

CHAPTER IV

RESULTS AND DISCUSSION

In this research, microwave-induced esterification of paper mulberry for degradable film preparation with DMAP as catalyst and lauroyl chloride as modify substance was studied, the results were analyzed and divided mainly into two parts as follows:

- Esterification reaction of paper mulberry with DMAP as catalyst and lauroyl chloride as esterifying agent

- The effect of esterification reaction time and microwave power
- The effect of catalyst (DMAP)
- The effect of esterifying agent (Lauroyl chloride)

- Characterization of esterified paper mulberry and paper mulberry film

The details of the results were explained in the following.

4.1 Esterification reaction of paper mulberry with DMAP as catalyst and lauroyl chloride as modify substance.

4.1.1 The effect of esterification reaction time and microwave power

The effects of various esterification reaction times and power output of microwave on paper mulberry using 4-dimethylamino pyridine (DMAP) and lauroyl chloride were investigated. The esterification reaction was carried out in DMAc/LiCl, 0.5 equiv. of DMAP and 10 equiv/OH of lauroyl chloride, with five different esterification reaction times viz., 2.30 min, 2 min, 1.30 min, 1 min, 30 sec under seven different microwave powers viz., 90, 180, 270, 360, 450, 540, 630, and 720 watts. The results are summarized in Table 4.1 and the relationship between % yield and microwave powers are shown in Figure 4.1.

Table 4.1 % yield of esterification at various reaction times and microwave powers (0.5 equiv. of DMAP, 10 equiv/OH of lauroyl chloride)

Power output (W)	% Yield				
	2.30 min	2.00 min	1.30 min	1..00 min	30 sec
90	125	131	60	27	0
180	-	81	93	42	0
270	-	58	132	64	7
360	-	-	113	84	19
450	-	-	-	137	40
540	-	-	-	68	57
630	-	-	-	-	74
720	-	-	-	-	56

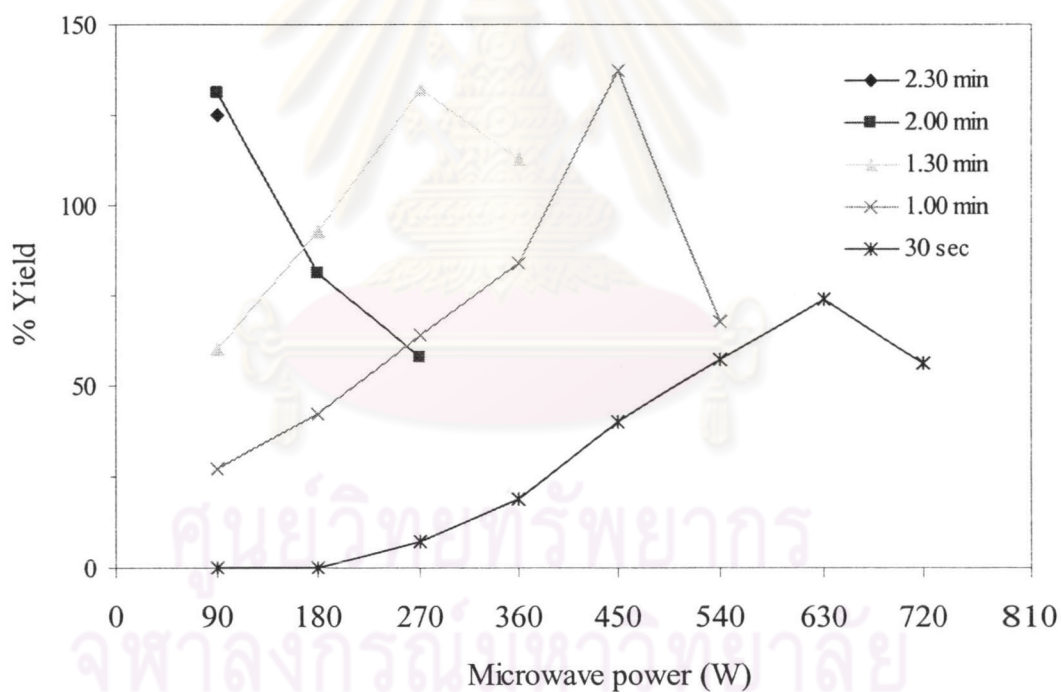


Figure 4.1 The relationship between % yield and microwave power (W) at different reaction times.

Figure 4.1 clearly shows that at reaction time of 30 sec, 1 min and 1.30 min, % yield of esterification reaction rapidly increases with microwave power until it reaches the optimum value and then gradually decreases. The optimum values of % yield of esterification at 30 sec, 1 min and 1.30 min were 74 %, 137 %, 132 % at microwave power of 630 watt, 450 watt and 270 watt, respectively. The decrease of % yield after the optimum value was reached indicated that the excess microwave power absorbed can cause cellulose degradation.

However, the similar trend of % yield of esterification respective to microwave power was not observed in case of 2 and 2.30 min reaction time. At reaction time of 2 min, it was found that % yield of esterification reaction gradually decreased with the increasing microwave power. The optimum value of 131 % yield was obtained at 90 watt microwave power. This was because of the inability to perform the esterification reaction below 90 watt due to the limitation of the microwave oven manufactured. It was believed that the % yield of esterification would initially increase with microwave power applied between 0 – 90 watt. The esterification reaction was further performed at 2.30 min and it was found that % yield of esterification was less than that at reaction time of 2 min under 90 watt microwave power.

The effect of reaction time on the % yield of esterification was also investigated. At any applied microwave power, the longer time the samples were irradiated, the higher % yield of esterification attained until it reached the optimum value. Beyond that point, samples started to degrade as indicated by the decreasing of % yield. For instance, under 270 watt microwave power, as irradiation time increased from 30 sec to 1.30 min, % yield increased from 7 % up to its critical value at 132 %. When sample was continued to heat until 2 min, cellulose degradation occurred and % yield dropped to 58 %. From these results, it can be concluded that the critical irradiation time before cellulose started to degrade under 0 - 90 watt, 90 - 270 watt, 270 - 450 watt, and 450 – 630 watt microwave energy were 2 min, 1.30 min, 1 min, and 30 sec, respectively.

Hence, when considered energy and time saving along with the reasonable % yield of esterification (131 %), the esterification reaction of paper mulberry should be performed under 90 watts microwave power for 2 min.

4.1.2 The effect of 4-dimethylamino pyridine (DMAP) as catalyst

The esterification reaction using various DMAP concentrations was studied. The esterification reaction was performed in DMAc/LiCl solvent system and 10 equivalent weight lauroyl chloride with four different equivalent weight of DMAP viz., 0.1, 0.5, 0.9, and 1.2. The esterification reaction was performed under 90 watts microwave power for 2 min. The results are summarized in Table 4.2. % Yield of esterification reaction and % esterification versus the equivalent weight of DMAP used is shown in Figure 4.2.

Table 4.2 % yield of esterification and % esterification at different equivalent weight of DMAP (10 equiv. weight of lauroyl chloride and 2 min 90 Watt)

DMAP (equiv)	% Yield	% Esterification*
0.1 equiv.	86	24.3
0.5 equiv.	127	36.3
0.9 equiv.	154	38.0
1.2 equiv.	138	11.0

* Details of calculation is described in Appendix C.

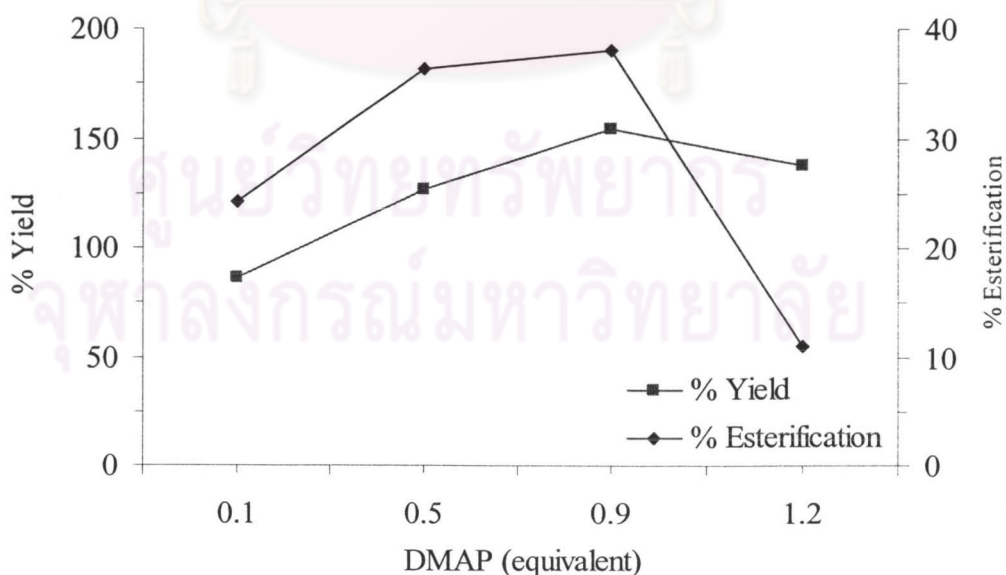


Figure 4.2 The effect of equivalent weight of DMAP on the % yield of esterification and % esterification.

As shown in Figure 4.2, both % yield and % esterification were greatly influenced by the amount of DMAP. % Yield of esterification reaction increased with the increasing equivalent weight of DMAP until maximum % yield value was reached at 0.9 equivalent weight of DMAP and then slowly decreased afterwards. The % esterification deduced from the IR spectroscopy study also had the highest value of 38 % at 0.9 equivalent weight of DMAP. This is obviously because N, N-dimethyl-4-aminopyridine (DMAP) acts as a powerful catalyst and activates esterification of paper mulberry, thus the reaction occurs rapidly.

At low amount of DMAP, the esterification reaction enhanced due to the diffusion of lauroyl chloride into main chain of cellulose. When DMAP was added more than 0.9 equivalents, both % yield and % esterification decreased. This was thought to be because of the reaction between DMAP and lauroyl chloride not allowed lauroyl chloride to act as an esterifying agent.

Therefore, the suitable amount of DMAP as a catalyst for the esterification reaction of paper mulberry under microwave power of 90 watt for 2 min is 0.9 equivalent weight. This result can be supported by the IR spectra presented in Figure 4.3.



