

CHAPTER IV

RESULTS AND DISCUSSION

In this study, the esterification of cotton under microwave energy was introduced by formation of the mixed carbonic/*p*-toluenesulfonic acid anhydride via the carboxylic acid / toluenesulfonyl chloride / pyridine method. Formation of mixed carbonic/*p*-toluenesulfonic acid anhydride represented the reactive species.

Under microwave radiation, the energy is rapidly increased in the system. Therefore, the first caution under microwave radiation is the ability of thermal stability of substance. The power generation and reaction time are important factor that should be considered.

4.1 Esterification of cotton

4.1.1 Effect of irradiation time and microwave power on esterification of cotton

The effects of various reaction time and power on esterification of cotton using stearic acid as modify agent, toluenesulfonyl chloride as a catalyst and pyridine as a co-catalyst /medium were investigated. The esterification reaction was conducted in DMAc/LiCl, 3 eq/TsCl of pyridine, 2eq/OH of stearic acid, and 2eq/OH of TsCl with five different reaction time and six different microwave power. The experimental results are presented in Table 4.1. The relationship between % yield of esterification and microwave power at different reaction time is illustrated in Figure 4.1.

Table 4.1 % yield of esterification at different power microwave and reaction time^a

Condition		%Yield
Time (min)	Microwave Power (watt)	
1.30	90	0
	180	0
	270	56.43
	360	73.27
	450	112.87
	540	102.97
2.30	90	8.91
	180	50.00
	270	81.19
	360	81.90
	450	56.43
	540	3.85
3.00	90	56.43
	180	96.04
	270	100.99
	360	95.05
	450	19.68
3.30	90	113.86
	180	126.73
	270	138.61
	360	99.01
4.00	90	77.67

^a Esterification condition: 3 eq/TsCl of pyridine, 2eq/OH of stearic acid, 2eq/OH of TsCl

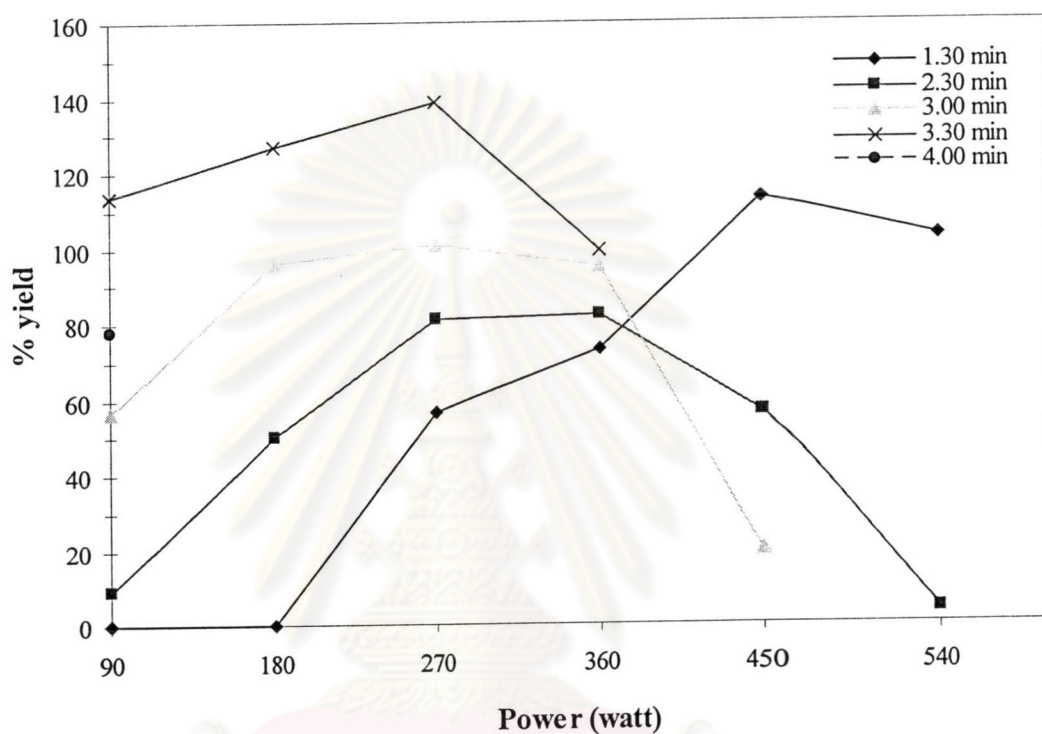


Figure 4.1 The relationship between % yield of esterification and power microwave power at different reaction time

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For reaction time of 1.30 min, % yield of esterification did not change significantly in at the early stage of microwave power and then rapidly increased with increase microwave power of 180 watt. The maximum % yield appeared at 450 watt. After that, % Yield of esterification decreased with increase microwave power. The increasing of power beyond 450 watt in this case led to an increase in temperature which resulted in cotton degradation as attested by drop in %yield of esterification of cotton.

For reaction time of 2.30 min, % yield of esterification increased with increasing microwave power until the maximum % yield was reached at 360 watt and then gradually. The drop of % yield was because the excess power can cause the degradation of cotton when comparing of % yield at different reaction times of 1.30 and 2.30 min under the same microwave power, it was found that when microwave power less than 360 watt was applied, % yield of 2.30 min -esterified cotton was higher than that of 1.30 min one due to higher microwave power absorbed.

The similar trend was found for microwave-esterification of cotton under 3 min. The maximum % yield can be reached at 270 watt. At power output of less than 360 watt, the longer time the samples were esterified, the higher microwave absorbed. This resulted in higher %yield of esterification as seen in Figure 4.1. Beyond power microwave of 360 watt, %yield of esterification of cotton obviously decreased. High temperature in system due to excess energy absorbed led to the degradation of cotton as well.

When cotton was esterified for 3.30 min under microwave power of less than 270 watt, %yield of esterification was higher than those of other reaction time and also increased with increasing microwave power. The highest % yield appeared at 270 watt and obviously decreased later.

The esterification was further conducted at 4 min. It was found that %yield of esterification was less than that performed at 3.30 min. The drop of %yield at 90 watt power microwave heating for 4.00 min was due to cotton degradation.

Although not graphically presented in this figure, %esterification did not significantly change among these esterified-samples.

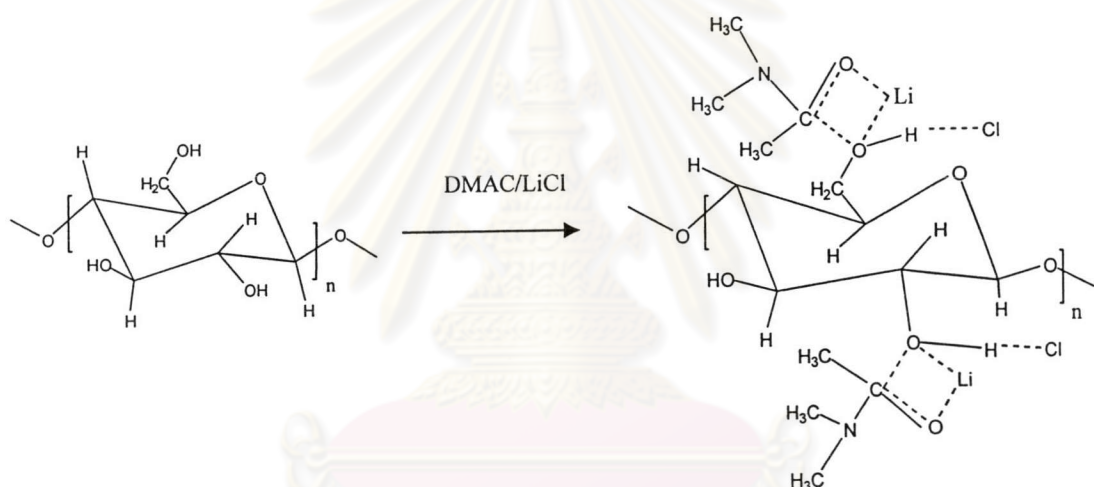
From these results, it can be seen that critical irradiation time before cotton degradation under 0-270 watt was 3.30 min. If cotton was to esterify between 270-360 watt, the suitable time between 2.30-3.00 min. Beyond 360 watt, cotton would have to be microwave-esterified for 1.30 min, only otherwise it would start to degrade.

However, when focussing on the highest %yield of esterification without-degradation of cotton along with the resonable energy and time used, the esterification of cotton should be performed under 270 watt microwave power for 3.30 min. This condition gave the highest %yield of esterification of about 138%.



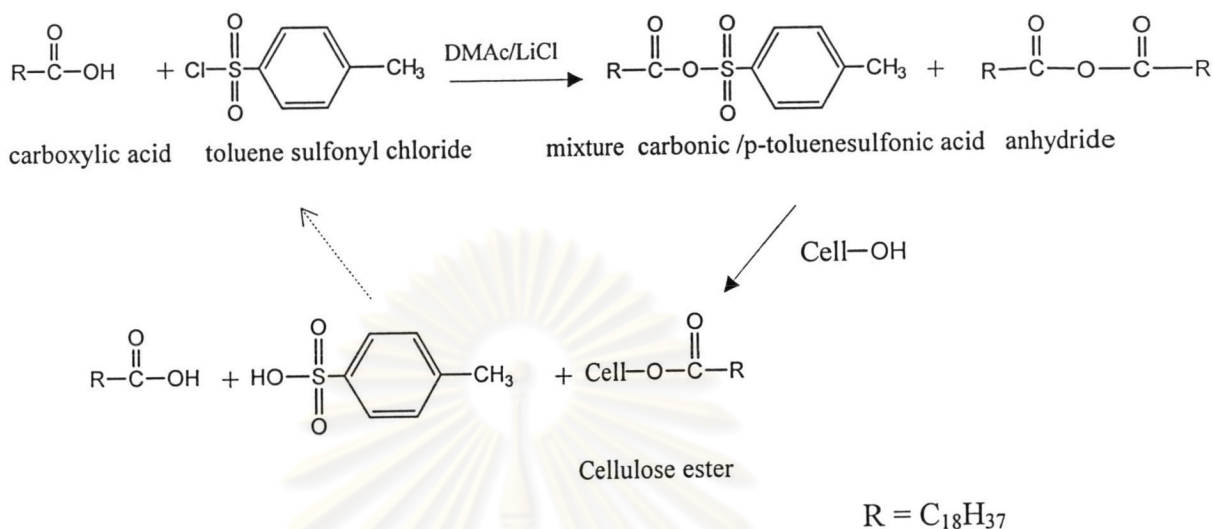
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In the esterification of cellulose, dissolution of cellulose in DMAc/LiCl solvent system may be accompanied by an interaction given in scheme 4.1. Stearic acid introduces to reaction with toluenesulfonyl chloride in DMAc/LiCl to form mixture of carbonic/*p*-toluenesulfonic acid anhydride as reactive species as show in scheme 4.2. Reactive species have alternatives to reaction, e.g., attack the secondary hydroxyl group first (due to the primary hydroxyl group is expected to be better solvated than secondary hydroxyl group), incorporate with pyridine or toluenesulfonyl chloride to attack solvated hydroxyl group of cellulose. Finally, the cellulose stearate was obtained.



Scheme 4.1 Possible interaction between cellulose and LiCl/DMAc system

T.Heinze and coworkers [7] offer the mechanism for formation of reactive species as shown in scheme 4.2. Aliphatic carboxylic acid, or stearic acid in this research, reacts with toluenesulfonyl chloride and then producing a mixture of carbonic/*p*-toluenesulfonic acid anhydride as reactive species. The increasing of temperature generates energy to increase reactive species and possibly to increase reaction rate of pyridine and toluenesulfonyl chloride in the system (see discussion in section 4.1.2) as resulted in increasing %Yield.



