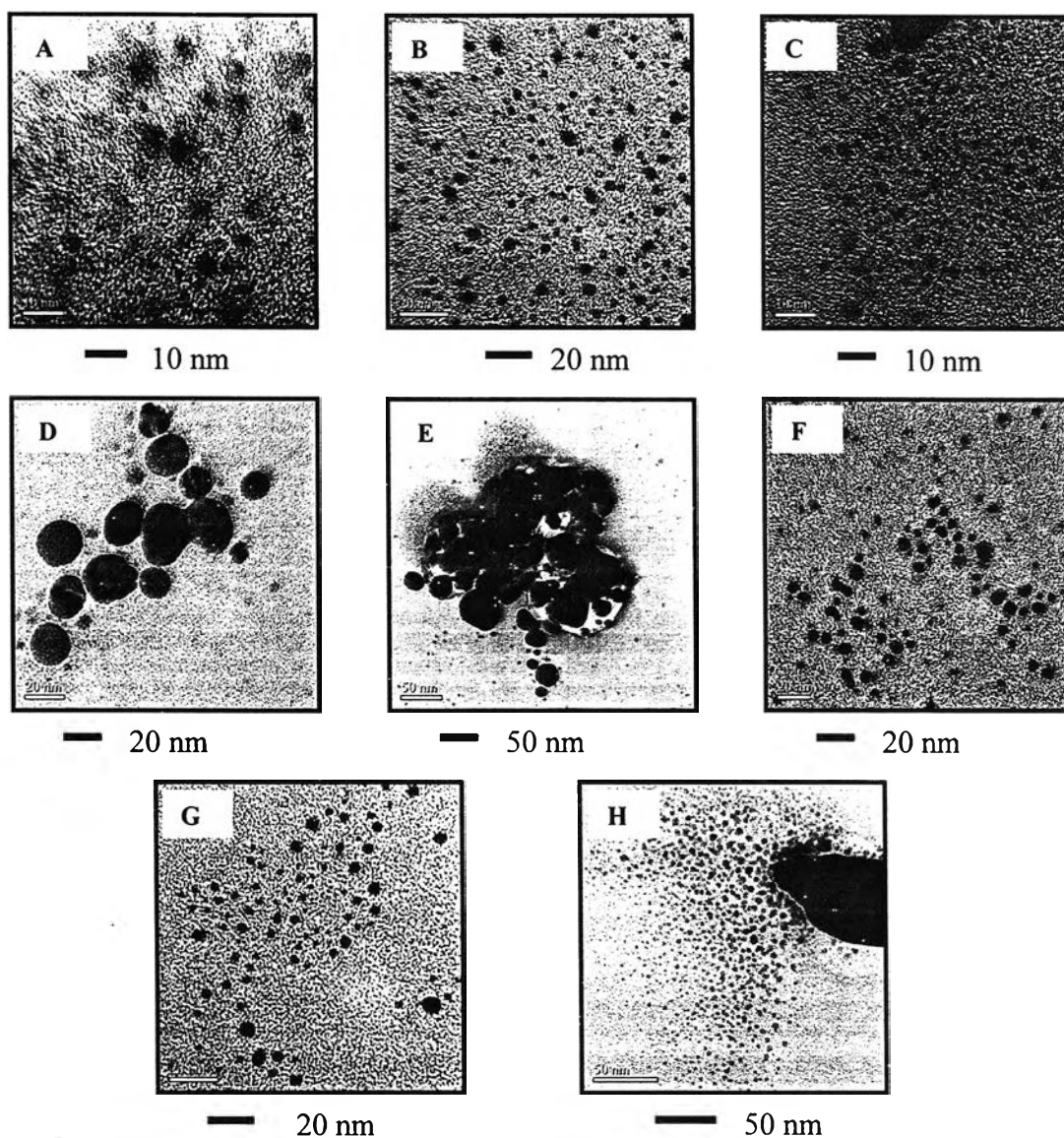


Figure 4.7 TEM images of silver particles at different type of polyelectrolyte of (A) PMA/AgNO₃ 10:10 mM brown solution at 10 nm (B) PMA/AgNO₃ 10:10 mM brown solution at 20 nm (C) PMA/AgNO₃ 10:10 mM yellow solution with ammonia at 10 nm (D) CoPSS/AgNO₃ 10:10 mM olive green solution at 20 nm (E) CoPSS/AgNO₃ 10:10 mM olive green solution at 50 nm (F, G) Alginate/AgNO₃ 10:10 mM olive green solution at 20 nm (H) Alginate/AgNO₃ 10:10 mM olive green solution at 50 nm

During the growth, particles presented a characteristic shape evolution. The particles were similar in shape for all type of polyelectrolyte. The well-dispersed sphere-like nanoparticles were obtained (Figure 4.7 A, B, C). The TEM images in Figure 4.7 C confirms that ammonia can remove the excess silver ions because small metal colloid size remained in solution comparing with Figure 4.7 A. [29]

4.2 Layer-by-layer Deposition on Textile Fibers

For the coating of nylon and silk fibers, the PMA capped Ag was alternately deposited with PDAD following the layer-by-layer deposit technique.

PMA capped Ag was used as the negative charge and PDAD was used as the positive charge. Then the sequential dipping of fibers in PDAD and PMA capped Ag solution led to the appearance of red color on fibers. The color was the result of the immobilization of silver nanoparticles onto the fibers. In order to monitor the layer-by-layer deposition of the silver nanoparticles, the K/S value provided by a reflectometer spectrophotometer was observed. This K/S value is calculated from the reflectance and scattering data and is commonly used in textile-related research to characterize the amount of dye fixation on fiber. Although silver nanoparticles can not be considered as a dye, the particles do absorb certain wavelength of light through the surface plasmon effect and a reflectometer can measure the increase in absorbance due to the deposition of the particles.

The growth of behavior of PEM was studied by following the change in their K/S at 480 nm. Figure 4.8 show that the increasing number of layers increased K/S value, it mean PEM thickness increased. The K/S value of PEM coated on silk fibers increased in a non-linear relationship because of the detection limit of the instrument.

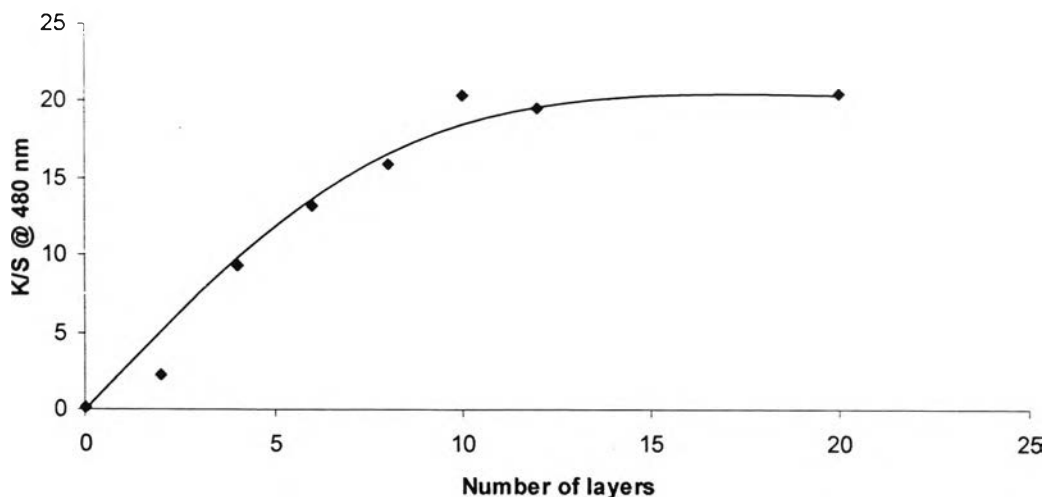


Figure 4.8 K/S value as a function of the number of PDAD-silver nanoparticle layer (See the condition p.52).