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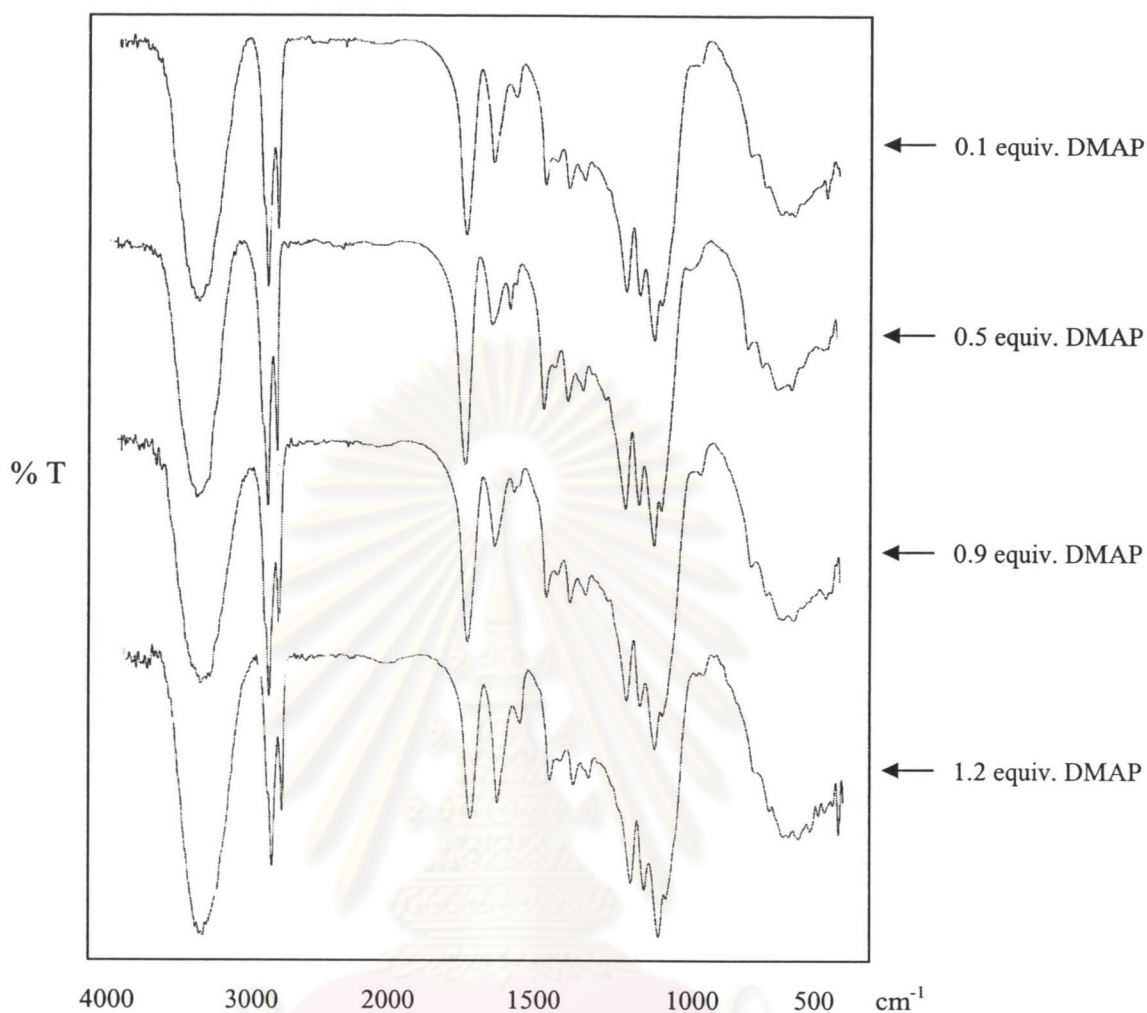


Figure 4.3 Infrared spectra of samples at different equivalent weights of DMAP.

From Figure 4.3, it was found that at 0.9 equivalent weight of DMAP, the intensity of the O-H bond vibrations at 3422 cm^{-1} decreased as compared to those at 0.1 and 0.5 equivalent weight. This was because hydroxyl groups in cellulose was substituted by alkyl groups from lauroyl chloride indicating fewer availabilities of O-H groups than those of a 0.1, 0.5, and 1.2 equivalent weight of DMAP solution.

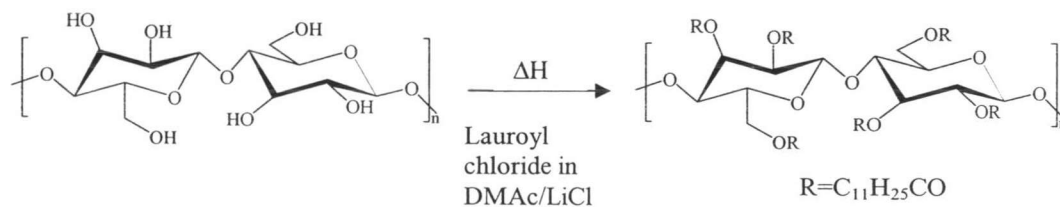


Figure 4.4 Acetylation of cellulose [78].

Figure 4.4 gives an overview of the esterification reactions of cellulose carried out under homogeneous condition in DMAc/LiCl. Lauroyl chloride was used as a esterifying agent and the reaction was performed under microwave energy. The hydroxyl groups in cellulose can be substituted by nucleophiles. Therefore, the esterification reaction investigated was always carried out with lauroyl chloride of the corresponding acids in order to exclude such side reactions. The free hydrochloric acid formed during the acetylation, on the contrary, is not an enough strong acid to hydrolysis of the products or not nucleophilic enough to attack the acetyl ester groups. This reason are in good agreement with work done by Heinze et al., [79]. The reaction mechanism involves an attacking of acyl carbon center by nucleophile such as DMAP and the removal of hydrochloric acid are shown in Figure 4.5.

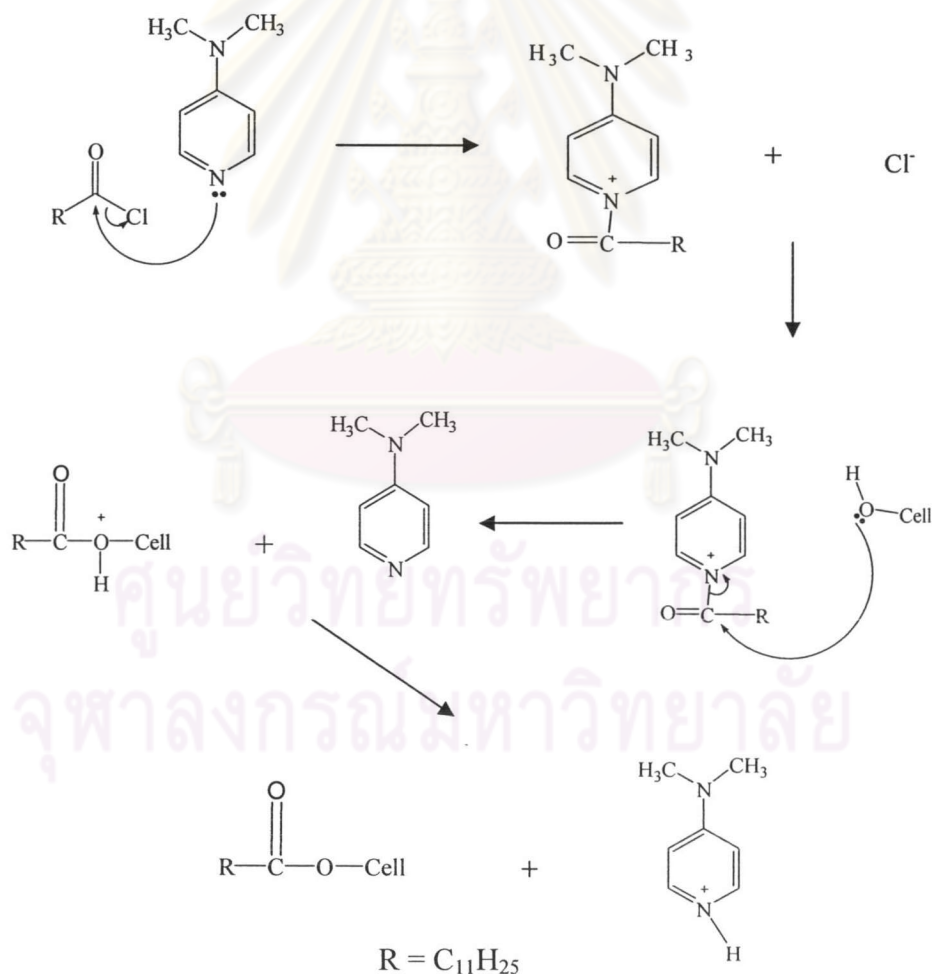


Figure 4.5 Mechanism of acetylation of cellulose.

The esterification of paper mulberry in this study might be similar to that of hemicellulose with acetic anhydrides and DMAP method studied by J. M. Fang et al., 2000. The mechanism for esterification of hemicellulose is presented in Figure 4.6.

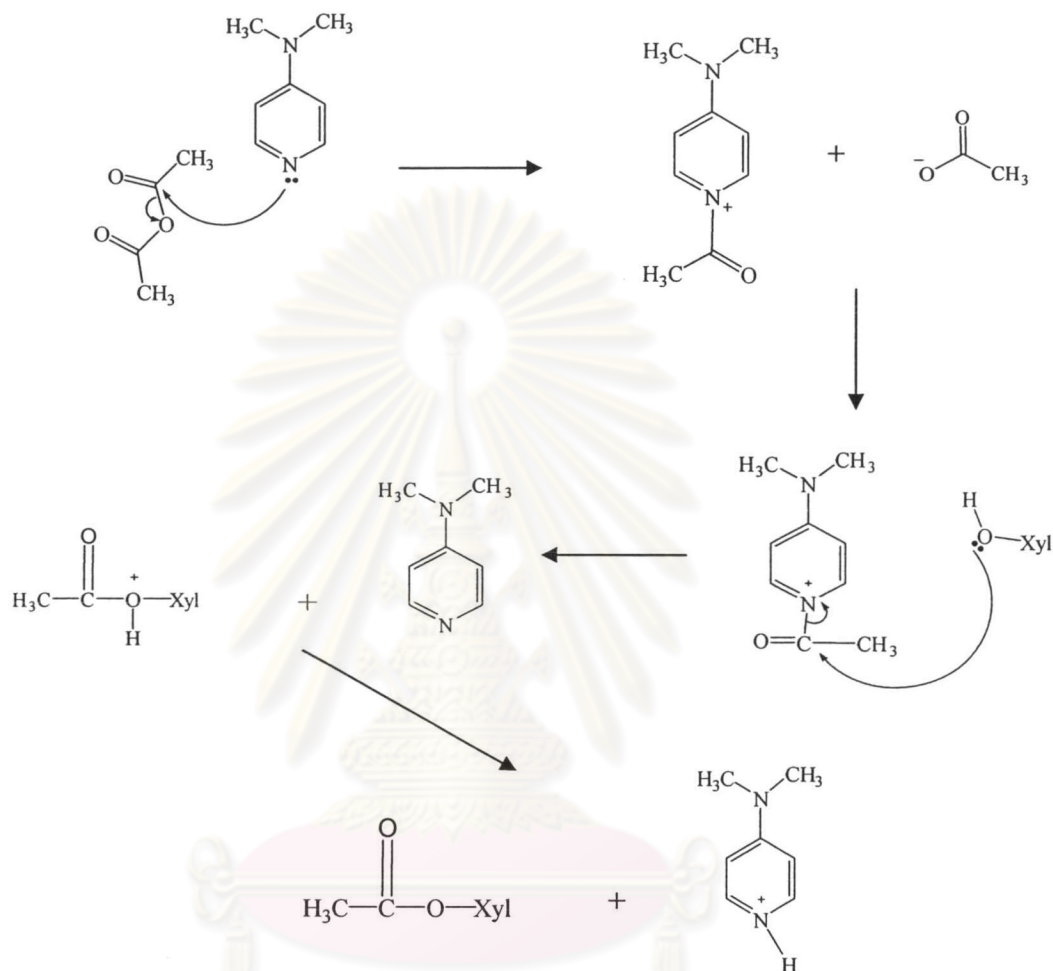


Figure 4.6 Mechanism of acetylation of wheat straw hemicellulose [79].

