สำนักงานวิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER IV
RESULTS AND DISCUSSION

In this research, preparation of crystalline cellulose reinforcing starch biocomposite film was studied. The results were analyzed and divided mainly into three parts as follows:

1. Selection of condition for crystalline cellulose preparation
    - Delignification condition
    - Bleaching condition
    - Hydrolysis condition
2. Characterization of crystalline cellulose
3. Evaluation of biocomposite film properties

4.1 Selection of Condition for Crystalline Cellulose Preparation

Crystalline cellulose was used as a reinforcing filler in starch biocomposite film. It was prepared from bagasse fiber and banana stem by delinification, bleaching, and hydrolysis processes, respectively. Therefore, the suitable condition of these processes were studied and identified.

4.1.1 Delignification Condition

4.1.1.1 Physical appearance

Bagasse fiber and banana stem were treated with 0.5, 1, and 2 M NaOH solution at 80-90 ^{o}C for 4 hours. The photographs of delignified fibrils treated with various NaOH concentrations were taken to investigate their structure as shown in Figure 4.1 and 4.2.

From Figure 4.1, bagasse fiber can be separated into fibrils at 0.5 M NaOH. Comparing among the treated ones, some parts of the bagasse fiber treated with

1 and 2 M NaOH solution were not changed into fibrils, probably due to the degradation of the fiber resulted from higher NaOH concentration.

For the banana stem, it can be saparated into fibrils at every NaOH concentrations, as shown in Figure 4.2. However, at 2M NaOH solution a small amount of dark fibrils also occured. The dark fibrils is probably resulting from degradation of cellulose at high NaOH concentration.

After alkaline treatment, fibrils exhibited slightly yellowish and brownish colors, which might be because partial lignin and hemicellulose still remained in the fiber. This probably occurs since sodium hydroxide solution is a mild delignification reagent, when comparing with solution other delignification reagent such as containing sulfur dioxide ion (i.e. sodium sulfide) [27]. In addition, lignin is dissolved as alkali lignin when wood fiber is treated with NaOH solution at 170 °C , or better alkali solution such as a mixture of NaOH and sodium sulfite solution. However, partial of lignin can be dissolved at temperature below at 170 °C from the fiber. Since both bagasse and banana stem were treated with mild reagent at low temperature, therefore, these fibrils were needed to be bleached to remove remainder lignin

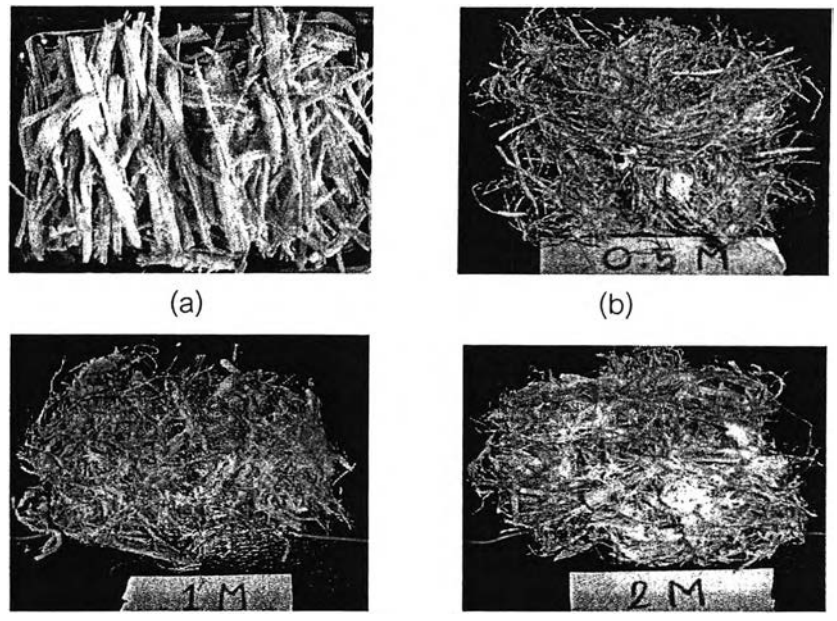


Figure 4.1 Photographs of (a) untreated bagasse and (b-d) treaeted bagasse with 0.5 M, 1 M , and 2 M NaOH, respectively, at 80-90 °C for 4 hours.

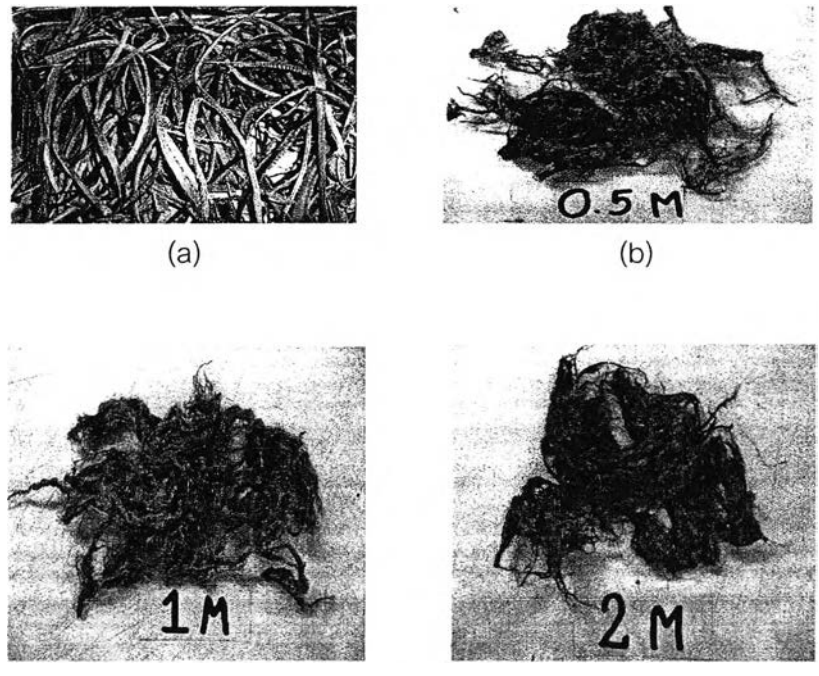


Figure 4.2 Photographs of (a) untreated banana stem and (b-d) treated banana stem with 0.5 M, 1 M, and 2 M NaOH, respectively, at 80-90 °C for 4 hours.

4.1.1.2 Thermogravimetric analysis

Figure 4.3 and 4.4 showed the TGA thermograms of delignified bagasse and banana stem fibrils, respectively, at various NaOH concentration comparing with the untreated bagasse and banana stem fibers. The decomposition temperatures of the samples obtained from TGA curves were summarized in Table 4.1. and 4.2. As presented in these two figures all of the samples displayed a decomposition temperature at nearly 100 °C due to moisture decomposition. As shown in Figure 4.3, the untreated bagasse fibers showed three main degradation steps. The first stage showed the Td (onset) in the range of 200-230 °C is due to hemicellulose degradation ; whereas, the second one occurred in the range of 240-300 °C is attributed to cellulose degradation. The last step appeared in the range of 360-380 °C is resulted from lignin degradation. After delignification with 0.5, 1, 2 M NaOH concentrations solution, the delignified bagasse showed one stage of decomposition that means partial of lignin can be removed from the fibrils. Moreover, there was no sign of hemicellulose left after delignicication. This is because hemicellulose is present mainly on an outer fiber surface from where it dissolves easily in the alkaline solution. In contrast, cellulose is located in the inner parts of the fibers and therefore is not easily dissolved.

From this figure, Td (onset) of delignified bagasse treated with 0.5 M NaOH solution was similar to that of the deligninfied bagasse treated with 1 M NaOH solution. The decomposition of delignified bagasse treated with 0.5 M and 1 M NaOH presented Td (onset) in the range of 250-300 °C was due to cellulose degradation [27]. The degradation of delignified bagasse treated with 2 M NaOH concentration solution occurred at lower temperature than that treated with 0.5 M and 1M NaOH concentration, resulting from the degradation of cellulose occurred at higher NaOH concentration solution. However, delignified bagasse treated with 2 M NaOH concentration had greater residue than the others.

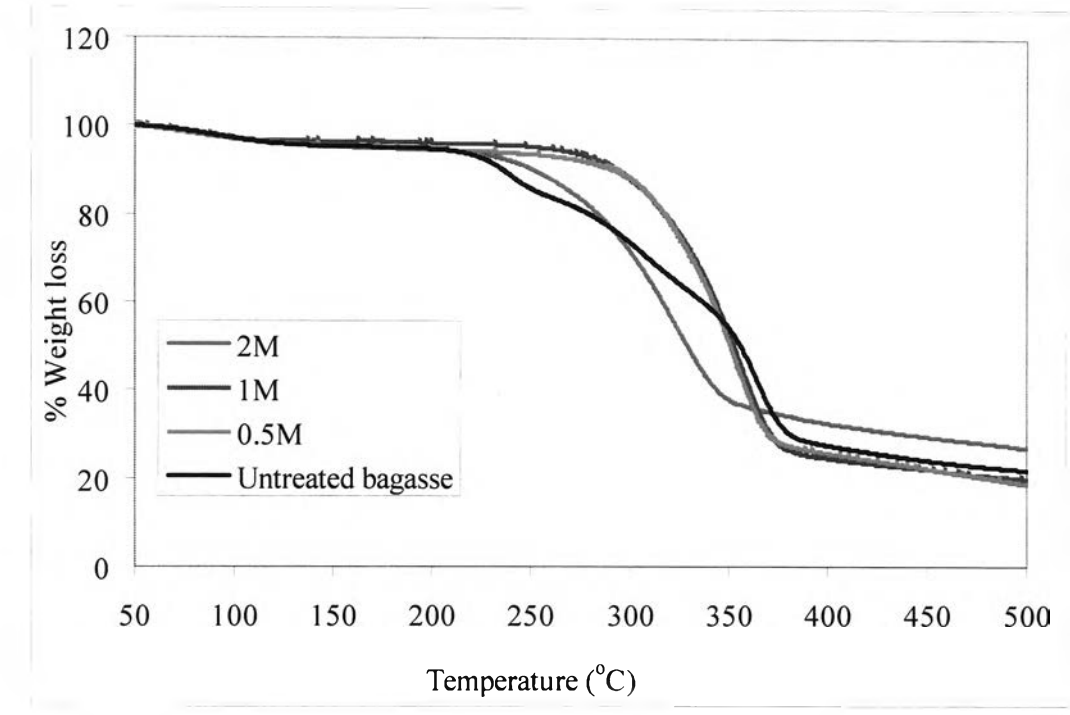


Figure 4.3 TGA curves of untreated and delignified bagasse fibrils with difference NaOH solution concentrations

Table 4.1 TGA Data of untreated and delignified bagasse fibrils

Sample bagasse	Td (°C) (Onset)			Percent weight Loss (%)		Residue (%)
	First	Second	Third	At 250 °C	At 350 °C	At 450
untreated	220.00	260.00	350	15.00	31.00	25.07
0.5 M	-	276.25	-	-	51.10	22.32
1 M	-	276.88	-	-	51.12	22.32
2 M	-	267.88	-	-	63.00	30.10

Unlike bagsse fiber, Figure 4.4 showed that untreated banana stem fibers had two main stages of degradation. The first stage of Td(onset) in range the of 170-230 °C is due to hemicellulose degradation, whereas the second step of Td (onset) in the range of 250-270 °C is probably due to cellulose and lignin degradation. After delignification, however, the delignified banana stem fibrils exhibited only one step of degradation ranging between 250-350 °C is due to the cellulose degradation [27]. Clearly of the Td (onset) banana stem treated with 1 M NaOH solution was higher than that of banana stem treated with 2 M and 0.5 M, respectively.

The delignification of the fiber is the important step to remove chemical composition (i.e. lignin, hemicellulose, and wax) for producing many fibrils. According to the results of photographs, the bagasse treated with 0.5 M NaOH solution can be separated into many fibrils than that of the bagasse treated with 1 M and 2 M NaOH solution. In addition, the TGA data showed that bagasse fiber treated with 0.5 M and 1M NaOH solution comparable Td (onset) but higher than that of bagasse treated with 2 M NaOH. Therefore, 0.5 M NaOH solution concentrations is the suitable condition for bagasse delignification.

Similarly, the suitable NaOH concentration for delignification of banana stem fiber was at 1 M. Since from the photographs presented in Figure 4.2, although banana stem can be separated into fibril at any concentration, but from TGA data, the bagasse fiber treated with 1M NaOH had greater Td (onset) than the bagasse fiber treated with 0.5 M and 2 M NaOH concentration. Therefore, the suitable condition for delignification of banana stem fiber was at 1 M NaOH.

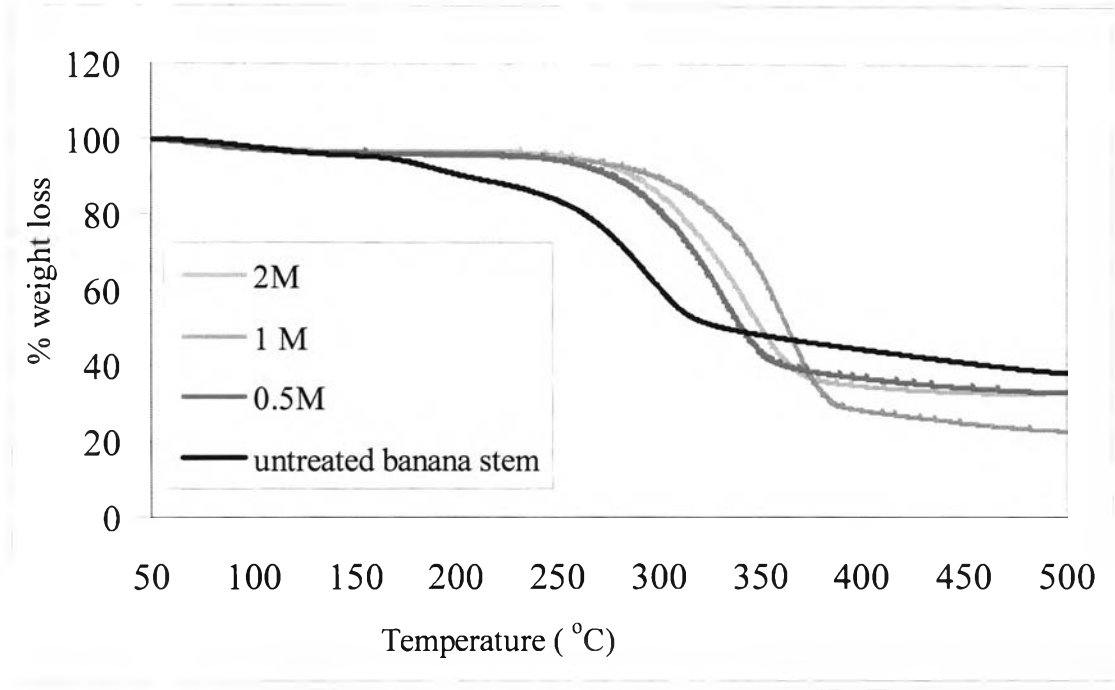


Figure 4.4 TGA curves of untreated and delignified banana stem fibrils with difference NaOH solution concentrations

Table 4.2 TGA Data of untreated and delignified banana stem fibrils

Sample banana	Td (°C) (Onset)			Percent weight Loss (%)		Residue (%)
stem	First	Second	Third	At 250 °C	At 350 °C	At 450
untreated	170.00	257.00	-	19.20	32.28	40.61
0.5 M	-	272.00	-	-	58.54	34.70
1 M	-	310.00	-	-	36.00	24.06
2 M	-	287.00	-	-	50.20	34.30

4.1.2 Bleaching Condition

4.1.2.1 Physical appearance

Figure 4.5 and 4.6 illustrated the photographs of bleached bagasse and banana stem pulp, respectively. Clearly, whiteness of the bagasse and banana stem pulp increased; when, the concentration of H_2O_2 increased. Comparatively, bleached bagasse pulp seem to have greater whiteness than bleached banana stem pulp. In addition, the bagasse pulp showed slightly yellowish at low H_2O_2concentration (i.e., 2% and 4%). But, when the H_2O_2 concentration was higher than 4%, the pulp became whiter. Further increased the H_2O_2 concentration upto 8-10% seemed to cause some degradation of pulp as evidenced by the occurrence of many short fibrils.

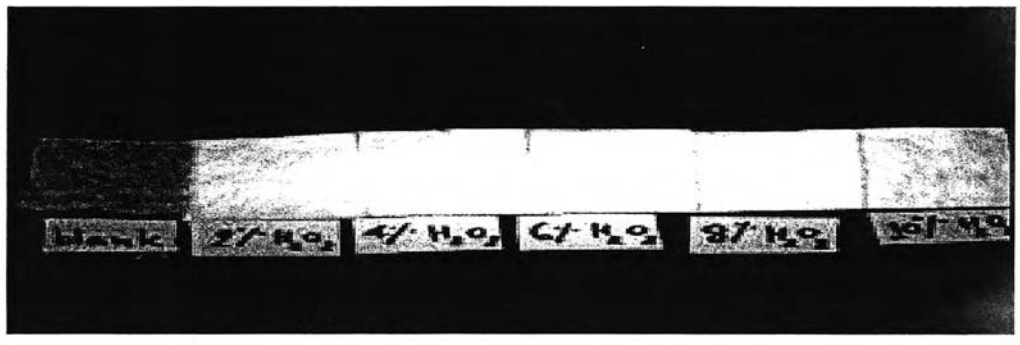


Figure 4.5 Photographs of bleached bagasse pulp at various H_2O_2 concentrations

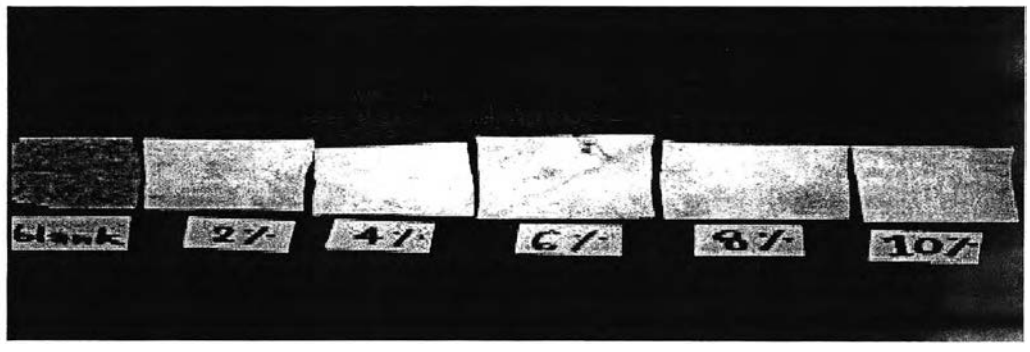


Figure 4.6 Photographs of bleached banana stem pulp at various H_2O_2 concentrations

4.1.2.2 Whiteness

Lignin, which is still left in the fibrils has influenced on the whiteness of pulp. Therefore, bleaching process is necessary to prepare crystalline cellulose. Bleaching process can remove the remianing lignin in the fibrils. Thus, whiteness of bagasse and banana stem pulp after bleaching was investigated.

After delignification, the bagasse and banana stem fibrils were bleached with 2, 4, 6, 8, and 10% H_2O_2 in alkali solution at 100 ^{o}C for 1 hour. Figure 4.7 and 4.8 showed that whiteness of bagasse and banana stem pulp were increased when the H_2O_2 concentration increased; whereas, the yellowness was drastically decreased. This is because hydrogen peroxide is used with alkaline solution or sodium hydroxide to produce high pH solution that is necessary to produce the active perhydroxyl ion, HOO^{-}. This ion is a mild oxidant resulting in pulp whiteness. Thus, the active perhydroxyl ion increased when the concentration of H_2O_2 was increased. This is resulting in an increase in whiteness of the pulp. However, the degradation of pulp occurred when the H_2O_2 concentration was higher than 6%.

Generally, the suitable condition for bleaching showed be the one that can remove higher amount of lignin from the fiber and yield high whiteness. Although, in this research, the high concentration of H_2O_2 (i.e. 8% and 10%) contributed to the high whiteness value but it led to some degradation of bagasse and banana stem pulp; Thus the suitable condition to bleach the both pulps should be at 6% H_2O_2 solution since this concentration attributed to high whiteness and low degradation of pulp.

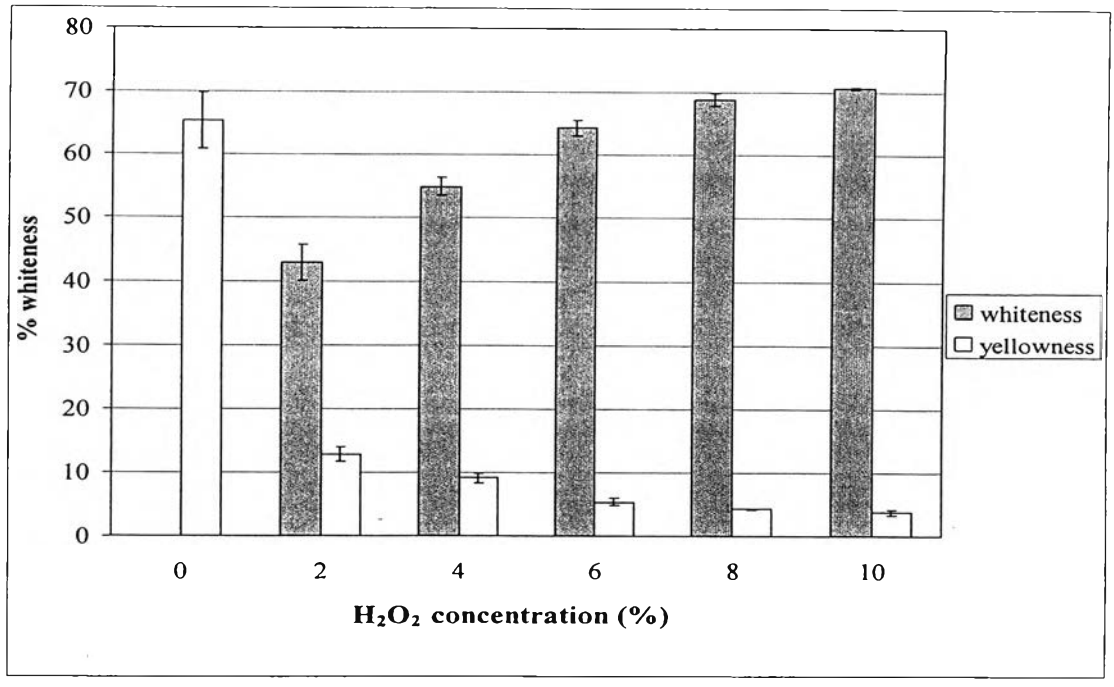


Figure 4.7 Whiteness and Yellowness of bleached bagasse pulp at various H_2O_2 concentrations

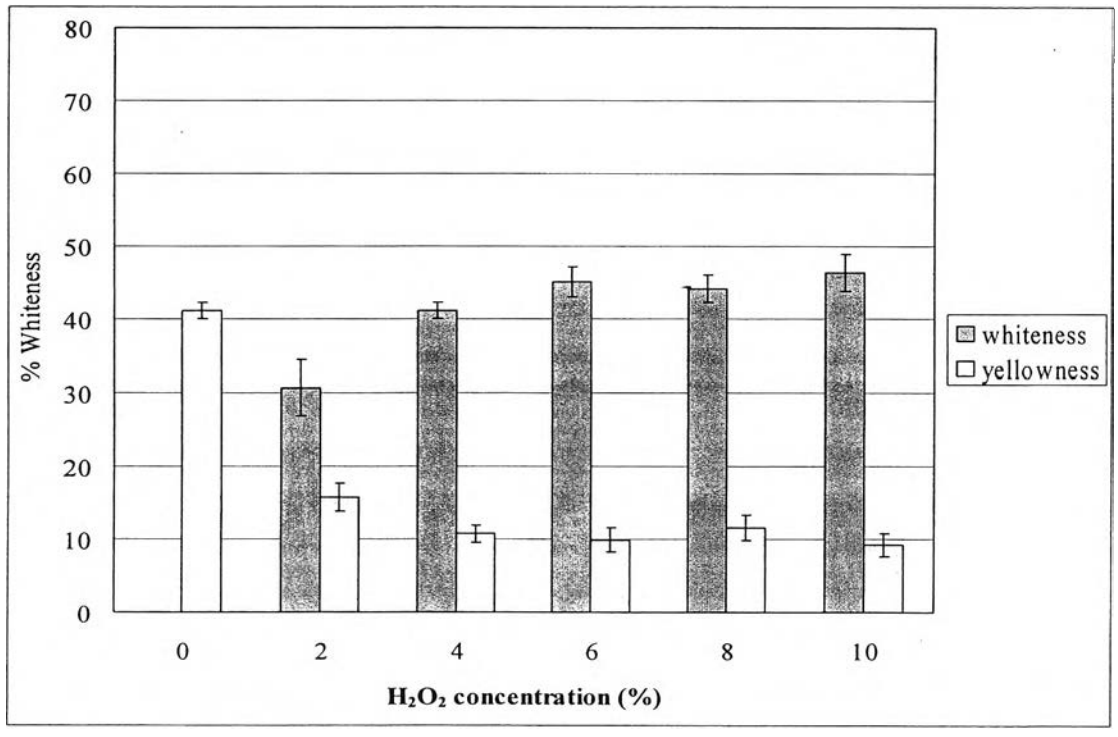


Figure 4.8 Whiteness and Yellowness of bleached banana stem pulp at various H_2O_2 concentrations

4.1.2.3 Thermal Properties

Investigation of the degradation temperature of fiber, delignified fibrils, and bleach pulp is very important since it could indicate processing and temperature condition for crystalline cellulose preparation without continuing or initiating a process of decomposition. Figure 4.9 and 4.10 show the TGA results obtained from untreated and chemical treated of bagasse and banana stem, respectively.

For bagasse fiber, as shown in Figure 4.9, after delignification and bleaching process, the delignified bagasse fibril and bleached bagasse pulp had higher the onset of thermal decomposition temperatures than untreated fiber. Both delignified and bleached bagasse samples exhibited one step of thermal degradation about 277 and 276 °C due to the cellulose degradation. No sign of hemicellulose and lignin was found. These thermograms comfirmed the appropriated conditions selected for delignification and bleaching process of bagasse fiber which were 0.5 M NaOH and 6% H_2O_2 concentration, respectively.

Similarly, Figure 4.10 showed that both delignified banana stem fibril and bleached banana stem pulp and higher thermal degradation temperatures than the untreated banana stem fiber. However, unlike bagasse fiber, after bleaching at 6% H_2O_2 concentration, the TGA thermogram of banana stem pulp slightly shifted towards lower temperature compared with the delignified banana stem fibrils. Nevertheless, the onset of thermal decomposition temperatures seemed to be not much difference (Table 4.4). Thus, regarding to the physical appearance and its whiteness as previously described, it can be indicated that the suitable condition for delignification and bleaching of banana stem fiber were 1M and 6% H_2O_2 concentration, respectively.

