

CHAPTER IV

RESULTS AND DISCUSSION

The modified cotton was prepared by admicellar polymerization using different types of monomers. The optimum conditions for each monomer were determined by adjusting LAS:monomer and initiator:monomer ratios. The thermal stability of the cotton was tested by Thermal Gravimetric Analyzer (TGA) and the coated surface was examined by Scanning Electron Microscope (SEM). Finally, washing fastness testing and rubbing fastness testing was used to test the durability of dye on cotton.

4.1 Admicellar Polymerization of 3,4-Dichloro-1-Butene

4.1.1 Effect of Adsolubilization Time

The effect of adsolubilization time was studied by fixing the polymerization time at 6 hrs and varying the adsolubilization time from 0-24 hrs. The results in Figure 4.1 show that the treated cotton started to show good water repellency at 15 hours.

4.1.2 Effect of Polymerization Time

In this experiment, the polymerization time was varied from 0 to 8 hrs. From Figure 4.2, it can be seen that the wetting time increased significantly with increasing in polymerization time and the optimum polymerization time was found at 6 hours. The coated polymer can be expected to be more uniform and has a higher molecular weight at longer period of polymerization. At low polymerization time, the polymer could not coat the fiber uniformly. Thus, there would be some gaps between the polymeric thin film that leads to the decrement of water-repellency.

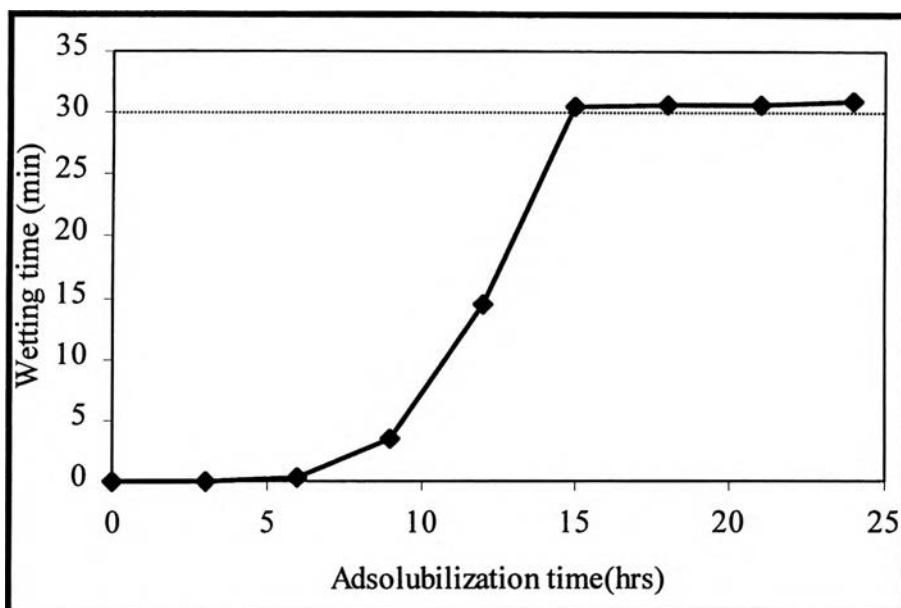


Figure 4.1 Wetting time of treated cotton with adsolubilization time [1000 μ M LAS, initiator:monomer ratio = 1:4, and polymerization time = 6 hrs at 80°C].

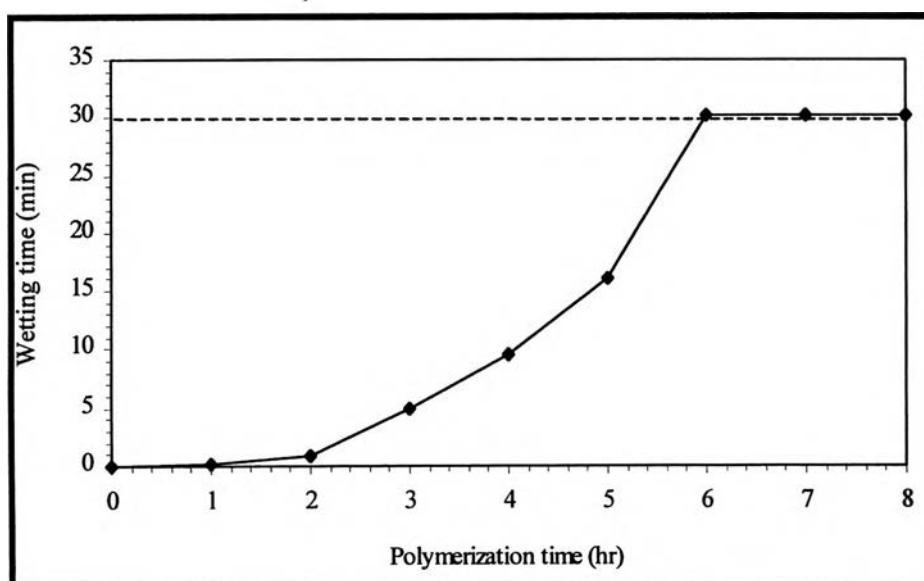


Figure 4.2 Wetting time with varying polymerization time [1000 μ M LAS, LAS:monomer ratio = 1:15, initiator:monomer ratio = 1:4, and polymerization at 80°C].