4.1.3 The effect of lauroyl chloride as esterifying agent

To investigate the effect of lauroyl chloride on the esterification of paper mulberry, the esterification reaction in DMAc/LiCl using 0.9 equiv DMAP as a catalyst with various amount of lauroyl chlorides was conducted. Esterification was carried out under microwave energy of 90 watts for 2 min. Four different equivalent weight of lauroyl chloride investigated included 5, 8, 10, and 14. The influences of lauroyl chloride on esterification reaction using DMAP as a catalyst are presented in Table 4.3 and Figure 4.7. The % esterification or yield was greatly influenced by the amount of lauroyl chloride. This findings is also been discussed elsewhere by C. Satge et al.[1].

Table 4.3 % yield of esterification and % esterification at different equivalent weight of lauroyl chloride

Lauroyl chloride (Equiv.)	% Yield	% Esterification
5 equiv.	106	23.24
8 equiv.	136	24.3
10 equiv.	154	38.0
14 equiv.	123	18.0

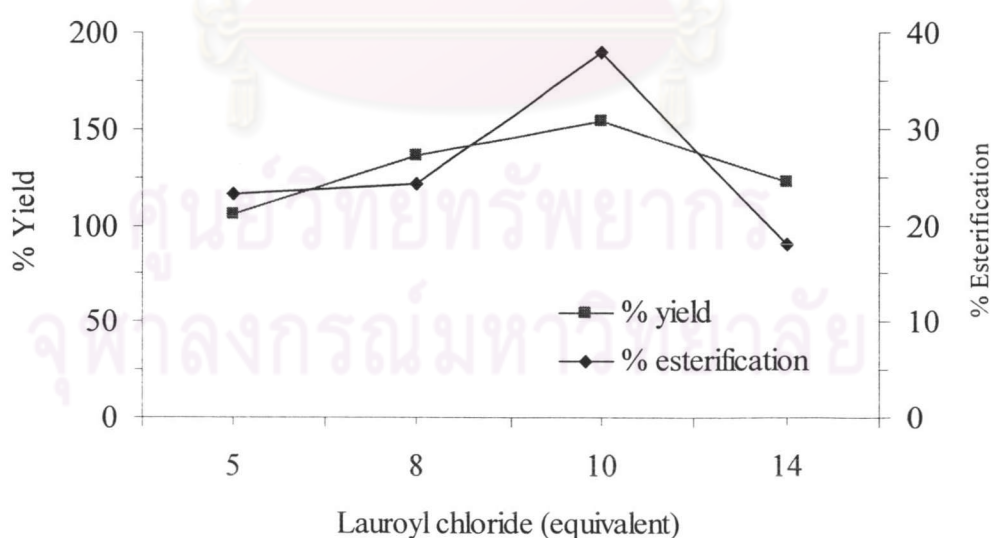


Figure 4.7 The effect of equivalent weight of lauroyl chloride on the % yield of esterification and % esterification of paper mulberry under 90 watt microwave energy for 2 min.

Figure 4.7 clearly shows that the maximum % yield of esterification reaction appears at 10 equivalent weight of lauroyl chloride. At less than 10 equivalent weight, lauroyl chloride reacted with hydroxyl groups in cellulose, thus % yield of esterification reaction increased almost linearly with the amount of lauroyl chloride. When more than 10 equivalent weight of lauroyl chloride was used, however, the % yield of esterification reaction decreased. This is because the excess amount of lauroyl chloride can lead to inhomogeneous system

Hence, It can be concluded that the optimum amount of lauroyl chloride is 10 equivalent for esterification reaction of cellulose under 90 watt-microwave for 2.00 min. These results are supported by IR spectras presented in Figure 4.8.

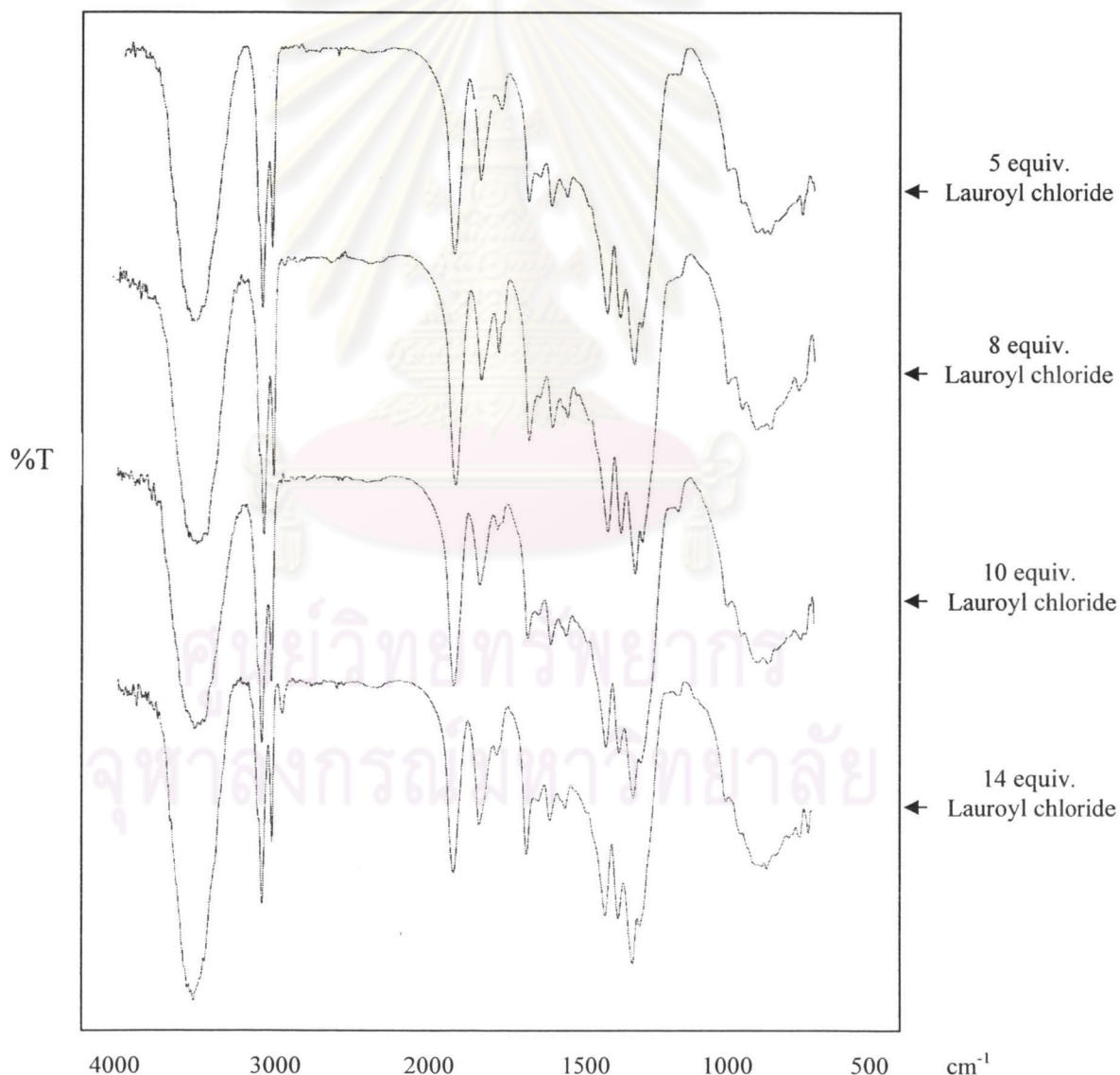


Figure 4.8 Infrared spectra of samples with different equivalent weight of lauroyl chloride.

Figure 4.8 shows the IR spectra of samples with different equivalent weight of lauroyl chloride. The smallest O-H bond vibration at 3422 cm^{-1} of 38 % esterified paper mulberry was shown, confirming the greatest increase of long chain fatty acid ester substituted at O-H group on cellulose.

The acetylation reaction of cellulose used lauroyl chloride as esterifying agent under microwave energy is shown in Figure 4.9 [B. Verneuil et al., 2002].

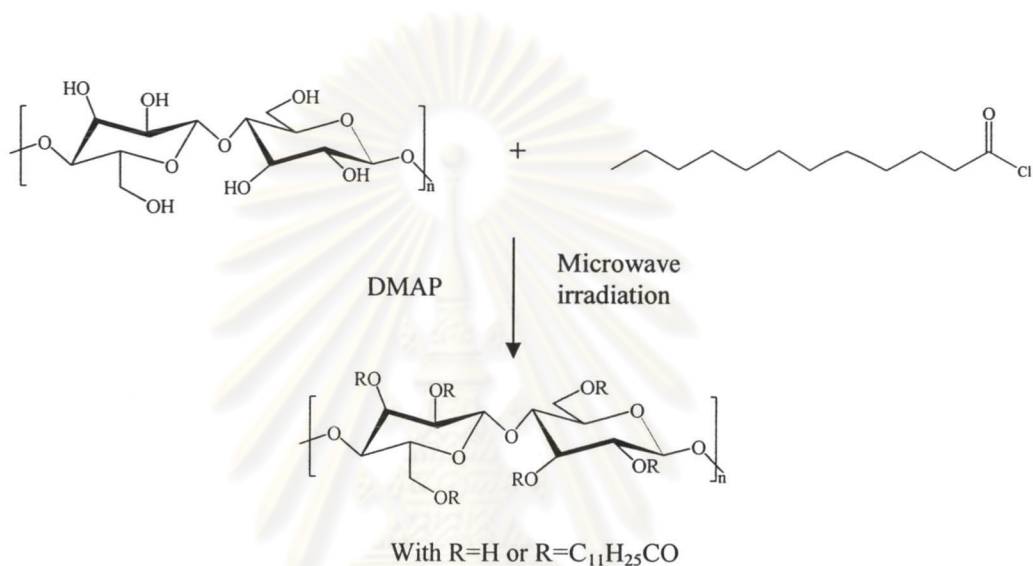


Figure 4.9 Acetylation reactions of cellulose [1].

The similar reaction was found in the acetylation of cellulose used dimethylformamide, pyridine, and octanoyl chloride as solvent, catalyst, and esterifying agent, respectively [Figure 4.10]. The reaction was performed on a hotplate at $130\text{ }^{\circ}\text{C}$ for 4 hours.