Scheme 4.2 Acylation of cotton in DMAc/LiCl using in situ activation of the carbonic acid by formation of the mixture of carbonic /p-toluenesulfonic acid anhydride

Finally, it can be concluded that the reason for this enhancement in acetylation upon increasing microwave power and duration reaction was probably due to the favorable effect of temperature on compatibility of reaction ingredients, diffusion of esterifying agent, mobility of the reactant molecules, and absorption of the reactant molecules and esterifying agent. The decrement in this yield could be ascribed by partial degradation of the cotton. Based on this work the recommended optimum microwave power and reaction time to esterify of cotton via the stearic acid/ toluenesulfonyl chloride / pyridine method under microwave irradiation are 270 watts and 3.30 min, respectively. Since under these conditions, the maximum %yield can be achieved using moderate power and reasonable reaction time.

4.1.2 Effect of equivalent weight of pyridine/TsCl on esterification of cotton

Esterification of cotton conducted in DMAc/LiCl system using TsCl as a catalyst and pyridine as a co-catalyst /medium at different equivalent weight of pyridine/TsCl was studied. Esterification was carried out at 270 watt for 3.30 min, 2eq/OH of stearic acid, 2eq/OH of TsCl, and with four different equivalent weight of pyridine/TsCl viz., 2, 3, 4, 5 and 6. The results are summarized in Table in 4.2. The relationship between % yield and %esterification with equivalent weight of pyridine/TsCl is shown in Figure 4.2 and Figure 4.3, respectively.

Table 4.2 % yield of esterification and % esterification at different equivalent weight of Pyridine/TsCl^b

Equivalent weight of pyridine/TsCl	%Yield	%Ester
2	0	0
3	126.47	49.27
4	151.96	69.45
5	159.80	73.1
6	175.49	81.11

^bEsterification condition: 2eq/OH of stearic acid, 2eq/OH of TsCl ,reaction time =3.30 min, power out put =270 watt.

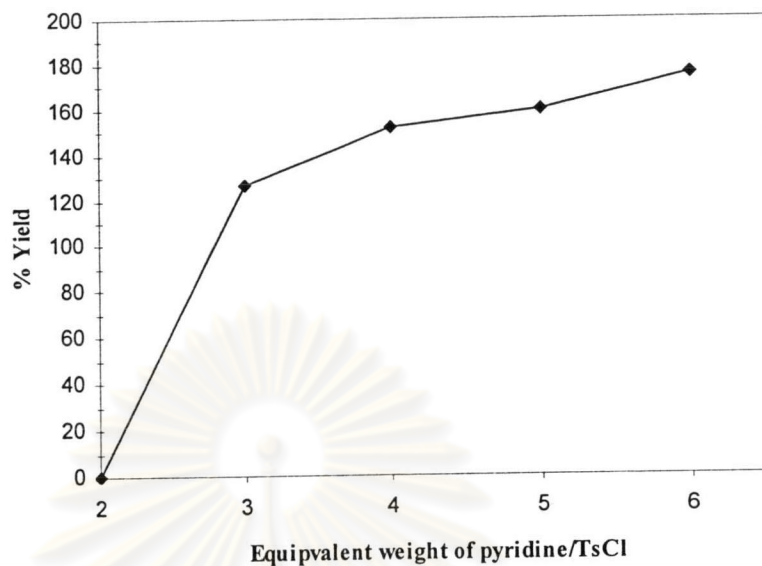


Figure 4.2 The relationship between % yield of esterification and equivalent weight of Pyridine/TsCl

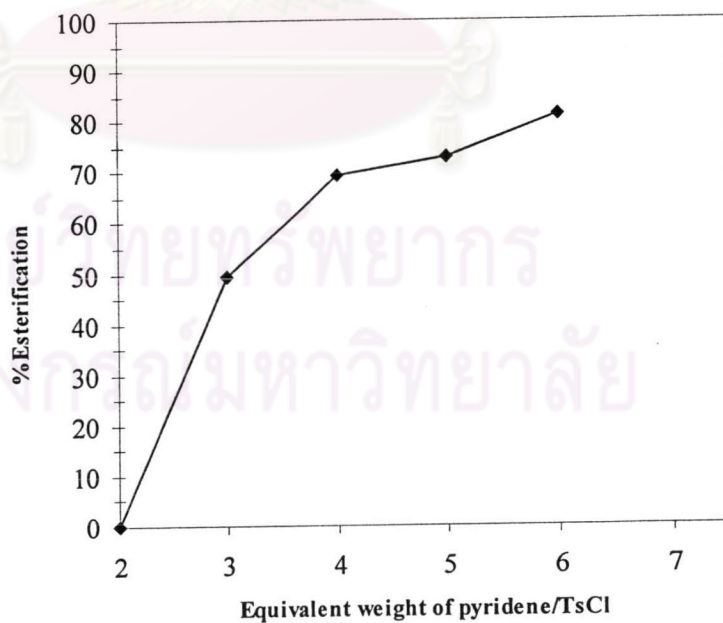


Figure 4.3 The relationship between % esterification and equivalent weight of Pyridine/TsCl

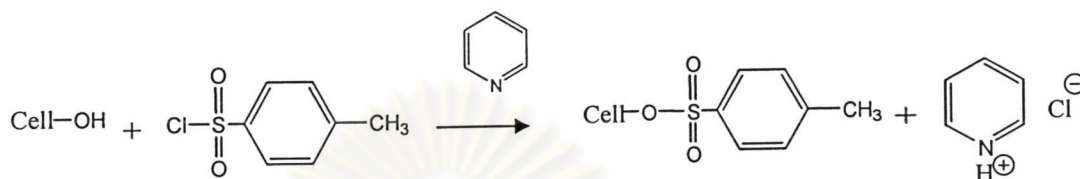
As shown in Figure 4.2 and 4.3, the %yield of esterification and %esterification strongly affected from the equivalent weight of pyridine/TsCl ratio. The % yield and %esterification increased with increasing equivalent weight of pyridine/TsCl ratio. Due to the activate energy for acetylation reaction of pyridine is less than that of TsCl so the concentration of pyridine have strong affect than TsCl [96]. As seen, under these conditions, the cotton could not be esterified at 2 eq. of pyridine/TsCl; i.e., %yield of esterification and % esterification were both zero. However, it was found that increasing of equivalent weight of pyridine/TsCl ratio more than 4 led to the undesirable side reactions and loss of homogenous in the system as attested by different size of esterified-cotton that obtained in final step. Moreover, for 5 eq. of pyridine/TsCl, the undesirable side reactions can be confirmed by the results from different scanning calorimetry showing several endothermic peaks besides the main melting temperature (see Figure 4.11 in section 4.2.2.2), and also from the XRF analysis showing the traces of sulfur and chloride atoms (Table 4.3).

Table 4.3 % Sulfur and chloride in side chain of cotton ester. (from XRF technique)

Equivalent weight of pyridine/TsCl	%Ester	% S	% Cl
2	0	-*	-
3	49.27	-	-
4	69.45	-	-
5	73.1	0.03	1.09
6	81.11	1.82	2.72

*- not found signal or less than .002%

According to the result of Gakkaishi and coworkers [69], they found that cellulose can be reacted with TsCl in pyridine to form tosylcellulose as shown in Scheme 4.3. Therefore, at higher concentration of pyridine (equivalent weight of pyridine/TsCl ratio more than 4), pyridine performs as acetylation medium leading to undesirable side reactions of tosylation.

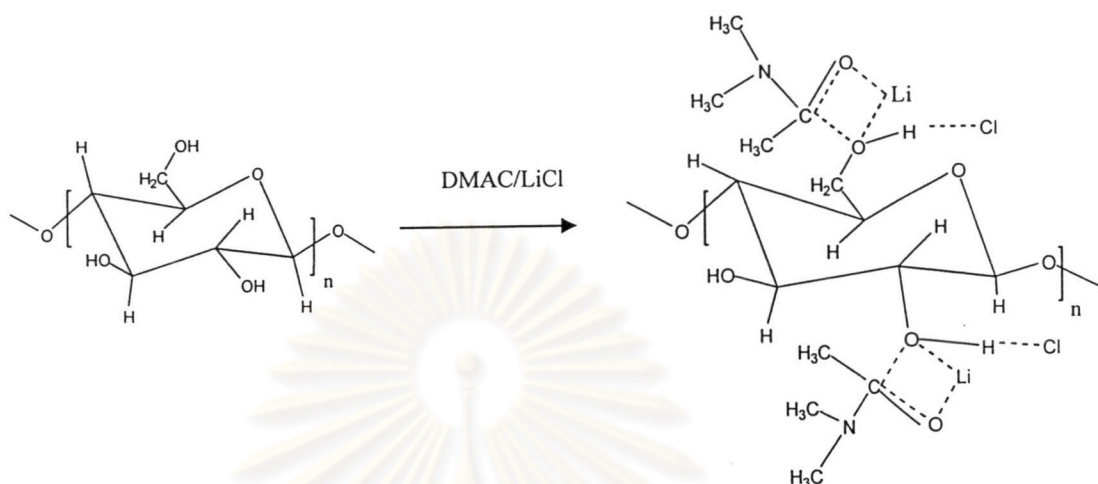


Scheme 4.3 Tosylation of cellulose in pyridine with toluenesulfonyl chloride

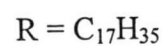
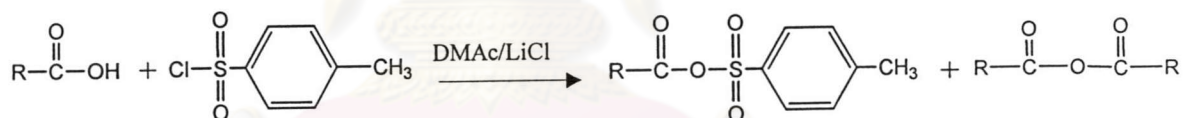
In the esterification of cellulose via the long chain carboxylic acid / toluenesulfonyl chloride / pyridine method, it was found that general mechanism for esterification was still under debate. However, B.Tosh and coworkers [96] offer mechanism for esterification of cellulose in DMAc/LiCl with acetic anhydride using TsCl and pyridine as catalyst. Therefore, similar to their work, instead of acetic anhydride. The overall tentative mechanism for this research is proposed in Scheme 4.4

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Step I : Dissolution of cellulose