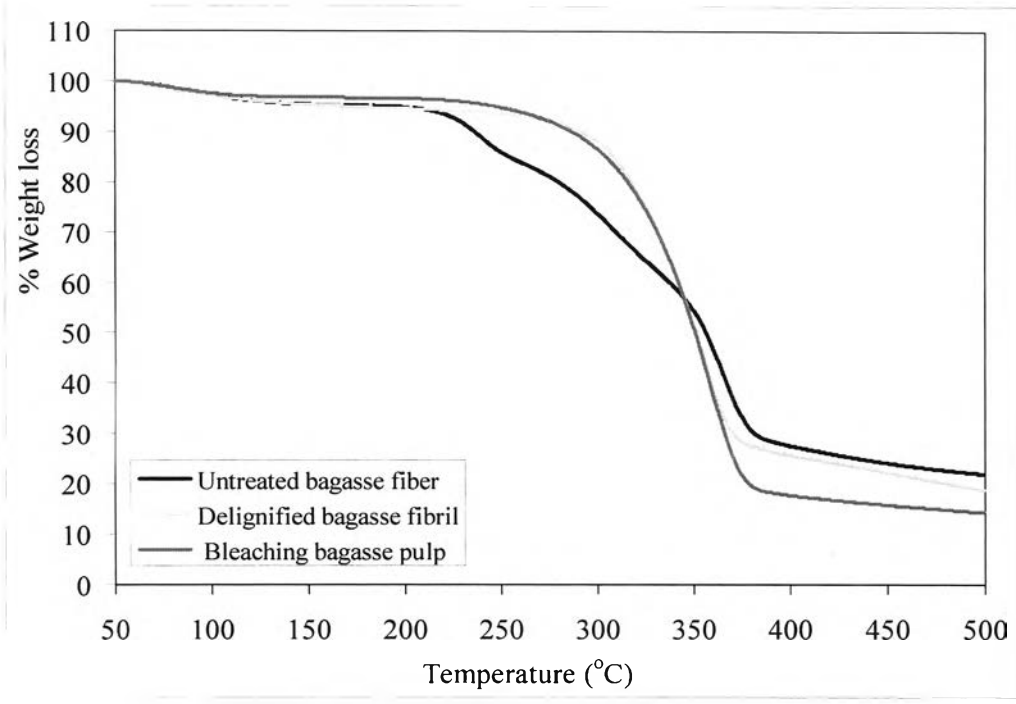


Figure 4.9 TGA curve untreated, delignified, and bleached bagasse sample

Table 4.3 TGA Data of chemical treated and untreated bagasse

Sample bagasse	Td (°C) (Onset)			Percent weight Loss (%)		Residue (%)
	First	Second	Third	At 250 °C	At 350 °C	At 450
untreated	220.00	260.00	350.00	15.00	31.00	25.07
delignified	-	276.25	-	-	51.10	22.32
bleached	-	262.30	-	-	51.39	15.87

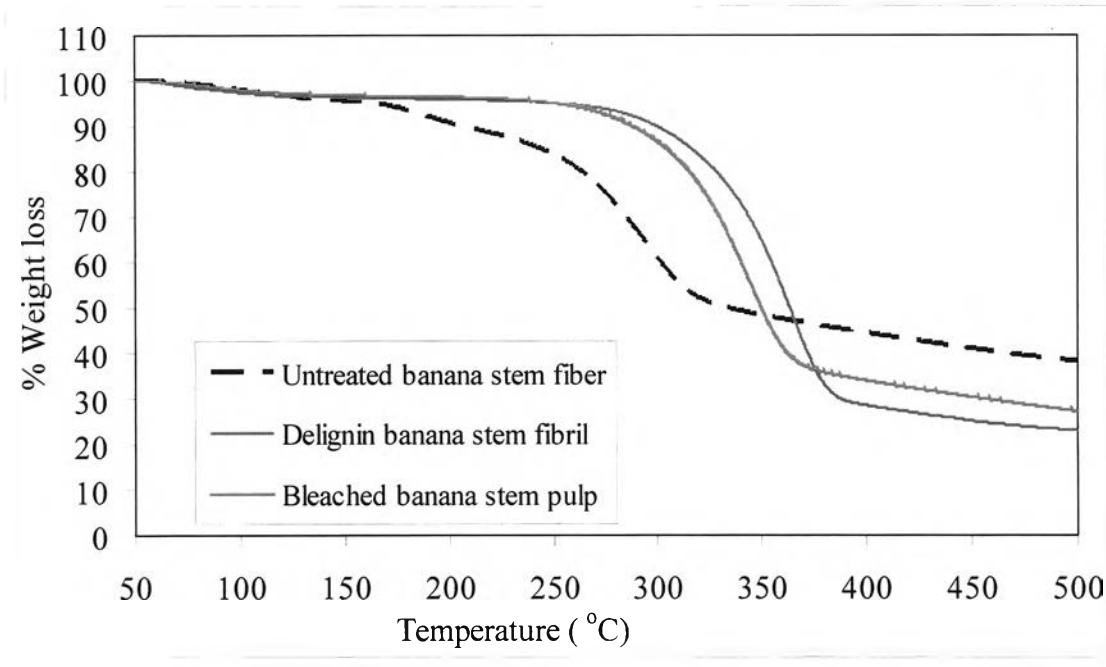


Figure 4.10 TGA curve untreated, delignified, and bleached banana stem sample

Table 4.4 TGA Data of chemical treated and untreated banana stem

Sample bagasse	Td (°C) (Onset)			Percent weight Loss (%)		Residue (%)
	First	Second	Third	At 250 °C	At 350 °C	At 450
untreated	170.00	257.00	-	19.20	32.28	40.61
delignified	-	310.00	-	-	36.00	24.06
bleached	-	300.00	-		35.31	30

4.1.2.4 Time for grinding

For some applications and several manufacturing processes of cellulose derivative, the use of ground microfibrils is advantageous or necessary to prepare crystalline cellulose. However, as shown in Figure 4.5 and 4.6, after bleaching, the pulp was filtrated and it tended to show an agglomeration, Similar to pulping process of making paper. Thus, these pulps needed to be ground prior to the hydrolysis, in order to reduce its particle size and agglomeration of pulp. Therefore, bleached bagasse and banana stem were ground for 1, 2, 3, 4, and 5 min to select the optimum time for grinding. The average particle size and morphology of bleached pulp were investigated.

4.1.2.4.1 Morphology

Figure 4.11 and 4.12 exhibited the SEM micrographs of bleached bagasse and banana stem pulp after grinding at various time. Figure 4.11 showed that the bleached bagasse pulp had shortening fiber and rod shape form with smooth surface. The length of the bleached pulp was decreased when the grinding time increased. Some part of the bleached bagasse pulp become into small particle or flake shape at longer grinding time (i.e. 5 min).

In case of banana stem pulp, Figure 4.12 showed that the bleached banana also had the rod shape form with smooth surface. Similarly, the length of banana stem bleached pulp decreased when the grinding time increased. However, at 5 min of grinding the bleached banana stem pulp still keeped its rod shape form.

Thus, comparatively, the bleached banana stem pulp had more rod shape form than the bleached bagasse pulp at the same grinding time. In addition, its was smoother than that of bleached bagasse pulp. Obviously, the particle size of bleached banana stem pulp was smaller than that of bleached bagasse pulp.

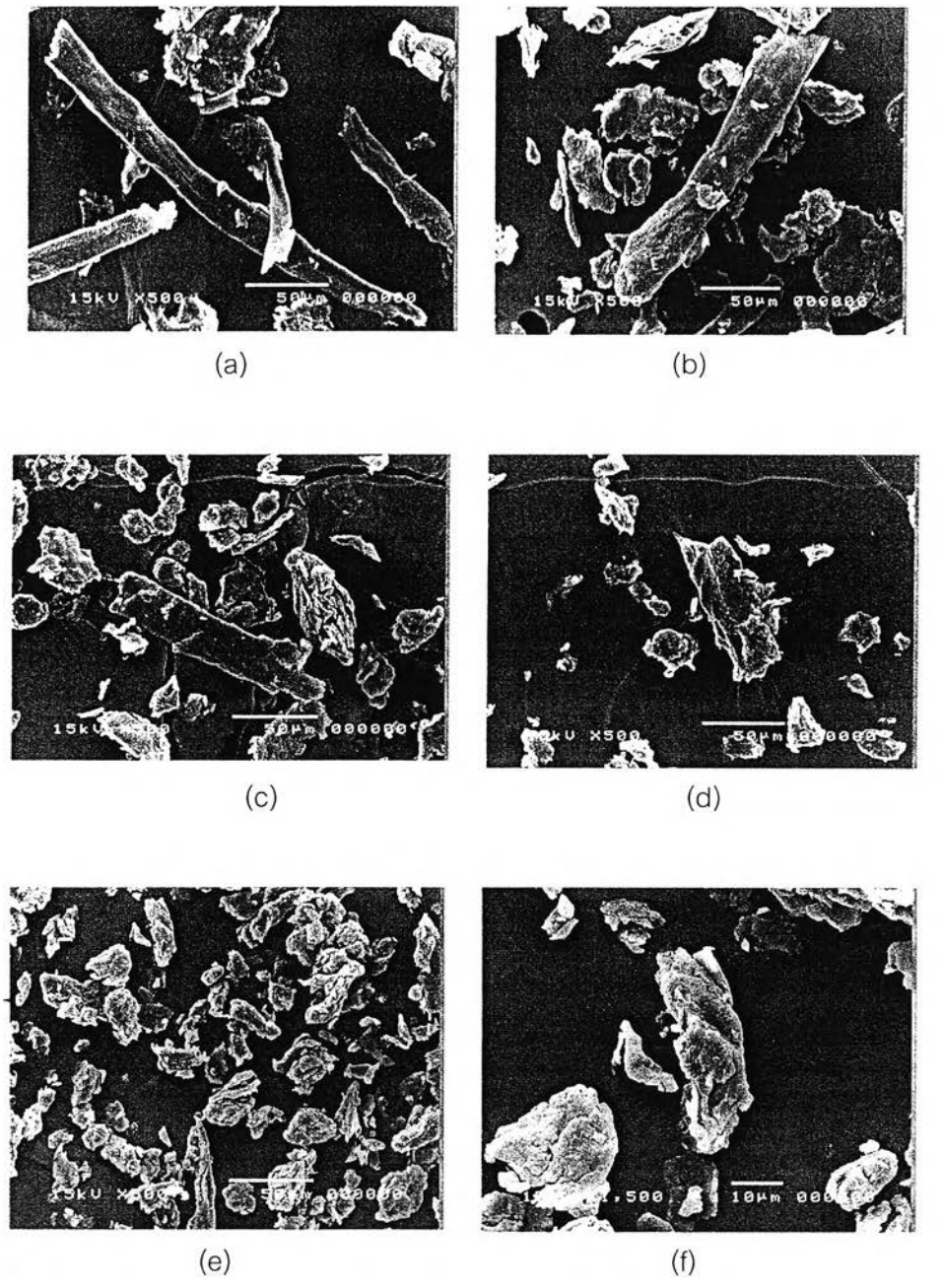


Figure 4.11 SEM micrographs of bleached bagasse at (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 min at magnificationx 500, and (f) 5 min at magnification X1500

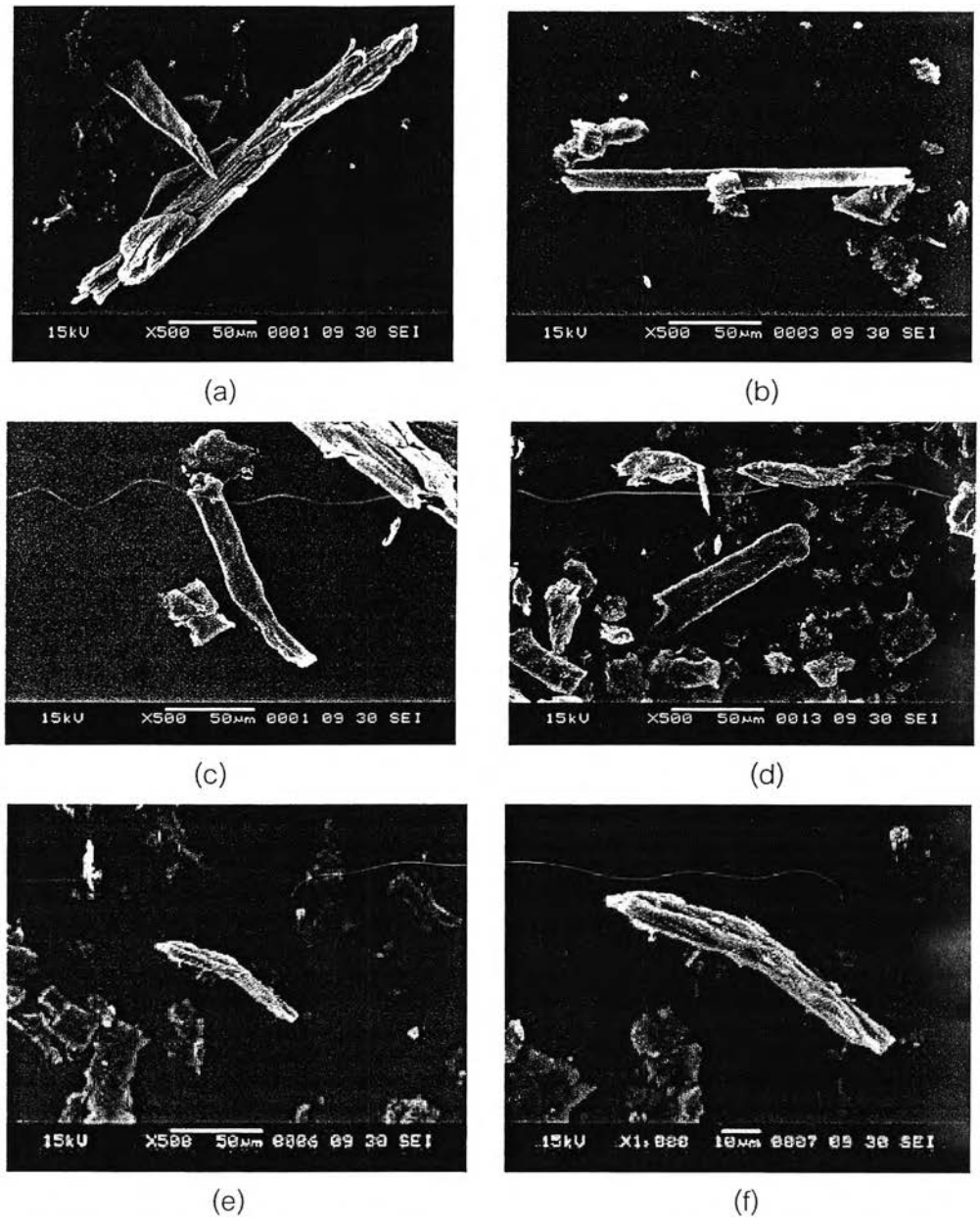


Figure 4.12 SEM micrographs of bleached banana stem at (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 min at magnification x500, and (f) 5 min at magnification x1000

4.1.2.4.2 Average particle size

Table 4.5 confirmed that when grinding time increased, the average particle size of bleached bagasse pulp decreased rapidly. However, when grinding time was raised from 4 to 5 min, the average particle size of bleached bagasse seemed to be slightly decreased.

In the same fashion, when the grinding time increased, the average particle size of bleached banana stem pulp was also decreased. However, upon increasing the grinding time from 4 to 5 min, the average particle size of bleached banana stem pulp was significantly increased owing to an agglomeration of small particle size as shown in Table 4.5

Therefore, the optimum condition for grinding time for bleached bagasse and banana stem pulp should be 4 min to avoid any agglomeration. Moreover, this optimum grinding time was also used as a grinding time for grinding hydrolyzed crystalline cellulose to prepare the crystalline cellulose as well.

Table 4.5 Average particle size of bleached bagasse and banana stem pulp

Time	Average particle size	
(min)	Bleached bagasse pulp (μm)	Bleached banana stem pulp (μm)
1	162.71	179.00
2	80.14	167.67
3	71.76	58.29
4	69.19	39.28
5	57.84	89.16

4.1.3 Hydrolysis Condition

Bleached bagasse and banana stem pulp were hydrolyzed with two different types of acid (i.e., 2.5 N HCl and 2.5 N H_2SO_4) at 30, 60, 120, and 180 min. The effects of acid types and hydrolyzed time on an average particle size, morphology, and degree of polymerization of all prepared crystalline cellulose were investigated. The results was also compared with those of commercial microcrystalline cellulose (CM MCC).

4.1.3.1 Morphology of microcrystalline cellulose

Table 4.6 and 4.7 showed SEM micrographs of bagasse microcrystalline cellulose (BG MCC) and, banana stem microcrystalline cellulose (BS MCC). As seen from these figures, all of prepared microcrystalline cellulose showed similar shape, which was a mixture between flake and pellet shape. As illustrated, the particle size of both BG MCC and BS MCC was decreased when the hydrolysis time or reaction time increased.

When comparing between microcrystalline cellulose treated with HCl and H_2SO_4, it was found that the particle size of the microcrystalline cellulose treated with H_2SO_4 seemed to be smaller than that of the microcrystalline cellulose treated with HCl. This result will be confirmed by the measurement of an average particle size as will be discussed in the next section.

Considering the effect of cellulose source, the particle size of bagasse microcrystalline cellulose treated by H_2SO_4 (H_2SO_4-BG) seemed to be larger than that of banana stem microcrystalline cellulose treated by HCl (HCl-BS) when hydrolyzed at 30 min. Nevertheless, the difference in the particle size of each type of microcrystalline cellulose will be clearly classified in 4.1.3.2.

Comparing with the commercial microcrystalline cellulose, Table 4.6 illustrated that the BG MCC showed a mixture between flake and pellet form with smooth surface; whereas, the commercial microcrystalline cellulose exhibited shortening fiber

and rod shape form with rough surface. The particle size of commercial microcrystalline cellulose seemed to be larger compared with the prepared microcrystalline cellulose. These results was agreed with the average particle size in 4.1.3.2.

Table 4.6 SEM micrographs of BG MCC hydrolyzed at 2.5 N HCl and 2.5 N H_2SO_4 at various time.

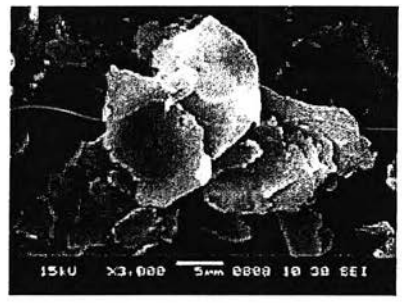
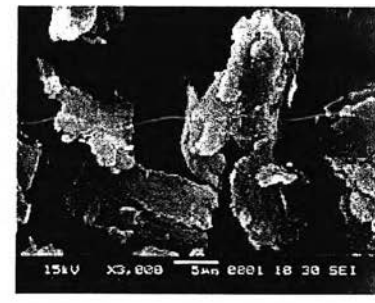
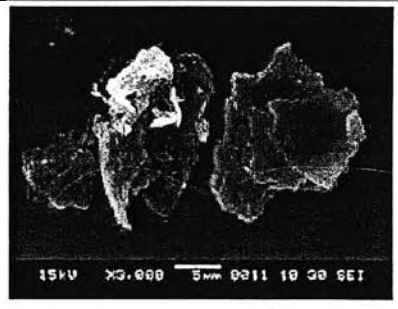
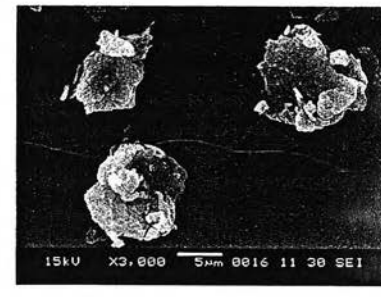
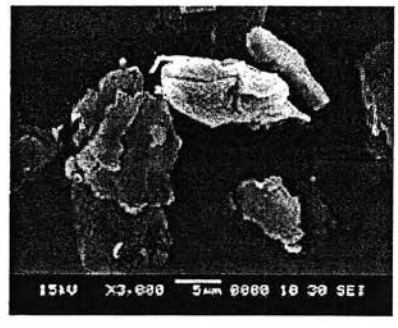
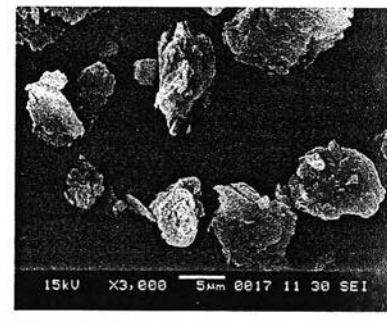
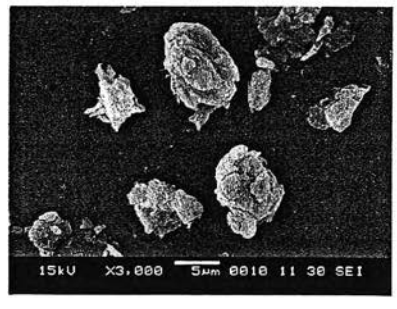
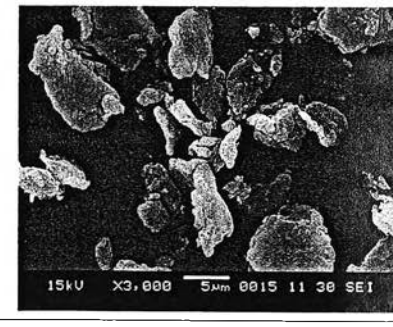
Time (min)	BG MCC prepared from HCl	BG MCC prepared from H_2SO_4
30		
60		
120		
180		

Table 4.7 SEM micrographs of BS MCC hydrolyzed at 2.5 N HCl and 2.5 N H_2SO_4 at various time

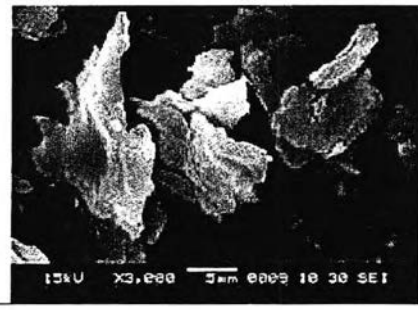
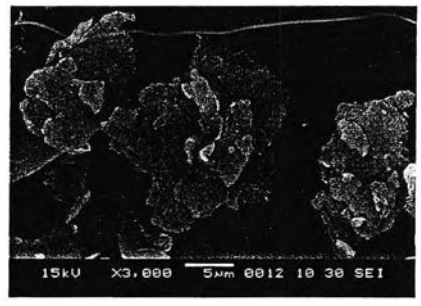
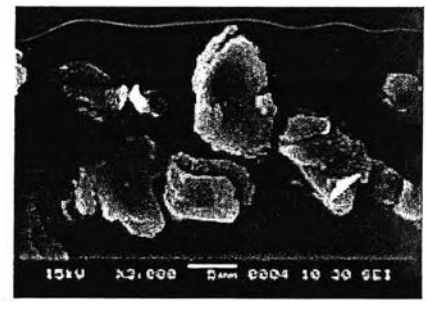
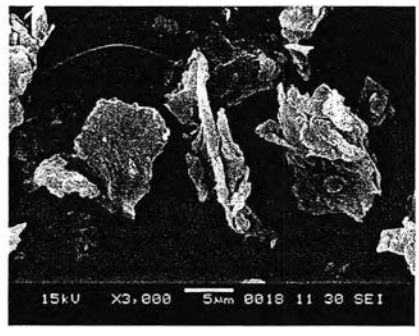
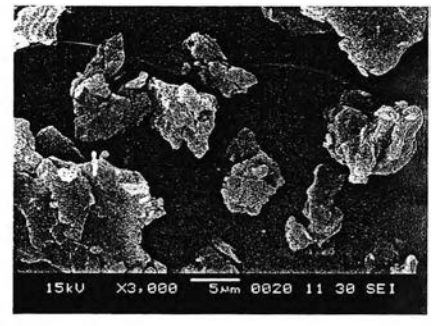
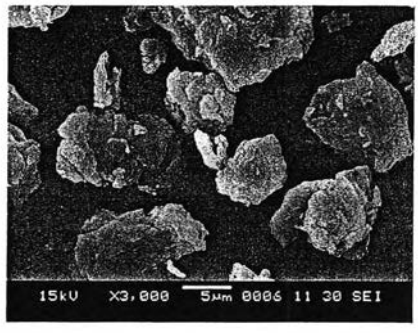
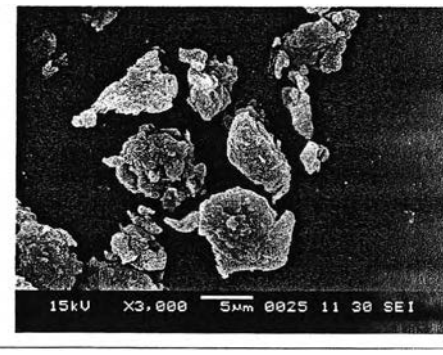
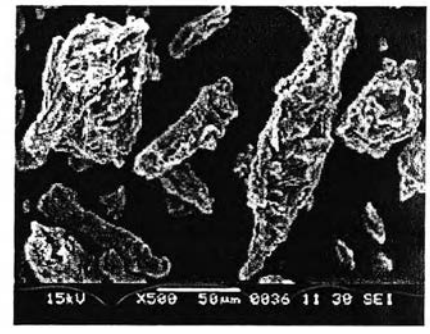
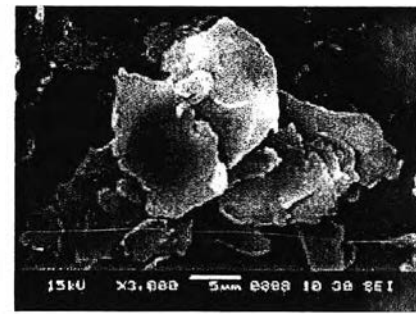
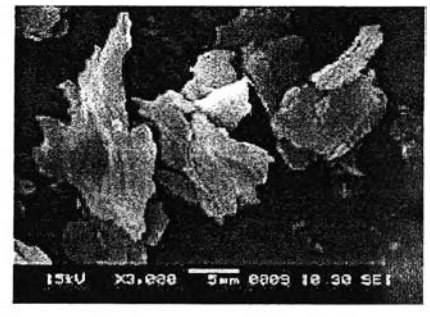
Time	BS MCC prepared from HCl	BS MCC prepared from H_2SO_4
30		
60		
120		
180		

Table 4.8 SEM micrograph of BG and BS MCC hydrolyzed at 2.5 N HCl and 2.5 N H_2SO_4 for 30 min and CM MCC

Hydrolysis Time (min)	Sample	
-	CM MCC	
30	HCl-BG MCC	
30	HCl-BS MCC	

4.1.3.2 Average particle size and particle size distribution

4.1.3.2.1 The Effect of hydrolysis time

The results of particle size analysis of crystalline cellulose samples are summarized in Table 4.9 and 4.10. These results showed that an average particle size and particle size range of hydrolyzed pulps were in the micro scale.