4.1.3 Effect of LAS:monomer

From Figure 4.3, the treated cotton displayed significant water-repellency at LAS:monomer ratio of 1:12 and resisted wetting for more than 30 minutes at ratio of 1:15. However, the monomer had a drawback in the corrosive property. The amount of added monomer in the solution caused the lowering of pH, and excessive monomer yielded cotton with poor strength.

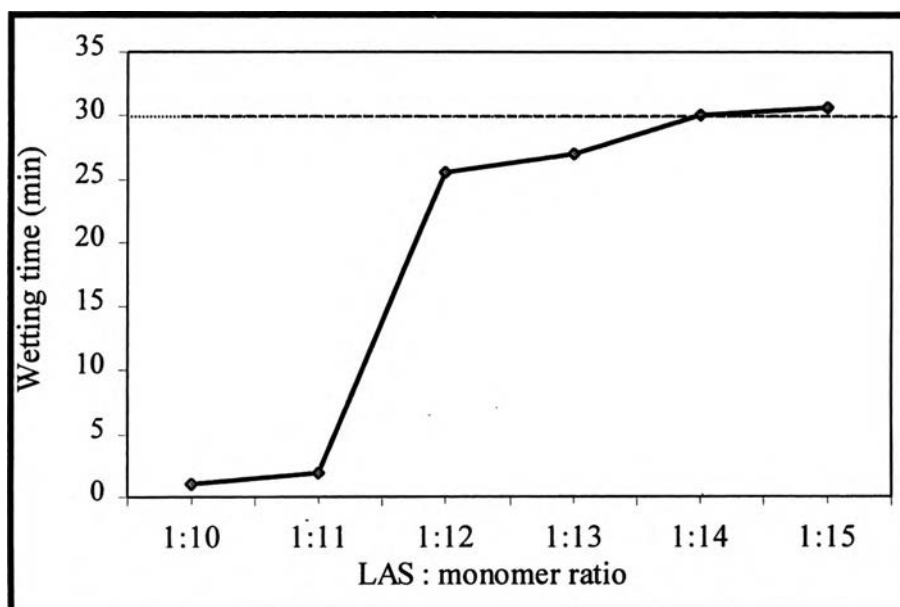


Figure 4.3 Wetting time of treated cotton with varying LAS:monomer ratio [LAS concentration 1000 μ M, adsolubilization time =15hrs at 30°C, and polymerization time = 6 hrs at 80°C].

4.1.4 Effect of Initiator:monomer Ratio

The results in Figure 4.4 show that the product did not demonstrate any significant water-repellency when the initiator:monomer ratio is below 2. Above the initiator:monomer ratio of 3.5, the treated cotton showed a high wetting time of almost 30 minutes. The results show that a high initiator:monomer ratio is required to obtain good water-repellency.

Unfortunately, excessive initiator caused yellowness in the treated cotton. From the experiment, the source of color in the treated cotton might come from the deposition of sulfate ion in the polymerization step. The

treated cotton started to become yellow when the amount of added initiator was up to $400\mu\text{M}$ and the color could be seen distinctively at $600\mu\text{M}$. Moreover, sodium persulfate had an influence on the decrement in pH. The lowering of pH in the solution depended on the quantity of initiator. The result showed that pH could be reduced to 1.8 at $400\mu\text{M}$ of initiator.

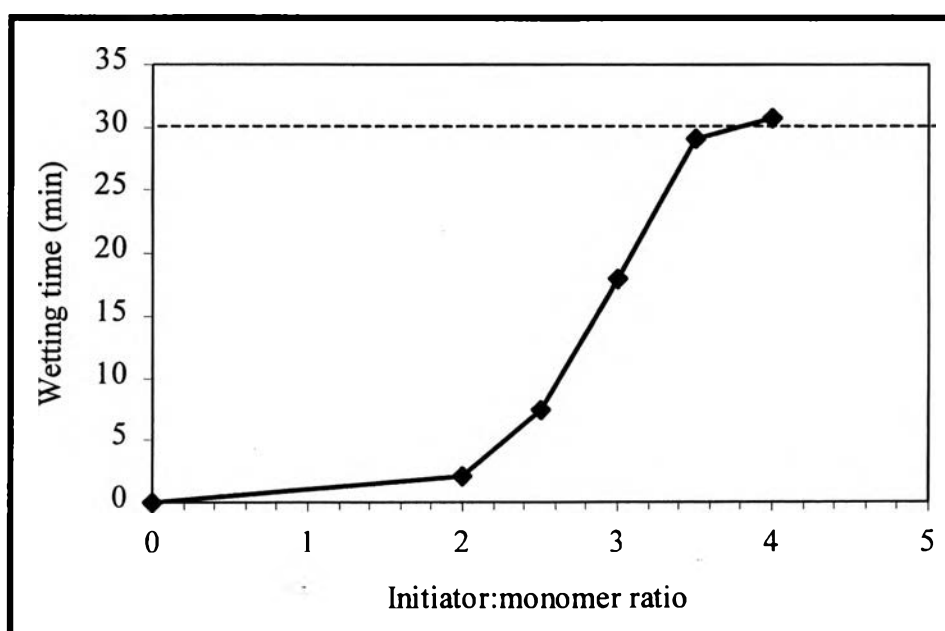
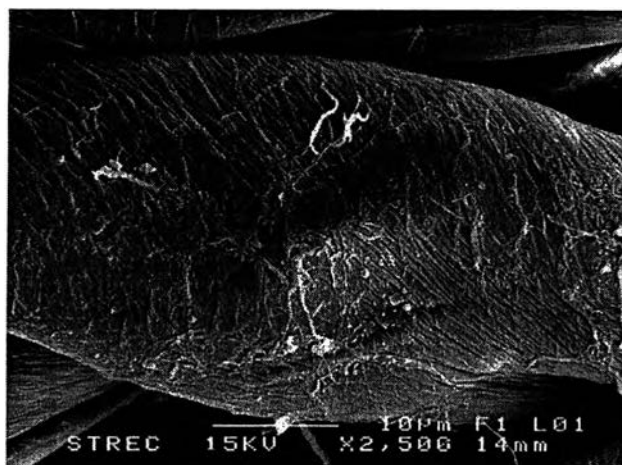