4.3 Effect of Primers

Polyelectrolyte multilayers are assembled from positive charge and negative charge of polymers on substrate by electrostatic attraction via layer-by-layer deposition.

The objective of this experiment was to improve efficiency of deposition. It was compared between the deposition PEM as a primer on fibers and without the deposition of primer. Nylon fiber has only limited amide groups thus presents lower charge density in molecular chains. Meanwhile, silk fiber is natural fiber with much more functional groups in molecular chains. The depositions with and without primer were compared. It was expected that the deposition of primer should provide high charge density for the fiber.

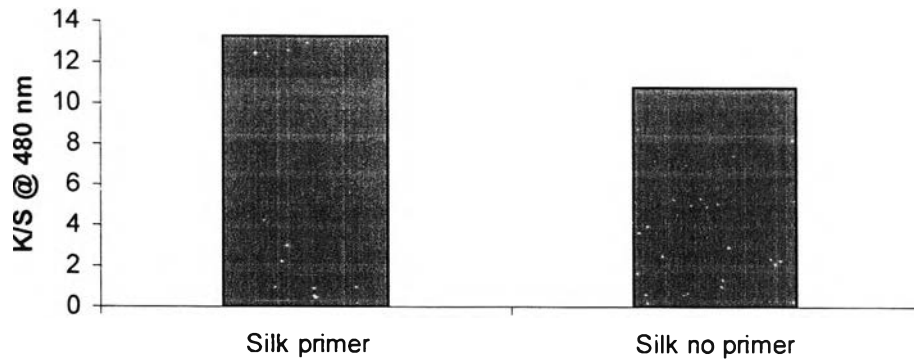


Figure 4.9 K/S value of silk primer and no-primer of PEM (See the condition p.52).

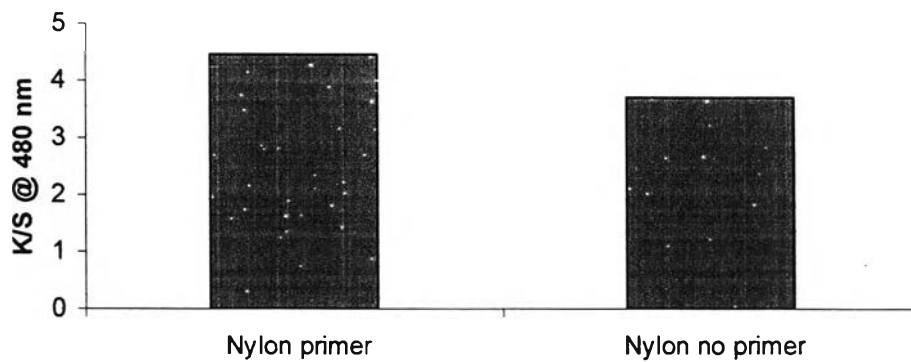


Figure 4.10 K/S value of nylon primer and no-primer (See the condition p.52).

Figure 4.9-4.10 shows that a higher K/S value at 480 nm of the deposition with PEM primer on both fiber were obtained comparing with the deposition without primer. However, this was not significant. In our subsequent experiments, the depositions were conducted without primer. [30]

4.4 Layer-by-layer Deposition of PMA capped Silver Nanoparticles on Fibers

The PMA capped Ag solution were diluted 10 times from mixed solution between PMA 10 mM and AgNO₃ 10 mM for built PEM on silk fiber with PDAD solution and successive dipping of silk in silver nanoparticle solution without the PDAD dipping step. For nylon fiber, the PMAcapAg solution non-diluted were alternately deposited with PDAD and nylon fibers were dipped in silver nanoparticles solution without the PDAD dipping step. During the dipping process, one might wonder if the silver nanoparticles are being deposited through interaction with cationic PDAD or if they are directly absorbed into fibers. To clarify this point the fibers dipped in silver nanoparticles solution without the PDAD dipping step was done.

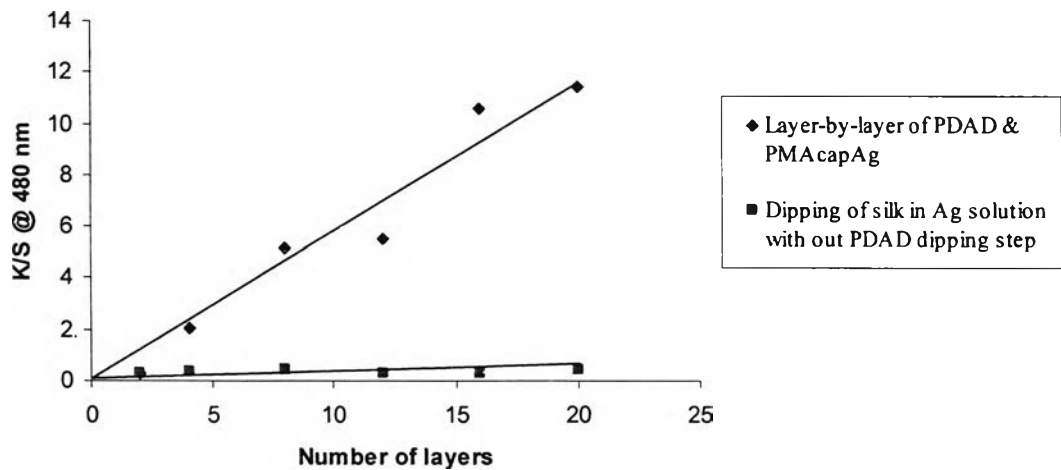


Figure 4.11 K/S value as a function of the number of PDAD-silver layer (PMAcapAg) (diamond) and number of silver layers without PDAD (square) on silk fiber(See the condition p.53).

Figure 4.11 and Figure 4.12 show the increase in K/S value of silk fibers as a function of number of deposited PDAD-PMAcapAg bi-layers. There is a large different between K/S of the fibers coated with PEM and the fibers dipped in silver nanoparticles solution. The K/S value of dipping nylon and silk fibers in silver nanoparticles solution without the PDAD dipping after various numbers of dipping

cycles showed no evidence of the presence of silver nanoparticles on fibers. This confirms that the deposition of the nanoparticles only occurs through the layer-by-layer deposition with oppositely charge PDAD.

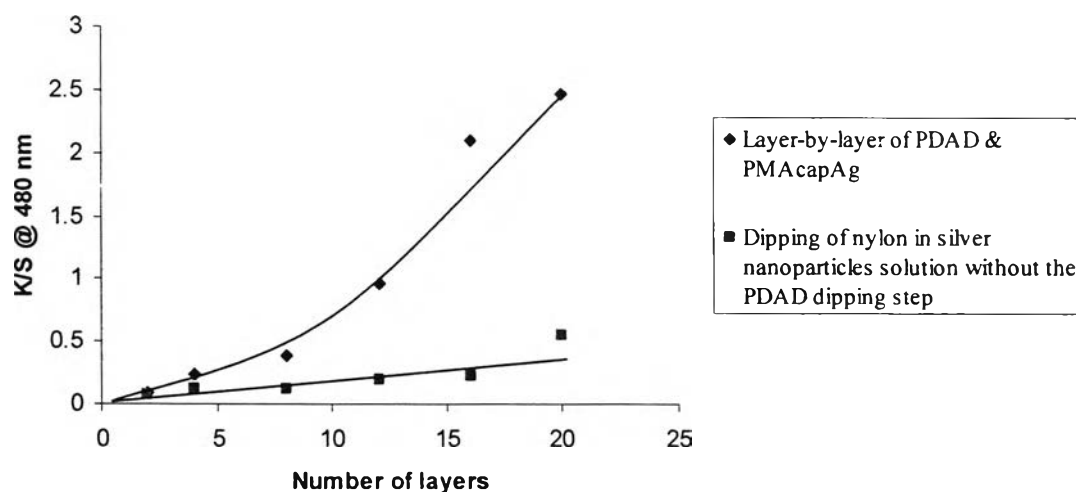


Figure 4.12 K/S value as a function of the number of PDAD-silver layer (diamond) and number of silver layers without PDAD (square) on nylon fiber(See the condition p.53).