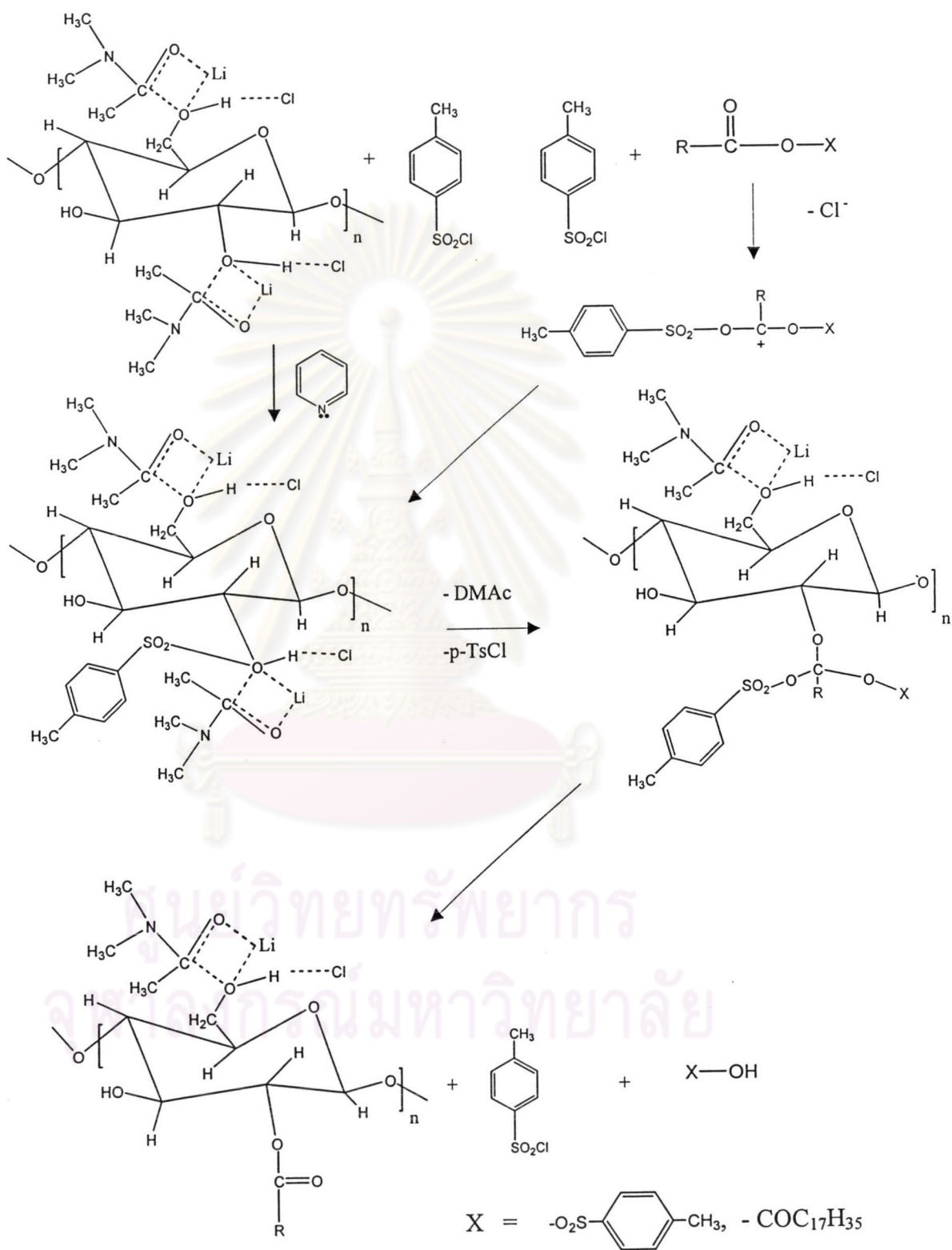
Step II : Formation of reactive species



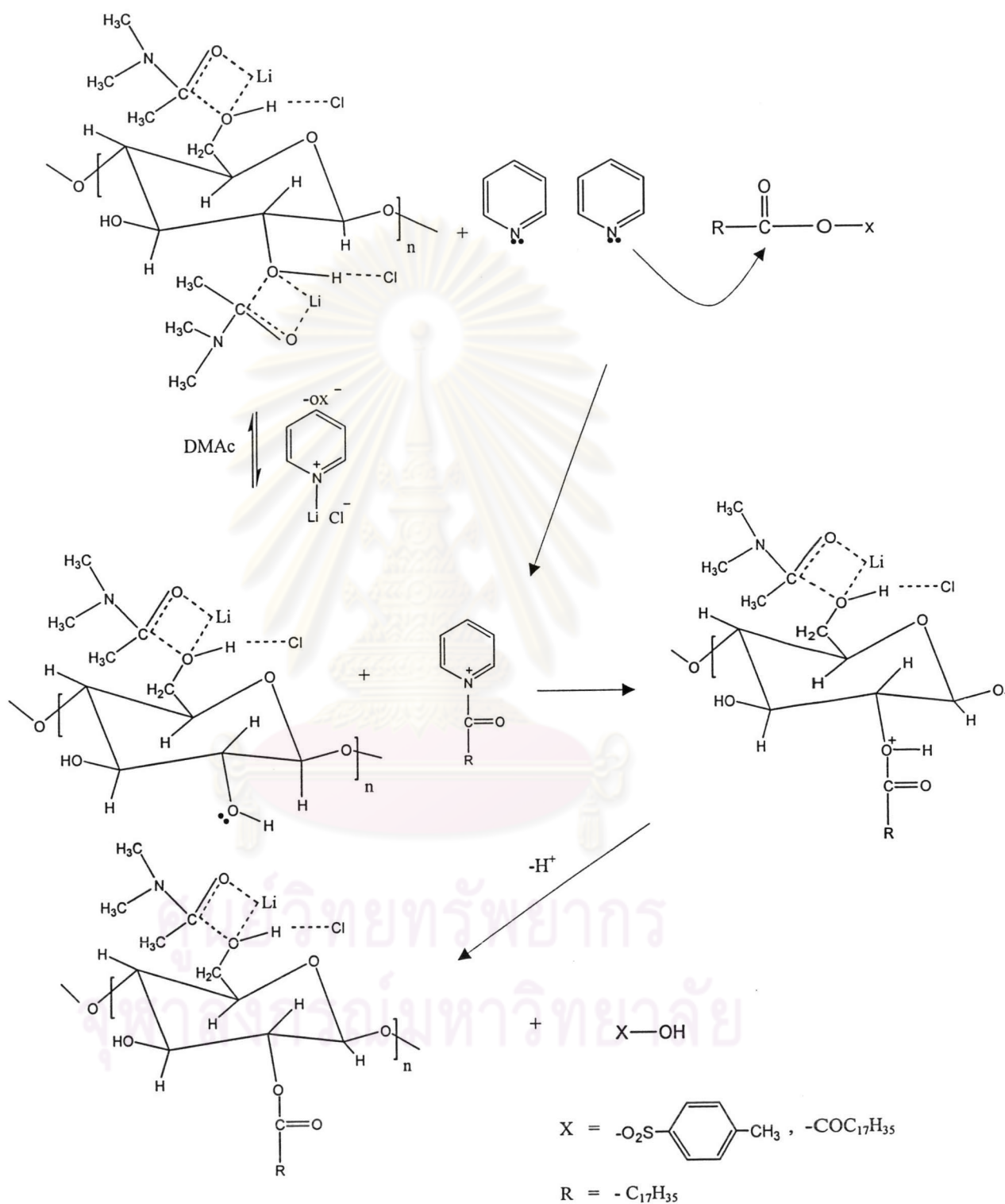
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Step III : Alkyl substituents

a) By toluenesulfonyl chloride



b) By pyridine



Scheme 4.4 Overall tentative mechanism of acylation of cellulose in DMac/LiCl using in situ activation of the carbonic acid by formation of the mixed carbonic/*p*-toluenesulfonic acid anhydride

4.1.3 Effect of concentration of stearic acid and toluenesulfonyl chloride on esterification of cotton

Esterification of cotton performed in DMAc/LiCl using stearic acid as an esterifying agent and TsCl as a catalyst at different equivalent weight of stearic acid and TsCl was investigated. Esterification was carried out at 270 watt for 3.30 min using 4 equivalent weight of pyridine/TsCl (base on the result from previous section), and four different equivalent weight of stearic acid and TsCl. The effect of stearic acid concentration was investigated at 0.5, 1, 2 and 3 eq/OH, whereas the concentration of TsCl was varied at 1, 2, 3 and 4 eq/OH. The results were summarized in Table 4.3. The effects of equivalent weight of TsCl and stearic acid on % yield and %esterification are shown in Figure 4.4 and Figure 4.5 respectively.



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Table 4.4 % yield of esterification and % esterification at different equivalent weight of stearic acid and toluenesulfonyl chloride^c

Stearic acid equivalents	TsCl equivalents				
	1	2	3	4	
0.5	% Yield	0	0	36.27	54.90
	% esterification	0	0	46.78	35.83
1	% Yield	0	134.31	111.76	96.08
	% esterification	0	55.14	63.32	46.47
2	% Yield	31.37	155.88	279.411	225.49
	% esterification	19.87	71.38	84.83	77.25
3	% Yield	0	84.31	123.53	401.96
	% esterification	0	41.66	49.87	88.92

^cEsterification condition: 4 equivalent weight of pyridine/ TsCl, reaction time =3.30 min, power out put =270 watt.

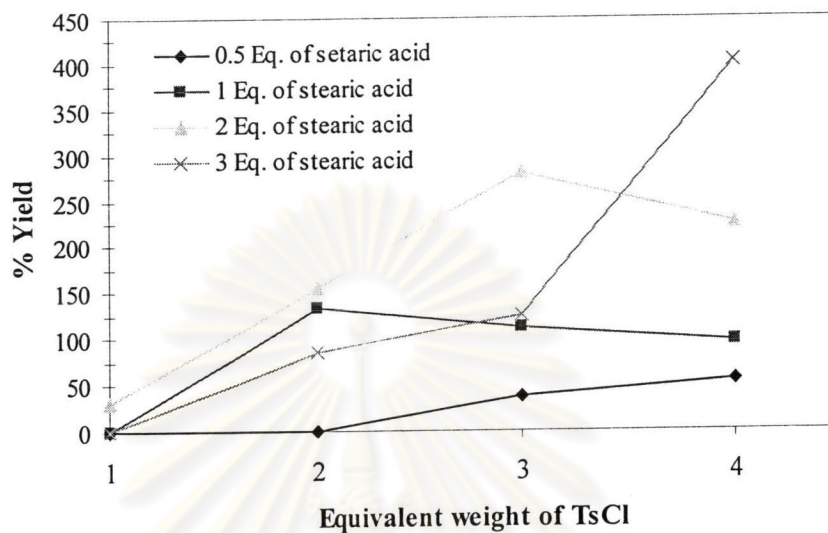


Figure 4.4 The relationship between % yield of esterification and equivalent weight of TsCl at different equivalent weight of stearic acid

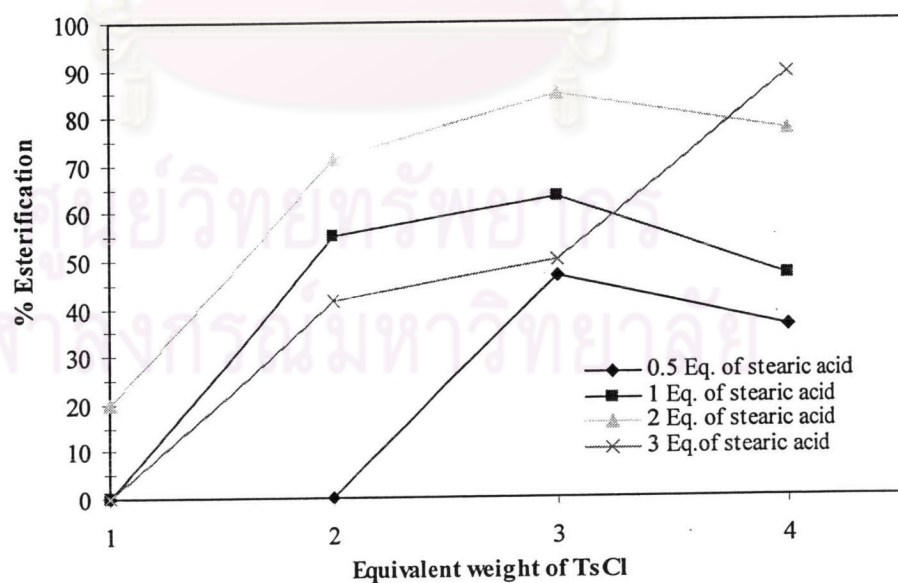


Figure 4.5 The relationship between % esterification and equivalent weight of TsCl at different equivalent weight of stearic acid

As shown in Figure 4.4 and 4.5, for 0.5 eq. of stearic acid, % yield and % esterification have no significant effect for 1-2 eq. of TsCl, however increasing amount of TsCl cause an increase in these values. The concentration of TsCl shows influence on esterification at lower amount of stearic acid. In this synthetic method, esterification reaction was controlled by concentration of stearic acid and TsCl via formation of stearic/*p*-toluenesulfonic acid anhydride as active species. The high concentration of TsCl at low concentration of stearic acid restricts the amount of active species in system but excess amount of TsCl acts like catalyst in the system (Scheme 4.4 a) resulting in increasing of %yield and %esterification at eq. of TsCl more than 2. However, undesirable side reactions of chlorination and tosylation (from XRF, Table 4.5) was also observed. At eq. of TsCl more than 3, clear signal of chloride was obtained because excess amount of the TsCl concentration in the system probably led to chlorination reaction.