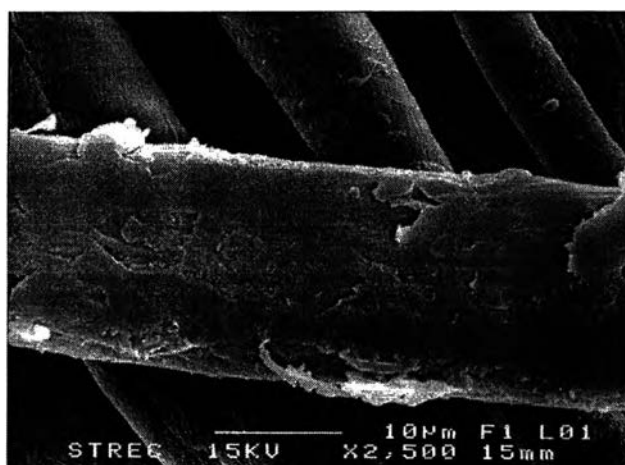
Figure 4.4 Wetting time of treated cotton with varying initiator:monomer ratio [LAS concentration $1000\mu\text{M}$, adsolubilization time = 15 hrs, and polymerization time = 6 hrs at 80°C].

4.1.5 Characterization of 3,4-Dichloro-1-Butene Coated Cotton by SEM

The treated cotton surface was examined by Scanning Electron Microscope (SEM). The results show that there is a polymeric thin film on the treated cotton fiber as shown in Figure 4.5.



(a)



(b)

Figure 4.5 Characterization of cotton surface by SEM (a) untreated cotton and (b) modified cotton.

4.1.6 Thermal Stability of Treated Cotton by TGA

The thermal stability of the treated cotton was examined by thermal gravimetric analyzer (TGA) as shown in Figure 4.6. From the Figure, it can be seen that the untreated cotton has greater %weight loss than the treated cotton. Hence, this result can confirm that the treated cotton has better thermal stability than original material which shows that the polymeric thin film helps to protect the fiber from the degradation by heat.

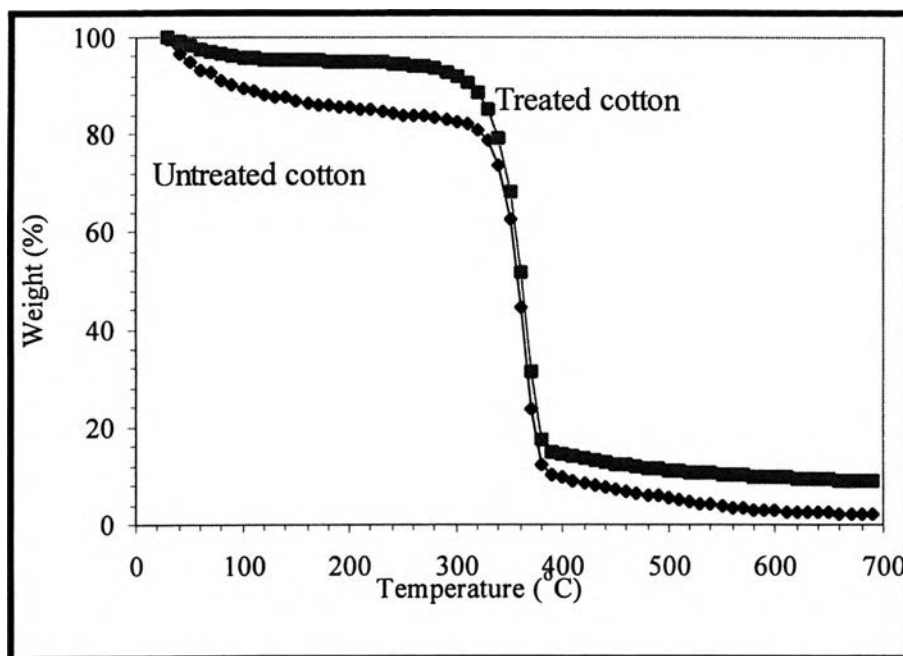


Figure 4.6 Thermal stability of untreated and treated cotton by TGA

◆ Untreated cotton and ■ Treated cotton.