From Figure 4.11 and Figure 4.12, it can be seen that the K/S value increase slower for the nylon fiber when compared with the silk fiber. This means that less silver nanoparticles are being deposited on the nylon fibers compared with the silk fiber. The difference in deposition is probably due to the lower charge density of synthetic nylon compared to that of silk. Surfaces having a lower charge density are known to lead to a slower growth the PEM. Nylon is a synthetic fiber. Their chemical structure usually does not allow for them to be deposited easily.[31] From this reason, subsequent experiments were focus only on the silk fibers. [32]

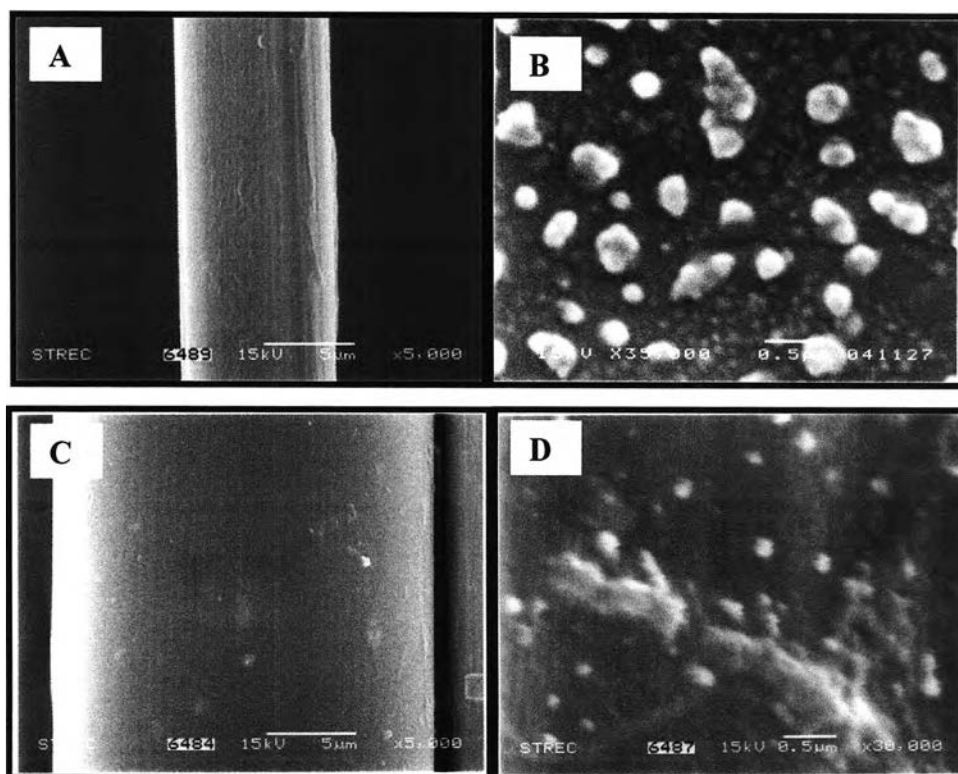


Figure 4.13 Scanning electron microscopy of the silk uncoated (A), silk coated 20 layer (B), nylon uncoated (C) and nylon coated 20 layer (D).

Figure 4.13 shows the picture of the silk, nylon fiber uncoated and the silk, nylon coated with 20 layers of PDAD/PMAcapAg nanoparticles. It can be seen that the silver nanoparticles were deposited on both fibers but it was not uniform in the case of nylon fiber. Figure 4.13 (B) and Figure 4.13 (D) shows the confirmation of K/S value result of the nylon fiber increased slower than the silk fiber.

From the experiment we found that the yellow color on fibers occurred when the experiment was done at night. Then, the red color on fiber appeared after exposure to light.

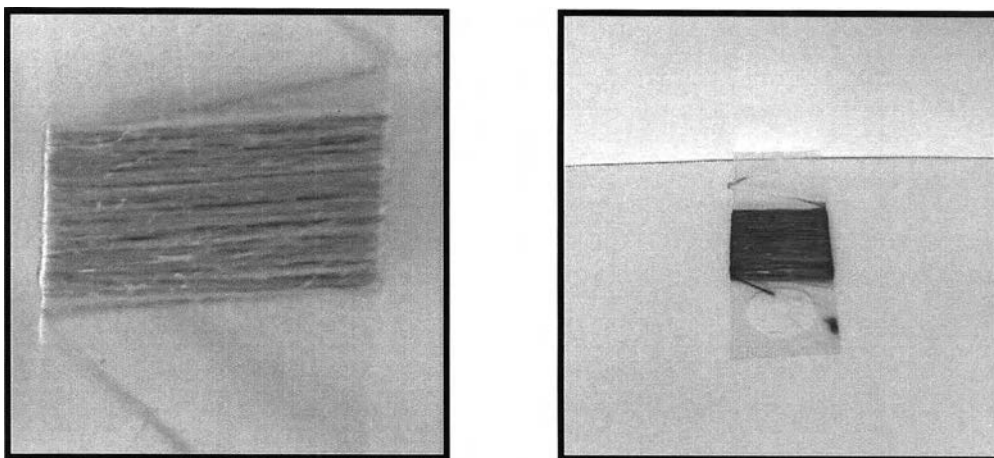
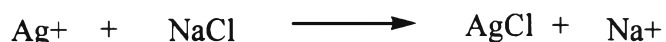


Figure 4.14 Silk fiber after deposited silver nanoparticles at night (left) and became red at next morning (right).

It seemed that not only silver nanoparticles were deposited on the fiber but also silver ions which remained inside. The silver ions can be reduced to AgCl in PDAD solution. AgCl was then trapped in multilayer together and reduced with the sun light.

This was confirmed by the following experiments. Firstly, silk fibers were dipped in PMAcapAg dilute 10 times (from 10 mM) and PDAD solution in day condition and night condition. Day condition showed red fibers and night condition showed yellow fiber. Then yellow fiber (night condition) was brought outside, led to the appearance of a red color on silk fiber.

Secondly, if the reducing reaction is low yield, there are plenty silver ions to react with salt. So, the mixed solution was neutralized by adding NaCl in mixed solution to remove silver ions. Then solution was centrifuged at 4000 RPM for 30 minutes to precipitate the complex of AgCl and clear solution was used for built PEM. The clear solution was assumed to contain only silver zero valent in solution.



Day condition showed red and night condition showed yellow fiber then became red fiber. Mixed slution became turbid because AgCl was formed by excess NaCl in solution. Then it was trapped in multilayer.

Silk fiber was dipped in 5 mM AgNO_3 and 10 mM NaCl . A purple color non silk fiber appeared.

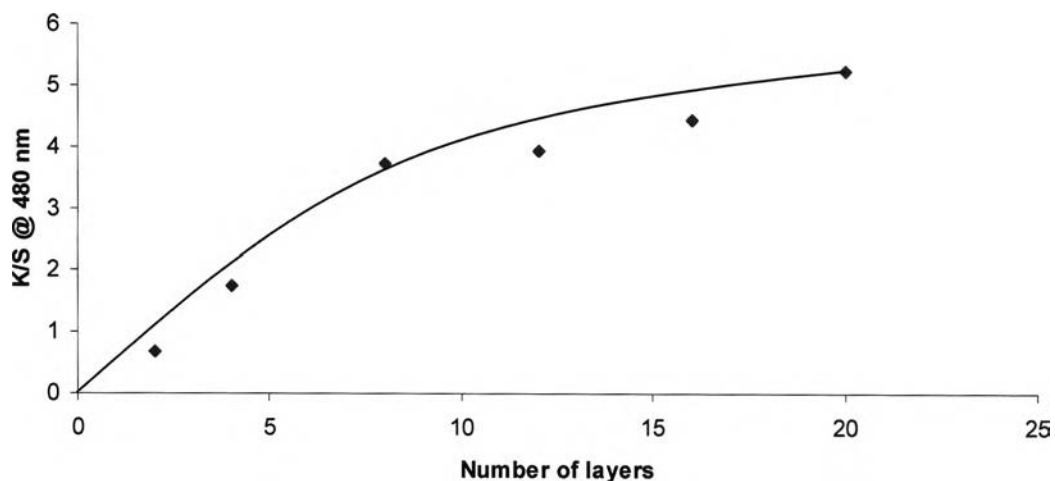


Figure 4.15 K/S value as a function of the number of AgNO_3 - NaCl cycle on silk fiber (See the condition p.54).