Considering the bagasse pulp, an average particle size and particle size range of bagasse pulp microcrystalline (BG MCC) decreased; with an increase of the reaction time. Especially, the average particle size and particle size range were decreased rapidly after hydrolysis with acids for 30 min to 60 min. However, upon further increased the reaction time, i.e., from 120 to 180 min, the average particle size of MCC seemed to be unchanged, having its values within the range of 6-7 μm

In case of banana stem pulp, similarly, an average particle size of banana stem microcrystalline (BS MCC) was decreased when the reaction time increased from 30 to 60 min. However, when the reaction time was increased from 60 to 180 min, the particle size of BS MCC treated with HCl seemed to be unchanged. The values of BS MCC treated with HCl were in the range of 7-8 μm. On the other hand, in case of H_2SO_4-BG MCC, when the reaction time was increased from 60 to 180 min, an average particle size was somewhat increased. This increasing of BS MCC particle size might be contributed to an agglomeration. According to the SEM micrographs of BS MCC in 4.1.3.1, the particle size of BS MCC treated with H_2SO_4 continously decreased when reaction time increased. Therefore, the increment of average particle size is believed to be due to an agglomeration of BS MCC particle.

4.1.3.2.2 The Effect of acid use

From Table 4.9 and 4.10, similar trend on average particle size was observed for both types of acid However, different kinds of acid had an effect on

the reaction time to reach unchanged or equilibrium value in the hydrolysis of each prepared MCC sample. The results showed that the optimum reaction time for bagasse pulp with HCl and H_2SO_4 hydrolysis was 120 and 60 min, respectively. Whereas, the optimum reaction time for hydrolysis of banana stem pulp with HCl and H_2SO_4 was 60 and 30 min, respectively. These results indicated that MCC prepared using H_2SO_4 required shorter reaction time to reach its constant value or equilibrium value than HCl. This result can be described by the fact that H_2SO_4 is a stronger acid than HCl since H_2SO_4 can give higher proton into water than HCl.

Comparing between these two pulps, the result indicated that bleached banana stem pulp seemed to be hydrolyzed easier than bleached bagasse pulp since the bleached bagasse pulp used longer time (i.e., 60 min) to reach the unchanged value; whereas, bleached banana pulp took only 30 min to obtain its constants value of average particle size when hydrolyzed with H_2SO_4. Similarly, when these two pulps were hydrolyzed with HCl, the approximately smallest particle size of BS MCC and BG MCC was obtained at 60 min and 120 min of hydrolyzed time, respectively.

In addition, the average particle size of all prepared BG and BS MCC was also compared with the commercial microcrystalline cellulose (CM MCC). Table 4.11 displayed average particle size and degree of polymerization of CM MCC. The result showed that all of the prepared BG and BS MCC had lower particle size than CM MCC.

Table 4.9 Average particle size of BG MCC at various hydrolysis reaction times

Time (min)	HCl		H_2SO_4	
	Average Particle size (μm)	Range (μm)	Average Particle size(μm)	Range (μm)
0	69.19	17.96 -261.10	69.19	17.96 -261.10
30	13.621	3.37 – 30.59	12.12	3.30 – 41.63
60	12.405	3.81 – 26.39	6.11	2.09 – 20.71
120	6.769	2.41 – 19.41	6.46	2.37 – 15.81
180	6.826	2.21 – 19.45	6.81	2.39 – 18.03

Table 4.10 Average particle size of hydrolyzed BS MCC at various hydrolysis reaction times

Time (min)	HCl		H_2SO_4	
	Average particle size (μm)	Range (μm)	Average particle size (μm)	Range (μm)
0	38.98	8.48 - 201.57	38.98	8.48 – 201.57
30	11.75	4.05 - 21.86	7.29	3.40 - 17.94
60	8.59	3.23 - 17.20	6.09	3.02 - 19.16
120	7.27	2.80 - 12.82	9.12	2.97 - 18.07
180	8.81	3.92 - 14.90	9.10	3.83 - 18.03

Table 4.11 Average particle size and degree of polymerization of CM MCC

Sample	Average particle size	Degree of polymerization (DP)
CM MCC	20	345

4.1.3.3 Degree of polymerization (DP)

Hydrolysis process is the most important process for preparing MCC. The degradation of cellulose by hydrolysis is known to occur through the degradation of glycosidic bonds of cellulose chain. This behavior is effected on the degree of polymerization or DP. Moreover, the DP is correlated to the average particle size of microcrystalline cellulose. In this study, the DP of hydrolyzed bleached bagasse and banana stem pulp using 2.5 H_2SO_4 or 2.5 HCl were investigated.

4.1.3.3.1 Effect of hydrolysis time

Table 4.12 showed that the degree of polymerization of BG and BS MCC was decreased when the reaction time increased. Considering, BG MCC prepared using HCl (HCl-BG MCC), the result showed that when the hydrolyzed time was increased, from 0 to 30 min, the DP of BG MCC was decreased rapidly. However, after 60 min, the DP of HCl-BG MCC slightly decreased and seemed to reach its equilibrium DP value within the range of 237-238. In case of the BG MCC prepared using H_2SO_4 (H_2SO_4- BG MCC) presented that, from 0-30 min, the DP of BG MCC was also drastically decreased when the reaction time increased from o to 30 min. But, after 30 min, the DP of BG MCC was slightly decreased and seemed to reach its equilibrium DP value, which was in the range of 231-233.

Similar result were also observed for BS MCC, The equilibrium DP value of HCl-BS MCC was in the range of 234-235, whereas the equilibrium DP value of H_2SO_4-BS MCC was in range of 231-234. These results indicated that the optimum reaction to hydrolyzed of both types of MCC were using HCl and H_2SO_4 was 120 and 60 min, respectively. At the conditions, the DP value of MCC reached its equilibrium or constant value.

4.1.3.3.2 Effect of acid use

As shown in Table 4.12, similar to average particle size, different type of acid had significant effect on the DP value. Regardless of MCC type, the MCC prepared using H_2SO_4 required shorter reaction time to reach its equilibrium DP value than the MCC prepared using HCl.

The DP value and equilibrium DP value of MCC prepared using HCl were higher than those of MCC prepared using H_2SO_4. For example, at 60min, the DP values of HCl-BG and HCl-BS were 340 and 303; whereas, those value of H_2SO_4-BG and H_2SO_4-BS MCC were 233 and 234.

Comparing between these two pulps, it seemed that similar trend was observed. The DP values obtained from each type of MCC were comparable when treated with the same acid.

Comparing with commercial the microcrystalline cellulose, the Table 4.11 and 4.13 showed that the DP value of CM MCC was higher than both BG and BS MCC. For example, at 60 min, the DP value of H_2SO_4-BG and H_2SO_4-BS MCC was 233 and 234, respectively; whereas, the DP value of CM MCC was 345.

Conclusively, the results of average particle size and degree of polymerization of microcrystalline cellulose revealed that the optimum of reaction time to reach the equilibrium average particle size and equilibrium values of BG and BS MCC was different. However, the suitable hydrolysis condition for bleaching BG and BS pulp should be considered mainly from the average particle size since the difference in particle size of the hydrolyzed MCC from each type of acid or cellulose source will affect differently to the mechanical and other properties of the biocomposite films. Therefore, the suitable hydrolysis conditions presented in Table 4.13 were selected based on the condition that yielded the smallest particle size.

Table 4.12 Degree of polymerization for hydrolyzed bagasse and banana stem

Hydrolysis Time (min)	Degree of polymerization (DP)			
	Hydrolyzed bagasse		Hydrolyzed banana stem	
	HCl	H_2SO_4	HCl	H_2SO_4
0	11685	11685	12024	12024
30	344	341	308	256
60	340	233	303	234
120	238	232	235	232
180	237	231	234	231

Table 4.13 The suitable hydrolysis condition of BG and BS MCC

MCC	Bagasse		Banana stem		CM
Acid use	HCl	H_2SO_4	HCl	H_2SO_4	None
Hydrolysis time (min)	60	60	30	30	None
Average particle size (μm)	12.41	6.11	11.98	7.30	20
DP	340	233	341	308	345

4.2 Characterization of Selected microcrystalline Cellulose

4.2.1 Crystallinity

Figure 4.13 showed the X-ray diffraction patterns of selected MCC samples prepared from bagasse (BG-MCC) and banana stem (BS-MCC) compared with that of the commercial sample (CM-MCC). As shown, all the samples showed crystallinity peak at $2\theta = 22^{\circ}$ and amorphous peak at $2\theta = 18.7^{\circ}$. This result is similar to work of Yu and co-work [47], this pattern is of α-cellulose in cellulose I. From this figure, both MCC prepared using H_2SO_4 (curves (a) and (b)) had higher intensity of crystalline peak than those prepared using HCl. This result may be implied that the prepared MCC using H_2SO_4 had higher degree of crystallinity than those prepared using HCl. This result is unlike the work reported by M.El-Sakhawy and M.L. Hasson [36]. In their work, it was found that the kind of acid used had no effect on crystallinity of the prepared MCC. Nevertheless, the effect of acid used on the crystallinity of MCC in this work is correlated well with the properties (i.e., transparency and water absorption) of the prepared biocomposite film as will be discussed in the next section. When comparing with the CM-MCC, it seemed that the crystalline peak ($2\theta = 22^{\circ}$) of CM-MCC had slightly higher intensity than those of prepared MCC, in particular for these hydrolyzed with HCl which exhibited relatively broader crystalline peak (curve (b) and (d)). Therefore, CM MCC had higher degree of crystallinity than the prepared microcrystalline cellulose. However, this conclusion needs to be further verified by other techniques such as DSC.

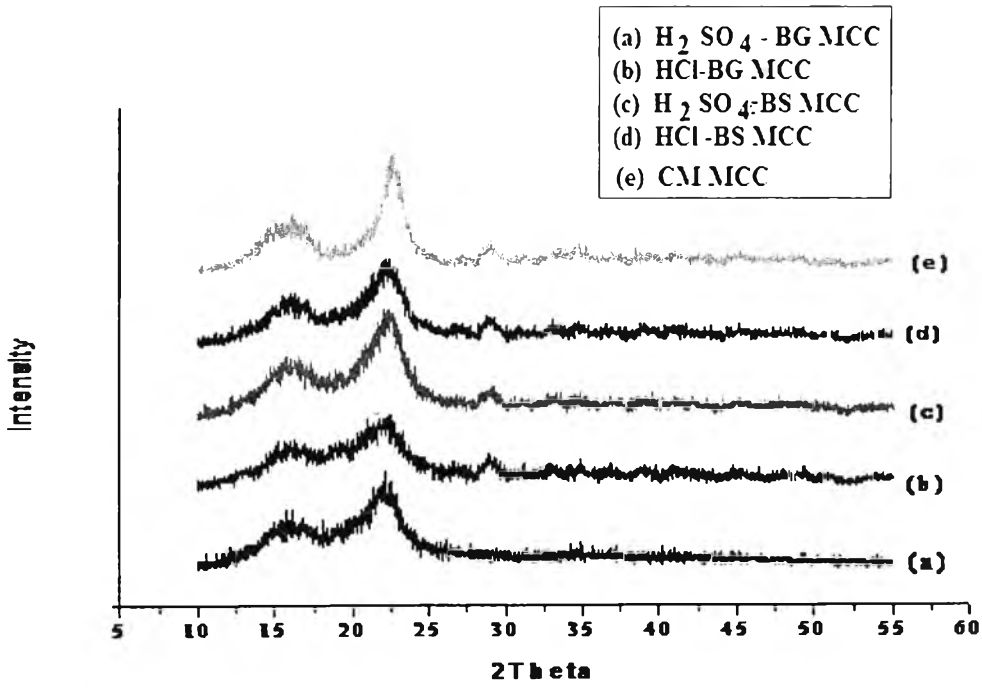


Figure 4.13 X-ray diffraction patterns selected microcrystalline cellulose

4.2.2 Thermogravimetric analysis (TGA)

4.2.2.1 Effect of acid use

Thermal stability decomposition of the different MCC samples was investigated using Thermogravimetric analysis (TGA). The samples selected were commercial microcrystalline commercial (CM-MCC), bagasse microcrystalline cellulose (BG-MCC) prepared using 2.5 N HCl and 2.5 H_2SO_4 for 60 min, and banana stem (BS MCC) prepared using 2.5 N HCl and 2.5 H_2SO_4 for 30 min. Figure 4.14 showed the TGA thermogram of the prepared MCC and CM MCC and Table 4.14 presented the data obtained from these curves.

As shown in this figure, MCC prepared using HCl showed one main stage of degradation at approximately 290-350 °C, which was due to the cellulose degradation, regardless of any MCC type. However, the MCC prepared using H_2SO_4 seemed to two degradation steps, with higher amount of residue than the MCC prepared from HCl. Obviously, both BG and BS MCC prepared using H_2SO_4 started to degrade easiler. According to M. El-sakhavy and M.L. Hansson [20] and Revol et [22], using H_2SO_4 in the preparation of MCC resulted in formation of sulfate groups onto cellulose chains. Thus the first stage of thermal decomposition for BG and BS MCC occurred at 200 °C and 160 °C , respectively, was probably due to the decomposition of those sulfate groups. The second decomposition step occurred at higher temperature around 290 – 350 °C was due to the degradation.

4.2.2.2 Effect of MCC type

Comparing between each type of MCC as already mentioned, as already mentioned, it was shown that there is no significant difference between the TGA curves of MCC prepared using HCl. Both BS-MCC and BG-MCC had nearly the same onset of degradation temperature at approximately 290-350°C. This onset of degradation was slightly lowered than that of CM-MCC; however, the prepared MCC had slightly higher residue, as shown in table 4.14. Considering the MCC prepared

using H_2SO_4, it was found that H_2SO_4 had on influence on thermal stability of MCC. Obviously, the BS-MCC started to decompose at about but upon further increasing the temperature, its thermal stability seemed to be greater than BG-MCC.The difference in the thermal stability of each type of MCC hydrolyzed with H_2SO_4 was also reported by M.El-Sakhawy and M.L. Hassan[36], In their work, three types of MCC prepared using H_2SO_4 were compared and the results revealed that cotton stalks-MCC showed slightly higher onset of degradation temperature than bagasse and rice straw-MCC sample. Meanwhile, the TGA curve of rice straw-MCC showed higher ash content than the others. These results including ours suggest that each type of cellulose and acid had interac each other differently and resulting in different thermal stability of each MCC sample

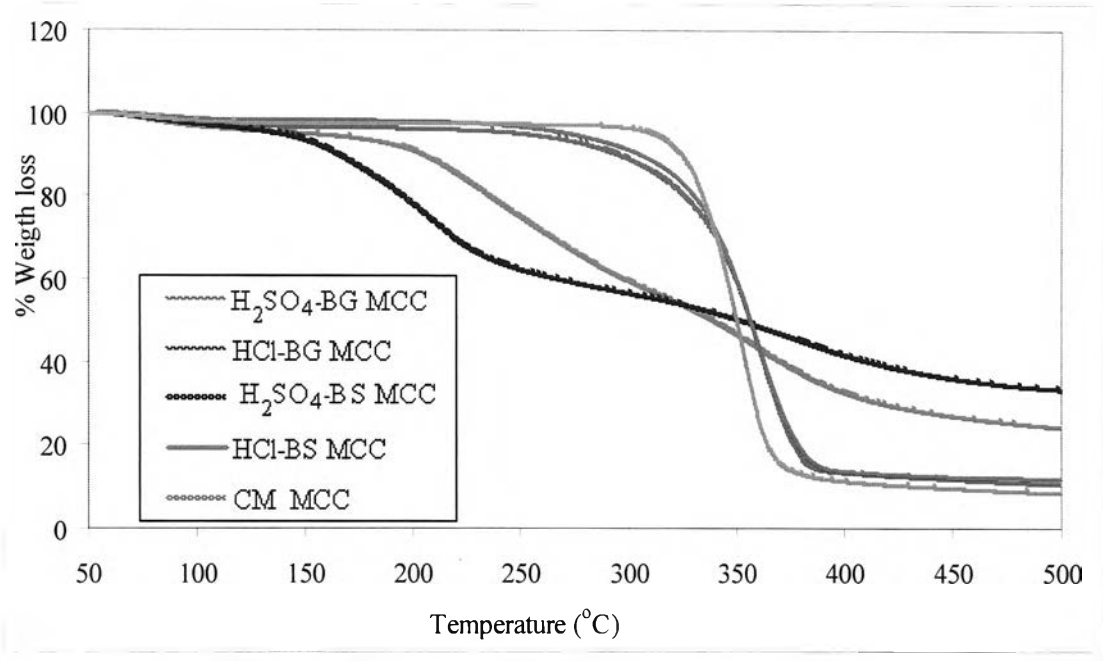


Figure 4.14 TGA thermograms of the selected microcrystalline cellulose

Table 4.14 TGA data of the selected microcrystalline cellulose

Sample	Td (onset) (°C)		Percent weight Loss(%)	Residue (%)
	First	Second	At 300	At 450 °C
HCl-BG MCC	-	304.68	10.98	12.47
H_2SO_4-BG MCC	200.00	290.51	33.51	27.30
HCl-BS MCC	-	303.76	10.30	12.44
H_2SO_4-BS MCC	160.00	290.33	37.03	36.24
CM MCC	-	310.00	3.37	9.81

4.3 Evaluation of Biocomposite film

4.3.1 Physical appearance

4.3.1.1 Appearance

The biocomposite film was prepared from plasticized starch reinforcing with microcrystalline cellulose (MMC) via casting method. Figure 4.15-4.19 display the photographs of prepared biocomposite films with various types and amount of MCC.The selected microcrystalline cellulose samples prepared from the suitable hydrolysis conditions were bagasse MCC hydrolyzed at 2.5 N HCl (HCl-BG MCC) and 2.5 N H_2SO_4 (H_2SO_4-BG MCC) for 60 min and the banana stem MMC hydrolyzed at 2.5 N HCl (HCl-BG MCC) and 2.5 N H_2SO_4 (H_2SO_4-BS MCC) for 30 min. The average particle size of the selected MCC condition was previously shown in Table 4.13. The plasticized cassava starch was reinforced with BG and BS MCC at 0, 5, 10, 15, 20, 25, 30, and 40 wt% (based on weight of starch). The thickness of prepared biocomposite films was appronmately lower than 0.3 mm.

Considering the effect of microcrystalline cellulose content, it was found that when the concentration of microcrystalline cellulose increased, the flexibility of biocomposite film was decreased. Moreover, at high concentration of MMC, over than 30 %wt, biocomposite film had rough surface and tended to crack when removing the film from casting mold. These results can be described by the flexibility of plasticized starch owing to the presence of presence of plasticizer which can help the molecular chain mobility of starch. However, upon increasing the amount of MCC, the MCC can decrease or restrain molecular chain motion of the starch matrix, as a result, the flexibility of biocomposite film decreased. Hence, the biocomposite film presented stiffness properties at high concentration of microcrystalline cellulose. From these photographs, it can be seen that the plasticized starch film was clearer than the biocomposite films. Moreover, when the content of MCC increased; the yellowness and browness of the biocomposite film increased.

Regarding the type of acid used to hydrolyzed or prepare MCC, Figure 4.15 and 4.16 show that the color of biocomposite film reinforcing with HCl-BG MCC presented yellow color. On the other hand, the biocomposite film reinforcing with H_2SO_4-BG MCC exhibited brown color. Similarly, the color of biocomposite films reinforcing with HCl-BS MCC had yellowness, whereas these films reinforcing with H_2SO_4-BS MCC had browness, as seen in Figure 4.17 and 4.18. These results were attributed to the color of microcrystalline which directly had an effect on the color of biocomposite film. Because the microcrystalline cellulose can disperse in the starch matrix it then made the starch films unclear and changed in their color. In other words, the color of biocomposite film presented yellowness when it was added with the microcrystalline cellulose prepared from HCl. Similarly, the biocomposite film showed browness when the microcrystalline cellulose prepared from H_2SO_4 was added into the starch matrix.

Considering the effect of cellulose source, Figure 4.15 and 4.17 showed that the color of biocomposite film reinforcing with HCl-BS MCC seemed to be yellowish than the biocomposite film reinforcing with HCl-BG. Similarly, as displayed in Figure 4.16 and 4.18, the biocomposite film reinforcing with H_2SO_4-BS MCC seemed to be brownish than H_2SO_4-BG MCC containing banana stem MCC. This result suggests that regardless of the type of acid, the biocomposite films containing banana stem MCC had darker in their color than those films having bagasse MCC. This is because the color of banana stem microcrystalline cellulose prepared from either HCl or H_2SO_4 acid was darker than that of bagasse microcrystalline cellulose.

Comparing with the biocomposite film reinforcing with commercial microcrystalline cellulose, Figure 4.19 shown that the biocomposite films reinforcing with the commercial microcrystalline cellulose had rough surface and exhibited many white spots on the film surface. These white spots on the biocomposite film are the whisker of commercial microcrystalline cellulose that was embedded in the starch matrix. The commercial microcrystalline cellulose can be obviously seen in the biocomposite film because of its larger paricle size comparing with the prepared MCC

in this research. In addition, the biocomposite film reinforcing with commercial microcrystalline cellulose had rougher surface than the biocomposite film reinforcing with bagasse and banana stem microcrystalline cellulose since the particle size of commercial microcrystalline cellulose was larger than those of bagasse and banana stem microcrystalline cellulose. The color of biocomposite film reinforcing with commercial microcrystalline cellulose presented white color. When the content of microcrystalline increased, the whiteness of biocomposite film increased because the commercial microcrystalline cellulose had white color. Comparing the color of biocomposite films, the biocomposite films reinforcing with the commercial microcrystalline cellulose had whiteness than those films reinforcing with bagasse and banana stem.

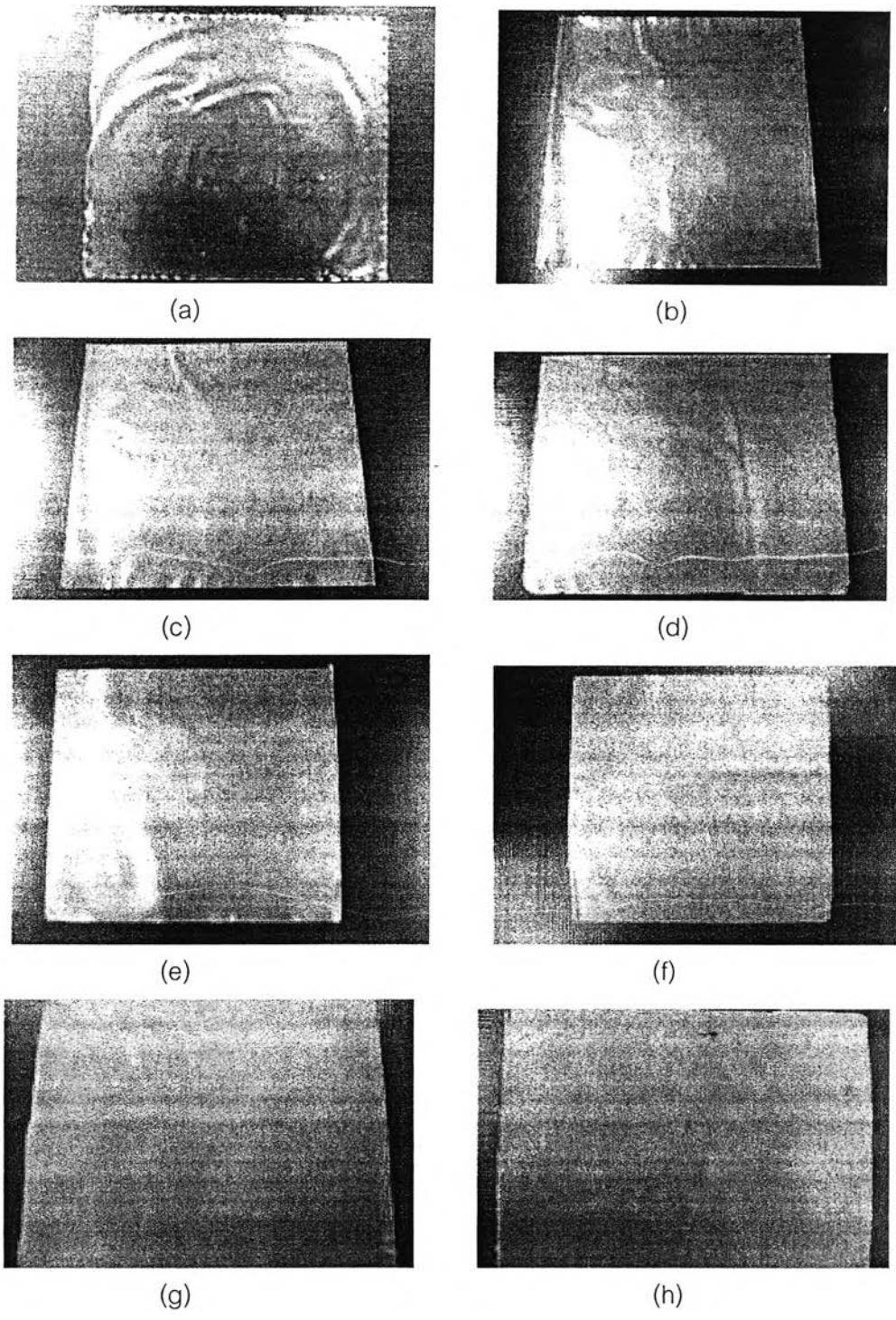


Figure 4.15 Biocomposite films reinforced with HCl-BG MCC at (a) 0, (b) 5, (c)10, (d)15, (e)20, (f)25, (g)30, and (h) 40 wt%