4.2 Admicellar Polymerization of 4-chloromethyl styrene

From the experiments, 4-chloromethyl styrene could not be coated on the cotton fiber and the treated samples did not show any water-repellency. The parameters that have been varied are shown in Table 4.1.

Table 4.1 The varied parameter in the admicellar polymerization of 4-chloromethyl styrene.

Variable parameters	Condition	Wetting time
Surfactant (LAS)	1000-1200 μM	0
pH	2-5	0
LAS:Monomer ratio	1:2 to 1:30	0
Monomer:Initiator ratio	0.5 to 4	0
Adsolubilization time	8 to 48 hours	0

Variable parameters	Condition	Wetting time
Polymerization time	2 to 6 hours	0
NaCl concentration	0 to 0.15 M	0
Extraction of inhibitor	With and without NaOH	0

There were some possible reasons that might explain why the monomer could not be coated on the cotton fiber. One reason is 4-chloromethyl styrene may have polymerized rapidly after the inhibitor was extracted out of monomer. In the experiment, it was found that the unpurified monomer formed transparent droplets in the solution. After purification, the droplets became translucent. This shows that there was polymerization of monomer in the solution because the translucent droplet has the white color as the polymer of 4-chloromethyl styrene in the emulsion polymerization.

4.3 Admicellar Polymerization of Sodium Styrene Sulfonate (NaSS)

4.3.1 Effect of NaSS Monomer

The effect of NaSS monomer was identified by varying NaSS concentration from 0 to 70000 μ M while monomer:initiator ratio was fixed at 1:1.

From Figure 4.7, it can be seen that the color strength is low at low NaSS concentration below 20000 μ M due to the charge density on the cotton surface is too low. Thus, the amount of cationic dye that can be adsorbed on the surface is limited by negative charge of monomer on cotton surface. After this concentration, the color strength of dye increases sharply and rises slowly when the NaSS concentration is higher than 50000 μ M. So, the concentration of NaSS at above 50000 μ M is required for optimum condition.

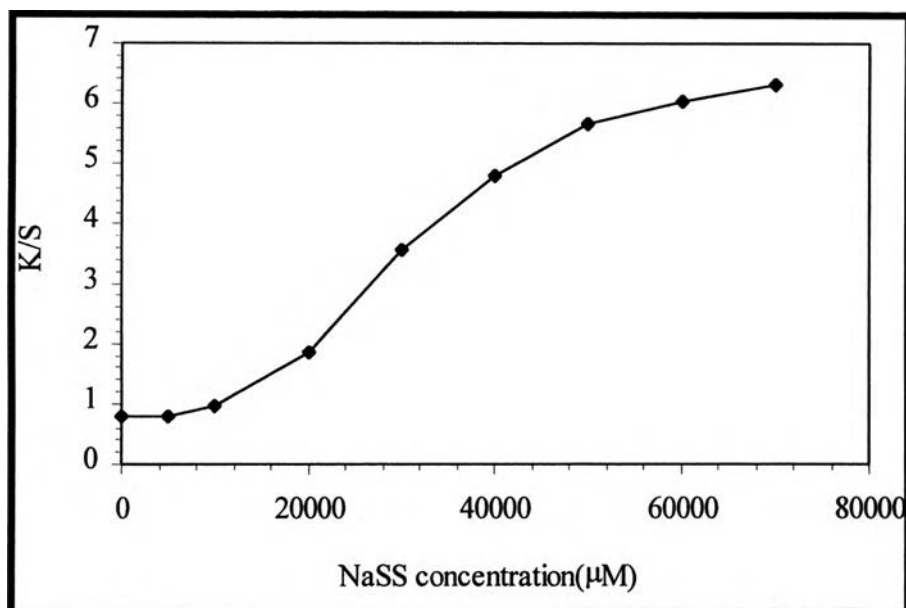


Figure 4.7 Color strength of treated cotton with varying NaSS concentration [initiator:monomer ratio = 1:1].