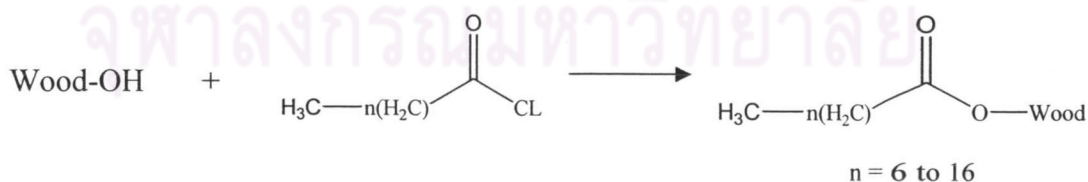


Figure 4.10 Acetylation reaction of sawdust [78].

Previous work done by C. Gourson et. al also showed the similar trend. In their works, hydroxyl groups of the cellulose contained in the maize bran were esterified by fatty acid chlorides as shown in Figure 4.11.

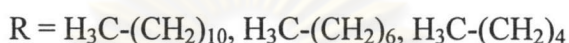
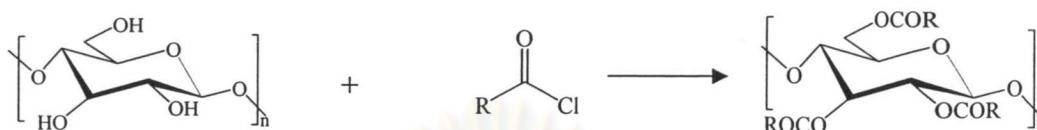


Figure 4.11 Esterification of maize bran by fatty acid chlorides [4].

In this experiment, the highest % esterification obtained was 38 %. It was expected that the % esterification should be much higher. However, it was thought that noncellulosic compound including heteroxytan, protein, and lignin embedded in cellulose microfibrils would probably prevent esterification of cellulose. G. Chauvelon et. al reported that irrespective to the initial cellulose used, the esterification of cellulose samples containing lignin gave cellulose laurate and also quite a large amount of residual particles. This suggested that lignin was probably also esterified but remained insoluble in toluene and chloroform besides chemical composition of cellulose laurate. [81].

The insoluble particles were probably constituted by unsubstituted cellulose or by other components such as lignin. Lignin may also be esterified because their constituting monomers bear hydroxyl groups. Antal and Micko reported that hemicellulose, lignin, and cellulose can be substituted to various extents [5]. However, the esterification of lignin probably did not lead to the formation of films. During esterification, lignin could be a competitor for the esterification reagents and/or could have a major influence on cellulose accessibility, as it can form an amorphous network with embedded cellulose microfibrils. Wang and Tao esterified pure cellulose with long-chain fatty acids (mixtures of palmitic, stearic, and linoleic acids) and obtained a high yield [77]. Therefore, it is possible that the low yield obtained in this work might be due to the noncellulosic components of the residue, which were probably esterified and eliminated but also prevented the esterification of the cellulose.

Hence, in this study, it can be concluded that the esterification of paper mulberry using 0.9 equivalent weight of DMAP as a catalyst and 10 equivalent weight of lauroyl chloride as an esterifying agent was performed successfully under 90 watt microwave energy for 2 min. This resulted in a maximum 154 % yield and 38 % esterification. In the next section, the characterizations of paper mulberry film prepared under these conditions were investigated.



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4.2 Characterization of esterified paper mulberry

4.2.1 Characterization of cellulosic film

4.2.1.1 Chemical Structure

The substitution reaction of hydroxyl groups of glucosyl units of cellulose from paper mulberry by esterification reaction was detected by IR spectroscopy. Characteristic bands of the IR spectra of paper mulberry before and after esterification with lauroyl chloride are given in the Table 4.4.

Table 4.4 Infrared vibrations and band assignments for cellulose and cellulose laurate

Major IR Bands of components	
Wave number (cm ⁻¹)	Band Assignments
Paper mulberry	
3342.11	O-H stretching with absorbed water
2905.23	C-H stretching due to CH ₂
1641.67	C=C stretching
1339.19, 1373.64	C-H bending due to CH ₂ and CH ₃
1031.25	C-O stretching (C-O-C and C-O-H)
Paper mulberry laurate	
3422.01	O-H stretching with absorbed water
2926.32, 2855.30	C-H stretching due to CH ₂ and CH ₃
1746.78	C=O stretching (ester)
1648.85	C=C stretching
1319.59, 1379.04	C-H bending due to CH ₂ and CH ₃
1062.38	C-O stretching (C-O-C and C-O-H)

The comparison of FTIR spectra of cellulose and cellulose laurate are summarized Figure 4.12. The IR spectra of cellulose modified by lauroyl chloride displayed different bands from the cellulose spectra. Obviously, after acyl substitution of long chain aliphatic from lauroyl chloride in the cellulose, two significant peaks can be observed at $2855.30\text{-}2926.32\text{ cm}^{-1}$ as C-H stretching and 1746.78 cm^{-1} as C=O stretching (ester).

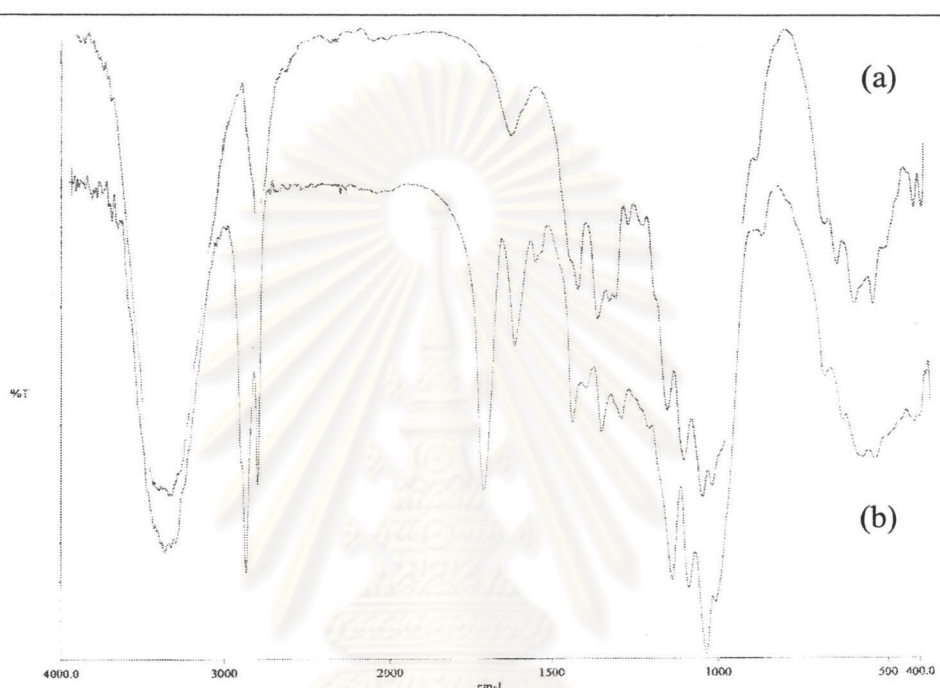


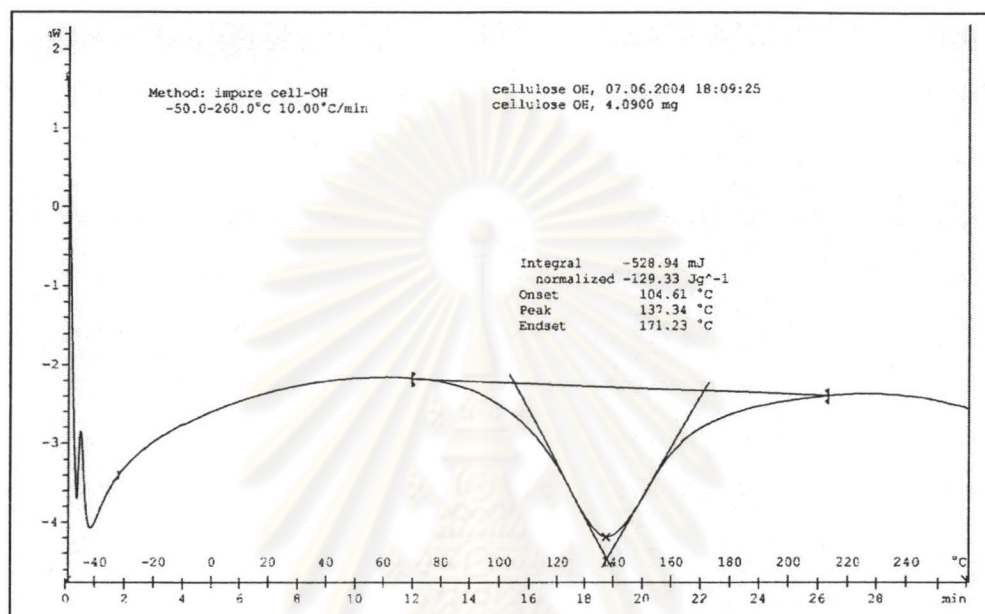
Figure 4.12 Infrared spectra of paper mulberry before (a) and after (b) esterification with lauroyl chloride.

In addition, when comparing to the IR spectra of cellulose, the intensity at 3422.01 cm^{-1} due to the O-H stretching peak decreased because hydroxyl groups was substituted by alkyl groups from lauroyl chloride (esterifying agent), indicating fewer availabilities of O-H groups remaining in the esterified cellulose. Whereas those of the increase in the intensity of the bands at $2855.30\text{-}2926.32\text{ cm}^{-1}$, due to the presence of a long- chain of alkyl groups from lauroyl chloride is substituted by hydroxyl groups. The presence of a new band at 1746.78 cm^{-1} is the characteristic peak of a carbonyl of ester group indicating the carbonyl group [S. Thiebaud et al., 1995 and C. Gourson et al., 1999].

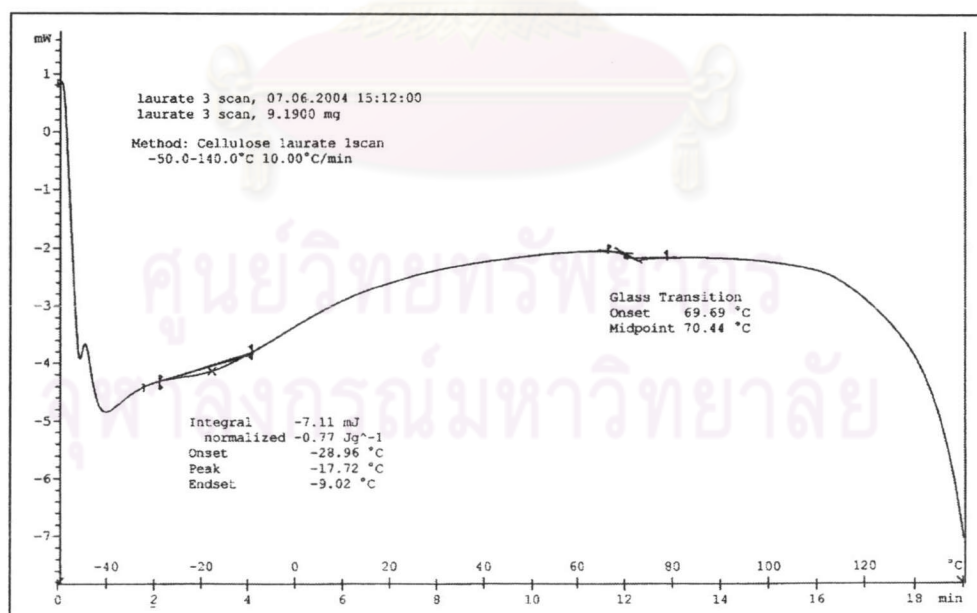
4.2.2 Thermal Properties

4.2.2.1 Different Scanning Calorimetry (DSC)

Thermal transition temperature was characterized by differential scanning calorimetry (DSC). The first heating of DSC thermograms for cellulose and cellulose laurate are displayed in Figure 4.13.