For 1 eq. of stearic acid, % yield increases with increasing eq. of TsCl more than 1 until maximum % yield is reached at 2eq. of TsCl, and decreases later while % esterification reaches its maximum at 3 eq. of TsCl. The drop in % esterification at eq. of TsCl more than 3 is probably due to excess amount of TsCl, leading to the loss of homogenous in system and/or to the decreasing of active species (caused by competition of side reaction of chlorination as shown by signal of chloride in XRF, Table 4.5). Comparing to the lower eq. of stearic acid, it is found that increase concentration of stearic acid leads to an increase in the reaction of stearic acid with the TsCl, causing an increase in the formation of stearic/*p*-toluenesulfonic acid anhydride into the esterification reaction. In addition, at eq. of TsCl more than 3, the reduction in signal of chloride can be found (from XRF, Table 4.5) because of the reduction of excess amount of TsCl in the system.

For 2 eq. of stearic acid, % yield and % esterification increase with increasing eq. of TsCl until maximum value are reached at 3 eq. of TsCl and then decrease. It can be clearly observed that the optimum ratio of eq. of stearic acid and TsCl had mark influenced on esterification via formation of stearic/*p*-toluenesulfonic acid anhydride and reduced side reaction of chlorination. However, increasing of %sulfur can be probably due to side reaction of tosylation, and it is possible to occur via formation of *p*-toluenesulfonic acid anhydride in system. The drop in % yield and % esterification at eq. of TsCl more than 3 is probably due to excess of TsCl and stearic acid leading to the loss of homogenous in the system and/or the declination of active

species (caused by competition of side reaction of chlorination and tosylation as attested by signal of chloride and sulfur in XRF, Table 4.5).

For 3 eq. of stearic acid, % yield and % esterification increase with increasing eq. of TsCl. The comparative effect of stearic acid concentration between 2 and 3 eq. at same eq. of TsCl was observed. At 2 eq. of stearic acid, show better results in terms of higher % yield and % esterification, and lower undesirable side reactions can be found, clarifying high conversion of cotton to cotton stearate. The drop in % yield and % esterification at 3 eq. of stearic acid is because excess amount of TsCl and stearic acid leads to the loss of homogenous in system and/or the competition of side reaction as chlorination and tosylation.

Table 4.5 % Sulfur and chloride in side chain of cotton ester (from XRF technique)

Stearic acid equivalents	TsCl equivalents	1	2	3	4
0.5	%S	-*	-*	0.22**	0.22**
	%Cl	-*	-*	8.22	7.39
1	%S	-*	-*	0.13**	0.17**
	%Cl	-*	-*	2.82	4.07
2	%S	-*	-*	2.97	2.26
	%Cl	-*	-*	1.24	2.02
3	%S	-*	0.03**	1.26	2.72
	%Cl	-*	0.04**	3.79	6.00

* not found signal or less than .002%

** could be neglectful

Finally, it can be concluded that the optimum ratio of eq. of stearic acid and TsCl had mark influenced on formation of stearic/*p*-toluenesulfonic acid anhydride, and can reduce undesirable side reactions of tosylation and chlorination. Based on these results, the recommended optimum conditions for esterification cotton via the stearic acid / toluenesulfonyl chloride / pyridine method under microwave energy are 2eq/OH of stearic acid, 2eq/OH of TsCl, 4 equivalent weight of pyridine/TsCl, at 270 watt for 3.30 min. From this condition the optimum %yield and %esterification can be achieved without degradation of cotton and undesirable side reactions.



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4.2 Characterization of cotton stearate powder

4.2.1 Chemical Structure

Functional groups of the cotton stearate were characterized using FTIR technique. The IR vibrations of cotton and cotton stearate are given in Table 4.6. Spectra of cotton and cotton stearate are shown in Figure 4.6.

Table 4.6 Infrared Vibration and Assignments for cotton and cotton stearate [4,7]

Major IR Bands of Components	
Wavenumber (cm ⁻¹)	Assignment and Remarks
Cotton	
3000-3650	O-H stretching
2900	C-H stretching due to CH ₂
1638	O-H bending
1431,1372,1338,1319	C-H bending
1164,1032	C-O bending
1113	C-O bending due to 2° alcohol
1059	C-O bending due to 1° alcohol
Cotton stearate	
3000-3650	O-H stretching
2925, 2854	C-H stretching due to CH ₂ and CH ₃
1752	C=O stretching
1468,1380	C-H bending
1238,1165, 1116, 1060, 1035	C-O bending due to C-OH and C-OR

The comparison of FTIR spectra of cotton and cotton stearate is presented in Figure 4.6. The IR spectra of cotton stearate powder displays different bands from the cotton spectra. The spectrum of cotton stearate provides evidences of esterification by showing the presence of two important ester bands at 2850 (C-H stretching) and 1752 (C=O ester) cm^{-1} . Moreover, another evidence can be seen by the intensity at 3000-3650 cm^{-1} (O-H). The presence of carbonyl (1752 cm^{-1}) and methyl band (2850 cm^{-1}) results from acyl substitution of long chain aliphatic on hydroxyl group of celluloses. Whereas, the decrease in the intensity of hydroxyl groups of cellulose (3000-3650 cm^{-1}) results from the absence of hydroxyl groups, which replaced by long chain aliphatic of stearic acid.

Obviously, as %esterification of cotton stearate increased, the IR exhibits strong carbonyl of ester (1752 cm^{-1}) and methyl absorption (2850 and 2900 cm^{-1}) with considerable decrease in the intensity of hydroxyl group of cotton (3000-3650 cm^{-1}), as shown in Figure 4.7

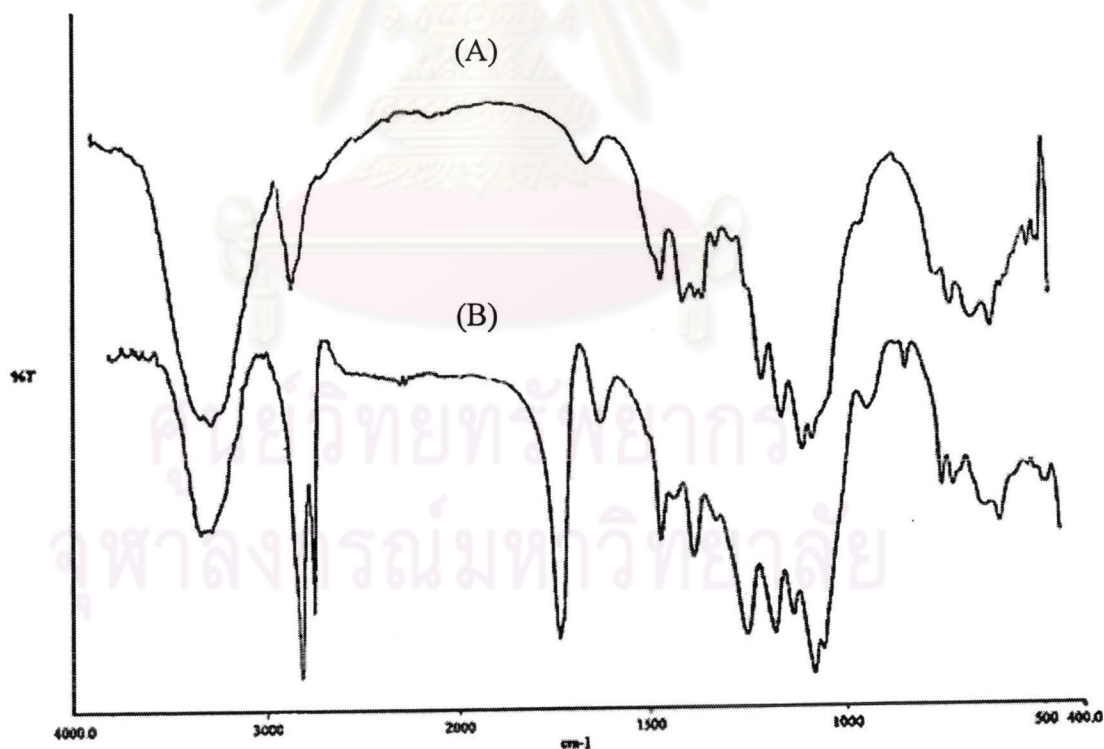


Figure 4.6 Infrared spectra of (a) cotton and (b) cotton stearate powder

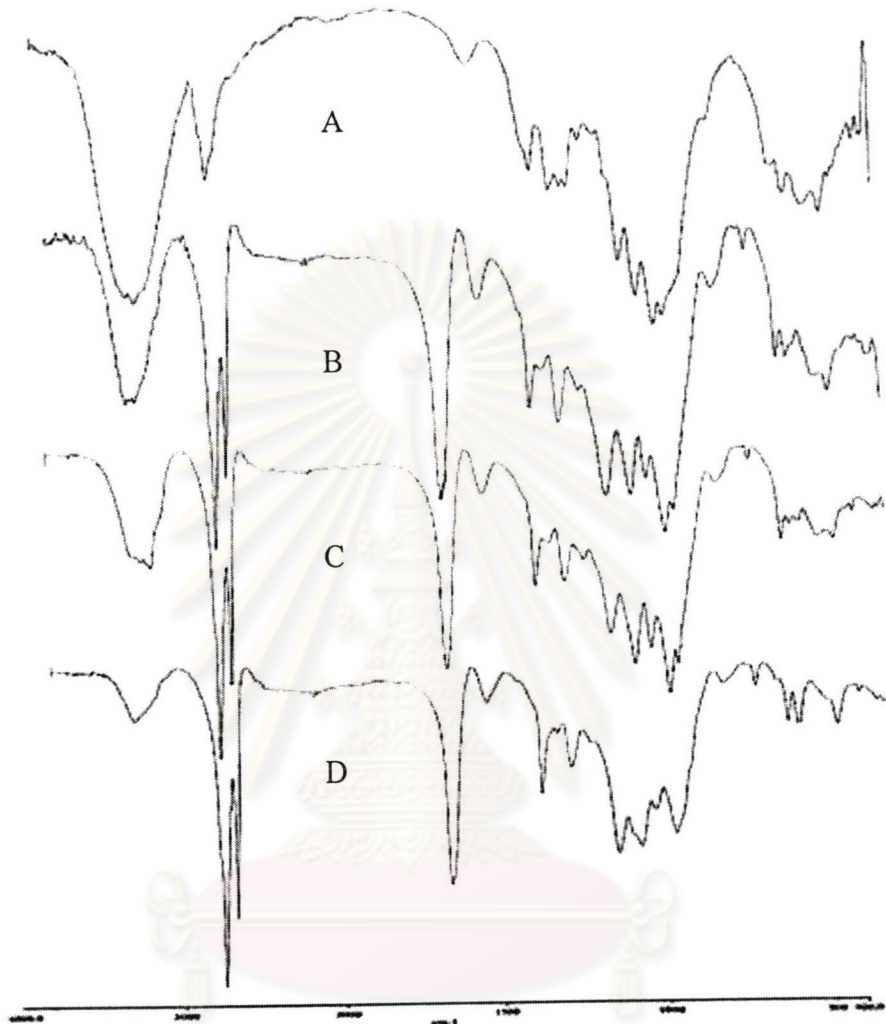


Figure 4.7 Infrared spectra of cotton and cotton stearate powder at different % esterification (a) pure cotton (b) 45.41 % (c) 55.14% (d) 71.38%

4.2.2 Thermal Properties

4.2.2.1 Thermogravimetric Analysis (TGA)

The decomposition temperatures of cotton and cotton ester powder were determined by thermogravimetric analysis. TGA curves of cotton and cotton stearate are showed in Figure 4.8. The onset of decomposition temperature and percent weight loss of cotton and cotton ester are summarized in Table 4.7

The TGA curve of cotton powder (Fig 4.8a) shows two significant steps of weight loss. The first decomposition step occurring approximately at 90-100 °C must be corresponding to the decomposition of moisture in cotton. At higher temperature, the 76.27% of weight loss at the temperature between 260 and 370 °C corresponds to the decomposition of cellulose [70,97]. The 5.50% residue products are possibly due amount of lignin and other carbonized products.