Figure 4.15 shows that silver particles were immobilized on fiber when number of layer was increased, the K/S value increased. It was confirmed by SEM micrographs shown in Figure 4.16.

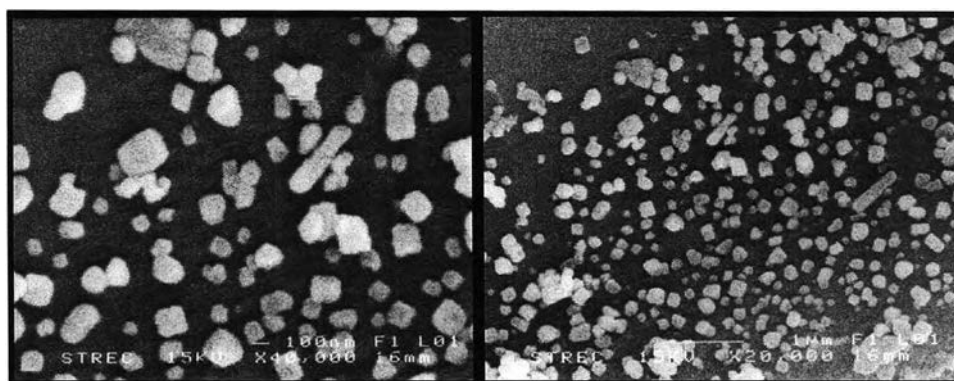


Figure 4.16 Scanning electron microscopy of the silk dipped in AgNO_3 and NaCl .

Figure 4.16 shows that silver crystallines deposited on silk fiber and presented various shapes and sizes. Comparing with the coatings in Figure 4.13 (B), there were clearly different shapes; it presented a spherical shape which it is character of silver

metal. Figure 4.17 shows silver chloride in cubic structure. Thus, it can be assumed that sphere-like shape is silver nanoparticles and cubic-like shape is silver chloride crystalline. [33]

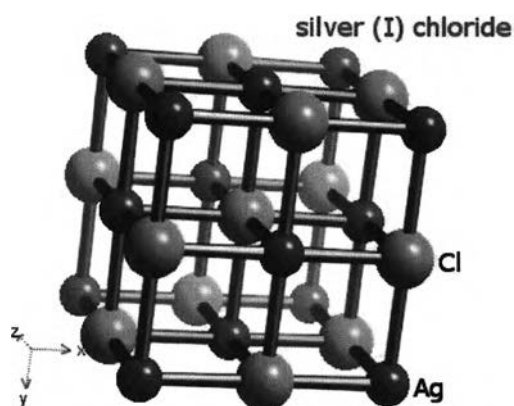


Figure 4.17 Cubic structure of Silver chloride

As stated earlier, AgCl can be removed by ammonia. Silk coated with AgNO_3 and NaCl was dipped in 1% w/w ammonia solution. The color of the fiber changed from purple to yellow since some AgCl was reduced to silver zerovalent nanoparticles.

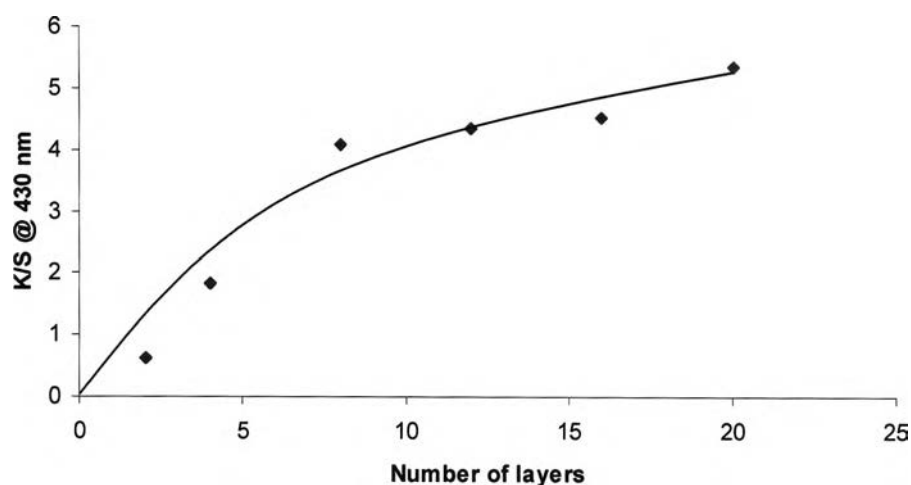


Figure 4.18 K/S value as a function of the number of AgNO_3 -NaCl layer on silk fiber and dipping of silk in 1% w/w ammonia solution on the last step (See the condition p.54).

Figure 4.18 shows that the kinetic of multilayer thin film formation of AgNO_3 and NaCl with the ammonia dipping step was in the same trend as that without ammonia dipping step. However, the maximum K/S value was found at different wavelength because the different color on fiber was presented.

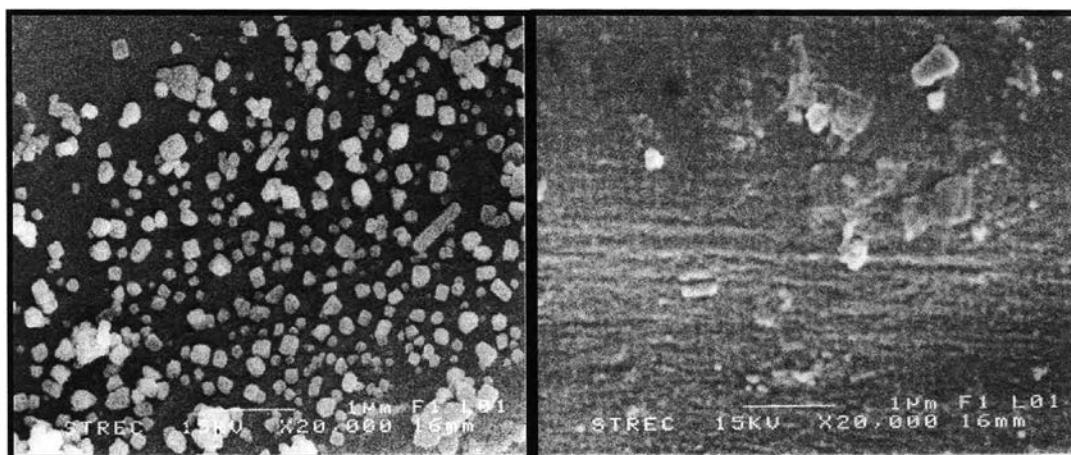


Figure 4.19 Scanning electron microscopy of the silk dipped in AgNO_3 and NaCl (left) and dipping of silk in 1% w/w ammonia solution on the last step (right).

Figure 4.19 shows the smooth surface of silk fiber after dipped in 1% w/w ammonia solution. It can be confirmed that AgCl was removed by ammonia. The silver nanoparticles remained on fiber can not be seen by SEM because of the limitation of SEM resolution. Although, it can be confirmed by the TEM micrograph shown in Figure 4.7 (C).