(a)



(b)

Figure 4.13 Differential scanning calorimetry (DSC) analysis of paper mulberry (a) before and (b) after esterification with lauroyl chloride.

From Figure 4.13(a), the DSC thermogram shows one significant transition occurring at about 137 °C. This endothermic peak is the melting temperature of crystalline structure of paper mulberry. As expected, due to high degree of inter- and intra- hydrogen bonding, paper mulberry did not show a second-order transition temperature, or T_g , due to its high crystallinity. After modified by lauroyl chloride, the DSC thermogram revealed two transitions for cellulose laurate: a broad T_g occurring at about 70.44 °C and a broad low-temperature melting endotherm (peak temperature designated as $T_{m, L}$) occurring below the T_g at 17.72 °C. The second order transition at around 70.44 °C was designated as T_g of cellulose laurate that occurs from long-chain substitution of lauroyl chloride at hydroxyl groups of cellulose causing an increase in amorphous region and decrease the crystalline structure of cellulose. In details, since the esterification reaction results in the opening of some of the hydrogen bonded cellulose chains thus producing the formation of amorphous cellulose. The acid chloride diffuses into these new amorphous regions to react with accessible hydroxyl groups and consequently generate more amorphous cellulose. The appearance of low- temperature endotherm ($T_{m, L}$) of cellulose laurate is resulted from melting of side- chain crystallization of long chain aliphatic substituent which is lauroyl ester in this case.



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4.2.2.2 Thermogravimetric analysis (TGA)

The thermal decomposition temperature (T_d) of cellulose and cellulose laurate were characterized by a thermogravimetric analysis (TGA). The values of the onset of the decomposition temperature are significant for producing of cellulosic films. Thermogravimetric analysis of cellulose and cellulose laurate are presented in Figure 4.14.

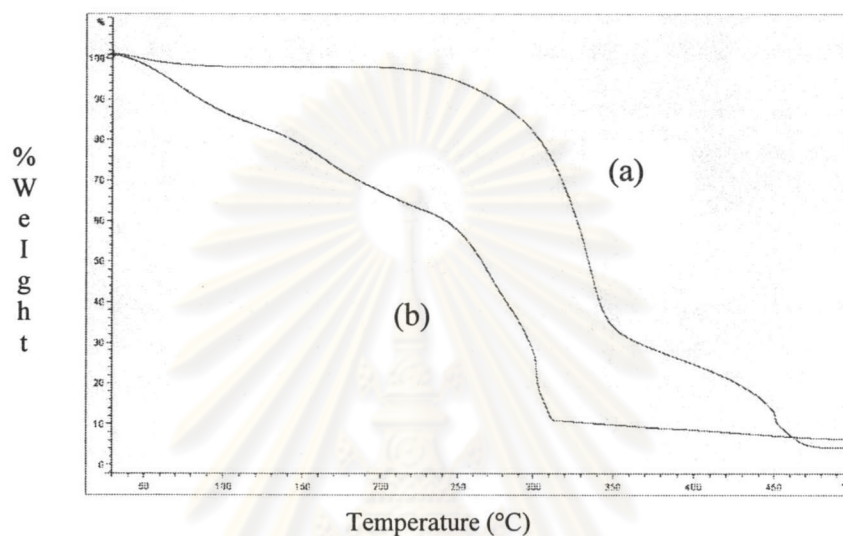


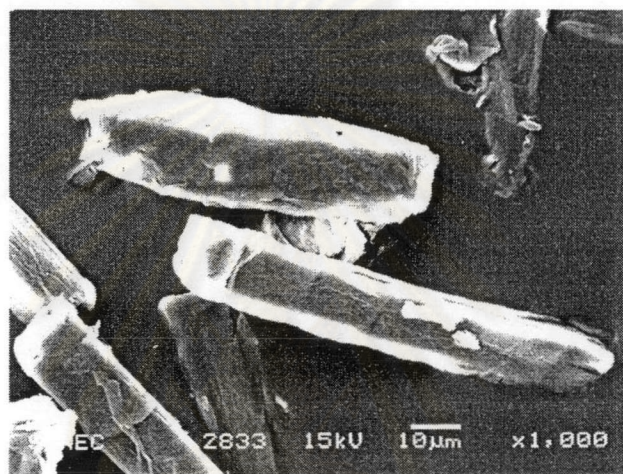
Figure 4.14 Thermo gravimetric analysis of (a) untreated paper mulberry sample, (b) paper mulberry sample esterified with lauroyl chloride.

Figure 4.14(a) shows three decomposition stages of untreated paper mulberry. The first stage (3.25 %) in the range of 70-90 °C is due to water decomposition. The second stage (70.29 %) in the range of 220-400 °C is due to hemicellulose and cellulose decomposition [Nguyen et al., 1981; Bouchard et al., 1986]. The third stage (21.18 %) in the range of 410-470 °C is due to lignin decomposition [S. Thiebaud et al.]. In contrast, after esterification reaction, it was found that five decomposition stages of cellulose laurate occurred. The first stage (17.51 %) in the range of 50-100 °C is due to water decomposition. The second stage (20.71 %) in the range of 150-200 °C is due to lauroyl chloride as esterifying agent substituted at hydroxyl groups of cellulose decomposition. The third stage (22.88 %) in the range of 220-285 °C is corresponded to decomposition of the more thermally fragile hemicellulose [Nguyen et al., 1981]. The fourth stage (30.30 %) in the range of 285-340 °C is due to cellulose decomposition. It has affected to thermal decomposition temperature (T_d) of cellulose decrease. Finally, the last stage occurring

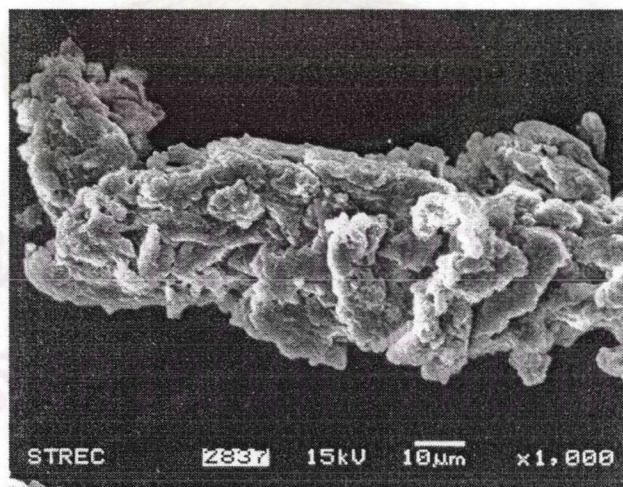
at temperature above 350 °C is corresponded to lignin decomposition. It is unexpected to find that the thermal degradation temperature of hemicellulose, cellulose, and lignin of the esterified paper mulberry are lower than those of untreated sample.

4.2.3 Morphological Studies

The difference between surface morphology of cellulose and cellulose laurate were analyzed using a scanning electron microscope. The SEM micrographs of non-esterified and esterified paper mulberry samples are presented in Figure 4.15.



(a)



(b)

Figure 4.15 SEM micrographs of paper mulberry : (a) non-esterified. (b) esterified with lauroyl chloride at 38 % esterification.

After acid hydrolysis process, paper mulberry pulp was hydrolyzed and can be seen as white powder. However, SEM micrographs (Figure 4.15a) revealed interesting characteristics of paper mulberry. From SEM micrograph, it can no longer be considered as paper mulberry powder since instead of powder it appears as a short fiber. Obviously, while the untreated or unesterified paper mulberry (Figure 4.15a) shows smooth surface, the laurate paper mulberry (Figure 4.15b) reveals rough surface. In the latter case, about one-third of hydroxyl groups in the paper mulberry have been laurated resulting in 38 % esterification. The acyl substitution on the hydroxyl groups of paper mulberry by lauroyl chloride causes an aggregation of acyl group on the paper mulberry surface.

4.3 Characterization and Testing of Paper Mulberry Film

4.3.1 Gloss

The physical appearance of the paper mulberry laurate film in term of surface properties, particularly gloss, were measured as a function of % esterification. The results of this experiment are shown in Table 4.5.

Table 4.5 Gloss values of paper mulberry laurate film at different % esterification

No.	Condition		% Esterification	Gloss (degree)
	DMAP (equivalent)	Lauroyl chloride (equivalent)		
1	0.9	5	23.24 %	17.54 ± 0.78
2	0.5	10	36.30 %	25.66 ± 0.94
3	0.9	10	38.00 %	31.30 ± 0.35

From the results, gloss values increases with an increase in % esterification indicating that the surface of the laurate films becomes smoother upon increasing % esterification. The highest gloss value obtained for 38 % esterification of cellulose laurate film is due to the fact that, when preparing the film, this cellulose laurate can be completely dissolved in chloroform, whereas for the 23.24 % esterified paper mulberry film, inhomogeneity between chloroform and cellulose laurate causes some difficulties in achieving the smooth surface. In other words, this result implies

that at lower % esterification the rougher surface is obtained. Since the light can be reflected from the smooth surface more than from the rough surface, which providing the higher gloss value. Therefore, 38 % esterified paper mulberry film yielded the greatest gloss value owing not only to the homogeneous between solvent and cellulose laurate but to the smoothness of the obtained surface as well.

4.3.2 Surface Property: Wettability

Surface or wettability of the esterified paper mulberry films was evaluated by means of contact angle measurement. The effect of % esterification on the wettability of the surface or the contact angle values of esterified paper mulberry films are shown in Table 4.6, and graphically compared with % water absorption in Figure 4.16.