In contrast, at 71.38% esterification, the cotton stearate was obtained using stoichiometric ratio of 2 equivalents of stearic acid/OH, 2 equivalents of TsCl/OH, and 4 equivalent of pyridine/TsCl. The TGA thermogram shows different degradation temperature profile, as shown in Figure 4.8b. Three significant stages of weight loss can be observed. The first decomposition at about 220 °C corresponds to the decomposition of aliphatic hydrocarbon chain of stearic acid (9.82%), the second decomposition between 230 and 350 °C corresponds to the decomposition of cellulose (63.66%), and the last decomposition between 430 and 460 °C corresponds to decomposition of lignin (12.74%) [70]. The decrease in decomposition temperature of lignin compared to the experimental result of Thiebaud et al [97] probably due to the partially dissolution of lignin structure in DMAc/LiCl solvent. The less amount of residue content (3.9%) compared to cotton powder can be explained according to the experimental result of Thiebaud et. al [97], that acyl groups in the esterified samples were eliminated in the form of volatile product and did not contribute to carbonized residue.

Moreover, it was found that content of TsCl and pyridine has affect on the thermal degradation behavior of cotton ester. As presented in Figure 4.8c, at 81.11 % esterification, obtained using stoichiometric ratio of 2 equivalents of stearic acid/OH, 2 equivalents of TsCl/OH and 6 equivalent of pyridine/TsCl, large or board decomposition temperature can be observed ranging from 170 °C to 270 °C. This

degradation step is too large to be attributed solely to the single decomposition of aliphatic hydrocarbon chain of stearate. As evidenced from XRF analysis, it should also be the decomposition of sulphonate and chloride, as well. The decomposition temperature of cellulose itself is hardly seen from this thermogram, probably due to overlapping of its degradation temperature to those of stearate and sulphonate as mentioned earlier. According to the similar experiment reported by Yu-ichi et al. and Heinze et al.[69], it is probably due to undesirable side reactions such as tosylation as evidenced in XRF.

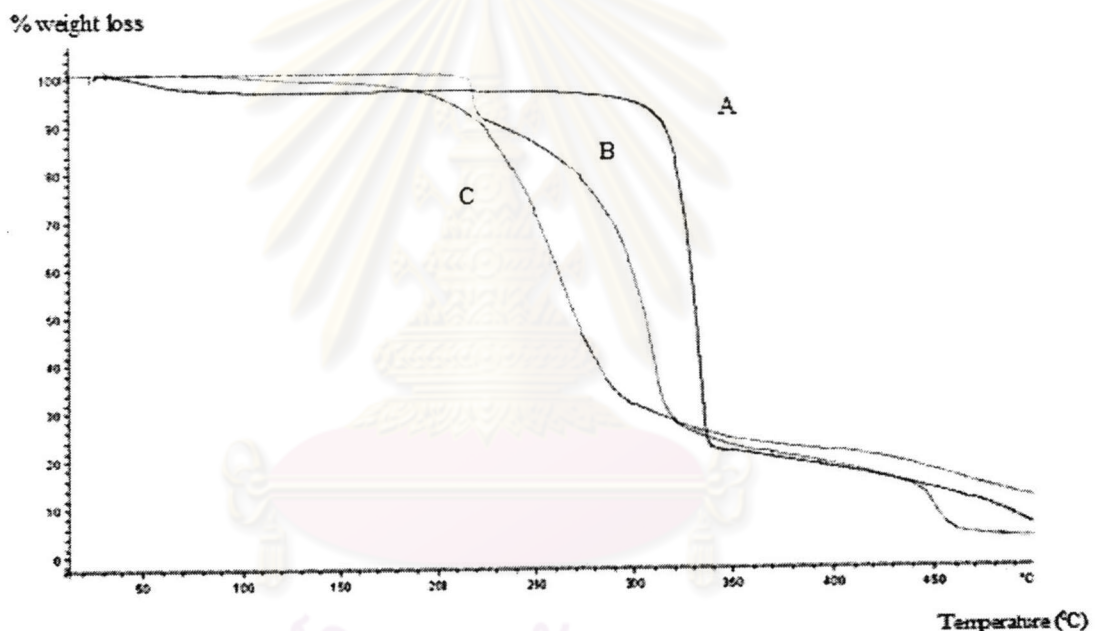


Figure 4.8 Thermal analysis of cotton and cotton ester; (a) cotton (b) cotton stearate at 71.38% of esterification (c) cotton derivative of-stearate, -sulphonate and -chlorinate at 81.11% of esterification

4.2.2.2 Different Scanning Calorimetry (DSC)

Thermal transition temperature was characterized by a differential scanning calorimetry (DSC). The melting temperature (T_m) of the cotton stearate powder was taken as the maximum of the endothermic peak from third heating scan.

The heating cycle of DSC thermogram for cotton is demonstrated in Figure 4.9. Thermogram of cotton reveals distinct transition that occurring at a temperature of 129.14 °C. This large endothermic peak corresponds to melting temperature of cotton and is designated as $T_{m,H}$ or high-temperature melting endothermic peak. However, as expected, cotton did not show second-order transition temperature or T_g due its to high crystalline structure.

For cotton stearate with 71.38 % esterification, the DSC thermogram reveals two separate transition temperatures as shown in Figure 4.10. The first melting endothermic peak occurred at a temperature of 24.82 °C, whereas the second-order transition temperature is barely seen at 128.69 °C. The acyl substituent on hydroxyl groups of cotton destroys or decreases the crystallization of hydrogen bond in cotton stearate as attested by the absence of large high-temperature endothermic peak of cotton. The appearance of low-temperature endothermic peak 24.82 °C is resulted from melting of side-chain crystallization designated as $T_{m,L}$. These results are in good agreement to the work of Sealey et al [70] and can be concluded that low-temperature endothermic peak was attributed to melting of side-chain crystals of long chain aliphatic substitute (stearic acid). In addition, it was found that the appearance of barely visible second-order high-temperature (128.69 °C) is an effect of the few hydroxyl groups remaining. It is possible due to enthalpy relaxation associated with T_g . (Although it is difficult to be sure without X-ray diffraction experiment)

In contrast, at 81.11% derivatives cotton ester (stearate, chloride and sulphonate), undesirable side reactions of tosylation and chlorination occurred. The DSC thermogram reveals four separated of transition temperatures as presented in Figure 4.11. These four endothermic peaks occurred at a temperature of 22.46, 31.29, 45.78, and 70.16 °C. It is difficult to identify these endotherms without X-ray diffraction. However, it may be possible to believe that the first endotherm resulted from melting of side-chain crystals, whereas the other three endotherms might be resulted from melting of undesirable side reactions of crystals, such as chloro- and

sulphonate derivatives (it is possibly due to enthalpy associated each other). The values obtained for all samples are summarized in Table 4.7.