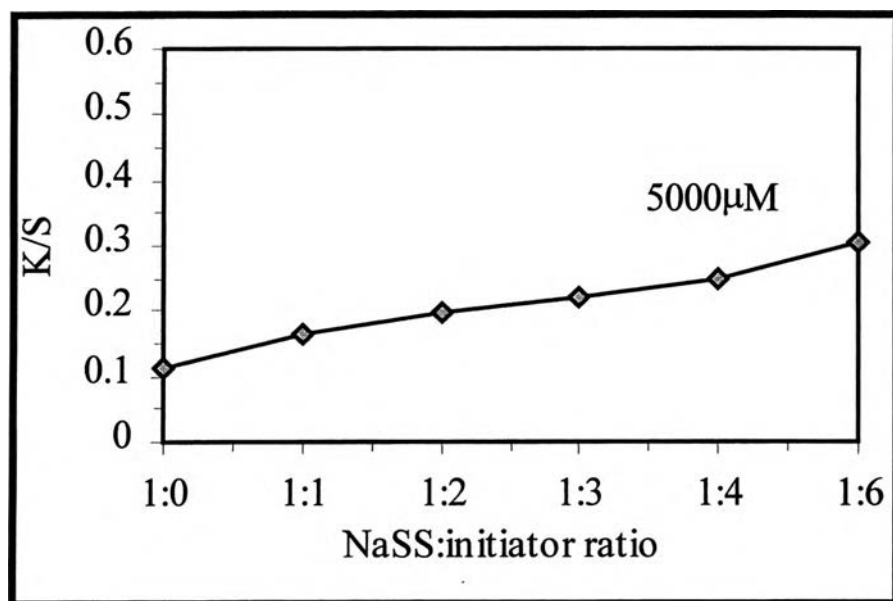
4.3.2 Effect of Initiator

Initiator:monomer ratio was varied for studying the effect of initiator on the polymerization. In order to study this effect, the initiator was varied while NaSS concentration was fixed at 5000 and 15000 μM as shown in Figures 4.8 (a) and (b), respectively.

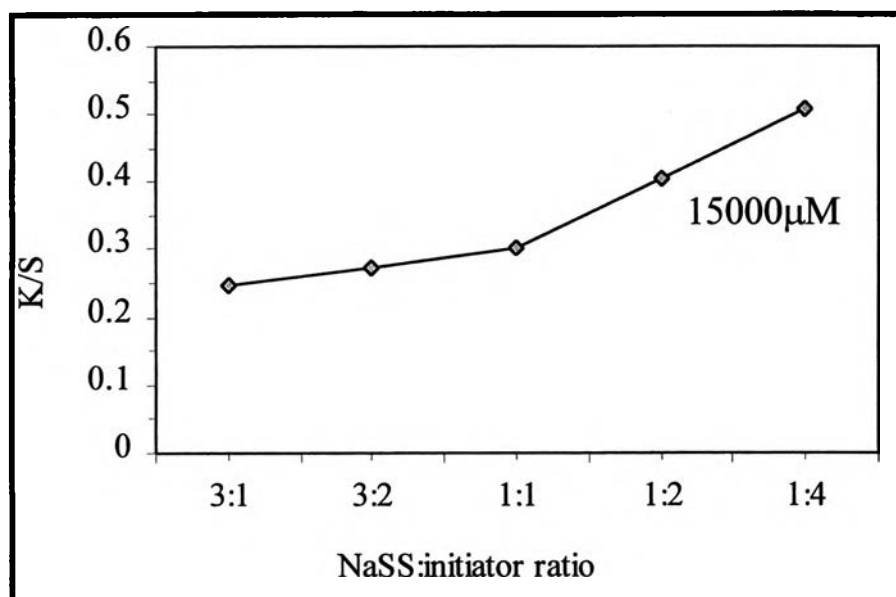
In Figure 4.8 (a), the color strength of treated cotton increases gradually when NaSS:initiator ratio increases. However, at NaSS 15000 μM, the color strength of treated fabric increases sharply when monomer:initiator ratio is above 1:1 as shown in Figure 4.8 (b). The results show that increase in the amount of initiator leads to increase in the polymerization of the monomer in the admicelle.

The problem from initiator in the experiment is the treated fabric becomes yellow and brittle when the large amount of initiator was added in the system. Therefore, the appropriate initiator:monomer ratio in the system is

taken as 1:1 since the treated cotton did not show any yellowness at this condition and the cotton strength remained the same after the polymerization process.



(a)



(b)

Figure 4.8 Color strength of treated cotton with varying NaSS:initiator ratio [NaSS concentration (a) 5000 μM and (b) 15000 μM].

4.3.3 Effect of Salt

In order to analyze the effect of salt to color strength, NaCl was altered from 0 to 0.15M while the NaSS concentration and initiator:monomer ratio were maintained at 20000 μ M and 1:1 respectively as shown in Figure 4.9.

The results show that color strength of dyed cotton increased with increasing NaCl concentration. The reason for this case is the added salt will shield the charge portion between NaSS molecule in the admicelle causing the closed packing of admicelle and increasing charge density on the cotton surface. Hence, the cationic dye can adsorb well and K/S shows larger value when the cotton surface has high negative charge density.