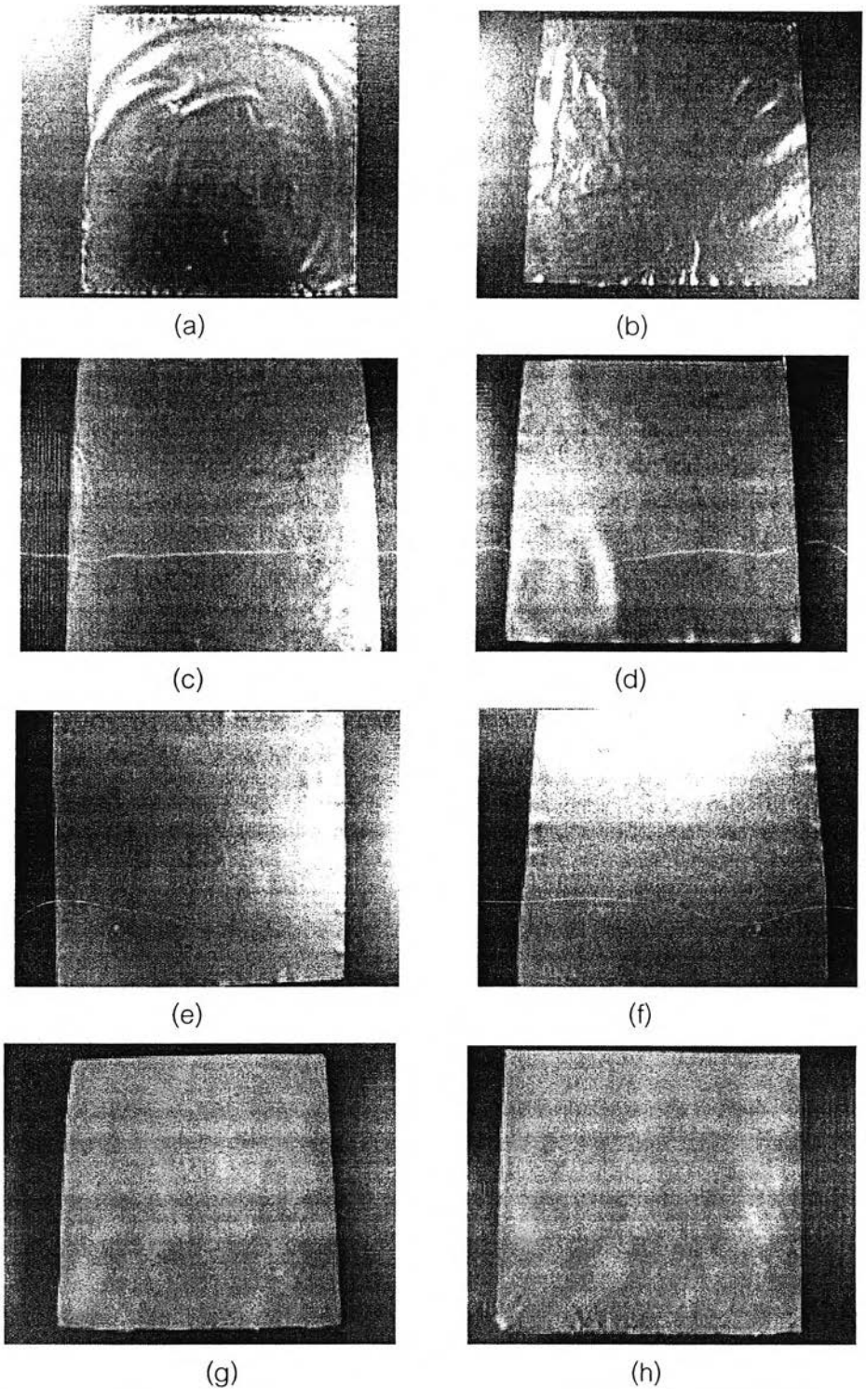


Figure 4.16 Biocomposite films reinforced with H_2SO_4-BG MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f)25, (g)30, and (H) 40 wt %

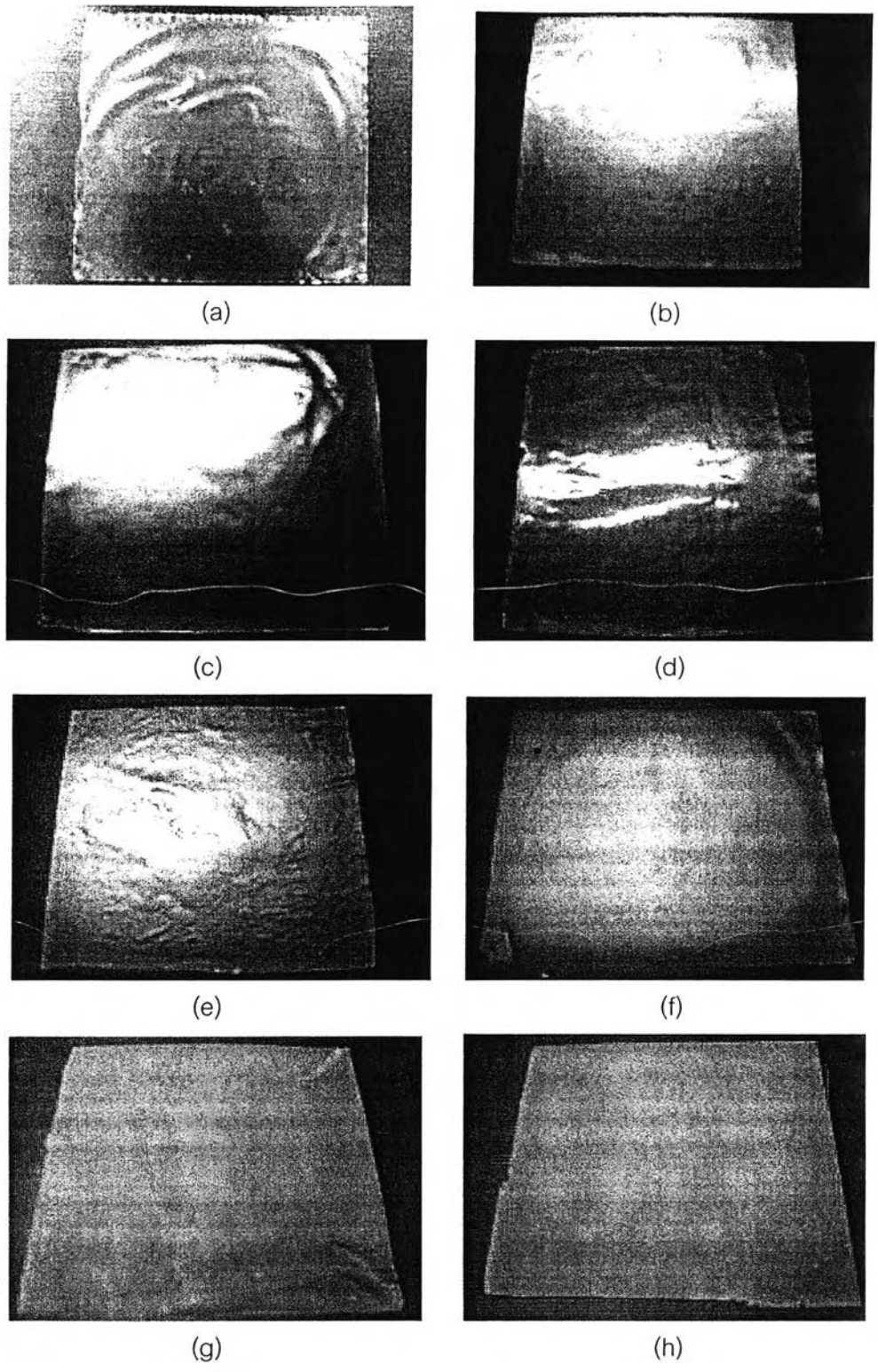


Figure 4.17 Biocomposite films reinforced with HCl-BS MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f)25, (g)30, and (h)40 wt %

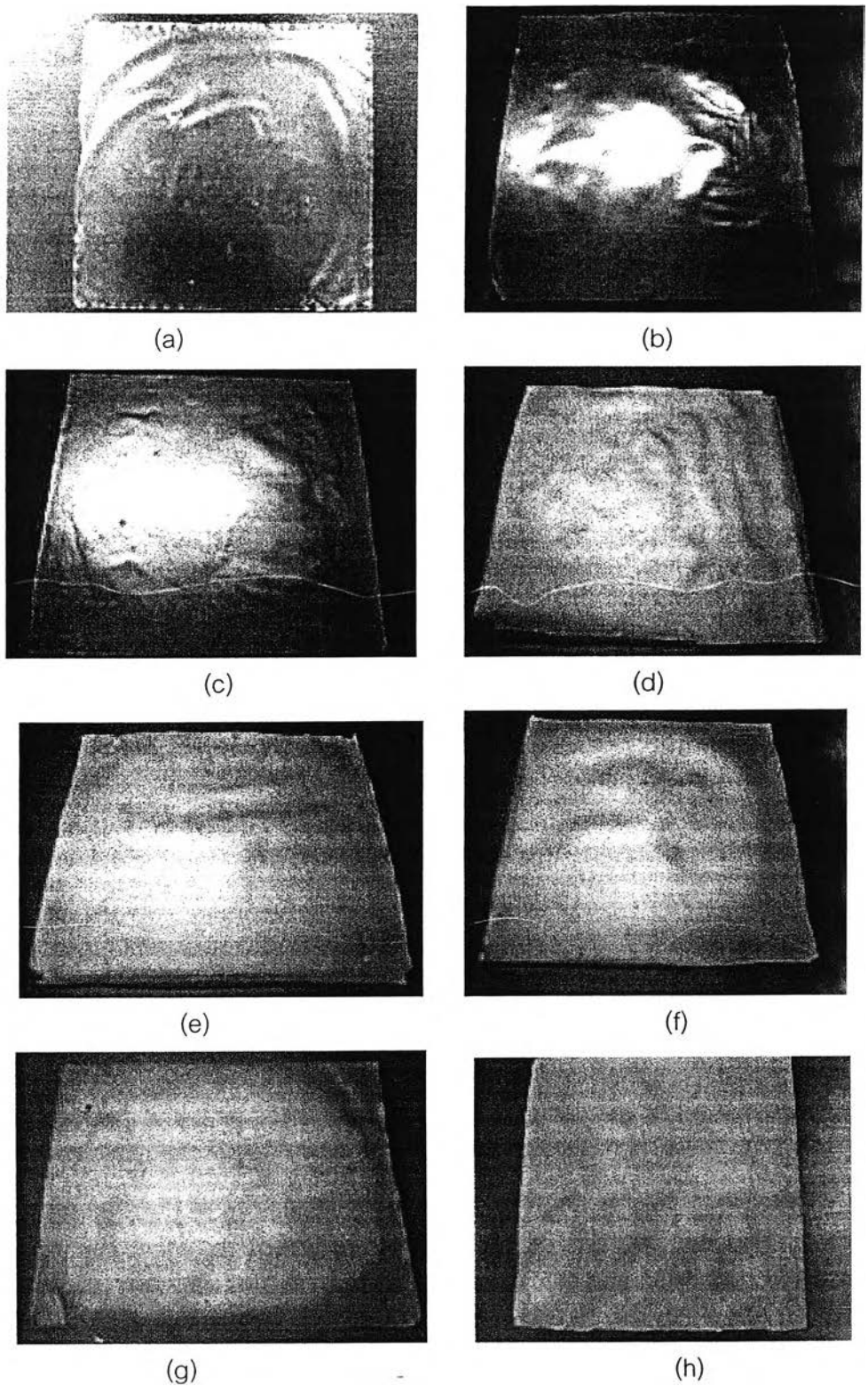


Figure 4.18 Biocomposite films reinforced with H_2SO_4-BS MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f)25, (g)30, and (h)40 wt%

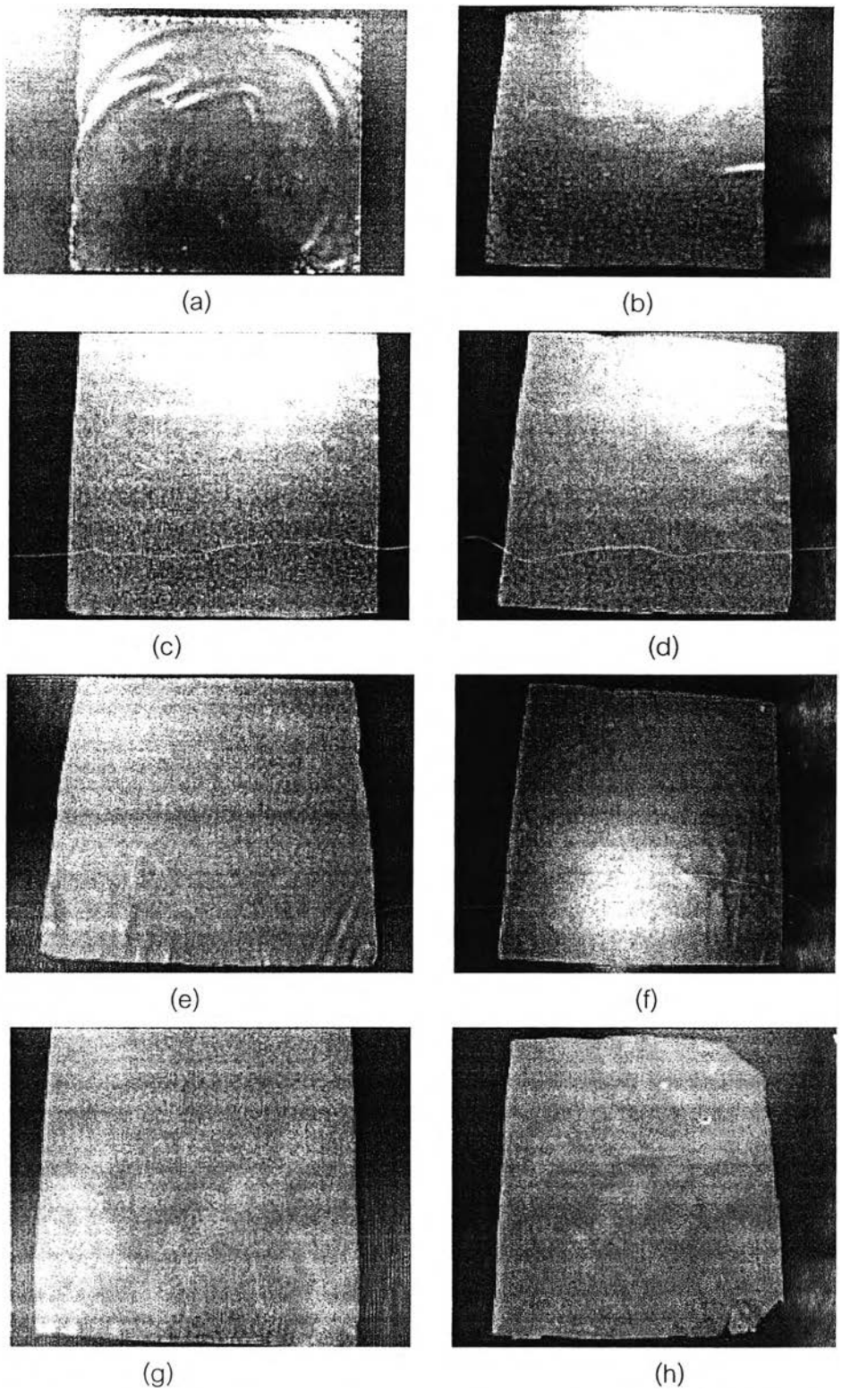


Figure 4.19 Biocomposite films reinforced with CM MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f)25, (g)30, and (h)40 wt%

4.3.1.2 Morphology of biocomposite film

The surface morphology of biocomposite film was investigated under scanning electron microscopy (SEM) in order to investigate the dispersion of microcrystalline cellulose in starch matrix. The bright spots on the SEM image presents microcrystalline cellulose embedded in starch matrix. The grey area on the SEM image presents starch matrix.

Considering the effect of microcrystalline cellulose, the smooth surface of pure starch film was disappeared when the MCC was presented. Obviously, the rough surface of biocomposite film was increased when the amount of microcrystalline cellulose was increased. Figure 4.20 and 4.21 show the SEM micrographs of biocomposite films reinforcing with HCl-BG and H_2SO_4-BG microcrystalline cellulose, respectively. It can be seen that microcrystalline cellulose has good dispersion in the starch matrix.

In addition, Figure 4.20 and 4.21 show that the surface roughness of biocomposite film reinforcing with HCl-BG microcrystalline cellulose was greater than that of biocomposite film reinforcing with H_2SO_4-BG microcrystalline cellulose. Figure 4.20 (g) shows that the HCl-BG microcrystalline cellulose was very well dispersed in the starch matrix. Upto 30 wt%. However, further increase in the amount of HCl-BG microcrystalline cellulose, the MCC tends to show an agglomeration at the microcrystalline content over than 30 wt%. For MCC hydrolyzed with H_2SO_4, Figure 4.21 (c) displays that biocomposite film reinforcing with 10 wt% of H_2SO_4-BG microcrystalline cellulose has good dispersion in the matrix. However, when the amount of MCC was higher than 10 wt%, an agglomeration of H_2SO_4-BG microcrystalline cellulose in the starch matrix occured. These results can be indicated that 30 wt% and 10wt% of microcrystalline content are the optimum content of HCl –BG and H_2SO_4-BG microcrystalline cellulose in the starch biocomposite film. This result is related to the tensile properties of biocomposite film, which will be described in 4.3.2.

Figure 4.22 and 4.23 show the SEM micrographs of the surface of biocomposite films reinforcing with HCl-BS and H_2SO_4-BS, respectively. Similarly, microcrystalline cellulose of banana stem was very well dispersion and had good compatibility in the starch matrix. In addition, the surface of biocomposite films reinforcing with HCl-BS microcrystalline cellulose had higher roughness than the biocomposite film reinforcing with H_2SO_4-BS microcrystalline cellulose. Figure 4.22 (e) and Figure 4.23 (e) show that HCl-BS and H_2SO_4-BS microcrystalline cellulose had good dispersion in the matrix at 20 wt% of microcrystalline cellulose content. But, higher 20 microcrystalline cellulose content (>20 wt%) contributed to the agglomeration of microcrystalline cellulose in the starch matrix. Thus, the optimum amount of HCl –BS and H_2SO_4-BS microcrystalline cellulose content in the starch biocomposite is 20 wt%. This result is also in agreement with the tensile properties of biocomposite film, as described in 4.3.2. The morphological behavior of these biocomposite films can be attributed to the good compatibility of MCC with starch matrix, which resulted from the good interaction of polar groups between molecular chain of starch and cellulose.

The particle size of microcrystalline cellulose had significant effect on the surface roughness of biocomposite film that was the large particle size had increased the roughness of the biocomposite film. Therefore, the surface of bicomposite film reinforcing with HCl-BG and HCl-BS microcrystalline cellulose had more roughness than the biocomposite film reinforcing with H_2SO_4-BG and H_2SO_4-BS, owing to the larger particle size of microcrystalline cellulose prepared from HCl.

In addition, the particle size of microcrystalline cellulose had influenced on the dispersion of microcrystalline cellulose in the starch matrix. The small particle size had good dispersion than the large particle size because the smaller particle size had more surface area and good interaction of hydrogen bondings between cellulose and starch molecule. Therefore, microcrystalline cellulose prepared from smaller particle size of H_2SO_4 seems to have good dispersion in the starch matrix than HCl-microcrystalline at the same content of microcrystalline cellulose. However,

microcrystalline cellulose tends to have an agglomeration in starch matrix when the amount of microcrystalline was increased over than the optimum content.

Regardingly, the effect of cellulose source, Figure 4.20 and Figure 4.22 show that the biocomposite film reinforcing with HCl-BG MCC had higher surface roughness than the film with HCl-BS MCC. Furthermore, when considering at the same content of microcrystalline cellulose, the HCl-BS MCC seemed to have good dispersion in the starch matrix than the HCl-BG MCC since particle size of HCl-BG microcrystalline cellulose was larger than that of HCl-BS MCC. Unlike, Figure 4.21 and 4.23 which present biocomposite film reinforcing with H_2SO_4-BG and H_2SO_4-BS MCC, it is very difficult to see any significant difference between these two figures. Although the average particle size of H_2SO_4-BG was slightly smaller than that of H_2SO_4 –BS MCC but the particle size distribution of these two microcrystalline cellulose seemed to be within the same range. In addition, the particle size of MCC treated by H_2SO_4 was much smaller (i.e.,~6-7 μm) than that of MCC treated by HCl (i.e., ~11-12 μm). Therefore, any differences on the morphology of biocomposite film reinforcing with H_2SO_4 –BS and H_2SO_4 –BG microcrystalline cellulose were hardly noticed.

Comparing with the commercial microcrystalline cellulose, Figure 4.24 shows SEM micrographs of starch biocomposite film reinforcing with commercial microcrystalline cellulose. Clearly, the surface roughness of biocomposite film increased when the content of microcrystalline cellulose increased. Furthermore, the biocomposite film with commercial microcrystalline cellulose had higher surface roughness than those films reinforcing with bagasse and banana stem microcrystalline cellulose. As seen in Figure 4.30 (c), when the amount of CM MCC was eaqual to or less than 10 wt%, the CM MCC had good dispersion in starch matrix. However, similar to other types of MCC, the CM MCC tens to show an agglomeration in the starch matrix, when the CM MCC content exceed 10 wt%. Thus, this result indicated that 10 wt% of CM MCC is the optimum amount for CM MCC in the starch biocomposite film. This result is correlated well with the tensile properties of the biocomposite film, as will be described in 4.3.2. In addition, the particle size of commercial microcrystalline cellulose was larger than those of

bagsse and banana stem microcrystalline cellulose; therefore, the commercial microcrystalline cellulose had lower dispersion in the starch matrix than the prepared bagasse and banana stem microcrystalline cellulose at the same content of microcrystalline cellulose.

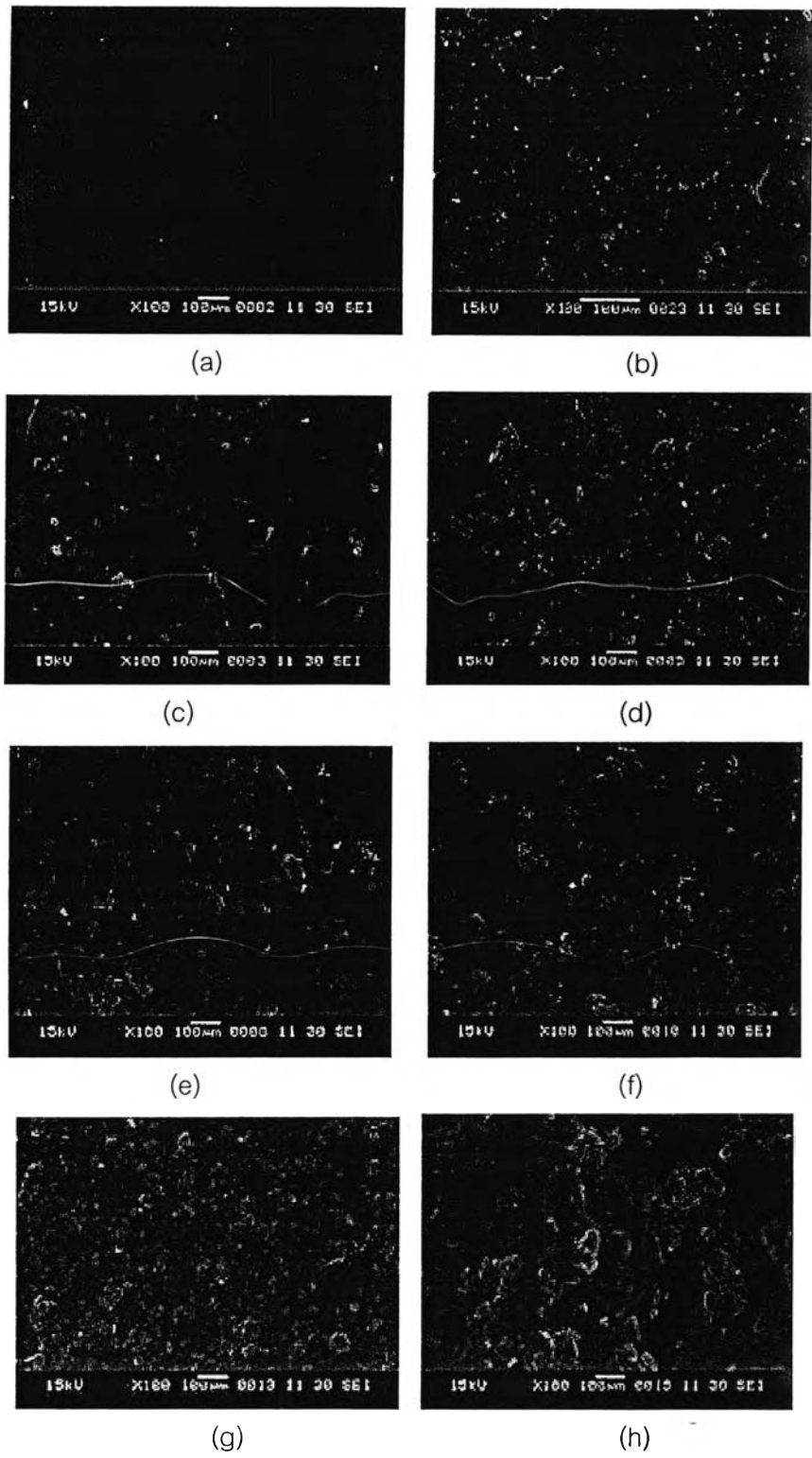


Figure 4.20 SEM micrographs of biocomposite film reinforced with HCl-BG MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f) 25, (g) 30, and (h) 40 wt%

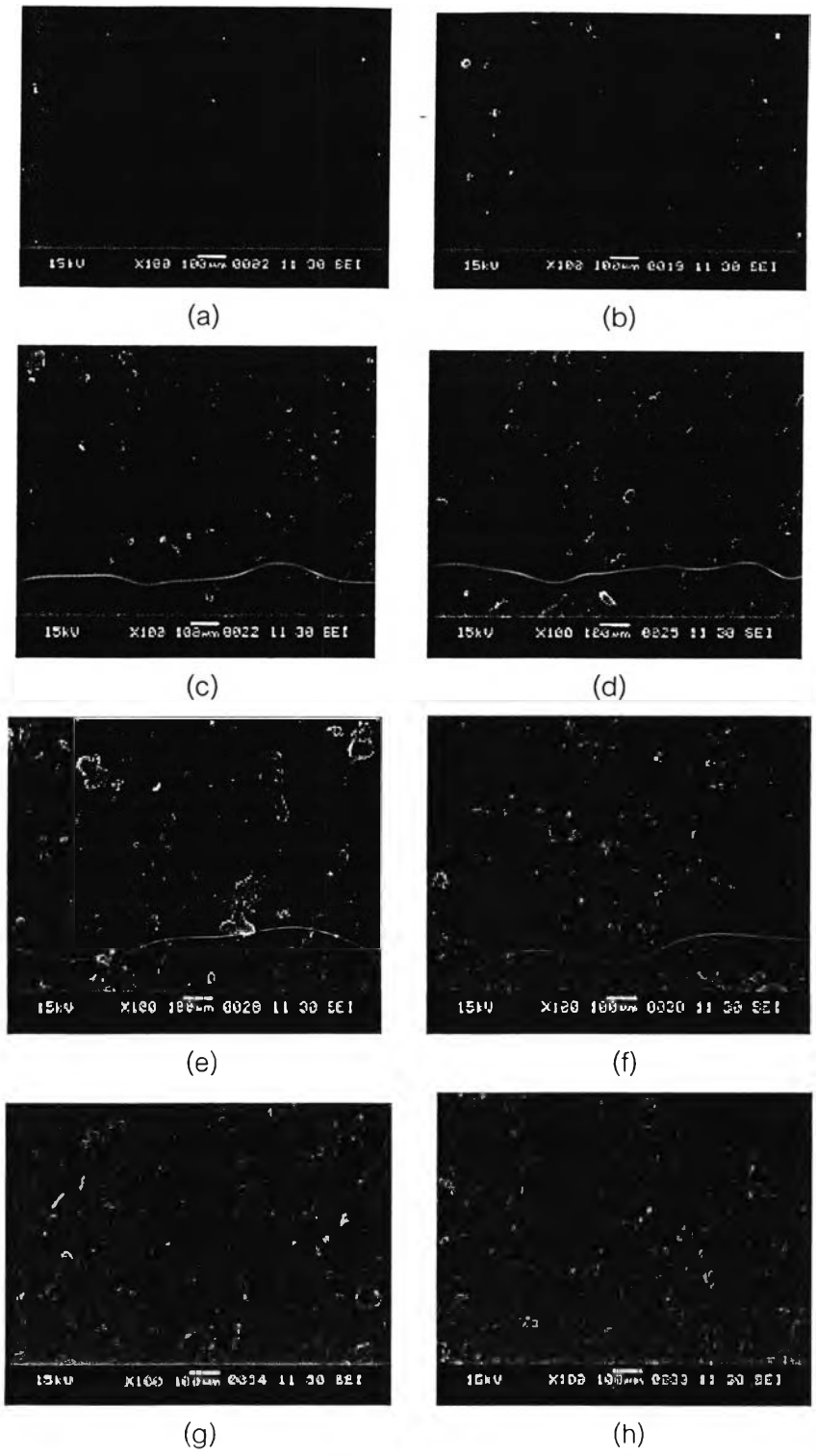


Figure 4.21 SEM micrograph of biocomposite film reinforced with H_2SO_4-BG MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f) 25, (g), 30 and (h) 40 wt%