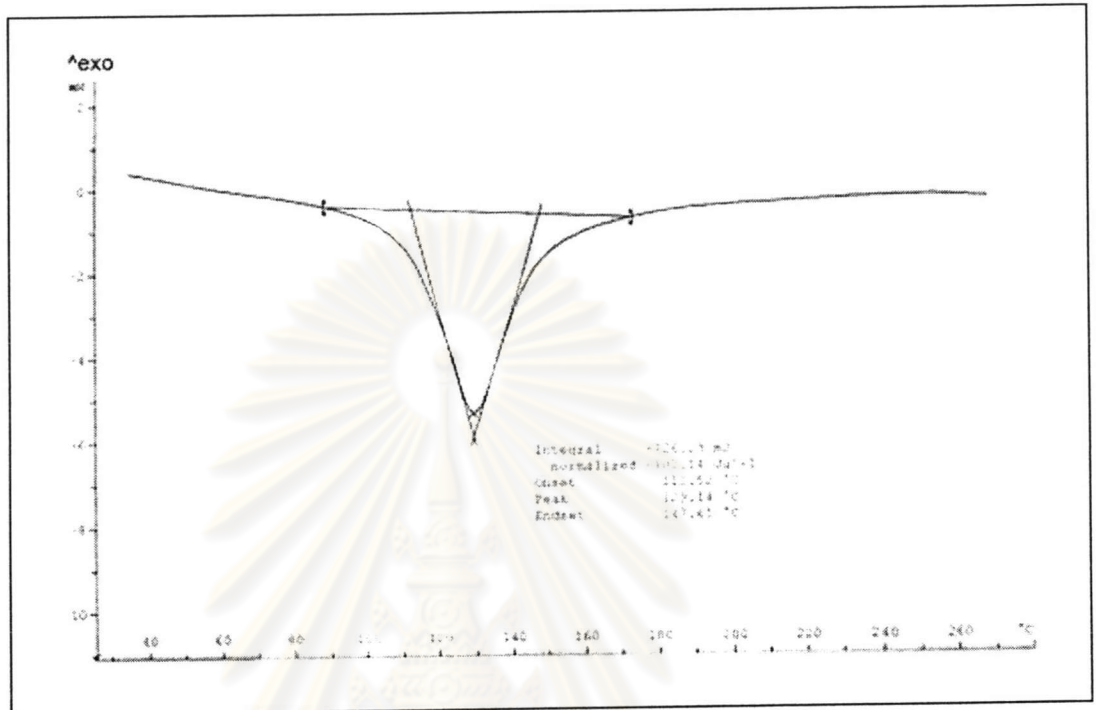


Figure 4.9 DSC thermogram for first heating scan of cotton

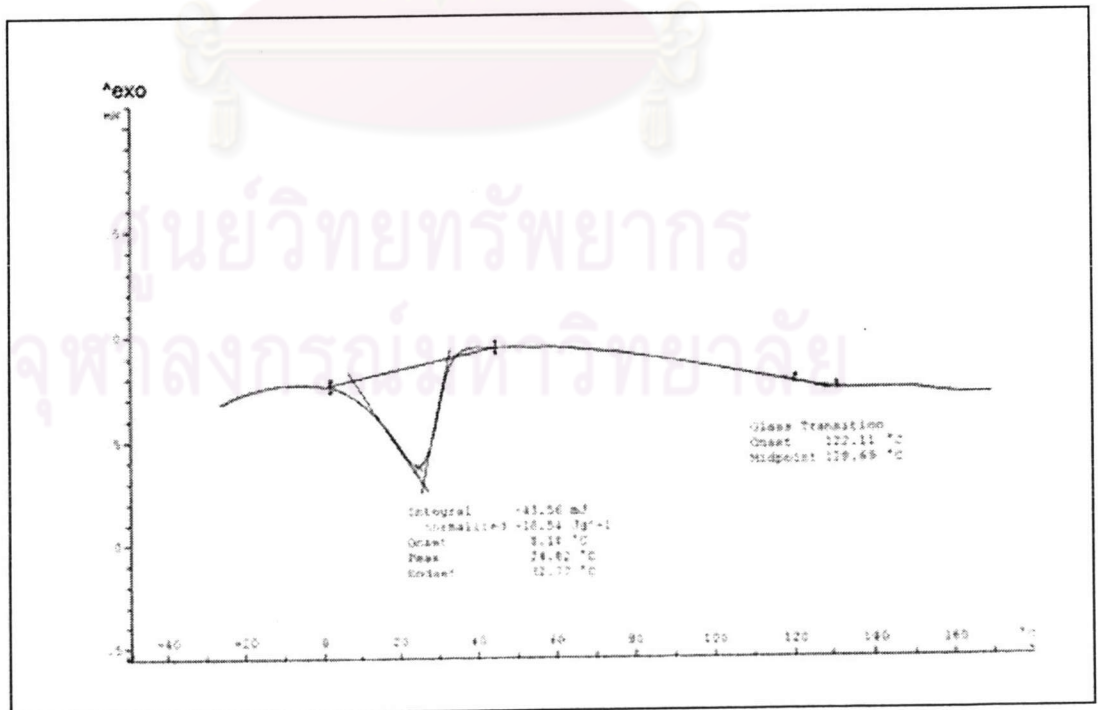


Figure 4.10 DSC thermogram for third heating scan of cotton stearate

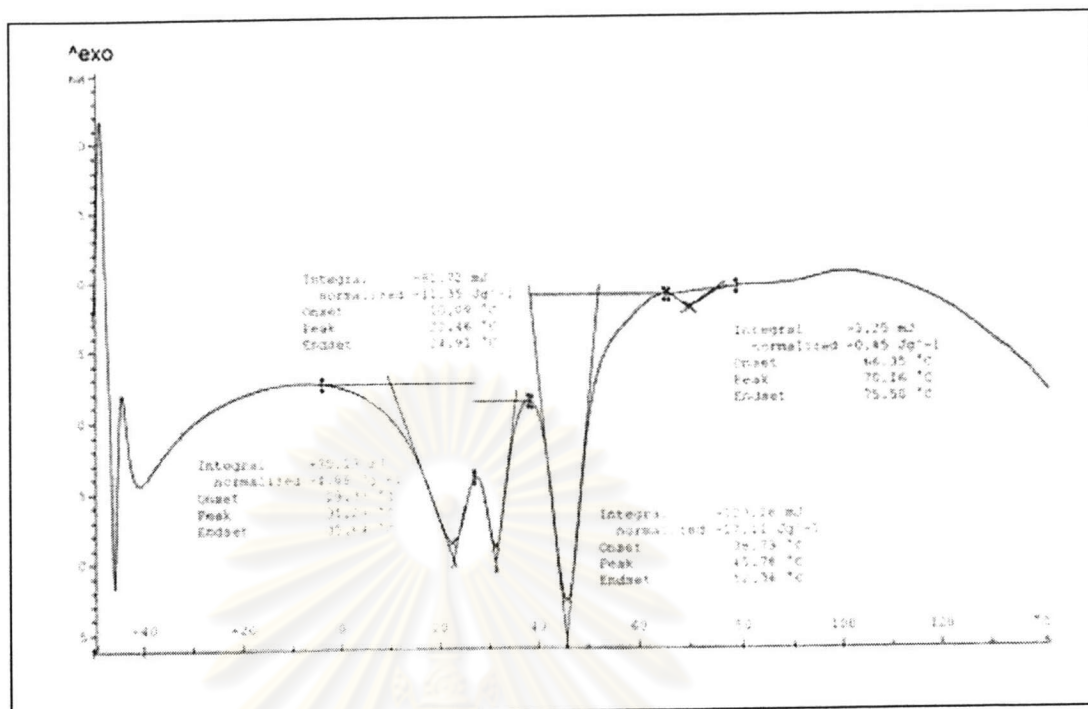


Figure 4.11 DSC thermogram for first heating scan of cotton derivative of -stearate, -sulphonate and -chlorinate

Table 4.7 Thermal of properties for cotton, cotton stearate and cotton derivative of -stearate, -sulphonate and -chlorinate

Sample	T _{m,l} (°C)	T _g (°C)	T _{m,H} (°C)
Cotton	-	-	129.14
Cotton stearate*	24.82	128.69	-
Cotton derivative**	22.46, 31.29, 45.78, 70.16 °C	-	-

* 71.38% of cotton stearate

** 81.11% of cotton derivative

4.2.3 Solubility

Solubility determination of cotton stearate was performed in common solvents and solvent mixture at a solvent-solid sample ratio of 25 to 1. If the samples were insoluble at room temperature, they were heated up to 100 °C or to the boiling point of solvent. The solubility of cotton stearate samples is shown in Table 4.8.

Table 4.8 Solubility of cotton ester at different % esterification

No.	%esterification	Acetone	DMSO	DMA	THF	DMF	Toluene	Chloroform
1	0 (cotton)	-	-	-	-	-	-	-
2	1.83*	-	-	-	-	-	-	-
3	11.01*	-	-	+	+	+	+	+
4	22.94*	-	-	++	++	++	++	++
5	55.14*	-	-	++	++	++	++	++
6	71.38*	-	-	++	++	++	++	++
7	88.92**	-	+	++	++	++	++	++

- Insoluble

+ partially soluble at 100 °C or at the boiling point of solvent

++ completely soluble at room temperature

* no sign of sulfur and chloride

** found sulfur contents in composition

From Table 4.8, the cotton is insoluble in any common organic liquids, whereas the cotton stearate begins partially dissolve in common solvents, like DMA, THF, DMF, toluene, and chloroform at 11.01 % of esterification. Due to the abundance of hydroxyl groups along the cotton of cotton chain, it has the tendency to form intra- and intermolecular hydrogen bonds with adjacent cotton chains, resulting in the formation of crystals. These crystals or crystallites make cotton insoluble in normal aqueous solutions as well as in common organic liquids. However, increasing of acyl substituents leads to the destruction of the highly organized hydrogen-bonding of cotton structure, and to increase the lipophilicity of polymer as results in sample completely dissolve in DMA, THF, DMF, toluene and chloroform of the cotton stearate at 22.94 % of esterification.

All samples except no.7 have no trace of sulfur and chloride atoms as evidenced from XRF analysis. This result suggested that no sign of tosylation and chlorination. However, it was found that sample no.7 contained sulfur and chloride atoms. It is probably due to undesirable side reactions such as tosylation and chlorination. Therefore, the partially dissolve in DMSO (polar solvent) of sample no.7 are resulted from introducing sulphonyl group into cotton structure. It can be concluded that sample no.7 showed weak polar group of cotton sulphonyl and lipophilic part of cotton stearate.

It can be concluded that the cotton stearate is more hydrophilic than cotton. In addition, it was found that the solubility is proportional to the %esterification.

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4.2.4 Morphological Studies

The SEM micrographs of cotton and cotton stearate are presented in Figure 4.12. After acid hydrolysis, waste cotton fabrics were hydrolyzed and became powder as seen by naked eye. However, under microscope, morphology of cotton revealed short fiber shape with approximately 10 μm in diameter, while the cotton stearate revealed granule shape and larger dimension. The different morphology between cotton and cotton stearate are resulted from acyl substitution of stearic acid. The acyl substituents on hydroxyl group of cotton stearate lead to aggregation of acyl group on surface of cotton stearate. Obviously, it can be seen that aggregation of acyl on surface of cotton stearate increased with an increasing of % esterification as shown in Figure 4.12 b and c.

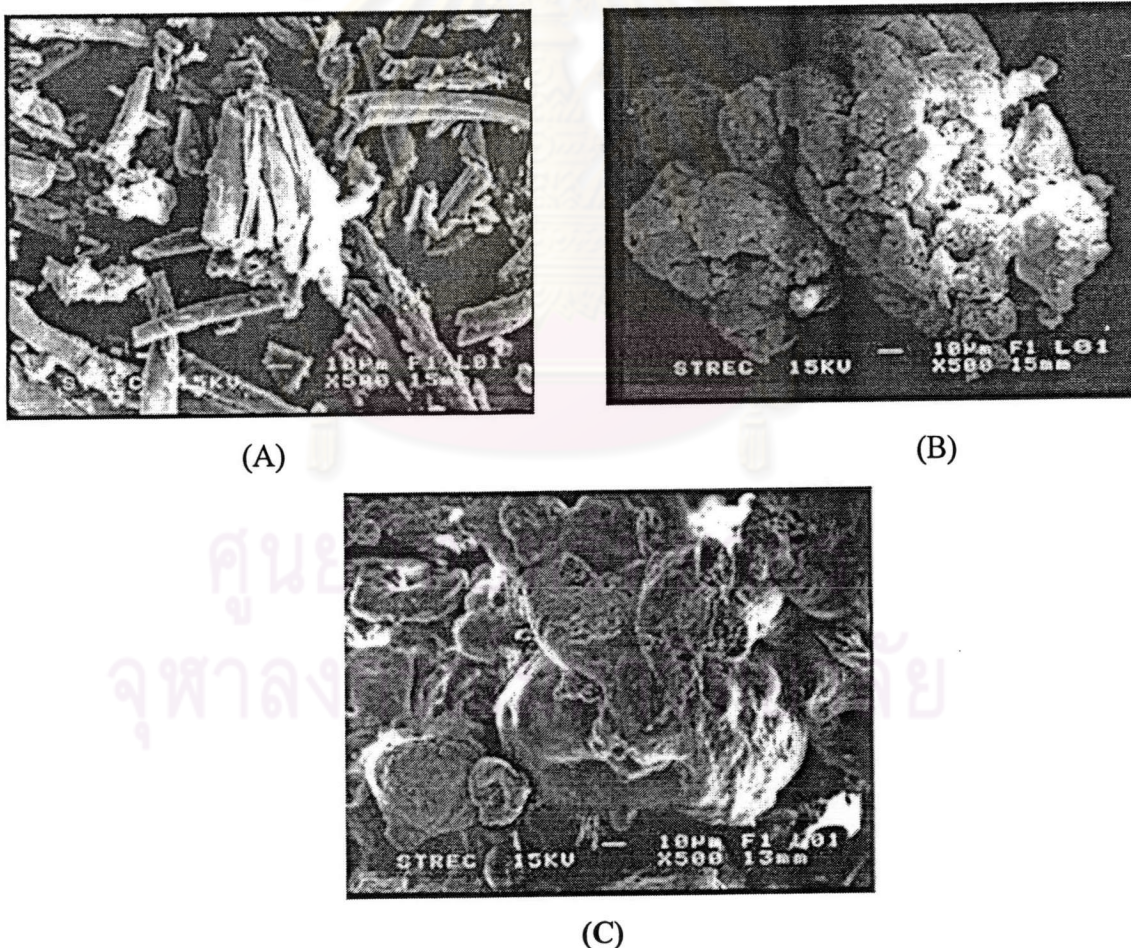


Figure 4.12 SEM Micrographs of cotton sample (a) cotton (b) cotton stearate at 55.14% of esterification (c) cotton stearate at 71.38% of esterification

4.3 Characterization of cotton stearate films

4.3.1 Gloss

The physical appearance of the cotton stearate film at difference %esterification in terms of surface properties were measured. The gloss values were summarized in Table 4.9.

Table 4.9 Gloss values at various %esterification of cotton stearate films

% Esterification	Gloss* (unit)
45.41	9.32 ± 2.07
55.14	51.28 ± 1.26
71.38	49.96 ± 1.60

*Gloss of standard black calibration = 95.1 units

From Table 4.9, gloss values of cotton stearate film increase with increasing % esterification of cotton and start level off or constant after 55.41%.