Table 4.6 Contact angles of paper mulberry laurate film at different % esterification

No.	Condition		% Esterification	Contact angle (units)
	DMAP (equivalent)	Lauroyl chloride (equivalent)		
1	0.9	5	23.24 %	90.00 ± 0.95
2	0.5	10	36.30 %	83.75 ± 2.06
3	0.9	10	38.00 %	74.75 ± 1.63

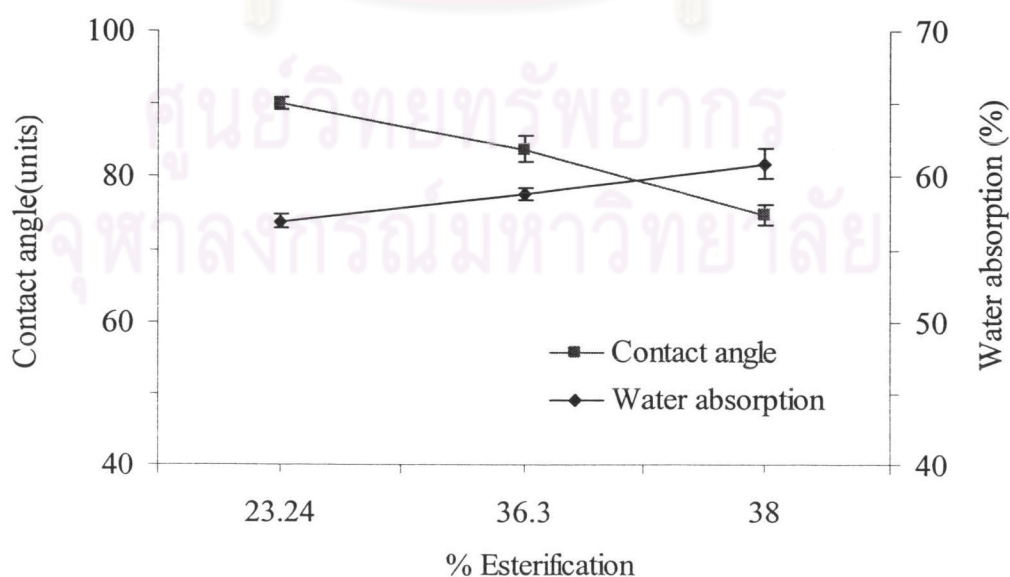


Figure 4.16 Effect of % esterification on contact angle and water absorption of the paper mulberry laurate film.

From figure 4.16, the contact angles values of paper mulberry laurate films decrease with increasing amount of % esterification, indicating the enhancement of wettability or hydrophilicity of the film surface. This result is clearly supported by the increasing in % water absorption as the % esterification increased.

Similar explanation to the water absorption results can be applied. Normally, structure of cellulose had more crystalline regions than amorphous regions and more hydrophobic. When cellulose was modified by lauroyl chloride into its hydroxyl groups, the crystalline regions decrease and amorphous regions increase. Since long chain fatty acid ester interfere with the intermolecular hydrogen bonding of the cellulose structure, therefore, water droplet can be easily absorbed on to the film surface as shown by decreasing in contact angle value.

4.3.3 Water absorption

Effect of % esterification on the water absorption values of paper mulberry are shown in Table 4.7. The results revealed that the % esterification had an effect on the % water absorption of cellulosic films.

Table 4.7 Water absorption at different % esterification of paper mulberry laurate films

No.	Condition		% Esterification	Water absorption (%)
	DMAP (equivalent)	Lauroyl chloride (equivalent)		
1	0.9	5	23.24 %	56.90 ± 0.49
2	0.5	10	36.30 %	58.80 ± 0.35
3	0.9	10	38.00 %	60.90 ± 1.05

As presented in table 4.7, % water absorption increased slightly with increasing % esterification. Only 4 % increasing in % water absorption was obtained upon increasing % esterification from 23.24 % to 38.00 %. However, an increasing in water absorption of the films can be explained in terms of cellulose structure. The hydroxyl groups of the cellulose contained in the paper mulberry were esterified by lauroyl chloride which is a long chain fatty-acid ester. After esterification, crystallites region decreases whereas its amorphous region increases because of increasing in free

volume of the system, consequently increasing the mass transfer of water through the paper mulberry laurate film. Therefore, water can easily access into cellulose structure. As a result, as % esterification increases, % water absorption increases.

4.3.4 Tensile Properties

The tensile strength and elongation at break of the cellulose laurate films at different degree of esterifications were listed in Table 4.8.

Table 4.8 The effect of % esterification of cellulose laurate on the mechanical properties of the films

No.	Condition		% Esterification	Tensile strength	Elongation (%)
	DMAP (equivalent)	Lauroyl chloride (equivalent)			
1	0.9	5	23.24	3.83 ± 0.49	4.20 ± 2.70
2	0.5	10	36.30	2.61 ± 1.18	10.55 ± 0.65
3	0.9	10	38.00	2.15 ± 0.13	14.57 ± 2.48

Figure 4.17 and Figure 4.18 graphically illustrate the effect of % esterification on the tensile strength and elongation at break of cellulose laurate films, respectively. Obviously, the tensile properties are dependent on the % esterification. The tensile strength decreases while elongation at break increases with increasing amount of % esterification.

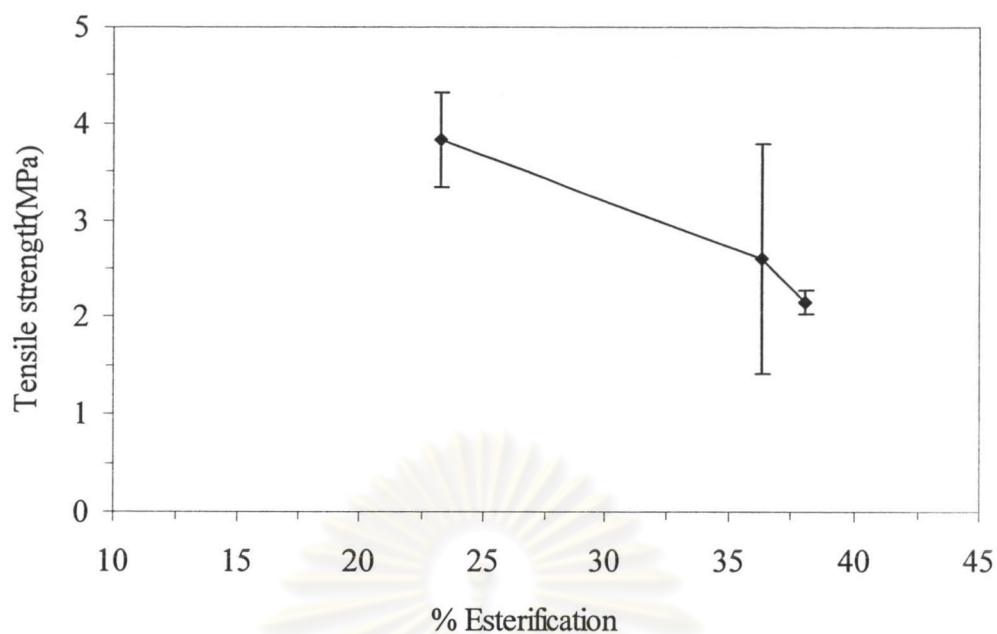


Figure 4.17 Tensile strength of cellulose laurate films at various % esterifications.

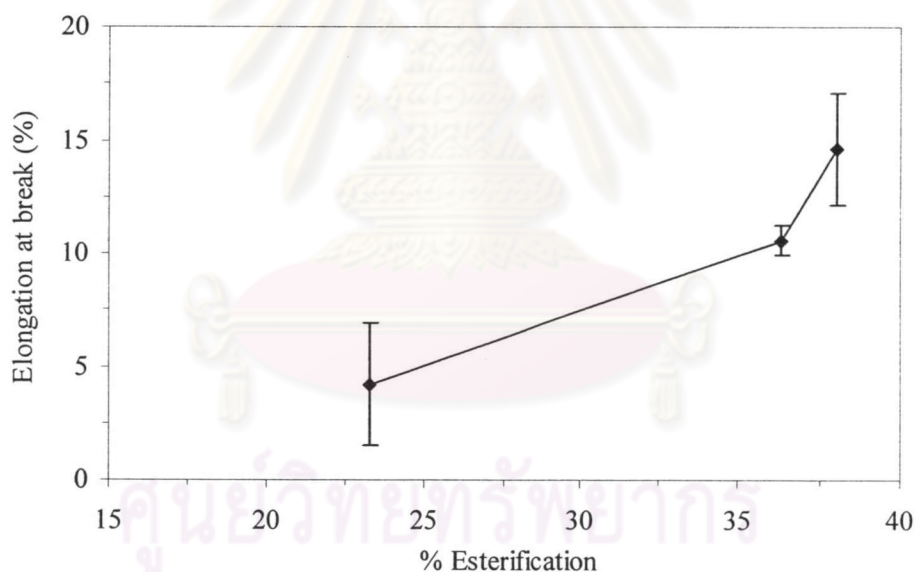


Figure 4.18 Elongations at break of cellulose laurate films at various % esterifications.

The lower tensile strength and higher elongation at break of cellulose laurate with increasing % esterification probably reflects decreased hydrogen bonding, or increased amorphous region, between cellulose laurate due to fewer hydroxyl groups on the molecule. High degree of hydrogen bonding between cellulose chains makes the polymer more rigid and then cellulose is a crystalline polymer. Hence, as explained earlier, when cellulose was esterified with lauroyl

chloride, its hydroxyl groups was partially replaced by this long chain aliphatic ester, which then caused the reduction of the crystalline region or increase the amorphous region. Similarly, when % esterification increases, amorphous region enhances leading to the decrease in tensile strength and increase in elongation at break. This is because a large substituent group into the cellulose due to cellulose laurate exhibited a plasticizing effect behavior without addition of any plasticizer unlike others biopolymer as starch.

In summary, esterified fatty acid seemed to act as an internal plasticizer for the long chain fatty acid cellulose ester, or cellulose laurate films, and thus resulted in increasing the elongation at break and decreasing the tensile strength upon increasing % esterification.

4.3.5 Degradation

Degradations of esterified paper mulberry films at different degree of esterification were performed by both soil burial test and accelerated exposure methods.

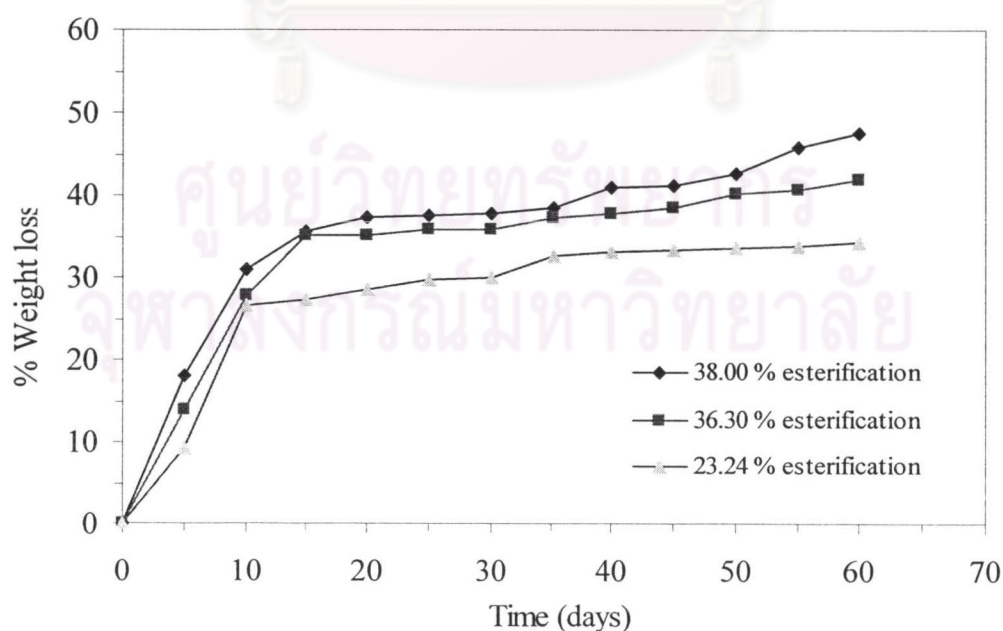
4.3.5.1 Soil burial test method

After being subjected to the soil, samples were removed for measuring the weight changes every five days. Biodegradation rate was evaluated by measuring weight loss of the films and the results are presented in Table 4.9 and Figure 4.19.