Ammonia solution was used in silk fibers coated with PDAD-PMA capped Ag bi-layers for every layer to remove AgCl on silk fibers, led to the appearance of a yellow color onto fiber. This was due to the fact that AgCl cannot be totally removed by ammonia only once in the last step since some AgCl may be trapped in each layer. [34]

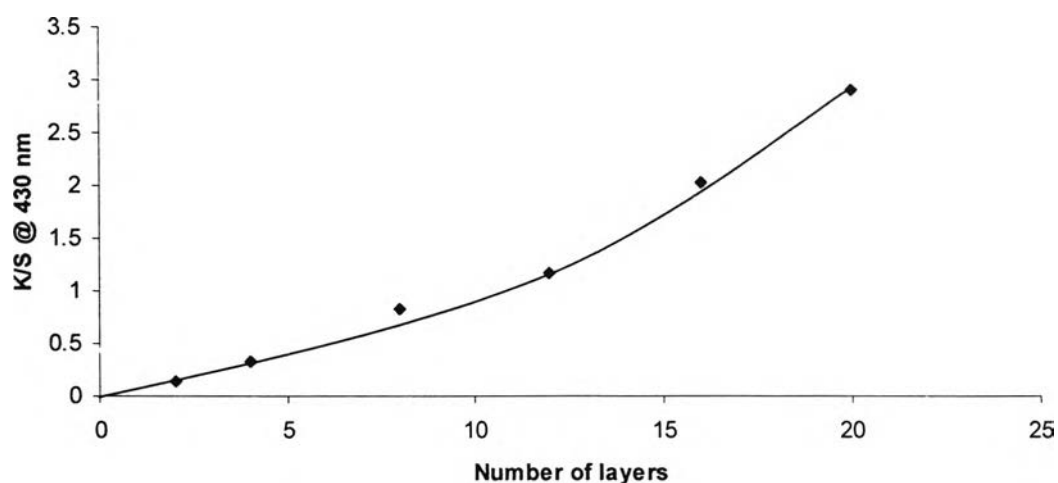


Figure 4.20 K/S value as a function of the number of PDAD-silver layer on silk fiber and rinsed with 1% w/w ammonia solution every layer (See the condition p.52).

Figure 4.20 shows that the increasing of K/S value when number of layers increased. This suggested that ammonia can remove AgCl and silver zerovalent nanoparticles were remained on fibers.

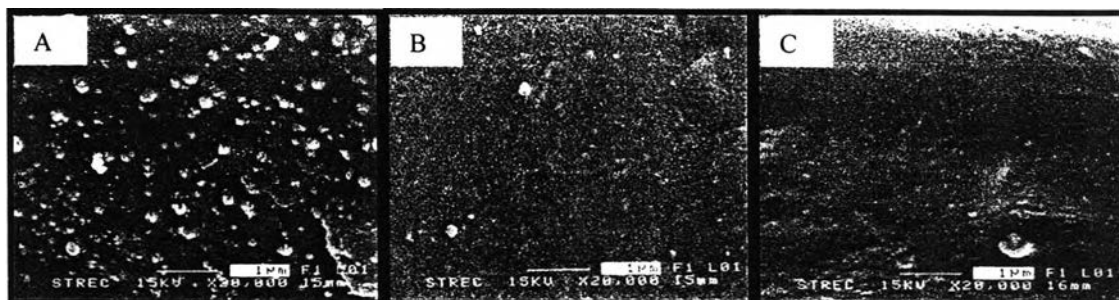


Figure 4.21 Scanning electron microscopy of the silk coated PDAD/PMAcapAg (A) and rinsed with 1% w/w ammonia solution every layer (B) and dipping of silk in 1% w/w ammonia solution on the last step(C).

It can be confirmed by Figure 4.21 (B) and Figure 4.21 (C) that ammonia can remove AgCl comparing with Figure 4.21 (A). From this figure, it can be seen that a small amount of particles remained on fiber. Silver nanoparticles remained on fiber cannot be seen by SEM because of its resolution limitation. [35]

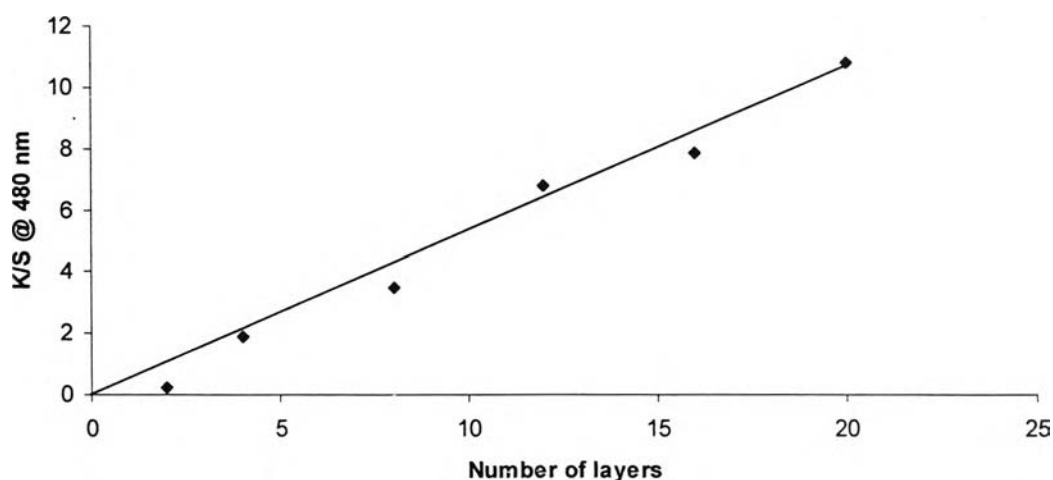


Figure 4.22 K/S value as a function of the number of PDAD-silver layer on silk fiber without salt in PDAD solution(See the condition p.52).

Figure 4.22 shows that the increasing number of layers increases K/S value which means that the thickness of PEM increases. PDAD solution was prepared

without salt to reduce the effect of AgCl. However, Cl^- counter ions of PDAD can be presented and a small amount AgCl can be formed. So, the maximum K/S value showed at 480 nm. PEM was prepared without salt in PDAD solution and dipping of silk in 1% w/w ammonia solution once only on the last step. The ammonia can remove AgCl and silver nanoparticles were immobilized on silk fiber.

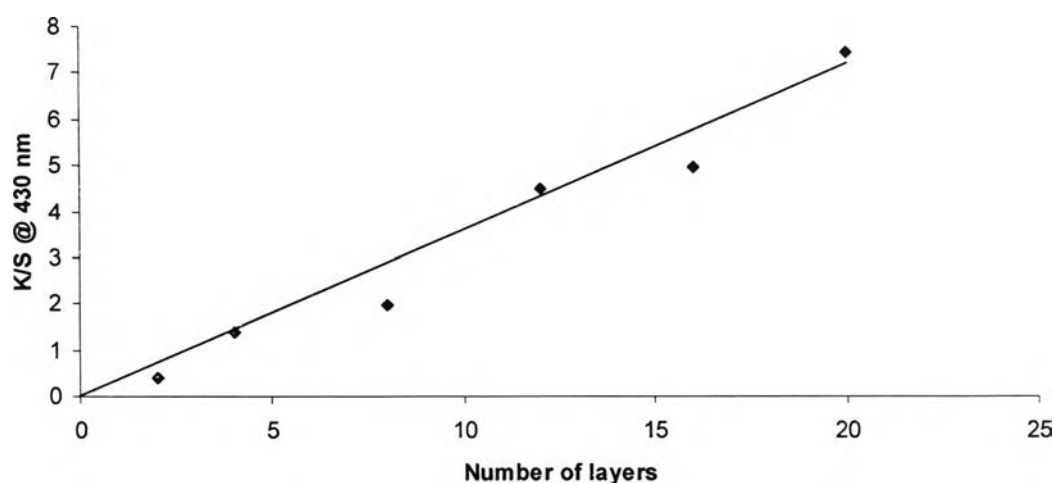


Figure 4.23 K/S value as a function of the number of PDAD-silver layer on silk fiber without salt in PDAD solution and dipping of silk in 1% w/w ammonia solution on the last step(See the condition p.52).