This result can be explained by the fact that gloss of materials is directly related to the smoothness of the material surface, which means that the smooth or even surface yields the greater gloss value. Increasing of acyl substitutes brings about a significant increase in gloss values of film. As shown previously, increasing acyl substitutes led to an increase in solubility of cotton stearate in chloroform. Therefore, at higher %esterification, smooth or even film surface can be obtained because of homogeneity between solvent and cotton stearate.

4.3.2 Wettability

The interesting property of film is surface hydrophilicity which was evaluated by means of contact angle determination. Three samples of cotton stearate film with different % esterification were measured and their contact angles are summarized in Table 4.10.

Table 4.10 Contact angle at various %esterification of cotton stearate film

% Esterification	Contact Angle (Degree)
45.41	85.6 ± 0.89
55.14	60.4 ± 0.89
71.38	68.4 ± 0.80

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From the above table, the contact angle decreased with increasing % esterification until the minimum value was reached at 55.41% and slightly increased later. In other words, wettability of the cotton stearate film increased with increasing the % esterification up to a certain limited value. This result can be explained in terms of the change in hydrophobicity of cotton surface upon esterification reaction, and will be further supported by the results of water absorption as presented in the next section.

In general, cellulose is intrinsically hydrophobic because the tendency of hydroxyl groups to form crystals utilizing extensive intra- and intermolecular hydrogen bonding. Crystallinity of cellulose has strong effect on penetration of water. Comparing to the cotton stearate at 45.14% esterification, at higher degree of esterification, 55.41%, the increasing of acyl substituents or decreasing hydroxyl groups in cellulose chain leads to the reduction in hydrophobicity and degree of crystallinity of cotton stearate. As a result, water can be absorbed on to the cotton surface easier as shown by decreasing in contact angle value. However, alkyl groups also have hydrophobic property. Upon increasing % esterification of cotton more than 55.41%, the presence of excess amount of hydrophobic aliphatic groups in cotton chain plays an important role in contributing to slight increase in contact angle value or hydrophobicity of cotton stearate film. In addition, the side-chain crystallization might be considered as the key factor as well.

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4.3.3 Water absorption

Water absorption of three cotton stearate films were evaluated by measurement of %water uptake. The effect of % esterification on water absorption of cotton stearate films is listed in Table 4.11 and graphically compared with contact angle values in Figure 4.13.

Table 4.11 Water absorption of cotton stearate film at various %esterification

% Esterification	Water absorption (%)
45.41	14.24 ± 1.33
55.14	30.89 ± 1.10
71.38	20.02 ± 2.52

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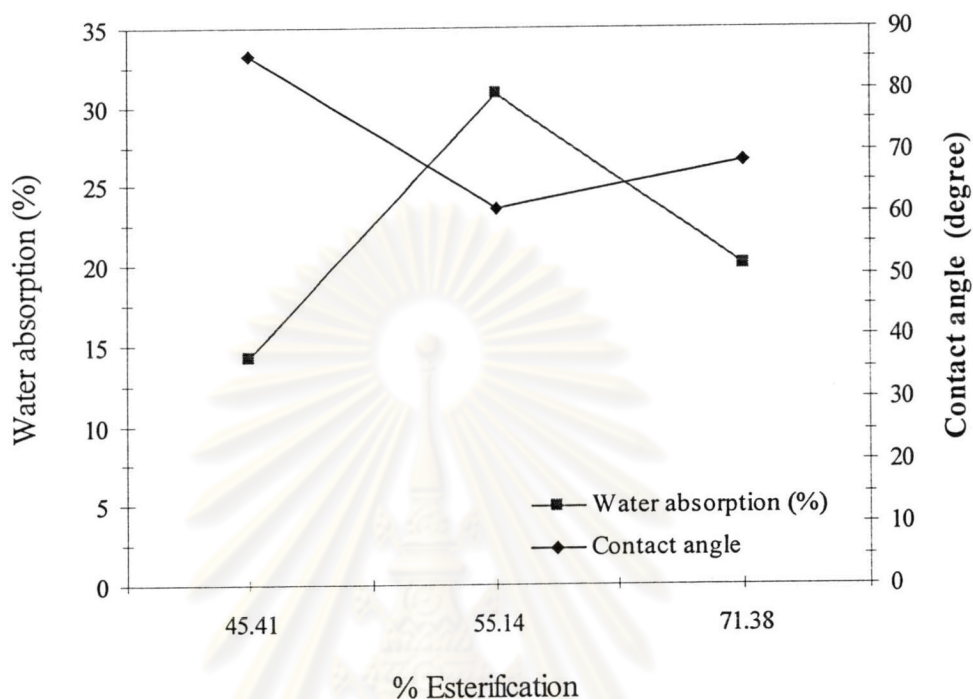


Figure 4.13 Effect of %esterification on water absorption (%) and wettability of cotton stearate films

Obviously, as shown in Figure 4.13, opposite trend was observed for the water absorption of films, compared to their contact angle values. The ability to absorb water of cotton stearate was increased with increasing % esterification until its maximum value was reached at 55.41% and decreased afterwards. This result is in good agreement with the result from contact angle measurement presented in previous section, and reason for these results is similar to that discussed earlier.

The interaction of hydroxyl groups of cellulose to form intermolecular hydrogen bonds between neighbouring cellulose chains results in the formation of crystallite strands. The hydroxyl groups of cellulose were partially replaced by long chain fatty acid of acyl substituents to produce cotton stearate. At higher % esterification, 71.38%, the ability to absorb water decreased. This probably due to the hydrophobicity and the side-chain crystallization of aliphatic chain in cotton stearate film.

4.3.4 Mechanical Properties Characterization:

Tensile Properties Evaluation

The tensile properties of cotton stearate film at various % esterification of cotton are summarized in Table 4.12. The effect of % esterification of cotton on tensile stress at maximum, tensile modulus, and % elongation at break are showed in Figure 4.14 , 4.15 and 4.16, respectively.

Table 4.12 Tensile properties of cotton stearate film at various %esterification

No.	% Esterification of cotton	Tensile strss at maximum load (MPA)	Tensile Modulus of elastic (MPA)	Elongation at break (%)
1	45.41	2.88 ± 0.44	147.73 ± 17.13	2.25 ± 0.46
2	55.14	4.64 ± 0.18	325.60 ± 16.71	3.06 ± 0.62
3	71.38	5.67 ± 0.41	330.81 ± 33.97	3.94 ± 0.28

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Figure 4.14, 4.15 and 4.16 illustrate the effect of acyl substituent of stearic acid content on the tensile properties of cotton stearate film. Obviously, the tensile properties of cotton stearate film are dependent on the amount of acyl substituent of stearic acid. As increasing % esterification of cotton, the tensile strength, tensile modulus and %elongation at break were increased. The increasing of tensile strength and tensile modulus as increasing of acyl substituent may be due to increase in side chain crystal thickness. Due to the parts of the side chain that overlap and crystallize become larger with increasing of acyl substituent. According to the experimental result of Sealey et al [70], they concluded that crystallization is limited to part of side chain extending beyond the first eight or nine methyl unit, and that crystals incorporate overlapping or interdigitated side chain from neighboring main chain. Therefore, increasing of acyl substituent as increase in side chain crystal thickness resulted in increasing of tensile strength and tensile modulus.

The slightly increasing of % elongation as increasing of acyl substituent may be due to the internal plasticization effect from non-alignment part or crystallized part of long chain aliphatic (stearic) leading to an increase in the mobility between chains.

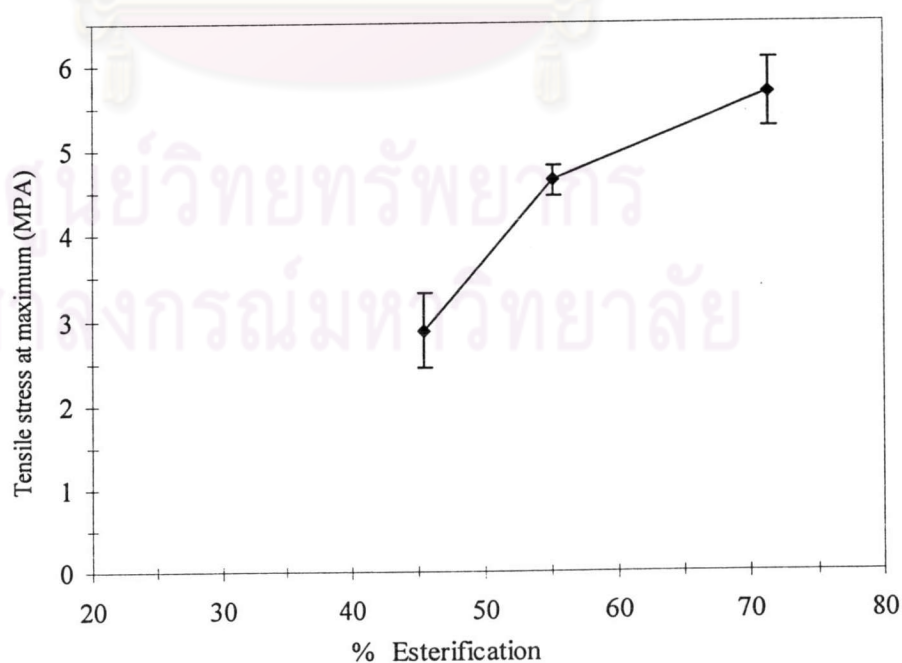


Figure 4.14 Tensile stress at maximum of cotton stearate film at various % esterification