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Table 4.9 Weight loss of samples with different % esterification during soil burial test

Time (Days)	% Esterification		
	38.00	36.30	23.24
5	18.20	13.80	9.27
10	31.08	27.91	26.53
15	35.58	35.02	27.36
20	37.37	35.03	28.57
25	37.55	35.92	29.74
30	37.75	35.95	30.00
35	38.57	37.40	32.62
40	40.92	37.74	33.21
45	41.20	38.76	33.47
50	42.80	40.21	33.72
55	45.90	40.75	34.01
60	47.54	41.84	34.50

**Figure 4.19** Effect of % esterification on weight loss of the films during soil burial test.

Obviously, as shown in Figure 4.19, it was found that % weight loss of the esterified films increased as a function of exposure time and % esterification. Among the three samples, the cellulose laurate film with 38 % esterification yielded highest value of weight loss of almost 50 % within 60 days of exposure. In addition, it was found that the degradation rate of all the films was relatively fast for the first period of exposure or 15 days. After that the degradation rate seemed to be slower. However, all the films exhibited high potential of further degradation after 2 months of exposure as well.

The mechanism for biodegradation of paper mulberry is similar to other biopolymers, such as starch. It depends on several factors such as microorganisms, temperature and humidity condition, and the structure of polymer itself. Generally, microorganisms, such as fungi and bacteria as seen in Figure 4.20, can degrade cellulose by diffusing into a part of amorphous region and then ingesting the carbon molecules that are the backbone of the cellulose in their digestive systems by enzymatic hydrolysis. Figure 4.21 illustrates the stepwise enzymatic hydrolysis of cellulose. Generally, each microorganisms produce different types of enzyme (endo- β -glucanase, cellobio-hydrolase, and β -glucanase) capable of hydrolyzing cellulose, hemicellulose, lignin, and acetyl groups under suitable temperature and humidity conditions to make the molecular chain break down. In addition, each enzymes are specific to hydrolyze different regions in the molecular chain.

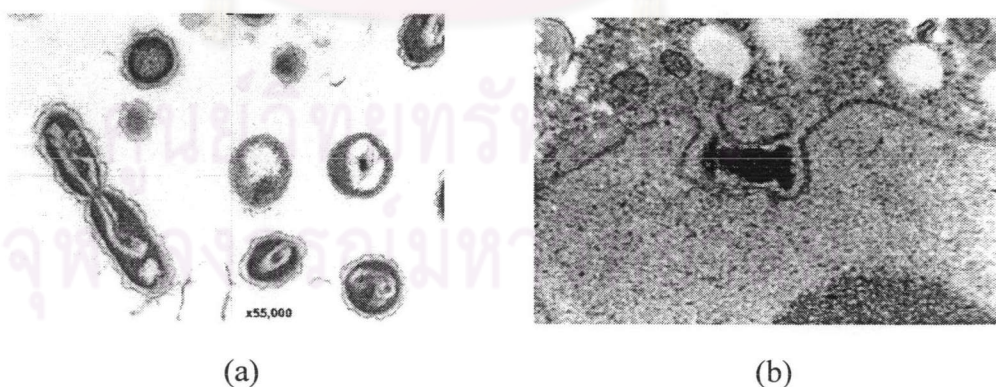


Figure 4.20 (a) Fungi and (b) bacteria.

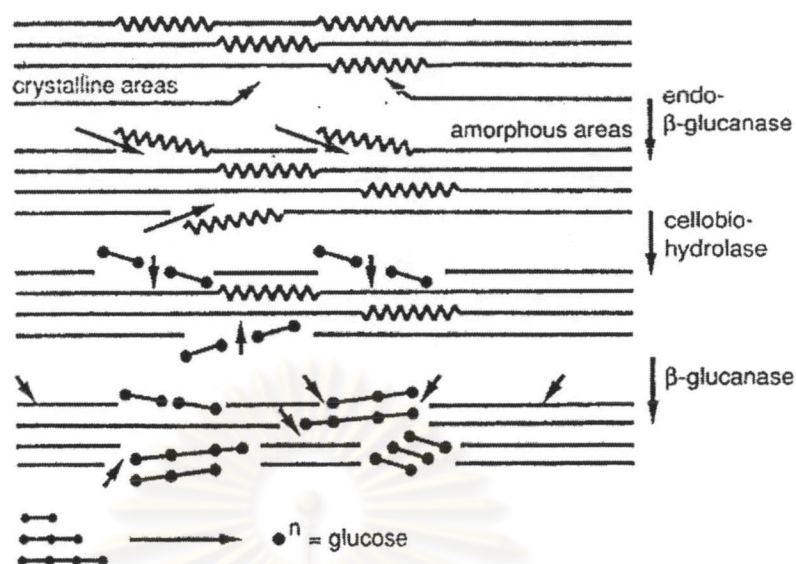


Figure 4.21 Schematic illustration of the stepwise enzymatic hydrolysis of cellulose [82].

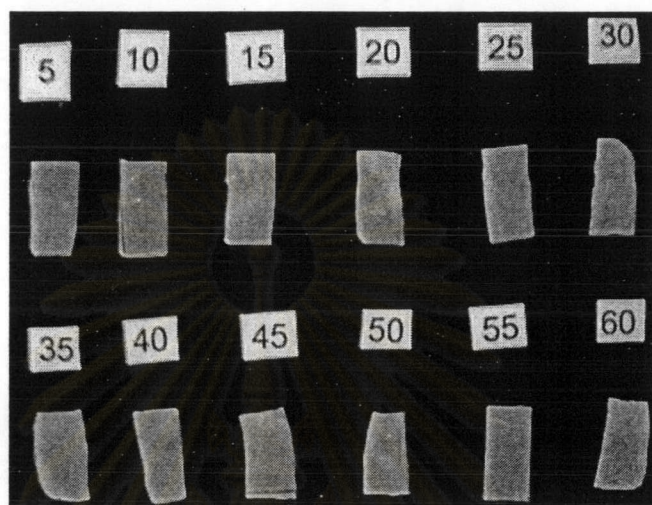
As shown in Figure 4.21, first, the endo- β -glucanase enzymes hydrolyze β -1, 4 linkage between amorphous region and crystalline region. Then, the cellobio-hydrolase enzymes hydrolyze amorphous region, whereas, the β -glucanase enzymes hydrolyze crystalline region. In addition, Yifang Ou et al [2] also found that besides cutting off $\beta(1-4)$ -D-glucoside bond, the microorganism can open the ring of glucose at the same time. Therefore, upon increasing the exposure time, the molecular chains became shorter, hence % weight loss of the film increased.

In addition, when considering the effect of % esterification, it was found that % weight loss increased as a function of % esterification. This is as mentioned earlier that the increase of long chain aliphatic ester due to the esterification reaction cause an increase in amorphous region which is the main portion that consumed by microorganisms. As a result the biodegradation rate is increased as a function of exposure time and % esterification.

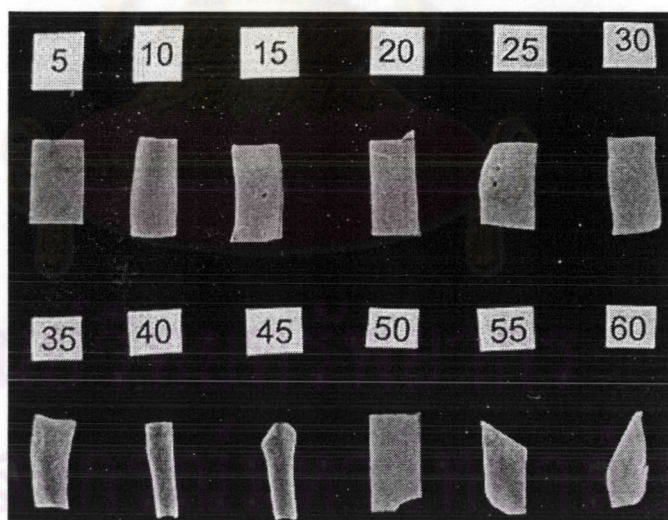
The physical appearance of paper mulberry laurate films after soil burial test for 60 days are presented in Figure 4.22. The SEM micrographs shown in Figure 4.23 were taken in order to confirm the above results. Obviously, after 45 days of exposure in soil, all the esterified-paper mulberry films exhibited a lot of holes or cavities which was contrast to the smooth surface of the film before soil

burial test. In fact, it can be seen that not only the number of cavities but also the size of the cavities, in particular, increased with increasing % esterification of the films.

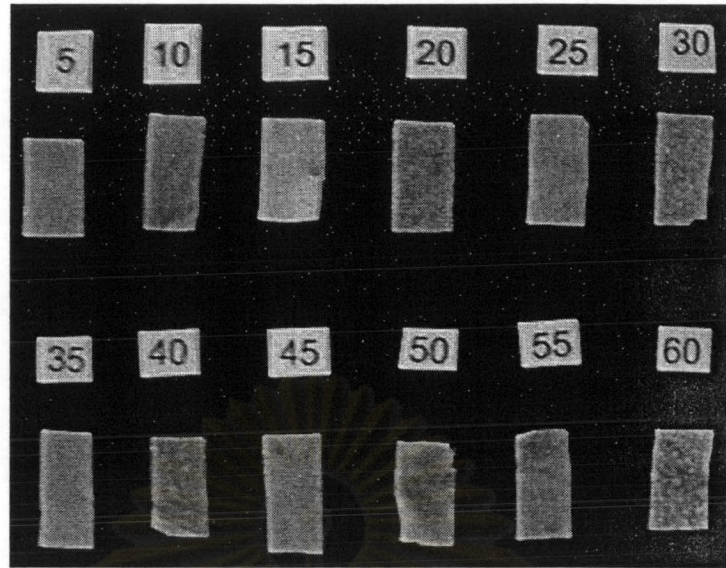
In summary, based on these results, the biodegradable plastic film can be prepared successfully from the esterified-paper mulberry film.