Figure 4.23 shows that the same increasing trend of K/S when the number of layers increased.

The error from PMA capped Ag experiment was due to silver ion reduction after immobilization since PMA capped Ag solution had a low yield reaction. Figure 4.4 shows that the CoPSS reaction reached the stable state faster PMA. This means that CoPSS capped Ag solution had higher yield when comparing with PMA capped Ag solution. As a consequent, for the next experiments, CoPSS capped Ag was used for the formation PEM.

4.5 Layer-by-layer deposition of CoPSS capped Silver Nanoparticles and Alginate capped Silver Nanoparticles on fibers

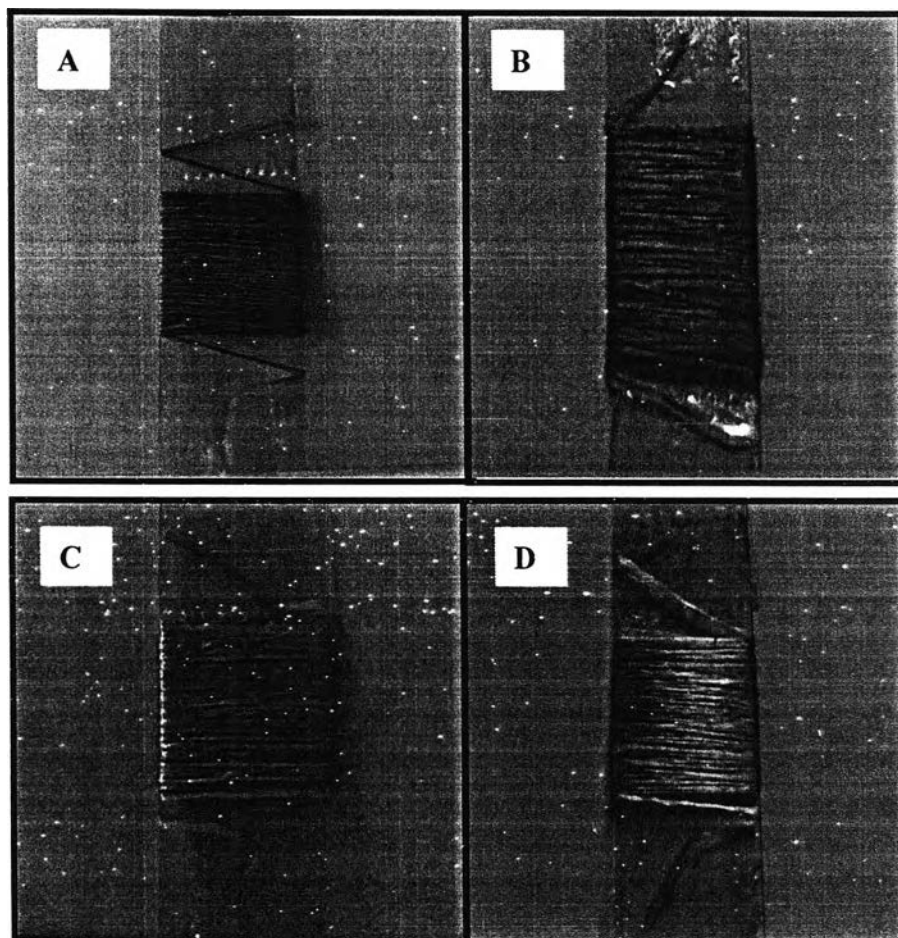


Figure 4.24 Picture of silk fiber dipped with :
chitosan and CoPSScappedAg day (A) and night (B) condition,
PDAD and CoPSScappedAg day (C) and night (D) condition.

Silk was dipped in 10-time diluted CoPSS capped Ag and PDAD (Figure 4.24 C, D) or chitosan (Figure 4.24 A, B). Chitosan is a weak polyelectrolyte, so PEM primer must be formed before the formation of PEM of 10-time diluted CoPSS capped Ag and chitosan. Both day condition and night condition were used for comparison. The results from day and night conditions were not much differed. Silk was deposited by 10-time diluted CoPSS capped Ag and chitosan. It gave a light purple color on silk fiber (Figure 4.24 A, B) because in PEM primer there was salt

inside which formed AgCl. Silk was deposited by 10-time diluted CoPSS capped Ag and PDAD, it gave a pale light yellow color on silk fiber. It can be assumed that the diluted CoPSS capped Ag had less amount of silver nanoparticles, so the color on silk was not dark. For the next experiment, PEM was prepared with non-diluted CoPSS capped Ag solution.

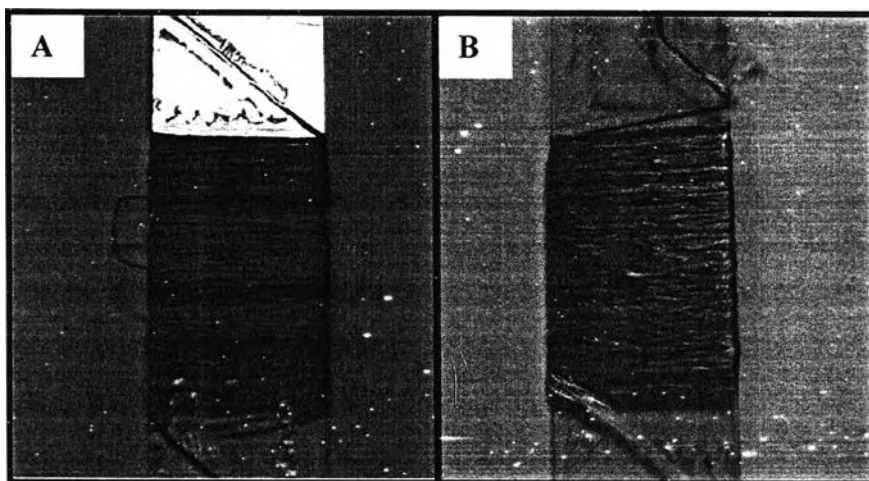


Figure 4.25 Picture of silk fiber dipped with : CoPSS capped Ag and PDAD with salt(A) and CoPSScapAg and PDAD without salt (B).

Figure 4.25 (B) shows that silver nanoparticles can be deposited on silk fiber without AgCl, which compared with Figure 4.25 (A), the silk fiber showed red color because AgCl was occurred by salt in PDAD solution. This confirmed the effect of AgCl. Figure 4.25 B and Figure 4.26 A showed, clearly, the amount of silver on fiber depended on amount of silver in solution.

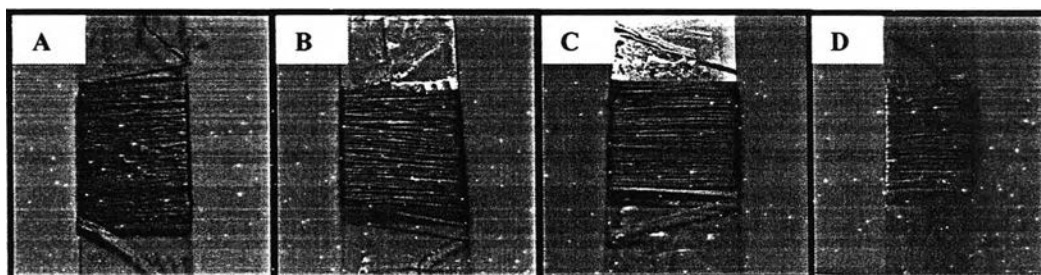


Figure 4.26 Schematic of silk fiber dipped with : CoPSScapAg and PDAD without salt : Non-dilute (10 mM) (A), dilute 2 times (B), dilute 5 times (C) and dilute 10 times (D).