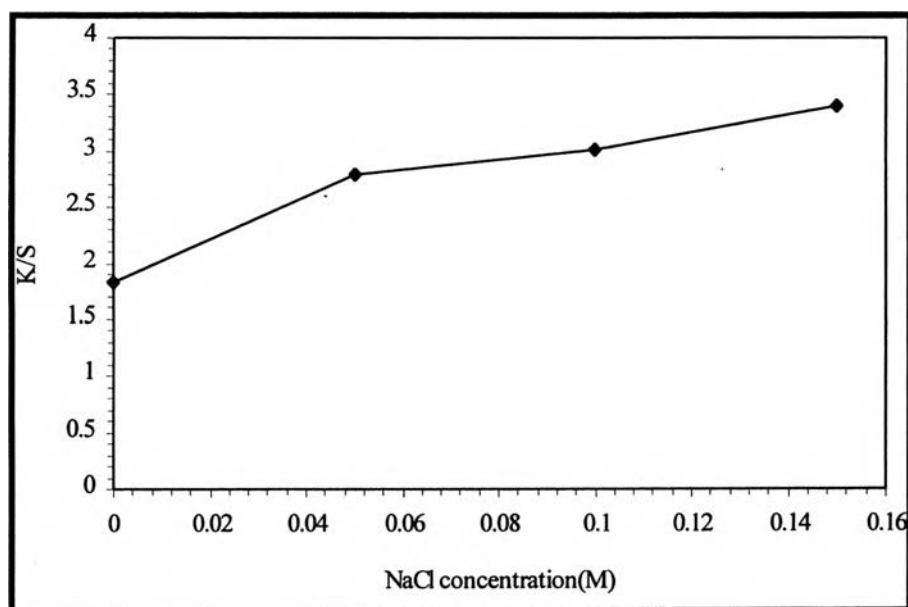


Figure 4.9 Color strength of treated cotton with varying NaCl concentration [NaSS concentration 20000 μ M, initiator:monomer ratio = 1:1].

4.3.4 Effect of pH

In the experiment, the color strength was expected to increase when pH is decreased because the monomer has a higher adsorption on the surface at low pH. Thus, pH in the solution was adjusted by adding

CH_3COOH and the color strength of treated cotton was then observed. Figure 4.10 shows the color strength and pH in the experiment. The results show that pH has an effect on the increment in color strength as expected. Generally, the cotton surface has negative charge in the water solution and it becomes more positive charge when pH is reduced. Hence, the color strength of treated cotton has maximum value at the lowest pH. Unfortunately, although the lower pH resulted in a higher value of K/S but the presence of acid also reduces cotton strength. Therefore, acid addition in the solution should be minimized and the optimum pH in this experiment is set at four.

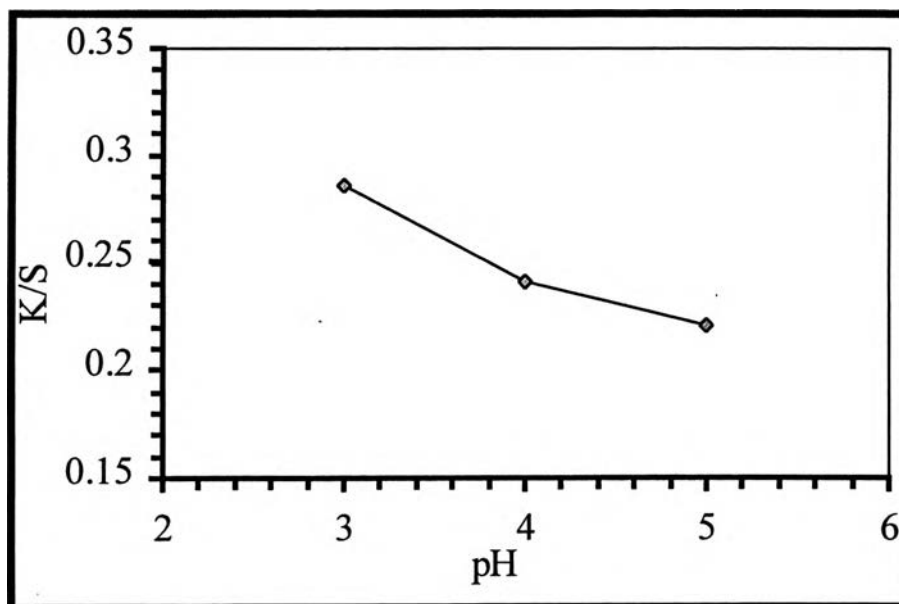


Figure 4.10 Color strength of treated cotton with varying pH [NaSS concentration $5000\mu\text{M}$, initiator:monomer ratio = 1:1].

4.3.5 Effect of Polymerization Time

The effect of varying polymerization time was studied to find the time required for a uniform coating of thin film on the cotton surface. Figure 4.11 shows the color strength of treated cotton at varying polymerization time from 0 to 180 minutes. The color strength of dyed fabric increases dramatically during the first hour and rises gradually after one hour.

This means that the monomer starts to form a uniform polymer layer rapidly during the first hour. After one hour, the curve rises slowly. Thus, the optimum polymerization time was taken as one hour.