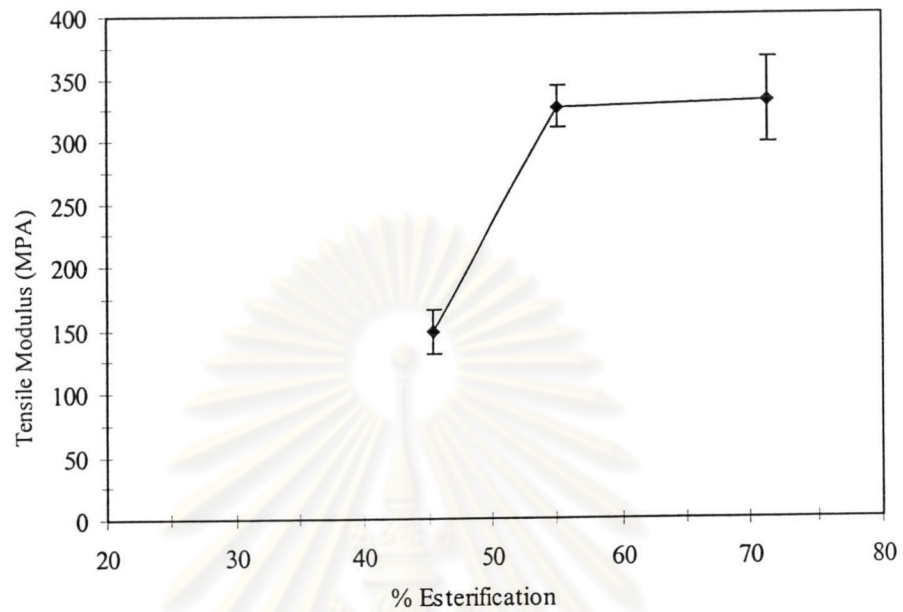


Figure 4.15 Tensile Modulus of cotton stearate film at various % esterification

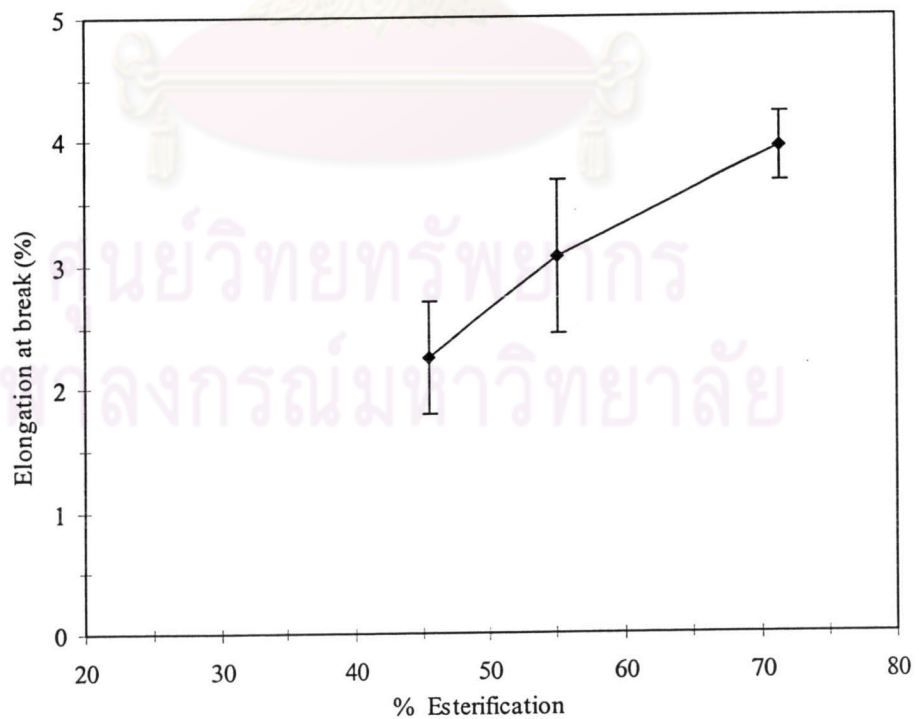


Figure 4.16 % Elongation at break of cotton stearate film at various % esterification

4.4.5 Biodegradation : Weight loss

Biodegradability of cotton stearate films was carried out by soil burial test under different exposure time. Evaluation of the biodegradability of the films was performed by weight loss measurement and SEM analysis. % Weight loss of cotton stearate films are summarized in Table 4.13 and graphically shown in Figure 4.17

Table 4 .13 %weight loss of cotton stearate films during soil burial test

%Esterification of cotton	Duration Time (Day)					
	5	10	15	20	25	30
45.41	1.60	1.89	5.14	4.96	9.94	15.20
55.14	1.77	1.92	5.71	8.31	12.73	18.31
71.38	1.93	3.08	5.74	10.58	12.56	21.16

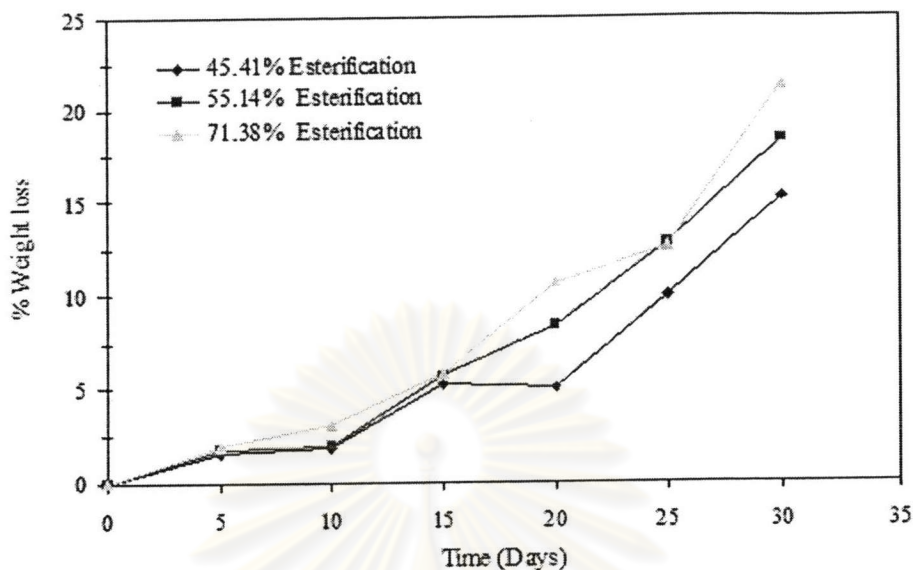


Figure 4.17 %weight loss of cotton stearate films during soil burial test

Clearly, from Figure 4.17, % weight loss the films increased with duration time of exposure in soil and % esterification of cotton. After 30 days, the greatest value of % weight loss was obtained from the cotton stearate film with 71.38 % esterification, which was as high as 21.16 %. The biological degradation of cotton can be explained in term of several factor such as their crystallinity or amorphous region, microorganisms, temperature and humidity condition, etc.

The weight loss of cotton stearate films are resulted from consumption of microorganism. Microorganisms, such as fungi and bacteria, can degrade cotton by ingesting the carbon molecules that are backbone of the cellulose in their digester system by enzymatic hydrolysis. Upon increasing the expuse time, the molecular chain become shorter in length due to the microbial degradation of backbone, hence % weight loss of the films increased.

In addition, when considering the effect of % esterification , it was found that % weight loss also increased as a function of % esterification. This result can be explained by the fact that the increasing of long chain aliphatic acid (stearic acid) contents led to an increase in amorphous region which is the portion that mainly consumed by microorganisms. Moreover, the amorphous region can faciliate the accessibility of water into the film which is also another factor promoting the biodegradable reaction. The appearance of cotton stearate films after soil burial

exposure at different time are revealed in Figure 4.18. Obviously, the remarkable change of the cotton stearate film at 71.38 % esterification can be observed within 15 days of exposure.

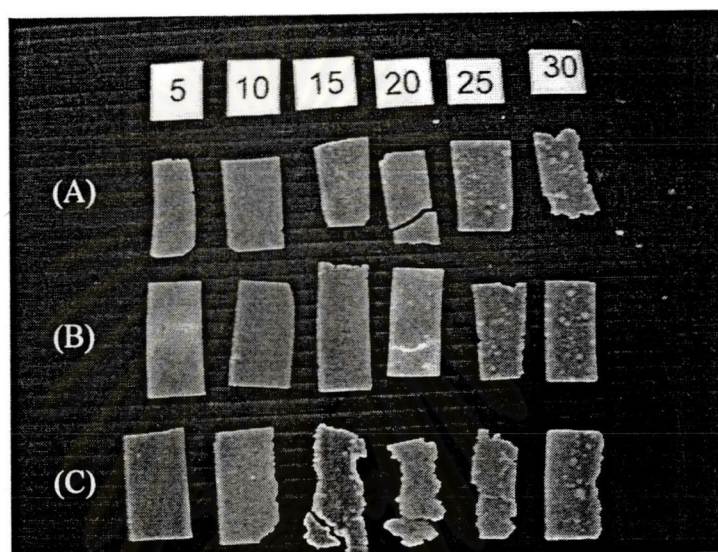


Figure 4.18 The appearance of cotton stearate films at different % esterification after soil burial at different exposure time (a) 45.41 % esterification (b) 55.14% esterification (c) 71.38 % esterification

To confirm these results, the SEM micrographs of cotton stearate film before and after 30 days of soil burial exposure were demonstrated in Figure 4.19. From Figure 4.19, cotton stearate films show cavities on the film surface and these cavities increase with %esterification. This result is similar to the result from soil burial test. Thus, it might be confirmed that long chain aliphatic acid (stearic acid) portion can be consumed by microorganisms.

Conclusively, upon increasing %esterification an increase in appearance of cavity on film surface because of an increasing of portion that can be consumed by microorganisms

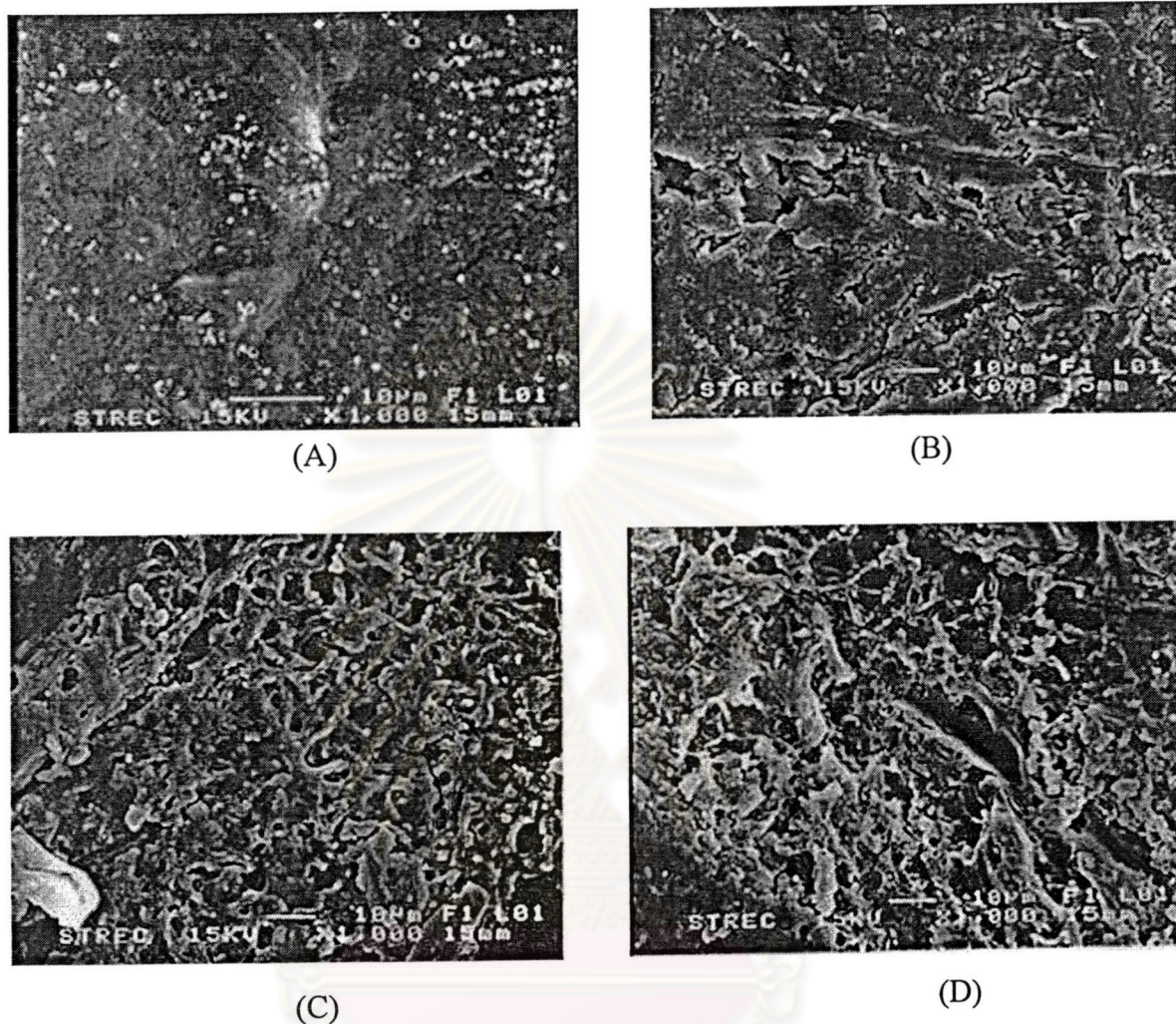


Figure 4.19 SEM micrographs of cotton stearate film at (a) 71.38% of esterification before soil burial, (b) 44.41% of esterification after 30 days of soil burial, (c) 55.14% of esterification after 30 days of soil burial, and (e) 71.38% of esterification after 30 days of soil burial