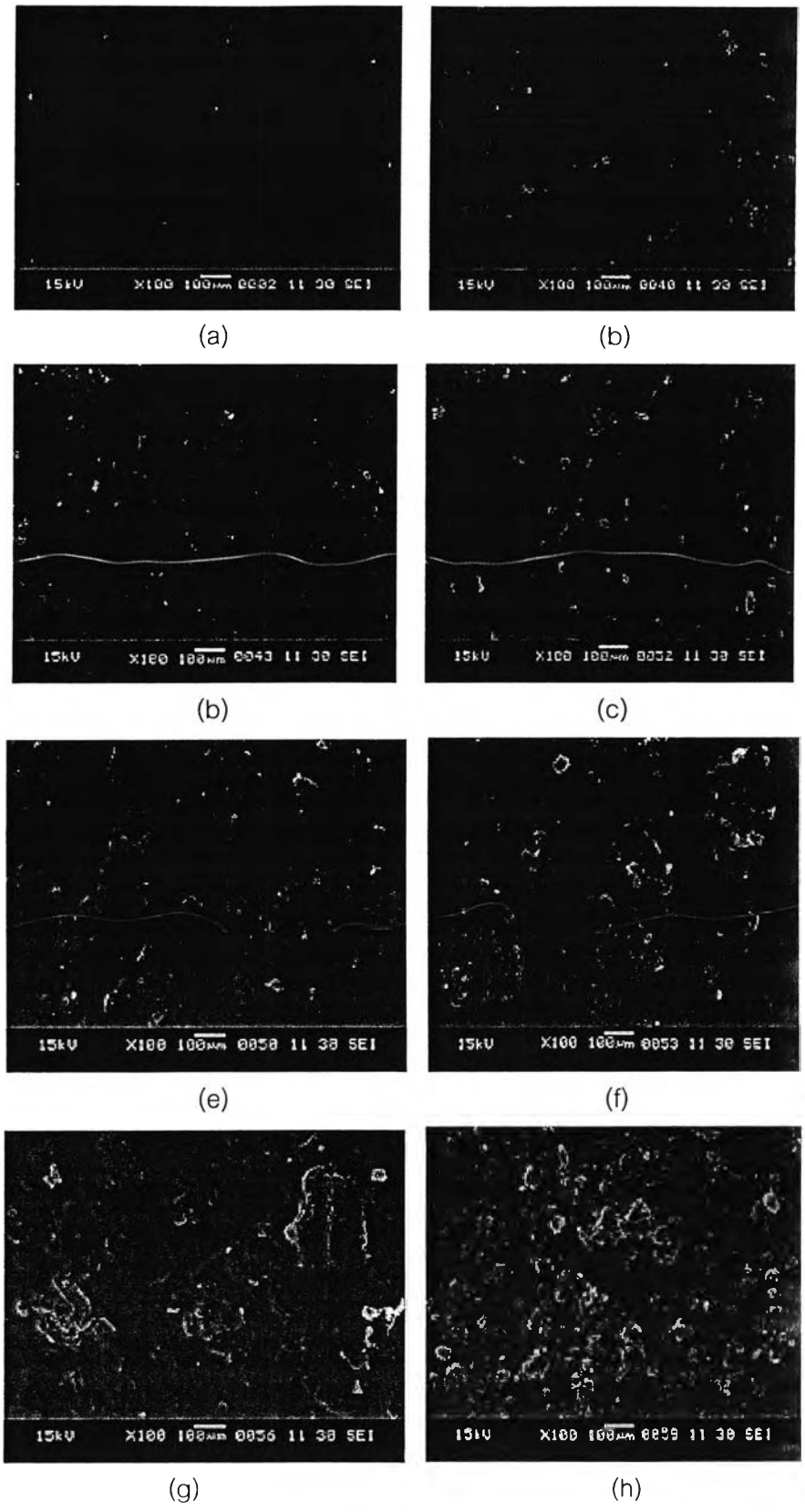


Figure 4.22 SEM micrograph of biocomposite film reinforced with HCl-BS MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f) 25, (g) 30 and (h) 40 wt%

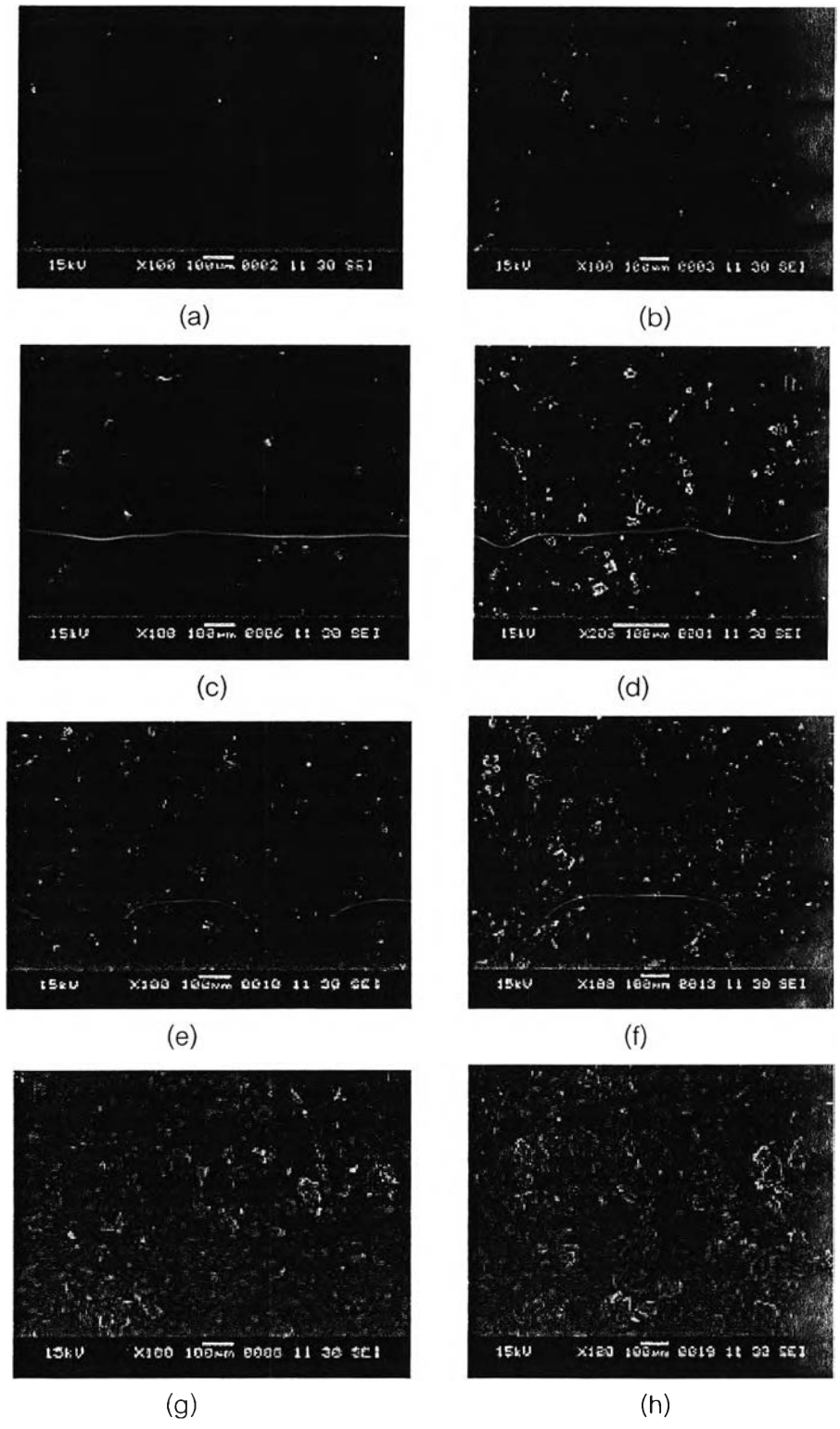


Figure 4.23 SEM micrograph of biocomposite film reinforced with H_2SO_4-BS MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f) 25, (g) 30 and (h) 40 wt%

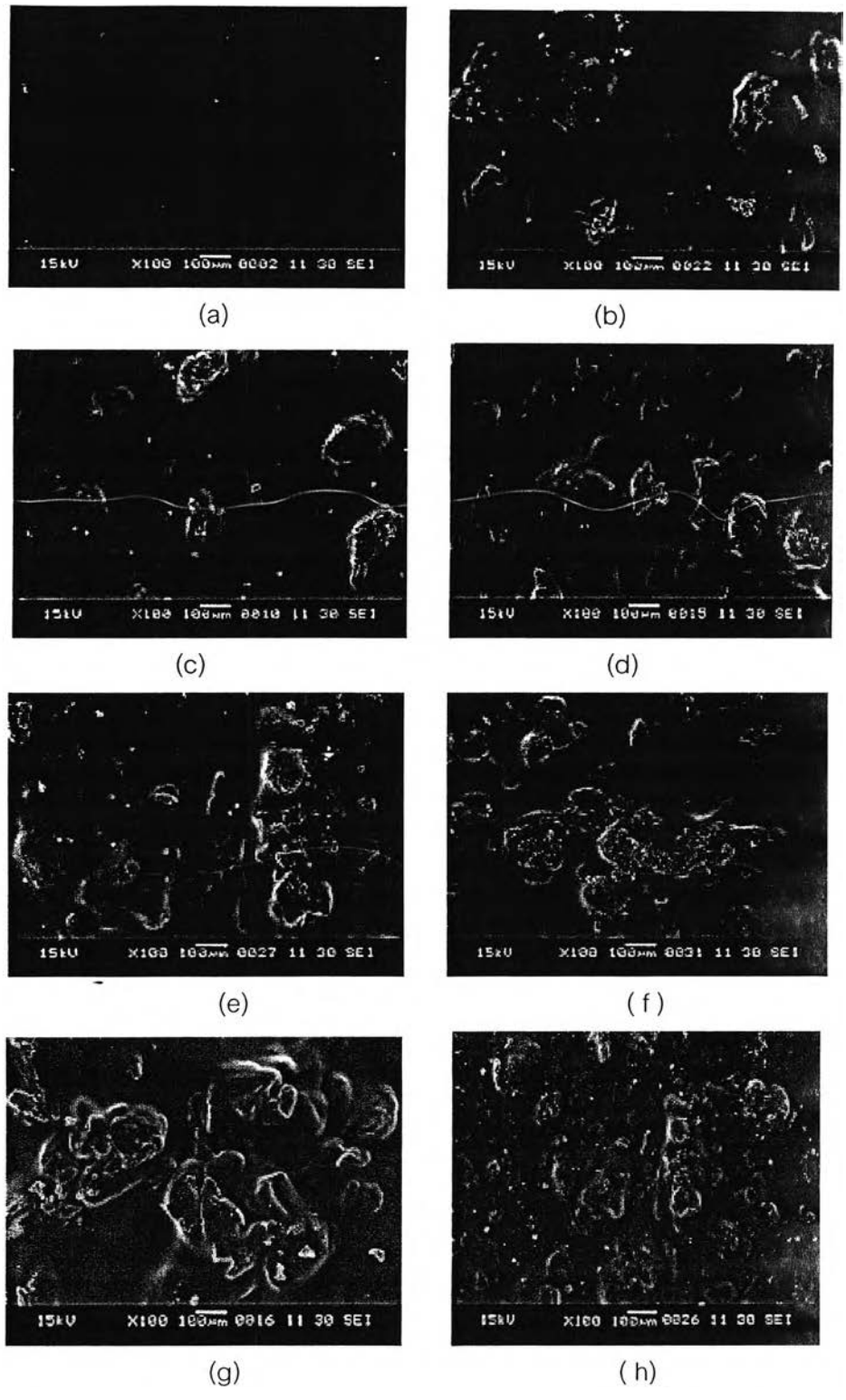


Figure 4.24 SEM micrographs of biocomposite films reinforced with CM MCC at (a) 0, (b) 5, (c)10, (d)15, (e) 20, (f) 25, (g) 30, and (h) 40 wt%

4.3.1.3 Haze

Haze value of biocomposite film had influenced on optical properties such as the transparency of biocomposite film. The lower haze values of the biocomposite film means the higher in its transparency. The haze values of the biocomposite film are presented in Figure 4.25.

Considering the effect of microcrystalline content, obviously, the haze values of the biocomposite films increased, when the content of microcrystalline increased. These results can be described that haze value of biocomposite film is a measure of the degree to which the biocomposite film looses its transparency due to the presence of suspended particulates in the film. Accordingly, if the film has more particle suspensed or dispersed in the film, it seems to have higher haze value. Therefore, the haze value of biocomposite film increased when the content of microcrystalline increased. For the effect of acid use, biocomposite films reinforcing with HCl-BG microcrystalline cellulose had lower haze value than those biocomposite films reinforcing with H_2SO_4-BG MCC. Similarly, the biocomposite films reinforcing with HCl-BS MCC had slightly lower haze values than thoes biocomposite films reinforcing with H_2SO_4-BS MCC. In other word, regardless of type of MCC added, the biocomposite films with HCl-treated microcrystalline cellulose had lower haze values or greater transparency than the films containing microcrystalline cellulose hydrolyzed with H_2SO_4.

The haze value of biocomposite film may be affected by various factors such as the larger particle size of reinforcing filler and the dispersion of reinforcing in matrix. The large particle size of reinforcing filler would hinder light transmittance that means the biocomposite film would have more haze value or lower transparency. Although microcrystalline cellulose prepared from HCl had larger particle size than microcrystalline cellulose prepared from H_2SO_4,when considering at the same content of MCC, it implied that the amount of HCl-MCC particles dispersed in the matrix were less than the number of smaller particle size H_2SO_4-MCC particles. Thus, as described earlier, the higher content of small H_2SO_4-MCC particles would obstruct

light transmittance in a greater extent. Therefore, biocomposite film reinforcing with microcrystalline cellulose prepared from HCl had lower haze value than biocomposite film reinforcing with microcrystalline cellulose prepared from H_2SO_4 at the same content of microcrystalline cellulose.

Considering the effect of cellulose source, Figure 4.25 displays that the haze values of biocomposite film reinforcing with HCl-BG were lower than those of the biocomposite film reinforcing with HCl-BS. This result can be supported by the SEM micrographs in 4.3.1.2 that because HCl-BG microcrystalline cellulose had very well dispersion in the starch matrix than HCl-BS. Similarly, the SEM micrographs in 4.3.12. show that H_2SO_4-BG microcrystalline cellulose had good dispersion in the starch matrix than H_2SO_4-BS microcrystalline cellulose. Therefore, the biocomposite film reinforcing with H_2SO_4-BS microcrystalline cellulose had higher haze vaules than biocomposite film reinforcing with H_2SO_4-BG microcrystalline cellulose. From these results, it can be implied that regardless of the type of the type of acid the biocomposite films containing bagasse MCC were more transparent or clearer then those films having banana stem microcrystalline , due to its better dispersion in starch matrix as evidenced by an SEM analysis

Comparing to commercial microcrystalline cellulose, the biocomposite film reinforcing with commercial microcrystalline cellulose had higher haze values than the biocomposite films reinforcing with bagasse and banana stem microcrystalline cellulose. This result was contributed to the particle size of commercial microcrystalline cellulose which was larger than those of bagasse and banana stem microcrystalline cellulose. Furthermore, it had low dispersion in the starch matrix. Therefore, the biocomposite film reinforcing with commercial microcrystalline cellulose had higher haze value or lower transparency than the biocomposite film reinforcing with bagasse and banana stem microcrystalline cellulose.

Conclusively, the decreasing in haze value or increasing in transparency of the biocomposite films were in the order of CM MCC/starch > H_2SO_4-BS

MCC/starch > H_2SO_4-BG MCC/starch> HCl-BS MCC/starch> HCl-BG MCC/starch. In addition, from these results, it can be concluded that the effects of MCC content had pronounced effect on the haze value of the biocomposite film, whereas the type of MCC (i.e., bagasse and banana stem) alone seemed to have insignificant influence on this property. However, when considering the type of MCC along with the kind of treated acid, several factors are involved (i.e., particle size, amount, and dispersion) and contributed to the transparency of these biocomposite films.

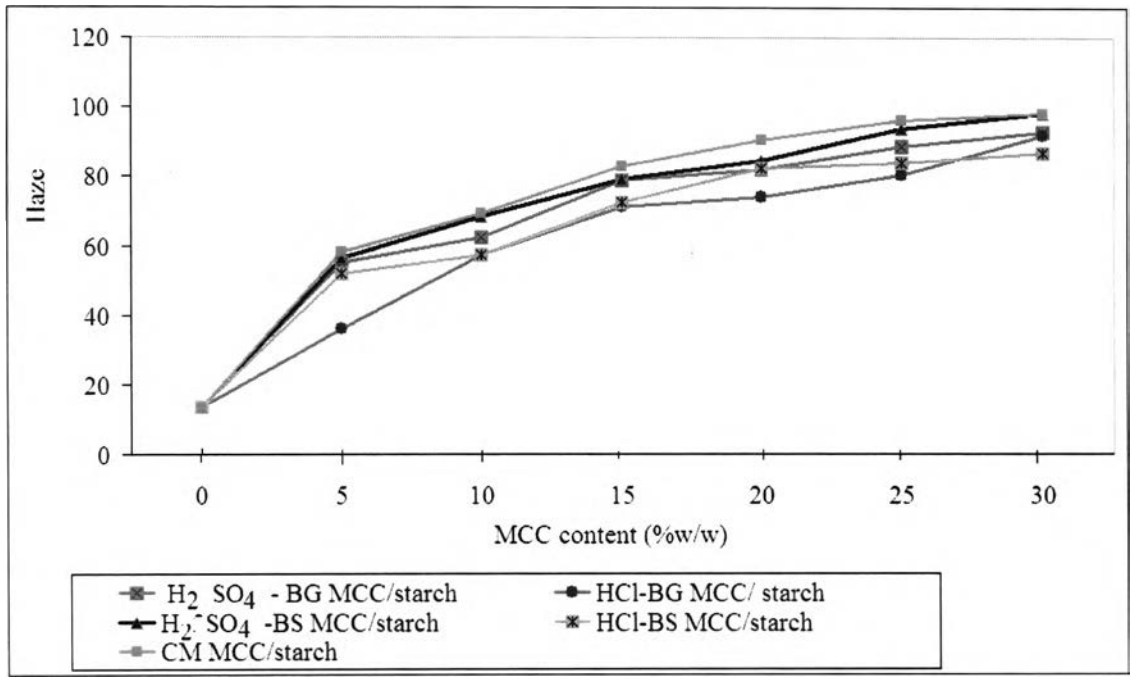


Figure 4.25 The percent haze of biocomposite films at various concentrations of microcrystalline cellulose

4.3.2 Tensile Properties

4.3.2.1 Tensile strength

The mechanical properties of biocomposite film were evaluated by tensile testing. Obviously, all the biocomposite films had higher tensile strength than plasticized starch film.

This means that the addition of microcrystalline cellulose was an effective method to reinforce the plasticized starch film. Considering the effect of microcrystalline content, Figure 4.26 and 4.27 display that the tensile strength of biocomposite film increased as a function of microcrystalline cellulose content upto a certain amount and then decreased or constant. The biocomposite films reinforcing with H_2SO_4-BG and HCl-BG microcrystalline cellulose reach to their maximum tensile strength of 11.72 and 11.5 MPa at 10% and 30% MCC content, respectively. For the biocomposite films reinforcing with H_2SO_4-BS and HCl-BS microcrystalline cellulose, obviously, the tensile strength of both biocomposite films increased; when, microcrystalline cellulose content increased from 0 to 20 wt%, and then decreased significantly. The maximum tensile strength obtained at 20 wt% of microcrystalline for the biocomposte films reinforcing with H_2SO_4-BS and HCl-BS microcrystalline cellulose was 15.36 and 13.74 MPa, respectively. After that, their tensile strength decreased to approximately 6 MPa, which was still higher than that of plasticized starch film.

The biocomposite films showed their maximum tensile strength at different amount of microcrystalline cellulose because of the effect of particle size. At the maximum tensile strength, all biocomposite film may have good dispersion of microcrystalline cellulose in the starch matrix, which contributed to the good interaction between microcrystalline cellulose and starch matrix. In case of biocomposite reinforcing with bagasse microcrystalline cellulose, at 10 wt% of microcrystalline cellulose content, the biocomposite film reinforcing with H_2SO_4-BG microcrystalline had higher tensile strength value than the film with HCl-BG microcrystalline cellulose.

However, over 10 wt% of microcrystalline cellulose, the tensile strength of biocomposite film was lower than that of biocomposite film reinforcing with HCl-BG microcrystalline cellulose. This result can be described that H_2SO_4-BG microcrystalline cellulose had smaller size than HCl-BG; hence, it seemed to have very well dispersion in starch matrix at 0-10%wt of microcrystalline cellulose content. However, the agglomeration of H_2SO_4-BG microcrystalline cellulose was occurred at over 10 wt% of microcrystalline cellulose, contributing to lower in the tensile strength of the biocomposite film. These result suggested that at lower microcrystalline cellulose content, H_2SO_4-BG microcrystalline cellulose had better reinforcing effect than HCl-BG microcrystalline cellulose due to its smaller size. Similar results were observed for the case of the biocomposite films with banana stem microcrystalline cellulose

Considering the effect of cellulose source, The results indicated that biocomposite films reinforcing with banana stem microcrystalline cellulose had higher tensile strength than the biocomposite films reinforcing with bagasse microcrystalline cellulose. This result is correlated to the SEM micrograph in 4.3.1.2 that the banana stem microcrystalline cellulose seems to have good dispersion in the starch matrix than bagasse microcrystalline cellulose. In addition, this data can also be explained by the DSC analysis in 4.3.3.2 that since the biocomposite film reinforcing with banana stem microcrystalline cellulose had higher degree of crystallinity than the biocomposite film reinforcing with the bagasse microcrystalline, resulted in the greater in tensile strength of the former.

Comparing to commercial microcrystalline cellulose, Figure 4.26 and 4.27 show that at 10 wt% microcrystalline cellulose, the maximum tensile strength of biocomposite film of about 10.77 MPa was obtained. The addition of microcrystalline cellulose more than 10 wt% resulted in a decrease in tensile strength because of the agglomeration as shown in the SEM micrograph in Figure 4.31. In addition, the biocomposite films reinforcing with either bagasse or banana stem microcrystalline cellulose had higher maximum tensile strength than biocomposite film reinforcing with commercial microcrystalline cellulose. This result was affected by the difference in the

particle size of reinforcing filler. Microcrystalline cellulose from bagasse and banana stem had smaller size and good dispersion in the starch matrix. Moreover, the small particle size microcrystalline cellulose had strong interaction with the starch matrix. Therefore, the biocomposite films reinforcing with microcrystalline cellulose from bagasse and banana stem had higher maximum tensile strength than the biocomposite film reinforcing with commercial microcrystalline cellulose. These results were in good agreement the DSC analysis that due to the lower in the degree of crystallinity, comparing with that of the biocomposite film with bagasse and banana stem microcrystalline cellulose, the biocomposite film with commercial microcrystalline had lower maximum tensile strength.

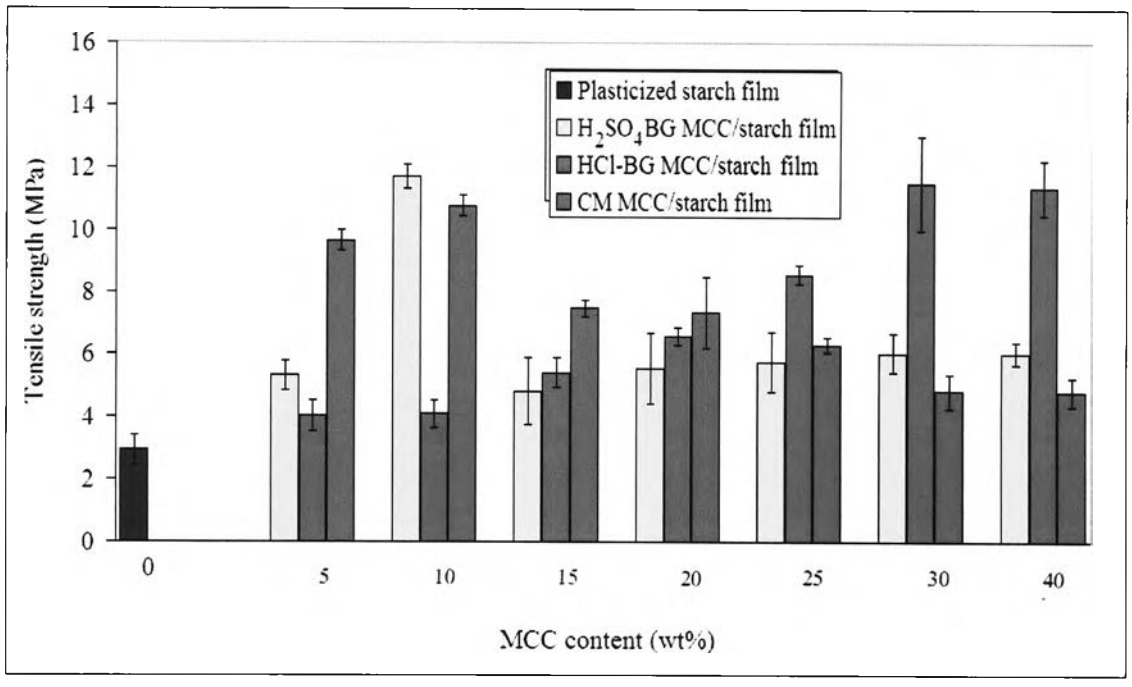


Figure 4.26 Tensile strength of plasticized starch and biocomposite film reinforcing with bagasse and commercial microcrystalline cellulose.