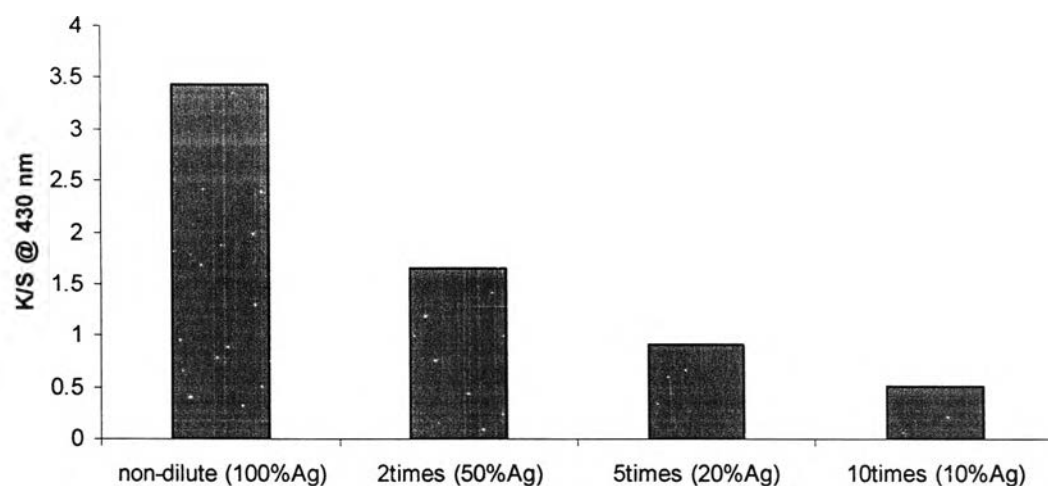


Figure 4.27 K/S value as a function of concentration of CoPSScapAg on silk fiber with PDAD : CoPSScapAg 10 mM (Non-dilute), dilute 2 times from 10 mM, dilute 5 times from 10 mM and dilute 10 times from 10 mM.

Figure 4.26 and Figure 4.27 shows that the amount of silver nanoparticles on silk fiber depended on concentration of CoPSScapAg solution. If silver nanoparticles solution was diluted, the amount of silver nanoparticles in solution decreased.

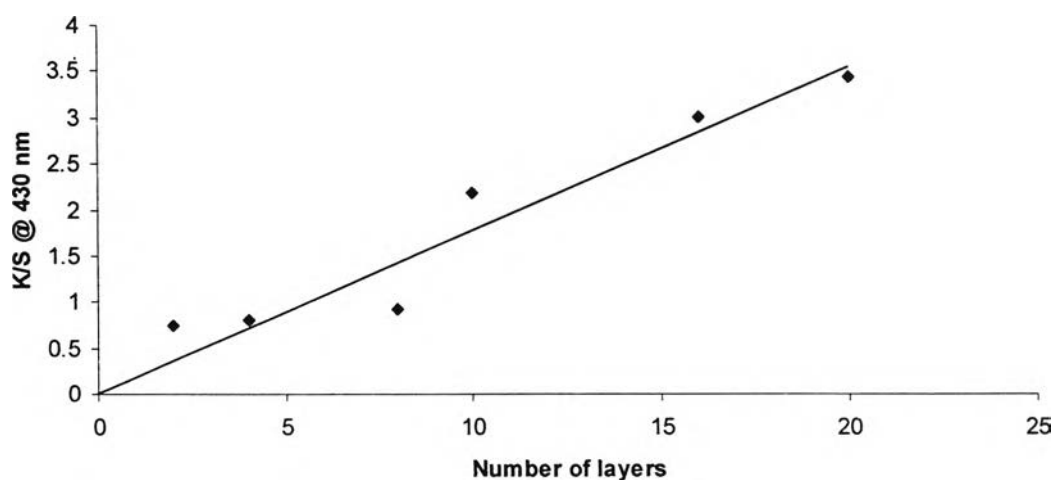


Figure 4.28 K/S value as a function of the number of PDAD-silver layer (CoPSScapAg) on silk fiber (See condition p.54).

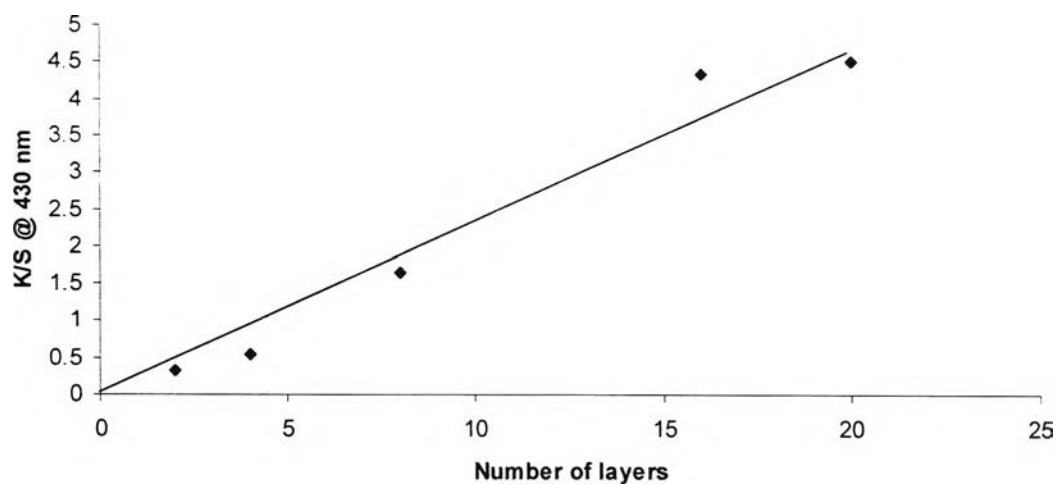


Figure 4.29 K/S value as a function of the number of PDAD-silver layer (AlginatecapAg) on silk fiber (See condition p.55).

Deposition of CoPSS capped Ag and alginate capped Ag gave yellow color on silk fiber due to the immobilization of silver nanoparticles onto silk fiber. Figure 4.28 and Figure 4.29 shows the increase in K/S value as a function of number of deposition. The increasing of K/S value demonstrated the layer-by-layer deposition of silver nanoparticles was occurred.

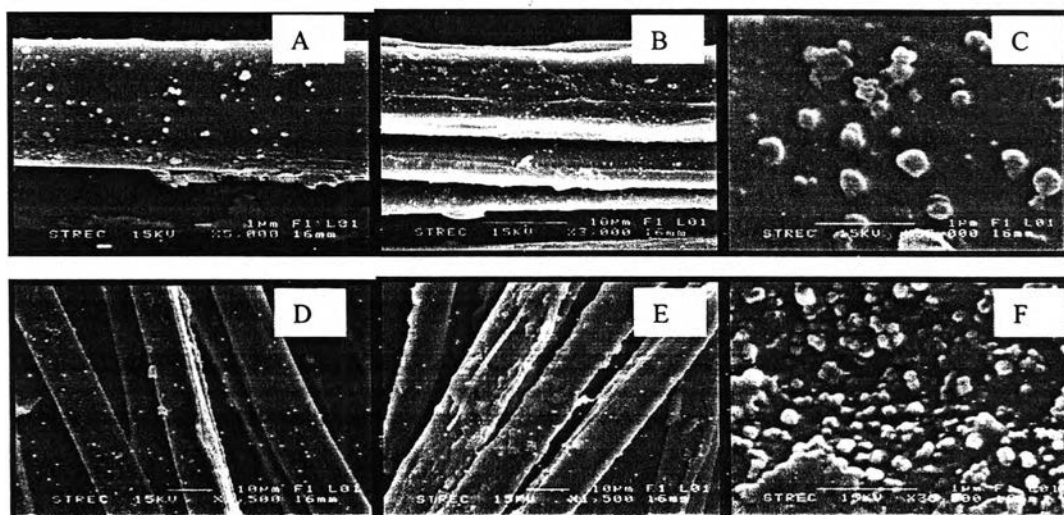


Figure 4.30 Scanning electron microscopy of the silk coated 10 layers PDAD/CoPSScapAg (A), 20 layers of PDAD/CoPSScapAg (B, C), 10 layers of PDAD/AlginatecapAg (D, F) and 20 layers of PDAD/AlginatecapAg (E).