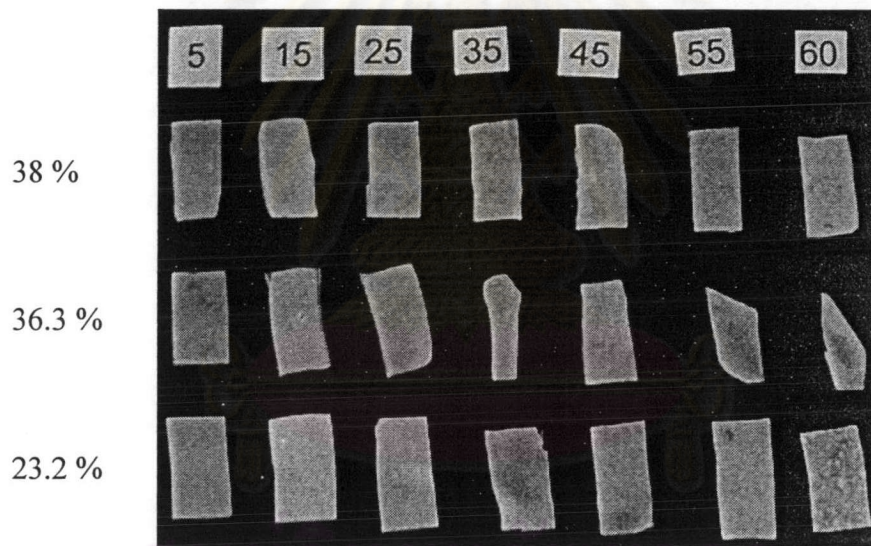
(a)



(b)



(c)



(d)

Figure 4.22 The physical appearance of the esterified-paper mulberry film after soil burial test for 60 days: (a) 38 % esterification, (b) 36.3 % esterification, (c) 23.24 % esterification, and (d) sum of different % esterification.

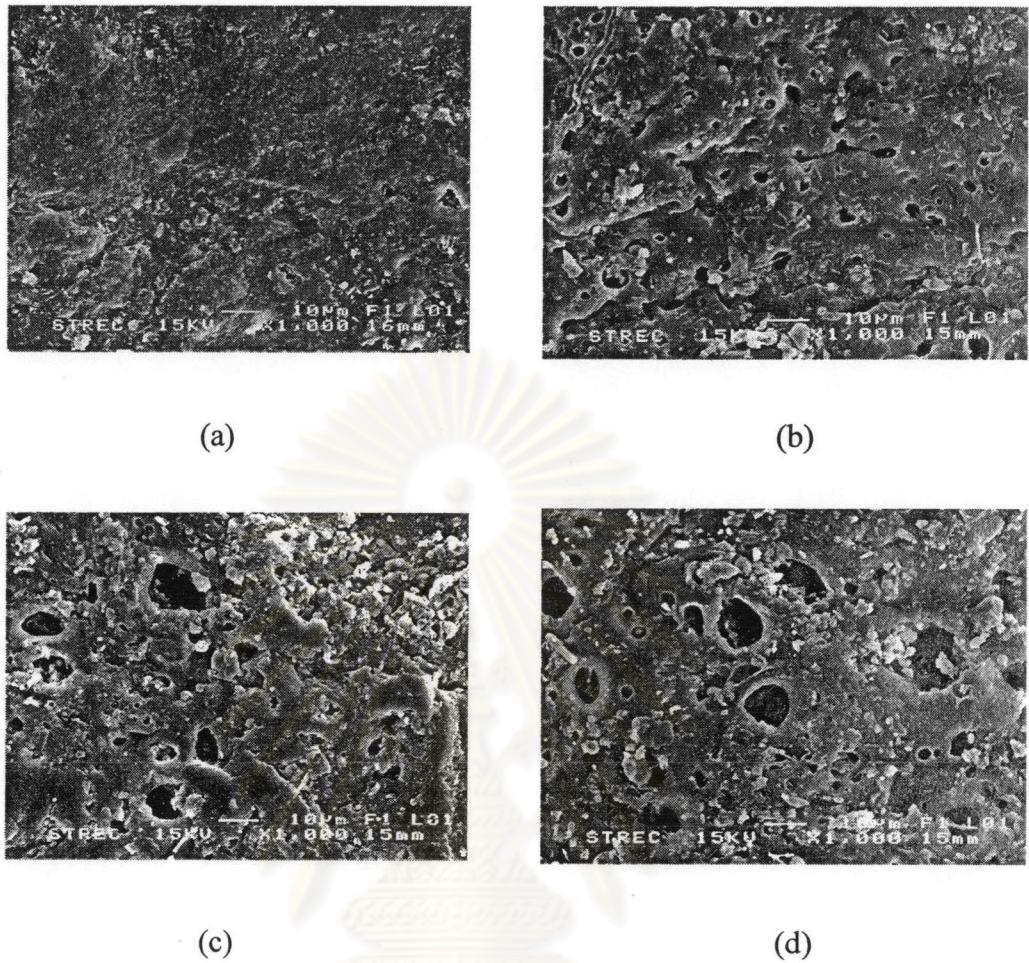


Figure 4.23 SEM micrograph of (a) cellulose laurate film before soil burial test and after 45 days of soil burial exposure for (b) 23.24 %, (c) 36.3 %, and (d) 38 % esterification.

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4.3.5.2 Accelerated exposure

Esterified-paper mulberry film samples were cut into 2 cm × 6 cm and put into the Xenotest Beta lamp chamber. All the films were conditioned at 25 °C and 76 % RH under UV light intensity of 100 watt/m² for 72 hours. The samples were removed for measuring the change in weight loss after 72 hours of exposure.

The comparison between outdoor exposure time and accelerated exposure time was calculated as follow:

$$\begin{aligned}
 \text{1 year UV radiation in Thailand} &= 328 \text{ MJ/m}^2 * (1 \text{ MJ} = 10^6 \text{ Watt sec}) \\
 &= 328 \times 10^6 \text{ Watt sec/m}^2 \\
 \text{Radiation in Xenotest Beta Lamp} &= 100 \text{ Watt/m}^2 \\
 \text{1 year of outdoor exposure equivalent to} &= (328 \times 10^6 \text{ Watt sec/m}^2) / (100 \text{ Watt/m}^2) \\
 &= 3.28 \times 10^6 \text{ sec in Xenotest Beta Lamp} \\
 &= 911.11 \text{ hrs. in Xenotest Beta Lamp} \\
 &= 38 \text{ days in Xenotest Beta Lamp}
 \end{aligned}$$

* Average data of 1 year UV radiation recorded during 1986-1995 by the Meteorological Department.

Hence, the exposure time of 72 hours in Xenotest Beta Lamp chamber is equivalent to the exposure time of 28 days under UV radiation.

Weight loss of the samples after 72 hours of exposure in Xenotest Beta Lamp chamber is shown in Table 4.10 and graphically compared with the result from soil burial test in Figure 4.24.

Table 4.10 Weight loss of samples with different % esterification

No.	Condition		% Esterification	Weight loss (%)
	DMAP (equivalent)	Lauroyl chloride (equivalent)		
1	0.9	5	23.24 %	10.23 ± 0.86
2	0.5	10	36.30 %	21.86 ± 1.93
3	0.9	10	38.00 %	26.66 ± 1.23

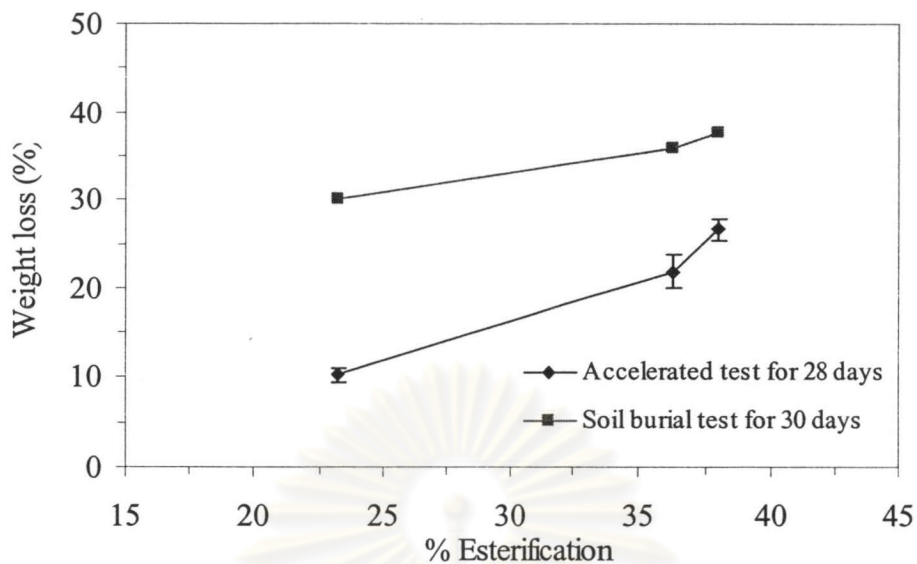


Figure 4.24 The relationship between weight loss and % esterification of esterified-paper mulberry.

Figure 4.24 shows the influence of UV light in Xenotest Beta Lamp chamber on the % weight loss of the films as a function of % esterification of the paper mulberry films. Similar to the soil burial test, % weight loss of cellulose laurate increases with increasing % esterification. Since increasing % esterification cause an increase in amorphous region of the film, the UV radiation and oxygen can easily diffuse or permeate into the film. As a result, the film with higher % esterification can be degraded faster. Figure 4.25 shows the mechanism of UV light and oxygen degradation of cellulose. Obviously, both UV and oxygen have a synergistic effect on the degradation of cellulose at the glucoside bond of the cellulose, which is relatively similar to biodegradation process. However, when comparing these two degradation tests, within approximately the same period of time, the esterified-paper mulberry films seemed to be degraded faster via biodegradation process due to several factors and mechanisms as previously described.

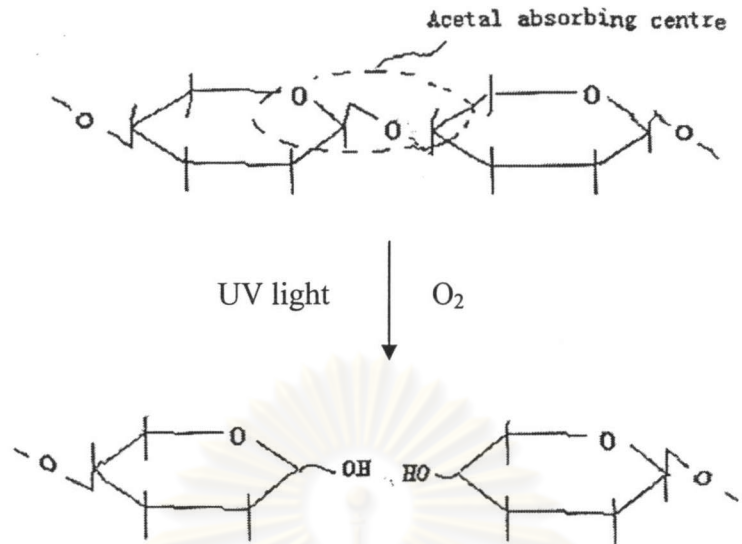


Figure 4.25 The mechanism of UV light and oxygen degradation of cellulose [2].

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