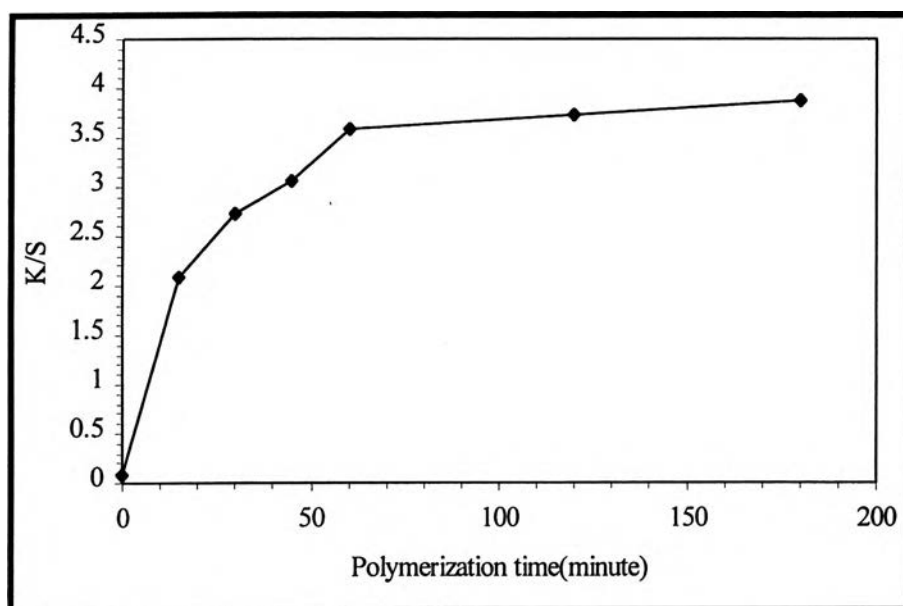


Figure 4.11 Color strength of treated cotton with varying polymerization time [NaSS concentration $15000\mu\text{M}$, initiator:monomer ratio = 1:1].

4.3.6 Effect of Dyeing Temperature

The temperature has an effect on the adsorption of cationic dye onto the cotton surface. As can be seen in Figure 4.12, the color strength of dyed cotton increases clearly at 30°C while dyeing treated cotton at 50°C gives lower color strength. This indicates that the dye adsorption is an exothermic reaction which can take place better at lower temperature.

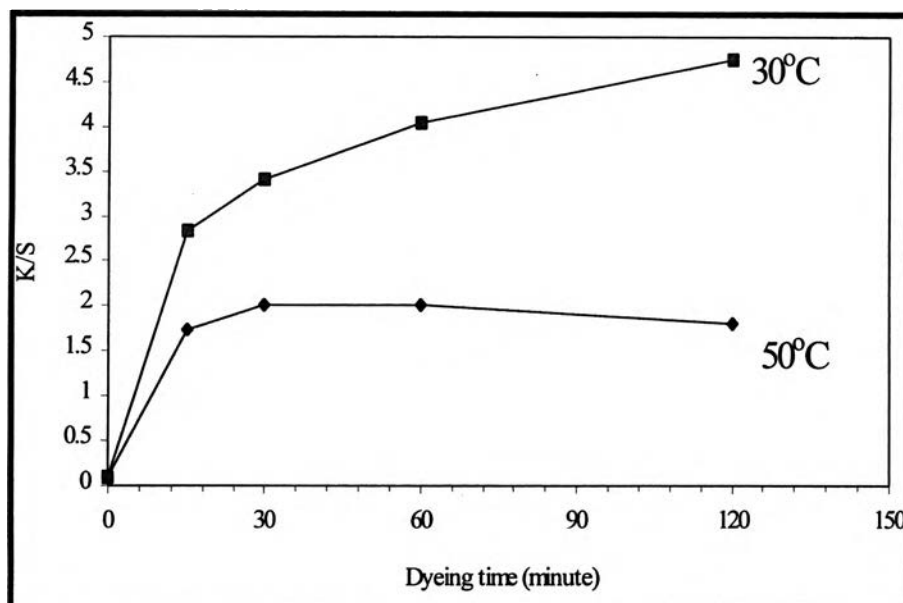


Figure 4.12 Color strength of treated cotton with varying dyeing time and temperature [NaSS concentration 30000 μ M, initiator:monomer ratio = 1:1, and polymerization time 2 hr].

4.3.7 Effect of Dye Concentration

From Figure 4.13, the percentage of dye was varied from 1 to 3 percent weight of dye based on cotton weight at NaSS concentration of 30000 and 60000 μ M respectively. The results show that the color strength increases with increasing percent dye and the highest strength value is 4.811. However, the color strength demonstrates a slow increment when the percent dye in the solution increases. This shows that the adsorption of cationic dye is near to its saturation value at high dye concentration.

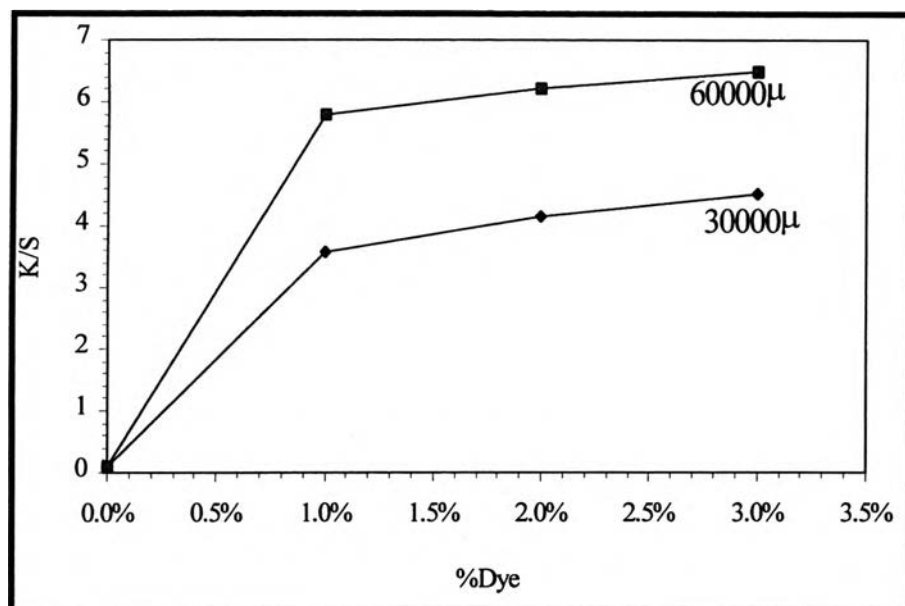


Figure 4.13 Color strength of treated cotton with percent dye in solution [NaSS concentration 30000 and 60000 μM , initiator:monomer ratio = 1:1, and polymerization time 2 h].