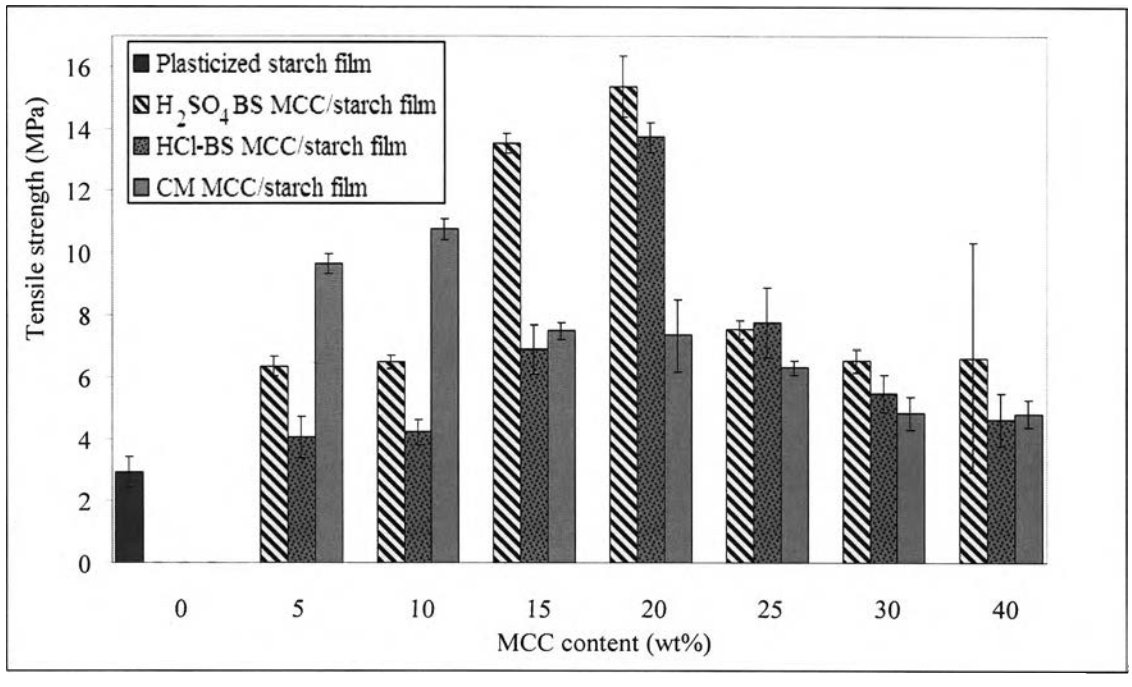


Figure 4.27 Tensile strength of plasticized starch and biocomposite film reinforcing with banana stem and commercial microcrystalline cellulose.

4.3.2.2 Young's modulus

Similar to tensile strength, the biocomposite films had significant greater young's modulus than the plasticized starch. An addition of microcrystalline cellulose significantly improved both tensile strength and Young's modulus.

Considering the effect of microcrystalline cellulose content, Figure 4.28 and 4.29 demonstrate that the Young's modulus of all the biocomposite films had similar trend to the tensile strength values that the Young's modulus increased as increasing microcrystalline cellulose content until it reached maximum values, and decreased afterwards. As shown in Figure 4.28, the maximum Young's modulus of the biocomposite films reinforcing with H_2SO_4-BG and HCl-BG microcrystalline cellulose obtained at 10 wt% and 30%wt of microcrystalline content was 651 and 630 MPa, respectively. Figure 4.29 illustrates that the Young's modulus of biocomposite film reinforcing with HCl-BS and H_2SO_4-BS microcrystalline cellulose was increased; upto 20 wt% of microcrystalline cellulose. The maximum values of the Young's modulus for the biocomposite films was reinforcing with 20 wt% of H_2SO_4-BS and HCl-BS was 716.37 and 662.43, respectively. After these maximum values, the Young's modulus were decreased but still greater than that of plasticized starch film.

These results can be described that the particle size and the dispersion of reinforcing filler had influenced on the Young's modulus of biocomposite film. The smaller particle size of microcrystalline cellulose had very well dispersion in the starch matrix; consequently, providing strong interaction between reinforcing microcrystalline cellulose and starch matrix. Therefore, the small particle size contributed to high Young's modulus value. In case of bagasse microcrystalline cellulose, the H_2SO_4-BG microcrystalline cellulose had smaller size than the HCl-BG microcrystalline cellulose. Thus, biocomposite film reinforcing with H_2SO_4-BG microcrystalline cellulose had higher maximum Young's modulus value than the biocomposite film reinforcing with HCl-BG microcrystalline cellulose. Similar result was observed for the biocomposite film reinforcing with banana stem microcrystalline

cellulose. This result indicated that microcrystalline cellulose prepared using H_2SO_4 led to higher Young's modulus value of the biocomposite film than the microcrystalline cellulose prepared using HCl.

Considering to the effect of cellulose source, the result showed that the biocomposite film reinforcing with bagasse microcrystalline cellulose had lower Young's modulus values than the biocomposite film reinforcing with banana stem microcrystalline cellulose. This result can be suggested that the bagasse microcrystalline cellulose had lower dispersion in the starch matrix than banana stem microcrystalline cellulose. These results were in good agreement with the tensile strength as previously described.

Comparing to the commercial microcrystalline cellulose, biocomposite film reinforcing with commercial microcrystalline cellulose reached its maximum Young's modulus value of 625.48 MPa at 10 wt% microcrystalline content and continuously decreased afterwards. In addition, it was found that the maximum Young's modulus value of the biocomposite film reinforcing with commercial microcrystalline cellulose was lower Young's modulus than that of biocomposite film reinforcing with bagasse and banana stem microcrystalline cellulose. Similarly, explanation can be used that because commercial microcrystalline cellulose had larger particle size, so it had low dispersion in starch matrix. Therefore, the biocomposite film reinforcing with commercial microcrystalline cellulose had lower Young's modulus than biocomposite film reinforcing bagasse and banana stem microcrystalline cellulose.

Nevertheless, when focusing at the lower amount of microcrystalline cellulose (i.e., before the maximum values of the Young's modulus were obtained) or regardless of the maximum value, the biocomposite film with commercial microcrystalline cellulose seemed to have higher Young's modulus; in particular, when compared to those of the film with bagasse microcrystalline cellulose. This is probably due to the shape of commercial microcrystalline cellulose, which was more fibril-like or

having higher aspect ratio than the prepared microcrystalline cellulose. These observation were also found for the tensile strength as well.

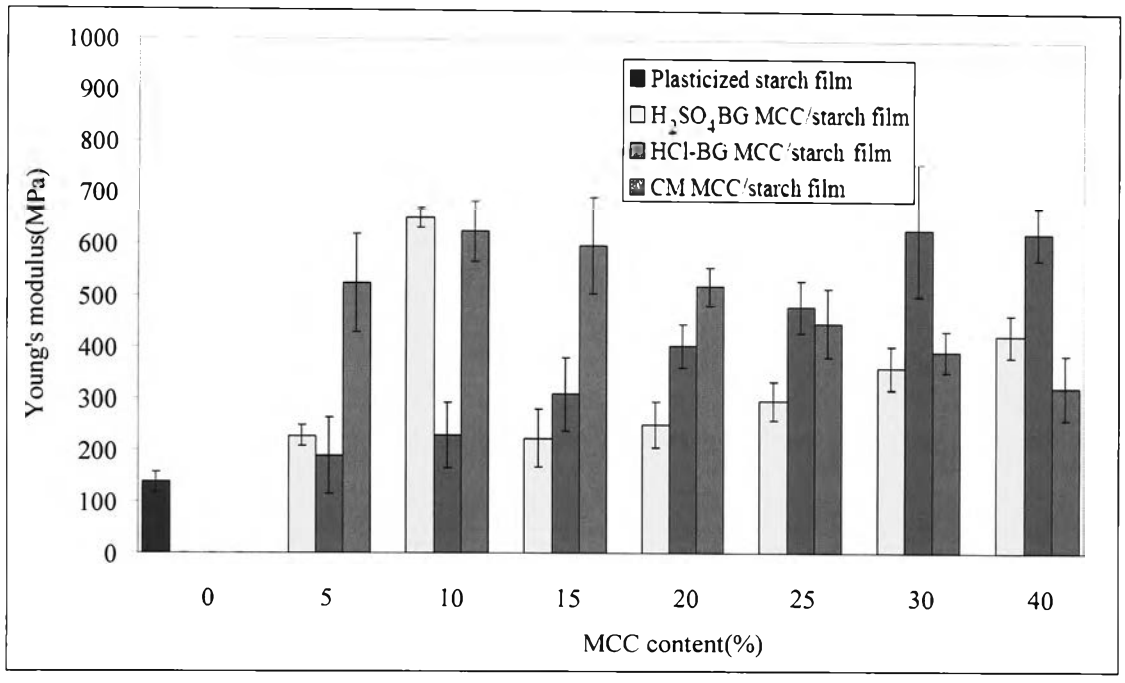
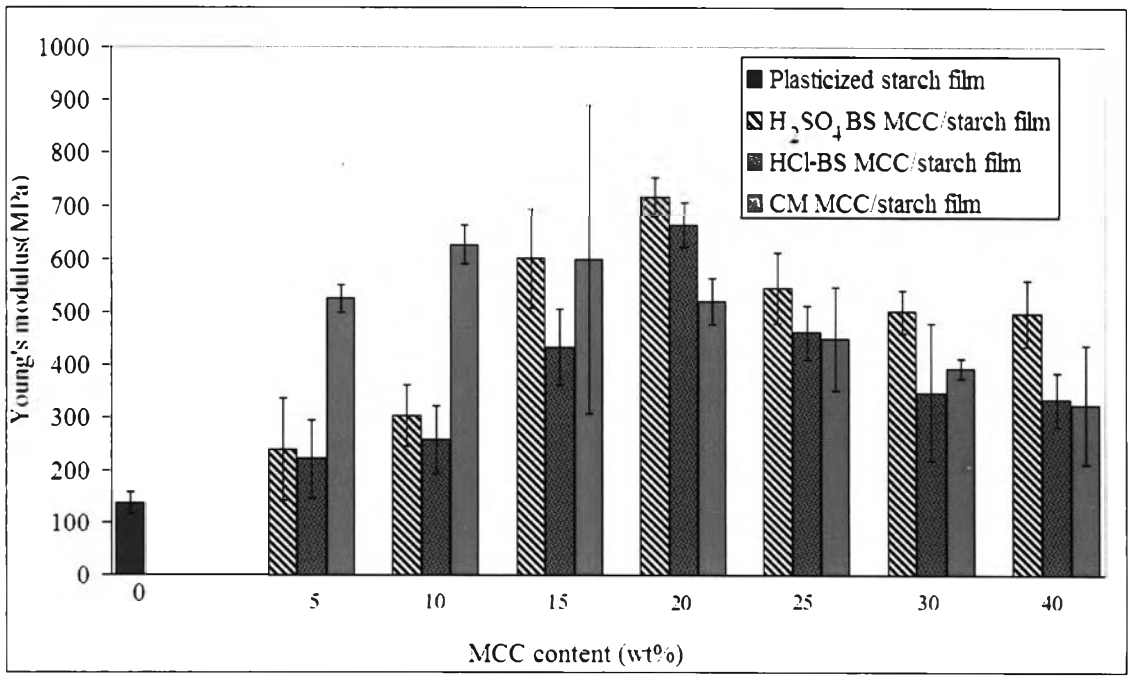


Figure 4.28 Young's modulus of plasticized starch and biocomposite film reinforcing with bagasse MCC, and commercial microcrystalline cellulose.



.Figure 4.29 Young's modulus of plasticized starch and biocomposite film reinforcing with banana stem MCC, and commercial microcrystalline cellulose.

4.3.2.3 % Elogation at break

In contrast to the tensile strength and Young's modulus, the biocomposite films had significant lower elongation at break than the plasticized starch film, indicating that the prepared biocomposite films were stiffer and stronger but less flexible than the plasticized starch film. Thus, as shown in Figure 4.30 and 4.31. The % elongation of biocomposite film reinforcing with any kinds of microcrystalline cellulose was decreased as a function of microcrystalline content.

These results may be described that microcrystalline cellulose can interfere and decreased the mobility of starch chain. Therefore, it contributed to the decrement of % elongation at break of the bicomposite films. Oviously, from these two figures, the % elongation at break of biocomposite film reinforcing with HCl-BS or HCl-BG microcrystalline cellulose was higher than the biocomposite film reinforcing with H_2SO_4-BS or H_2SO_4 –BG microcrystalline cellulose, particularly, the results were obviously noticed for the films with bagasse microcrystalline cellulose. The lower in % elongation at break of biocomposite film with H_2SO_4-BG or H_2SO_4-BS microcrystalline cellulose was probably due to the grater in the degree of crystallinity comparing with those films with HCl-BG or HCl-BS MCC. Generally, the film having high degree of crystallinity will behave as a strong and somewhat brittle material.

Considering to the effect of cellulose source, Figure 30 and Figure 31 display that the % elongation at break of biocomposite film reinforcing with bagasse microcrystalline cellulose was slightly higher than that of biocomposite film reinforcing with banana stem microcrystalline cellulose. According to the degree of crystallinity, since the biomposite film with banana stem microcrystalline cellulose had higher degree of crystallinity than the biocomposite film microcrystalline cellulose. Therefore, the biocomposite film reinforcing with banana stem microcrystalline had lower % elongation at break than the latter.

Comparing to commercial microcrystalline cellulose, the results showed that the biocomosite film reinforcing with commercial microcrystalline cellulose had significantly lower elongation at break than the plasticized starch and biocomposite films reinforcing with either bagasse or banana stem microcrystalline cellulose. These results implied that the biocomposite film reinforcing with commercial microcrystalline cellulose was more brittle than the biocomposite reinforcing with bagasse and banana stem microcrystalline cellulose. This was probably attributed to the large particle size and poor dispersion of the commercial microcrystalline cellulose in the starch matrix, as evidenced by SEM analysis.

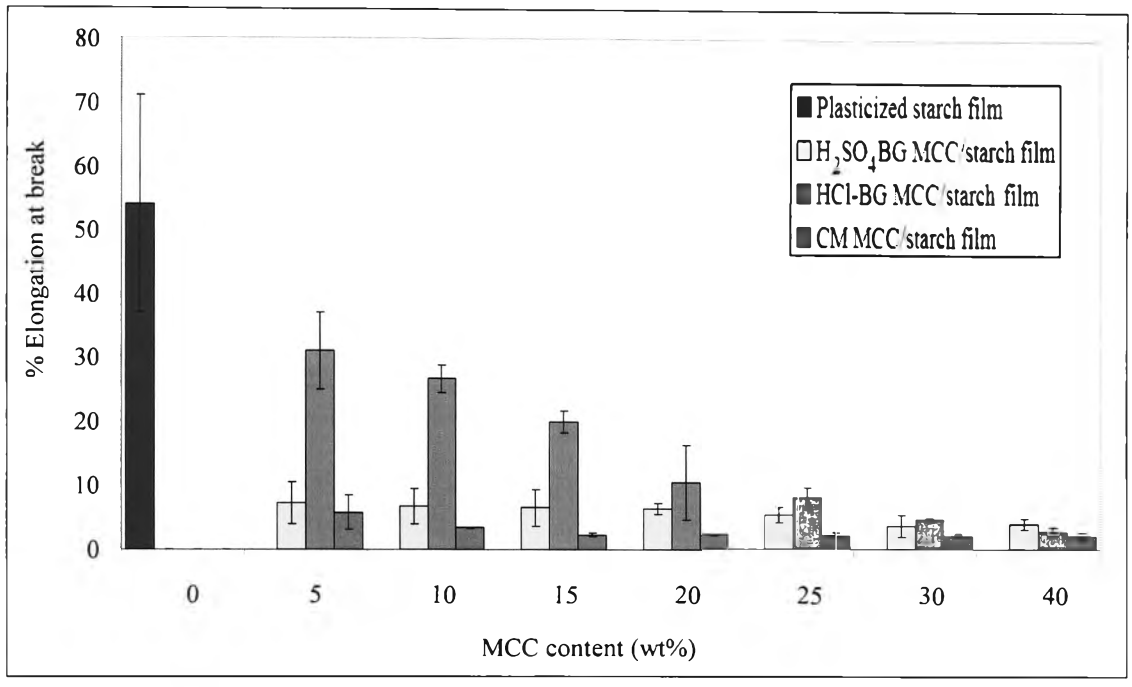


Figure 4.30 % Elongation at break of plasticized starch and biocomposite film reinforcing with bagasse and commercial microcrystalline cellulose.

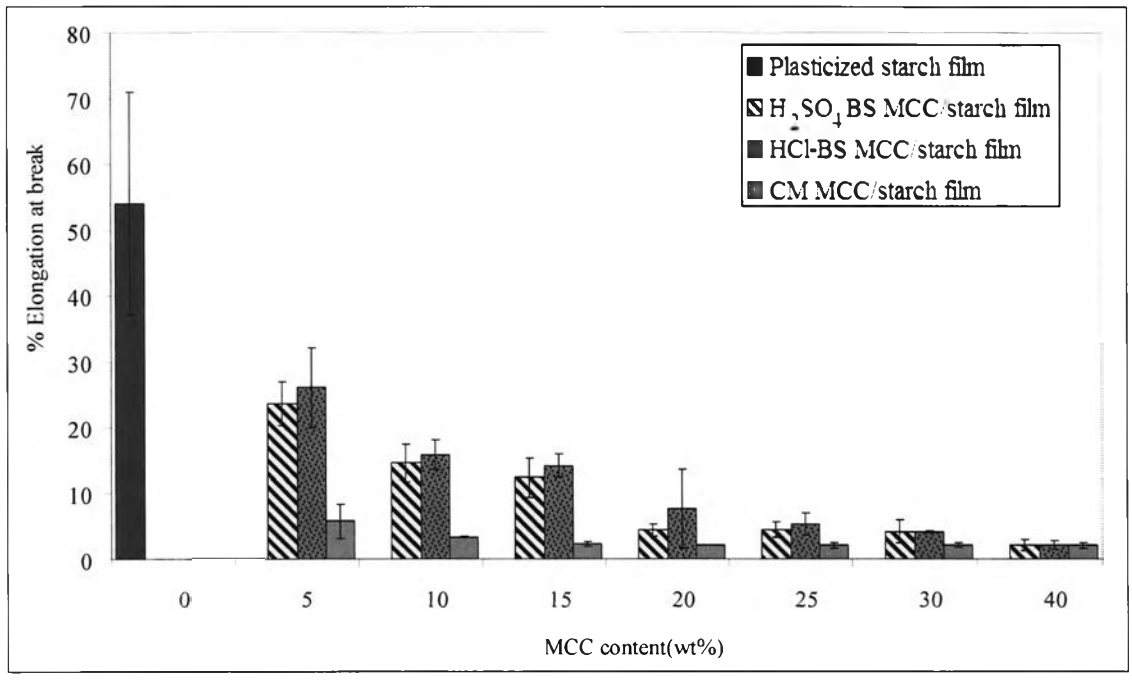


Figure 4.31 % Elongation at break of plasticized starch and biocomposite film reinforcing with banana stem and commercial microcrystalline cellulose

4.3.3 Thermal properties

4.3.3.1 Thermogravimetric Analysis (TGA)

The decomposition temperature (Td) is an important property of the film since it could indicate the processing and manufacturing temperature of polymer without an initiation of a process decomposition.

Figure 3.32 and 3.33 presented the TGA thermograms of biocomposite film at 20 wt% of bagasse and banana stem microcrystalline cellulose content, respectively. Table 4.15 summarizes the data obtained from the TGA curves. No evidence of glycerol decomposition around 150-200 °C was found in the all of films. This is probably due to the fact that the amount of glycerol is quite small compared with other compositions. As shown, all samples had the decomposition temperature at 100 °C due to moisture adsorption. Afterward, the plasticized starch presented the onset of degradation temperature Td (onset) at 290 °C with 21.08 % weight loss; whereas, the biocomposite film had two degradation steps. The Td onset of the first step of the biocomposite film reinforcing with HCl-BG microcrystalline cellulose presented around 280-290 °C was due to cellulose degradation. The result is correlated to the TGA of result of microcrystalline cellulose in 4.2.2.1. The second step occurring was around 280-290 °C was attributed to starch degradation. Similarly, for the biocomposite film reinforcing with H_2SO_4-BG microcrystalline cellulose, the first Td (onset) around 240-260 °C was due to cellulose degradation, while the second step of degradation occurred around 280-290 °C was owing to starch degradation.

Similarly results were also noticed for the biocomposite film reinforcing with banana stem microcrystalline cellulose. However, it was found that the biocomposite film reinforcing with H_2SO_4 -BS had only one step change ranging from. 240-310 °C, This may be because the Td (onset) of starch and cellulose were very closed. As shown in table 4.15 that of bleached banana stem was 281 °C, therefore, in

case of biocomposite film reinforcing with H_2SO_4-BS the overlapping of the Td (onset) of the starch and cellulose was occurred.

From the results although the biocomposite film started to degrade earlier than the plasticized starch film, they seem to have higher thermal stability than the plasticized starch considering with greater in the amount of residue at 500 °C, especially for the biocomposite films with BS microcrystalline cellulose. Comparing with the effect of acid type, the biocomposite films reinforcing with H_2SO_4 microcrystalline cellulose started to degrade earlier than the biocomposite films reinforcing with HCl microcrystalline cellulose, regardless of the type of microcrystalline cellulose. This is most likely due to the effect of acid hydrolysis used to produce the microcrystalline cellulose. The microcrystalline cellulose prepared from H_2SO_4 had lower degree of polymerization than the microcrystalline cellulose prepared from HCl as shown in 4.1.3.3. Thus, it tended to degrade easier than the microcrystalline cellulose prepared from HCl.

Regarding the effect of cellulose source, no significant difference in Td (onset) of the biocomposite film reinforcing with bagasse and banana stem microcrystalline cellulose at the same type of acid used to produce microcrystalline was observed.

Comparing with commercial microcrystalline cellulose, the biocomposite film reinforcing with commercial microcrystalline cellulose exhibited two steps of degradation. As opposed to the prepared microcrystalline cellulose, the starch matrix started to degrade prior to commercial microcrystalline cellulose filler. The first degradation step of the biocomposite film presents around 282 °C was due to starch degradation, whereas, the second degradation step at 310 °C was due to the cellulose degradation. The biocomposite films reinforcing with bagasse and banana stem microcrystalline cellulose started to degrade earlier than the biocomposite films reinforcing with commercial microcrystalline cellulose, probably because of the lower in degree of polymerization of bagasse and banana stem microcrystalline compared with

the microcrystalline cellulose. However, the percent weight loss at 250 °C and 300 °C of biocomposite film reinforcing with microcrystalline cellulose was lower than that of the biocomposite films reinforcing with bagasse and banana stem cellulose. Conclusively, plasticized starch and biocomposite containing microcrystalline celluloe showed similar thermal stability behavior, while the biocomposite film reinforcing with bagasse and banana stem although started to degrade at lower temperature but still had higher % weigh residue at higher temperature.

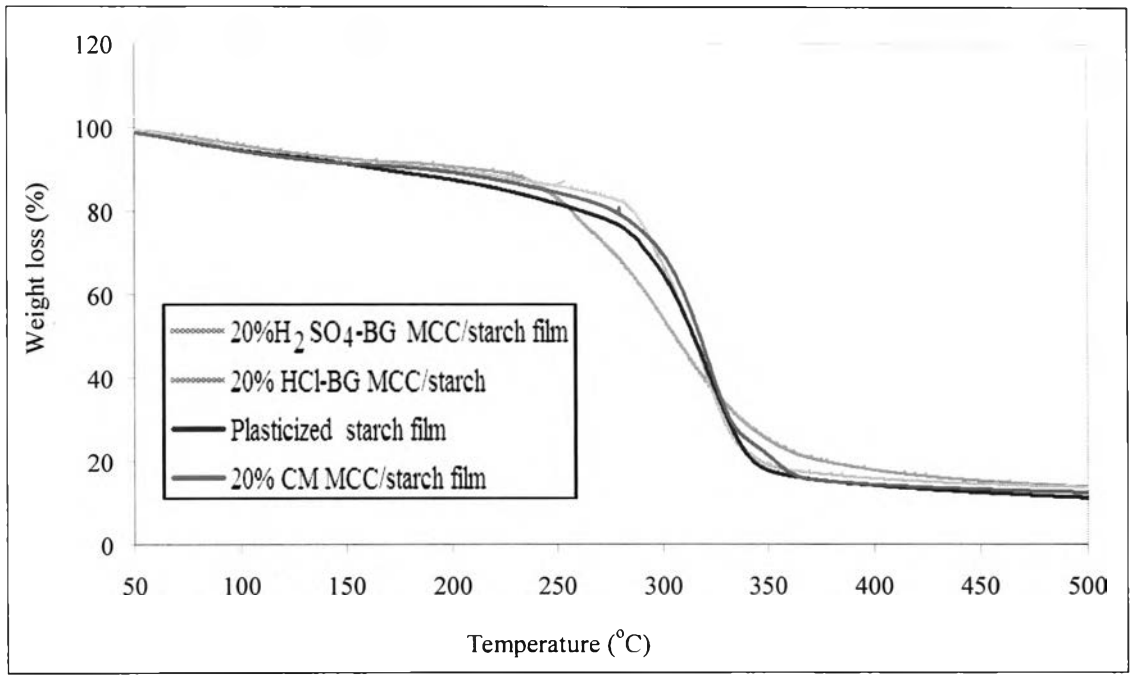


Figure 4.32 TGA curves of plasticized starch film and biocomposite film reinforcing with bagasse and commercial microcrystalline cellulose

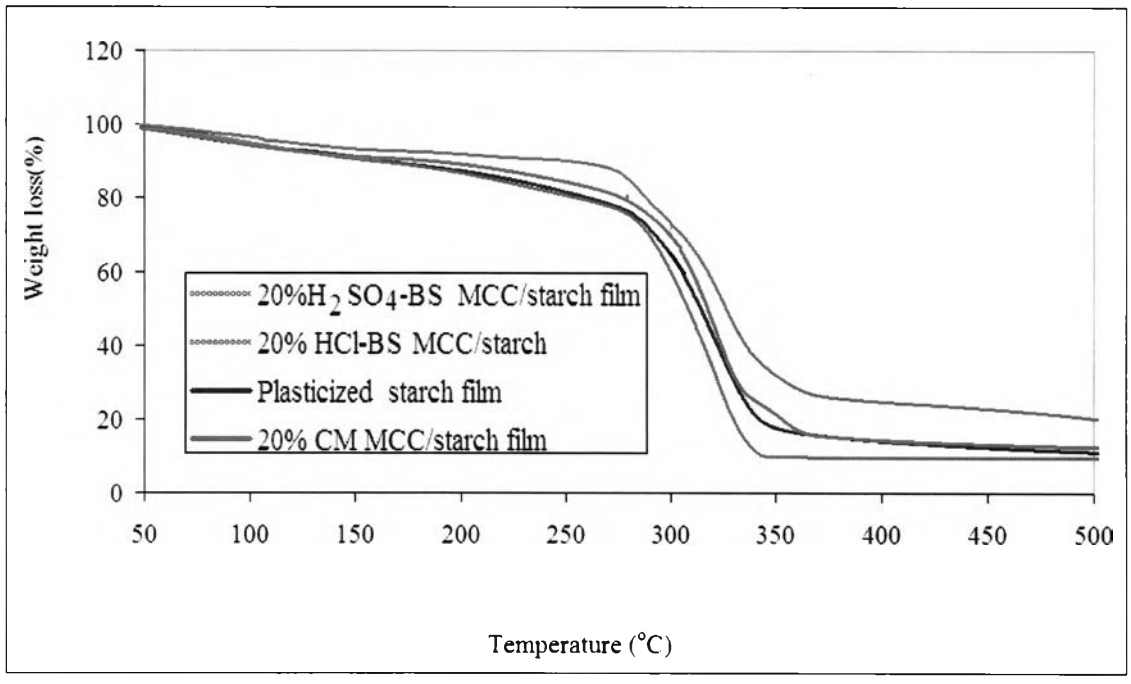


Figure 4.33 TGA curves of plasticized starch film and biocomposite film reinforcing with banana stems and commercial microcrystalline cellulose

Table 4.15 TGA data of plasticized starch and biocomposite films

Sample biocomposite film	Td (°C) (Onset)		Percent weight Loss (%)		Residue (%)
	First	Second	At 250 °C	At 300 °C	at 500 °C
Plasticized starch	-	290	-	31.54	10.92
HCl-BG/Starch	284.583	282.58	15.79	15.24	13.76
H_2SO_4-BG/Starch	240.49	282.25	18.41	28.35	13.74
HCl-BS/ Starch	264.63	294.29	10.19	17.12	18.97
H_2SO_4-BS /Starch	242.93	-	12.37	31.00	17.78
CM / Starch	282.00	310.00	18.17	30.16	12.40

4.3.3.2 Differential scanning calorymetry (DSC)

The thermal transition temperature was characterized by a differential scanning calorymetry (DSC). The melting temperature (Tm) of biocomposite films was taken as the maximum of the endothermic peak from the first heating scan. It is well known that the area enclosed under the melting endothermic peak called heat of fusion. These melting temperature and heat of fusion are correlated with the degree of crystallinity in the biocomposite films. If of the films have higher the heat of fusion, they will have greater degree of crystallinity.