Figure 4.30 shows that the silver nanoparticles were deposited on silk fibers in nanometer size. Figure 4.30 (D) and Figure 4.30 (E) shows the different density of silver nanoparticles between deposited 10 layers and 20 layer, which at 20 layer can not be seen the particles because a lot of particles were deposited on surface. [36]

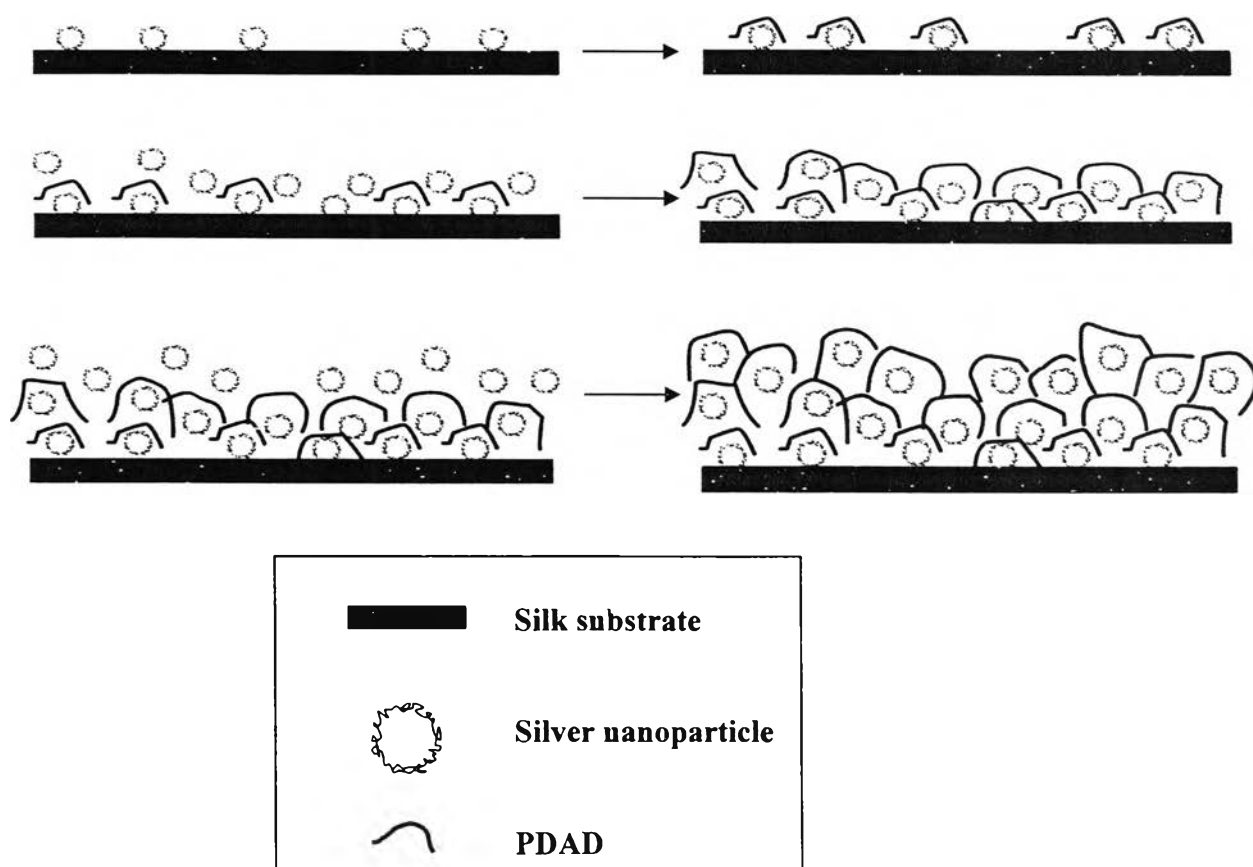


Figure 4.31 Schematic of layer-by-layer deposited of densed particles.

The structure of the multilayer assemblies of silver nanoparticles with polyelectrolytes was investigated with the emphasis on the control of the particle density in the adsorption layers. LBL of nanoparticles can occur via two modes of deposition, which are difficult to recognize following the standard optical density against the number of layers plots. One of the modes allows for the preparation of the multilayer stacks (normal growth mode), while the other one does not (lateral expansion mode). Film growth via the lateral expansion mode can be switched to the sandwich mode by organic modification of nanoparticles. [37] Figure 4.31 shows that when number of layer increased the surface area of silver nanoparticles decreased, which silver nanoparticles on first layer cannot diffuse to the surface. Separated

particles cannot be seen in SEM micrographs of silk coated with 20 layers of PDAD/Alginate capped Ag can not see to (Figure 4.31 (F)).

4.6 Antimicrobial Activity Test

The antimicrobial activity of particles deposited on fibers was tested against *staphylococcus aureus* bacteria. The result of test are showed in Table 4.2 and Table 4.3.

Table 4.2 Antimicrobial test on silk and nylon fibers coated with PMAcapAg and PDAD. (See condition p.53).

Sample	% bacterial reduction
Blank Silk	-
10 layers on silk	41%
20 layers on silk	80%
Blank Nylon	-
10 layers on nylon	0%
20 layers on nylon	53%

The percentage of bacteria reduction was increased as a function of the number of layers. The coated silk fibers gave the highest percentage of bacteria reduction. It showed 41% inhibition with 10-layer coating and 80% with 20-layer coating. This was the effect of not only silver nanoparticle colloids but also AgCl particles. The nylon fibers showed lower percentage of bacteria reduction when comparing with silk fiber. It showed 0% inhibition with 10-layer coating and 53% inhibition with 20-layer coating.

Table 4.3 Antimicrobial test on silk fibers coated with CoPSScapAg and PDAD. (See condition p.54).

Sample	% Reduction
Blank Silk	-
10 layers on silk	43
20 layers on silk	38

Table 4.3 shows percentage of bacteria reduction on silk fibers coated with CoPSS capped Ag and PDAD. The silk fibers showed 43% inhibition with 10-layer coating and 38% inhibition with 20-layer coating. The silk fibers coated with CoPSS capped Ag and PDAD can be show antibacterial properties but it was not different for 10-layer coating and 20-layer coating because the method of testing was applied from AATCC Test Method 100-1998. In AATCC method, when bacteria (*Staphylococcus aureus*) with 5 ml nutrient broth (media) are pipetted onto the fibers, the tubes will be shaken for 24 h. However, for this research, the tubes were shaken for 1 h, thus the bacteria cannot be grown enough in the nutrient broth.

Table 4.4 Antimicrobial test on silk fibers coated with AlginatecapAg and PDAD. (See condition p.54).

Sample	% Reduction
Blank Silk	-
10 layers on silk	50
20 layers on silk	48

Table 4.4 shows percentage of bacteria reduction on silk fibers coated with alginate capped Ag and PDAD. The silk fibers showed 50% inhibition with 10-layer coating and 48% inhibition with 20-layer coating.

The silk coated with 10 layers of PDAD/alginate capped Ag showed higher percentage of inhibition than silk coated with 20 layers because at silk coated with 10

layers had larger surface area to expose to bacteria. This was correlated with SEM micrographs. [38-39]