4.3.8 Effect of NaSS Concentration on Washing Fastness

The durability of the dyed cotton to washing procedure was observed by washing fastness testing method as shown in Table 4.2. From the Table, the results show that the treated cotton at higher NaSS concentration gives better fastness grade than the treated cotton at low NaSS concentration. This results may be due to the more uniform film of sodium styrene sulfonate polymer on the cotton surface at higher NaSS concentration.

Table 4.2 Washing fastness of dyed cotton at different concentrations of NaSS.

NaSS concentration	% Dye	Grade
20000 μM	1	3
40000 μM	1	4-5
70000 μM	1	4-5

4.3.9 Effect of %Dye on Washing Fastness

The percent of dye in the solution was varied for testing the durability of dyed on cotton at higher dye concentration. From Table 4.3, the results show that the fastness grade of treated cotton at low concentration of NaSS was found to decrease with increasing dye concentration. In contrast, the treated cotton at the higher concentration of NaSS gave good fastness at all dye concentrations. The results confirm that NaSS at higher concentration produces more uniform film of polymer than cotton treated with NaSS at lower concentration.

Table 4.3 Washing fastness of dyed cotton at different dye concentration.

NaSS concentration	% Dye	Grade
30000 μ M	1	4-5
30000 μ M	2	3-4
30000 μ M	3	3
60000 μ M	1	4-5
60000 μ M	2	4
60000 μ M	3	4-5

4.3.10 Effect of NaSS Concentration on Rubbing Fastness

The durability of the treated cotton to rubbing application was tested by rubbing fastness method. The results in Table 4.4 demonstrated that the treated cotton has excellent rubbing fastness at all NaSS concentrations with the dry rubbing test. However, the dyed cotton displayed lower grades with the wet rubbing test. Moreover, cotton treated in higher NaSS concentration showed a poorer grade. The possible reason is that the dye can dissolve in water. Thus, the large amount of dye on the cotton surface at the higher NaSS concentration has greater removal than the cotton treated at lower NaSS concentration.

Table 4.4 Rubbing fastness of dyed cotton at different concentration of NaSS.

NaSS concentration	% Dye	Dry rubbing test	Wet rubbing test
20000 μM	1	5	3-4
40000 μM	1	5	2-3
70000 μM	1	5	2

4.3.11 Effect of %Dye on Rubbing Fastness

The effect of rubbing on cotton dyed at different dye concentrations was studied in this experiment. The concentration of dye was varied from one to three percent by weight based on the weight of cotton. The results are shown in Table 4.5. From the Table, the rubbing testing with the dry method has excellent grade at all dye concentrations. However, the wet rubbing fastness was only fair and the wet fastness decreases with increase in dye concentration. The explanation for this is the same as in section 4.3.10

Table 4.5 Washing fastness of dyed cotton at different dye concentration.

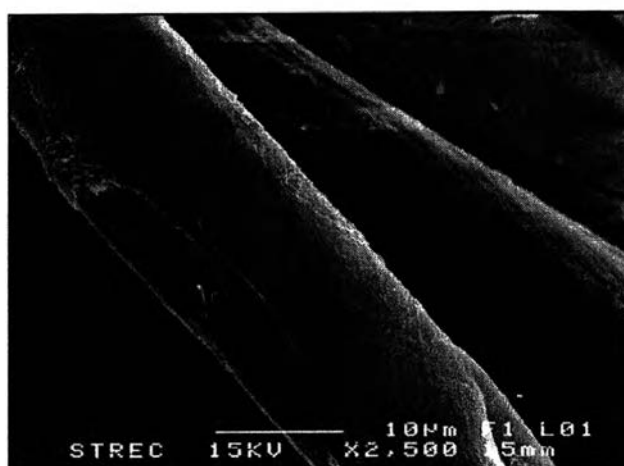
NaSS concentration	% Dye	Dry rubbing test	Wet rubbing test
30000 μM	1	5	3-4
30000 μM	2	5	3-4
30000 μM	3	5	3
60000 μM	1	5	2-3
60000 μM	2	5	2-3
60000 μM	3	5	2

4.3.12 Characterization of Cotton Surface

The treated cotton surface was examined by Scanning Electron Microscope (SEM). The results show that the treated cotton is covered by a uniform layer of polymer indicating that sodium styrene sulfonate can be admicellar polymerized along the cotton surface as shown in Figure 4.14.



(a)



(b)

Figure 4.14 Characterization of cotton surface by SEM
(a) untreated cotton and (b) NaSS coated cotton.