The DSC thermograms of all biocomposite films were displayed in Figure 4.34 - 4.38. Table 4.16 show melting temperature and heat of fusion of the films obtained from these DSC thermograms. Obviously, the melting temperature (Tm) peak of plasticized starch was sharp and had large peak area; whereas, the melting temperature of all biocomposite films were lower and broader than the plasticized starch film. In addition, from Table 4.16, the heat of fusion (ΔH_f) of all biocomposite films were lower that that of plasticized starch and decreased, when the amount of microcrystalline cellulose was increased. These results indicated that the plasticized starch film seemed to have more degree of crystallinity than the biocomposite films since its heat of fusion of was higher than all of biocomposite films. Because molecule of plasticized starch was formed into crystalline when it was cooling, this phenomenon was called retrogradation starch. When the microcrystalline was added into the starch matrix, it would obstruction the mobility of starch chain molecule and leading to lower crystallinity in biocomposite films. Therefore, the degree of crystallinity of biocomposite film was dereased when the amount of microcrystalline cellulose was increased because of the interference of the crystal formation of starch molecules.

In case of bagasse, the heat of fusion of biocomposite films reinforcing with HCl-BG microcrystalline cellulose was lower than that of the biocomposite films reinforcing with H_2SO_4-BG microcrystalline cellulose. Similar result was observed in the case of biocomposite films reinforced with banana stem

microcrystalline cellulose, In other words, the degree of crystallinity of biocomposite films reinforcing with microcrystalline prepared using HCl was lower than that of the biocomposite films reinforcing with microcrystalline prepared using H_2SO_4. This phenomena can probably be describe by the interaction between cellulose and starch matrix. The average particle size of microcrystalline cellulose prepared using H_2SO_4 was smaller than microcrystalline cellulose prepared using HCl. Therefore, it has high surface area than the large particle size, it leading to high interaction between filler and matrix. This phenomena can induced the recrystallization in the biocomposite film. The result is in agreement with those of Mathew and Dufresne [48]. Furthermore, the results showed that the heat of fusion of biocomposite films reinforcing with bagasse microcrystalline cellulose was lower than that of biocomposite film reinforcing with banana stem microcrystalline cellulose. This means that the degree of crystallinity of biocomposite films reinforcing with bagasse microcrystalline cellulose was lower than that of biocomposite films reinforcing with microcrystalline prepared using H_2SO_4.

Comparing with commercial microcrystalline cellulose, heat of fusion of biocomposite films reinforcing with bagasse and banana stem were higher than that of biocomposite reinforcing with commercial microcrystalline cellulose. This result can be confirmed the effect of average particle size of microcrystalline, as previous discribed. Since the average particle sizes of bagasse and banana stem were smaller than micorystalline cellulose; as aresult, they have higher surface area and can induce strength interaction between matrix and filler. Therefore, the degree of crystallinity of biocomposite films reinforcing with bagasse and banana stem was higher than that of biocomposite film reinforcing with commercial microcrystalline cellulose. These results can be supported the moisture absorption and biodegradation of biocomposite films as discribed in 4.3.4 and 4.3.5.

Table 4.16 The melting temperature and heat of fusion of the plasticized starch and biocomposite films

Film	% Loading	Tm (°C)	ΔH_f (J/g)
Plasticized starch	-	176.00	216.00
HCl-BG/starch	10	137.81	143.00
	20	131.47	122.82
	30	142.34	65.49
H_2SO_4-BG/starch	10	176.00	168.00
	20	156.00	116.00
	30	136.10	130.13
HCl-BS/starch	10	140.00	164.36
	20	156.51	167.36
	30	137.00	134.76
H_2SO_4-BS/starch	10	176.00	161.00
	20	156.00	170.00
	30	137.00	98.94
CMC/ Starch	10	186.17	124.12
	20	161.40	97.37
	30	138.40	79.67

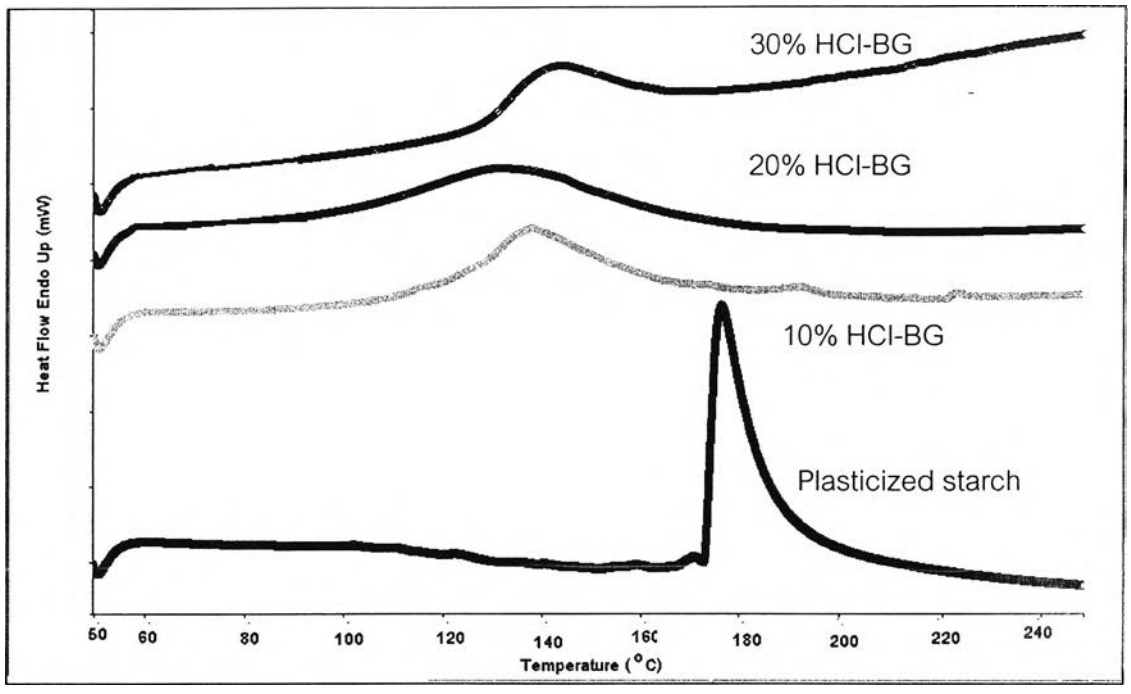


Figure 4.34 DSC thermograms of biocomposite film reinforcing with HCl-BG MCC

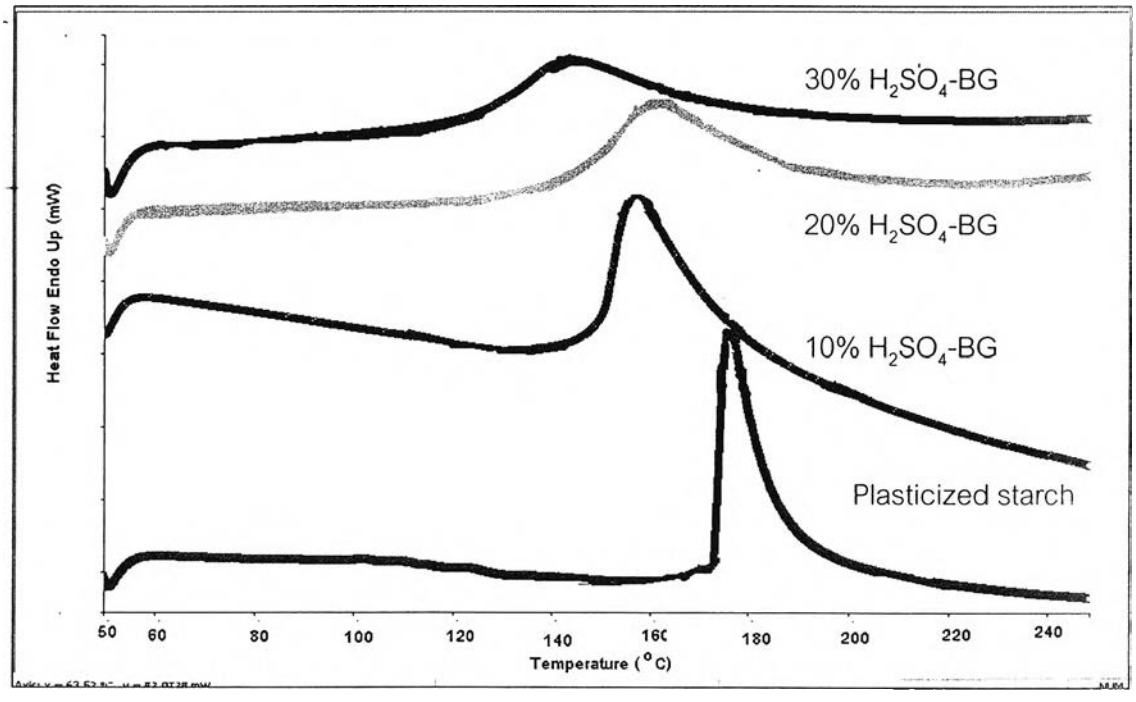


Figure 4.35 DSC thermograms of biocomposite film reinforcing with H_2SO_4-BG MCC

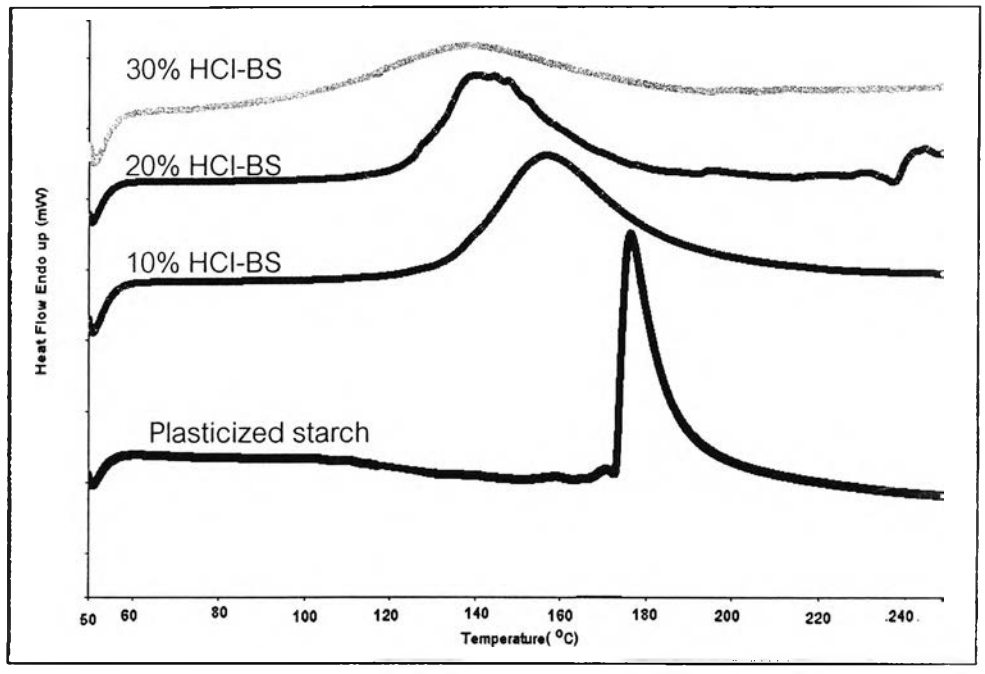


Figure 4.36 DSC thermograms of biocomposite films reinforcing with HCl-BS MCC

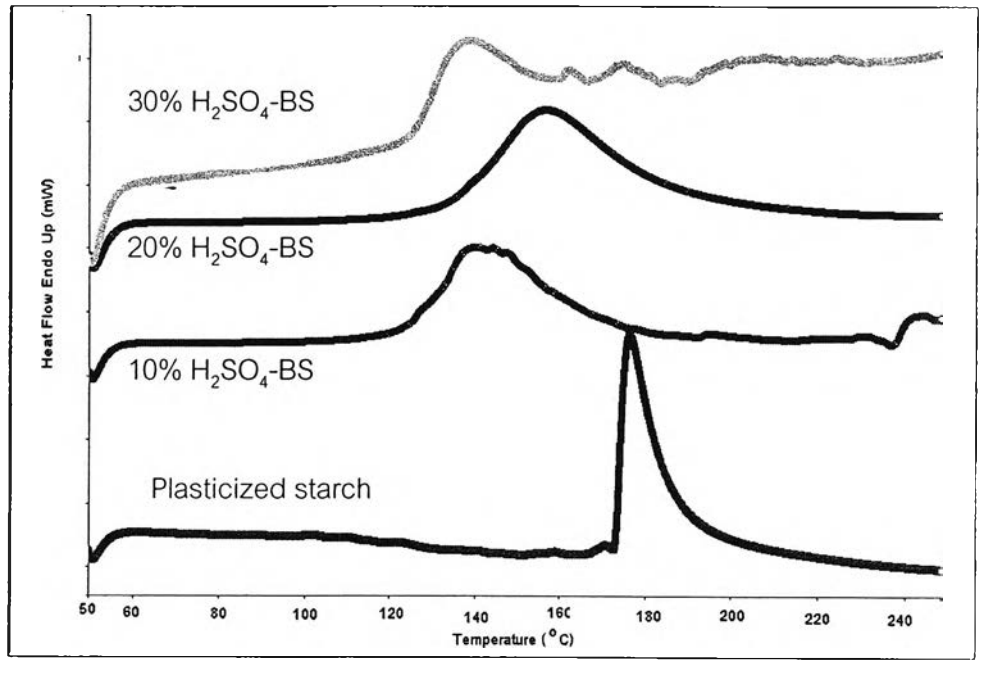


Figure 4.37 DSC thermograms of biocomposite films reinforcing with H_2SO_4-BS MCC

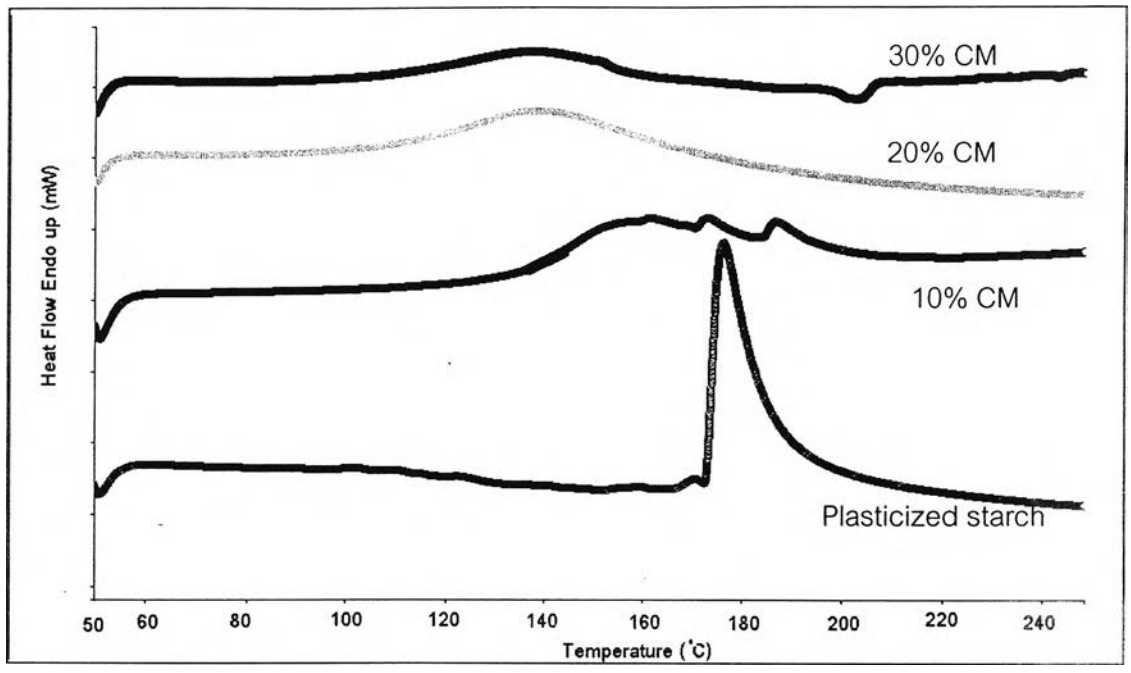


Figure 4.38 DSC thermograms of biocomposite films reinforcing with CM MCC

4.3.4 Water absorption

From Figure 4.39, water absorbsion of all the biocomposites films was higher than the plasticized starch film (0 wt % MCC). Upon increasing the amount of MCC, the water absorption of biocomposite films increased as a function of MCC content, regardless of type of MCC. The sensitivity to water of the biocomposite films should be resulted from the amorphous phase and its hygroscopic property of the microcrystalline cellulose. This amorphous phase can greatly absorb water; hence, the higher in the amount of MCC in the biocomposites films means the greater the amorphous phase compared with the pure or plasticized starch film. As a result, a pronounced effect on water absorption of the biocomposite films can be observed.

When comparing between the MCC treated with HCl and H_2SO_4, it was found that water absorption of the biocomposite films containing HCl-BG and HCl-BS microcrystalline cellulose was significantly higher than that of the biocomposite films reinforcing with H_2SO_4 – BG and H_2SO_4 – BS microcrystalline cellulose. This result was attributed to the difference in the degree of crystallinity or the amount of amorphous phase of the biocomposite films, which directly resulted from the crystallinity of the prepared MCC and the biocomposite films. As evidenced from X-ray diffraction pattern, the HCl-BG and HCl-BS microcrystalline cellulose seemed to have lower degree of crystallinity or higher amorphous phase. Therefore, these two microcrystalline cellulose should absorb water higher than the H_2SO_4-BG and H_2SO_4-BS MCC. In fact, this explanation was confirmed by the measurement of the degree of crystallinity of the biocomposite films as previously discussed that the degree of crystallinity of the bioconposite film was reinforcing with MCC prepared using HCl was lower than that of those films with H_2SO_4-MCC. Thus, the lower degree of crystallinity, the high amount of the amorphous phase; as a result, the greater value of water absorption for the biocomposite films containing HCl-microcrystalline was observed.

Regarding the effect of cellulose source, the water absorption of bagasse and banana stem MCC prepared from HCl and H_2SO_4 behaved differently.

Both HCl-BG and HCl-BS microcrystalline cellulose seemed to have comparable influence on the water absorption of biocomposite films. Whereas, in case of H_2SO_4, the bagasse MCC unexpectedly led to higher in water absorption value than the banana stem MCC throughout the MCC loading. According to the DSC results shown that the degree of crystallinity of biocomposite films reinforced with bagasse MCC was lower than that of the biocomposite film reinforcing with banana stem. Consequently, their water absorption values were higher.

Comparing with commercial microcrystalline cellulose, the water absorption biocomposite film reinforcing with commercial cellulose had higher than the biocomposite film reinforcing with bagasse and banana stem. This result can also be described by DSC analysis that the degree of crystallinity of the biocomposite film reinforcing with commercial microcrystalline cellulose was lower than that of biocomposite films reinforcing with bagasse and banana stem. Therefore, the water absorption of biocomposite films reinforcing with commercial microcrystalline was greater than that of the obviously biocomposite film reinforcing with bagasse and banana stem microcrystalline cellulose.

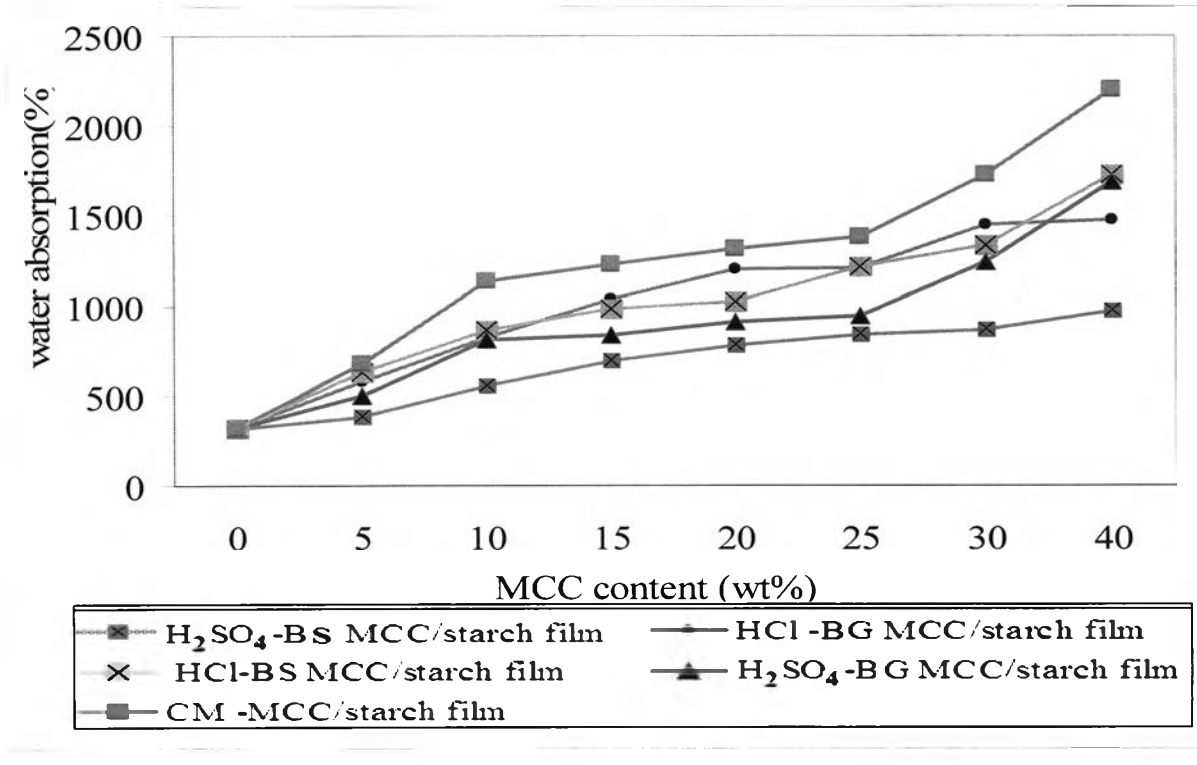


Figure 4.39 Water absorption of plasticized starch and biocomposite films

4.3.5 Biodegradation

4.3.5.1 Physical appearance

4.3.5.1.1 Appearance

The biodegradability of plasticized starch and biocomposite film was studied by soil burial test. The experiment was carried out up to 30 days. The physical appearance of both plastized starch and biocomposite films had been change significantly as shown in Figure 4.40-4.41

For the plasticized starch film, The Figure 4.40 displayed that the platicized starch had a relatively smooth surface with high transparency at the initial time (0 day). After 3 days, the plasticized starch showed deformation and expansion in its shape. Furthermore, the transparency of the film was decreased while it opacity was increased compared to the initial stage. After 9 days, the plasticized starch film tended to cracking and it was difficult to perform weight measurement. The plasticized starch film was completely disappeared into soil after 16 days of exposure.

The Figure 4.40 and 4.41 showed the physical appearance of the biocomposite films reinforcing with HCl-BG and H_2SO_4-BG microcrystalline cellulose. These figures illustrated that the deformation of all biocomposite films was increased when the exposure time increased. After 3 days, the biocomposite film become brittle material and had light weigh. Furthermore, the transparency of biocomposite film was decreased. All of biocomposite film reinforcing with bagasse microcrystalline disappeared after 16 days. In case of biocomposite film reinforcing with HCl-BG microcrystalline cellulose, at 5 and 10 wt % of microcrystalline cellulose content, the biocomposite film cracked into small pieces after 9 days and it is can not be weighed due to it is disappear in soil after 16 days. In addition, at 15 wt% of microcrystalline cellulose content, the biocomposite film cracked into small pieces eailer (after 6 days), Moreover, it was completely disappeared in the soil after 9 days.

At higher microcrystalline cellulose content (i.e. 20-30 wt %), the biocomposite film was cracked into small pieces and disappeared only after 3 days and 6 days, respectively.

Similarly, at low microcrystalline cellulose content (5-10 wt%), the biocomposite film reinforcing with H_2SO_4-BG microcrystalline cellulose cracked into small pieces after 9 days and disappeared in the soil after 16 days. At higher microcrystalline cellulose content (i.e. 15-30 wt%), the biocomposite film cracked into small pieces after 3 days and totally disappeared in the soil after 6-9 days.

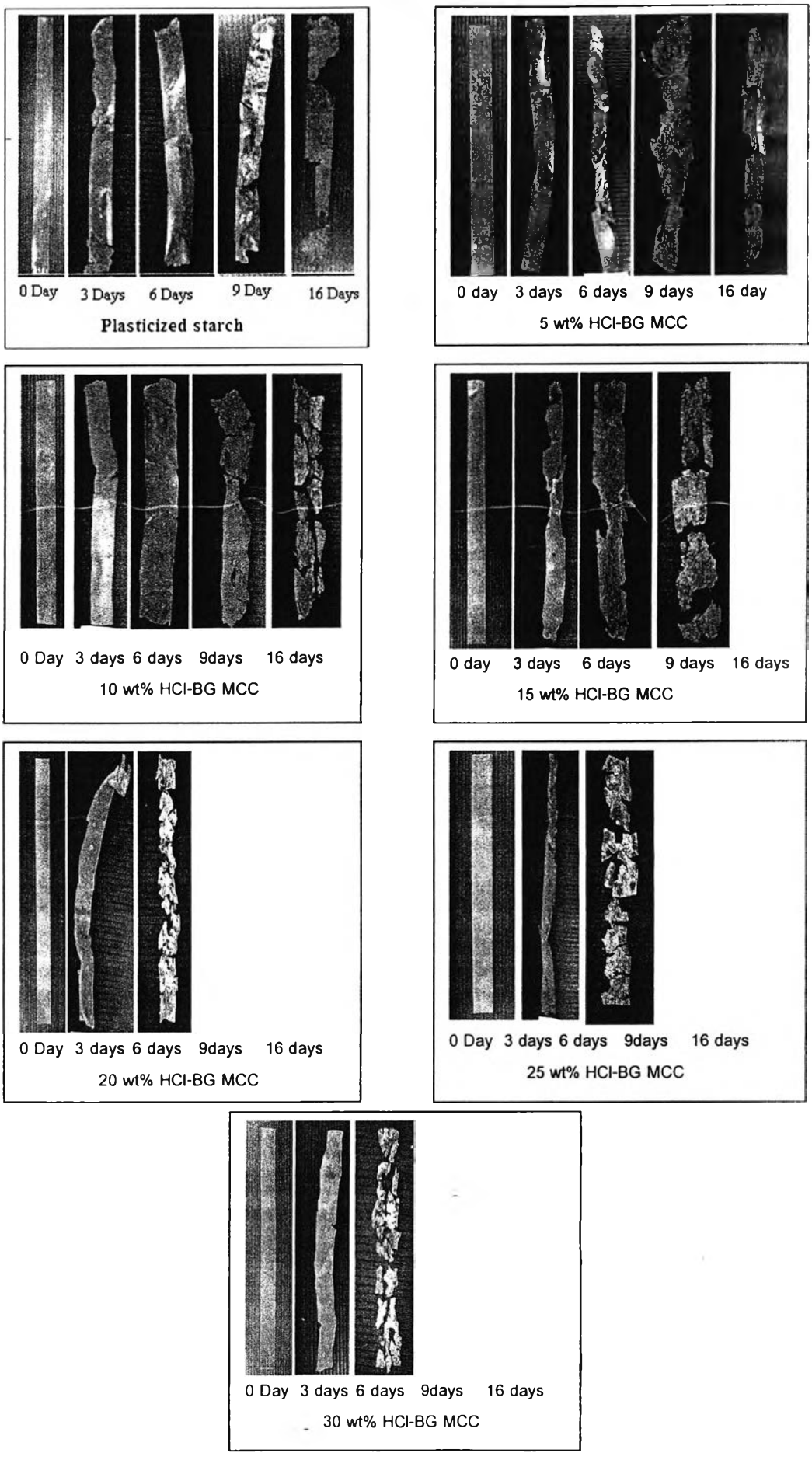


Figure 4.40 Physical appearance of biocomposite films reinforcing with HCl-BG MCC after burial test

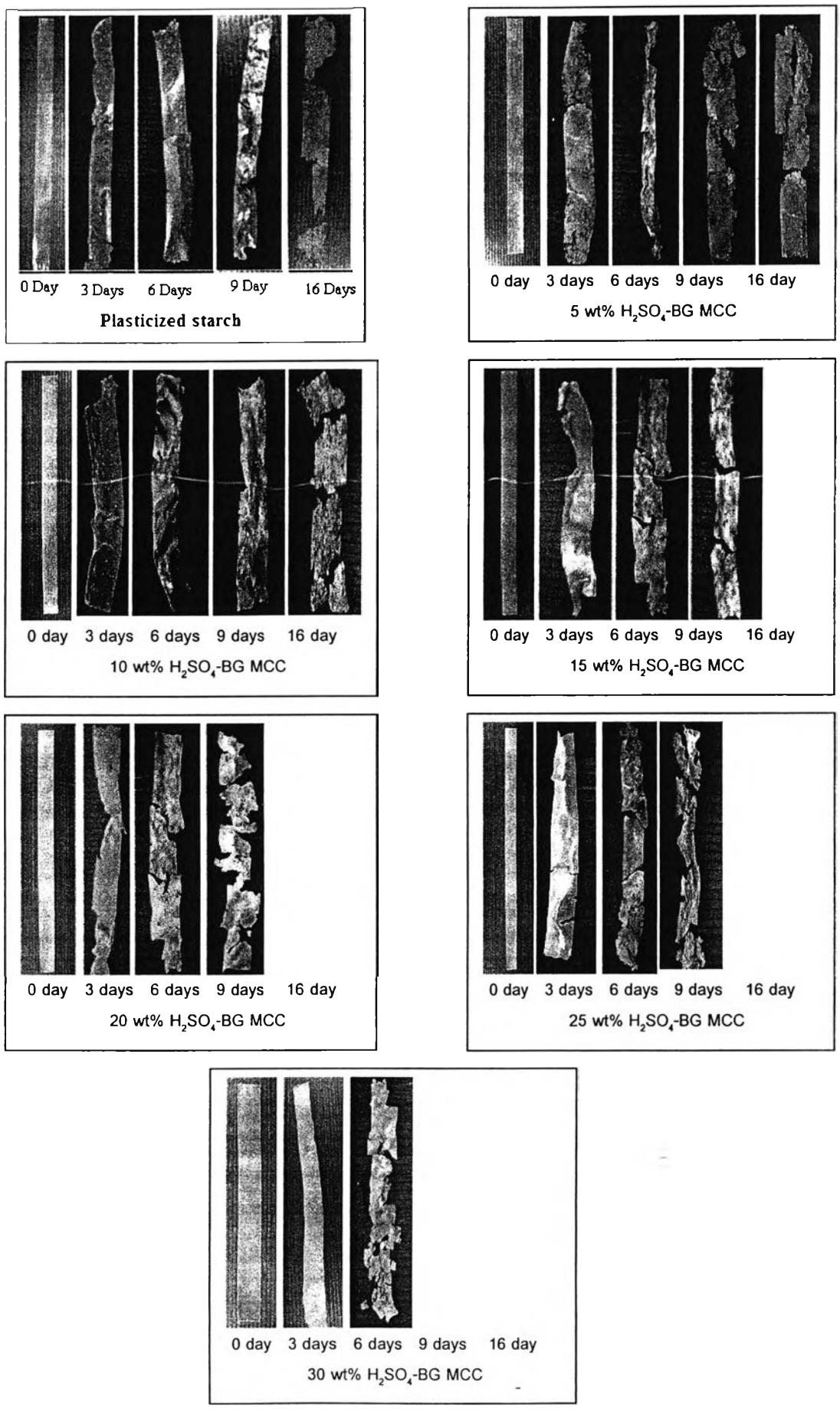


Figure 4.41 Physical appearance of biocomposite films reinforcing with H_2SO_4-BG MCC after burial test

For the biocomposite film reinforcing with HCl-BS and H_2SO_4-BS microcrystalline cellulose, Figure 4.42 shows 4.43 show that the deformation of biocomposite film was increased as a function of time. Figure 4.42 showed that at low microcrystalline cellulose content (i.e. 5-10 wt%), the biocomposite film cracked into small pieces after 9 days and disappeared in the soil after 16 days. In addition, the biocomposite film reinforcing at high contents of HCl-BS microcrystalline cellulose (i.e. 20-30 wt%) showed that it tended to cracked into small pieces and entirely disappeared in the soil after 3 days and 6 days, respectively. Similar results were observed for the biocomposite film reinforcing with H_2SO_4-BS microcrystalline cellulose.

These results can be indicated that the physical appearance changes as the deformation, crack, and disappearance of biocomposite film were noticeably obvious than the plasticized starch film. Furthermore, these changes increased when the amount of microcrystalline cellulose increased. The biocomposite film reinforcing with the microcrystalline cellulose treated by HCl had shown pronounced effect on the biodegradability of the biocomposite film than the biocomposite film reinforcing with microcrystalline cellulose treated by H_2SO_4.

These results were directly were directly correlated with the water absorption properties of the films, which attributed to the film swelling; as a result the deformation of biocomposite film was occurred. In addition, the water absorbed in the film allowed the microorganisms to grow and utilize the film, contributing to the deterioration in physical appearance of the biocomposite films. Moreover, the partial component such as plasticizer can be dissolved by water diffusion into the biocomposite films. This behavior leads to the biocomposite film having the stiffness properties and seems to be cracked easily. Accordingly, the biocomposite films had more hygroscopic properties than the plasticized starch film since the amorphous phase in microcrystalline cellulose attributed to the high water absorption. Therefore, the biocomposite film had greater deformation than the plasticized starch film. When the amount of microcrystalline cellulose increased that means the hygroscopic properties of

biocomposite film was increased. Thus, the deformation of biocomposite film was increased when the amount of microcrystalline cellulose increase.

From the water absorption results, the biocomposite film reinforcing with microcrystalline cellulose treated by HCl had greater hygroscopic properties than the biocomposite film reinforcing with microcrystalline cellulose treated by H_2SO_4. Therefore, the biocomposite film reinforcing with microcrystalline cellulose treated by HCl had higher deformation and biodegradbility the biocomposite film reinforcing with microcrystalline cellulose treated by H_2SO_4.

Regarding the effect of cellulose source with the same acid treatment, the biocomposite film reinforcing with bagasse microcrystalline cellulose had better hygroscopic properties than the biocomposite film reinforcing with banana stem microcrystalline cellulose. Therefore, the biocomposite film reinforcing with bagasse microcrystalline cellulose can be degradaded faster than the biocomposite film reinforcing with banana microcrystalline cellulose.

Comparing with the commercial microcrystalline cellulose, the biocomposite films reinforcing with commercial microcrystalline cellulose seemed to be degraded faster than the biocomposite film reinforcing with bagasse and banana stem microcrystalline cellulose at the same content of microcrystalline cellulose. From Figure 4.44, the biocomposite film was completely disappered after 6 days, even at 15 wt% of microcrystalline content.

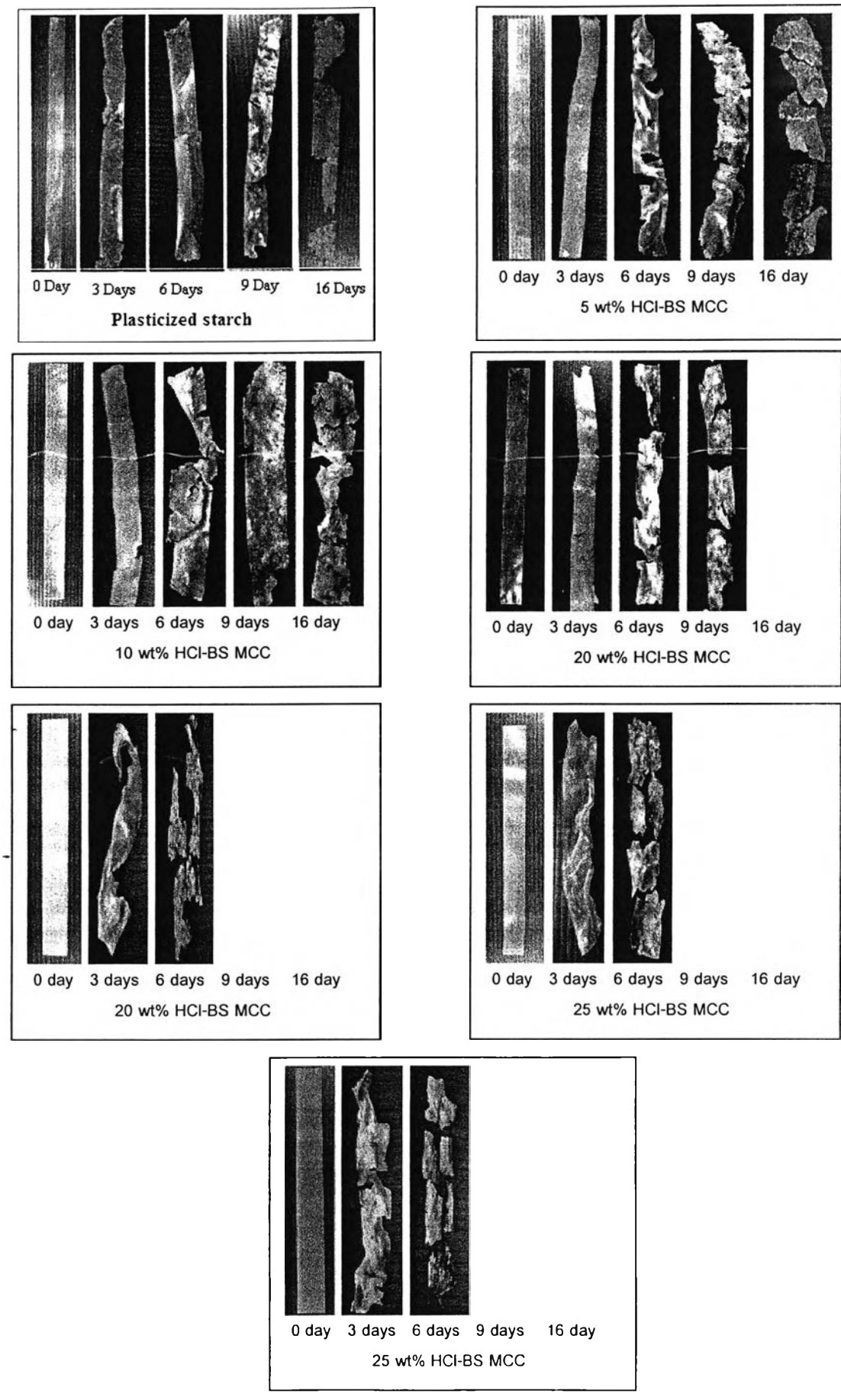


Figure 4.42 Physical appearance of biocomposite films reinforcing with HCl-BS MCC after burial test

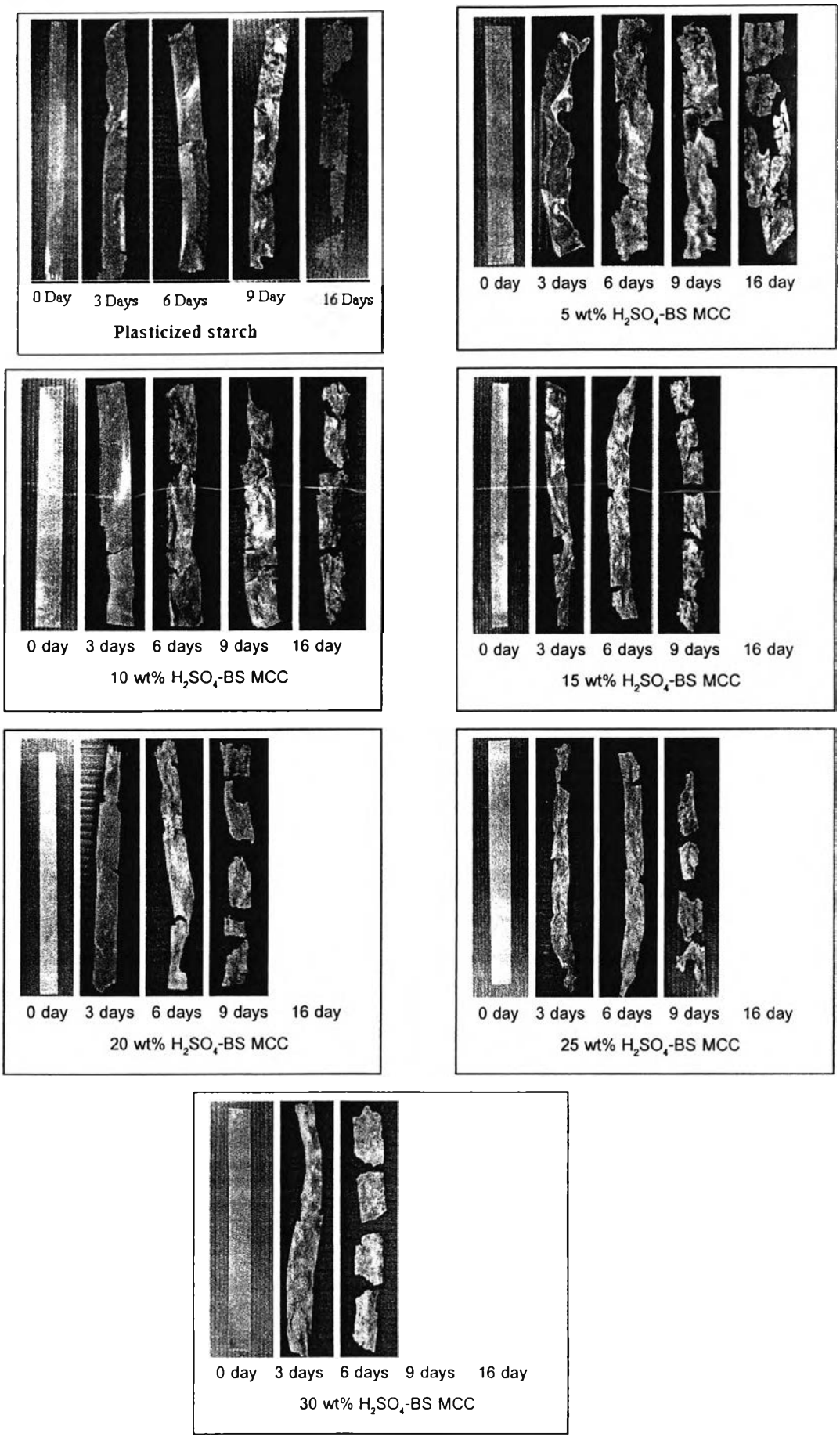


Figure 4.43 Physical appearance of biocomposite films reinforcing with H_2SO_4-BS MCC after burial test

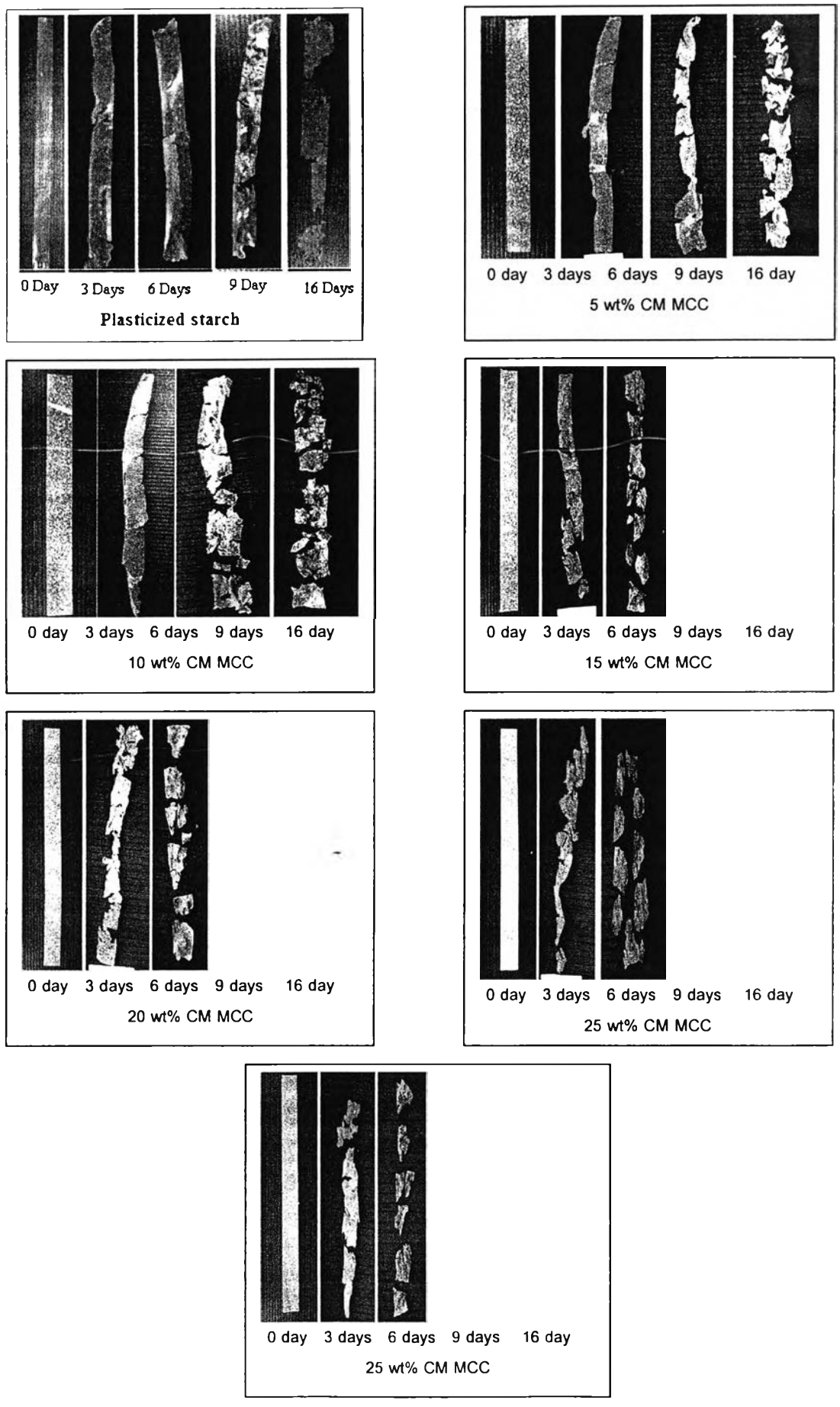


Figure 4.44 Physical appearance of biocomposite films reinforcing with CM MCC after burial test

4.3.5.1.2 Morphological behavior

The SEM micrographs of plasticized starch and biocomposite film before soil burial test were illustrated previously in Figure 4.45-4.49. After burial in soil, the biocomposite film had rough surface with a few number of small holes on the film surface. The biodegradability of all biocomposite films increased, as evidence by an increasing amount of these tiny holes. A small hole and surface roughness of biocomposite film were due to the degradable of the films, which resulted from attacking of microorganisms and the desolvation of the film component.

Comparatively, in case of bagasse, the surface roughness of biocomposite films reinforced with HCl-BG microcrystalline cellulose was higher than that of biocomposite films reinforced with H_2SO_4-BG microcrystalline cellulose. In fact,similar trend was also formed for the biocomposite films reinforcing with banana stem microcrystalline cellulose. These results confirmed that the biocomposite film reinforcing with microcrystalline cellulose prepared using HCl was more effective than microcrystalline cellulose prepared using H_2SO_4.

Considering the effect of cellulose source, the SEM micrographs of bagasse and banana stem did not show any significant difference. However, it seems to be that the biocomposite films with bagasse microcrystalline are more biodegrable than those films with banana stem microcrystalline cellulose.

Comparing with commercial microcrystalline cellulose, Figure 4.49 showed the SEM micrographs of biocomposite reinforced with commercial microcrystalline cellulose. The results showed that the biocomposite film reinforced with commercial microcrystalline cellulose had higher surface rougness with a great amount of holes than the biocomposite films with bagasse and banana stem microcrystalline cellulose, indicating the greater biodegradability than the latter biocomposite films.

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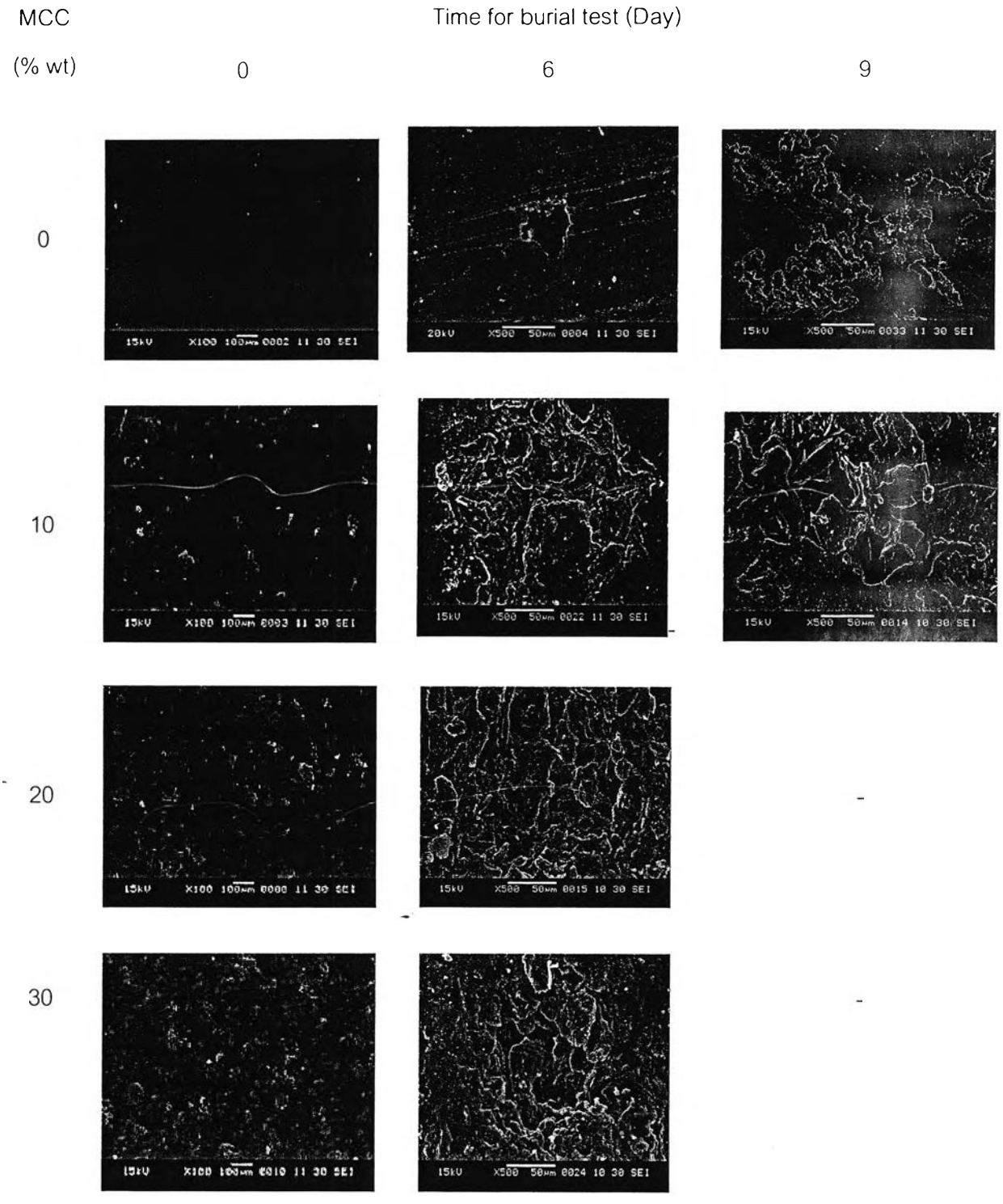

Figure 4.45 SEM micrographs of the surface of biocomposite films reinforced with HCl-BG microcrystalline cellulose after soil burial test for 6 days

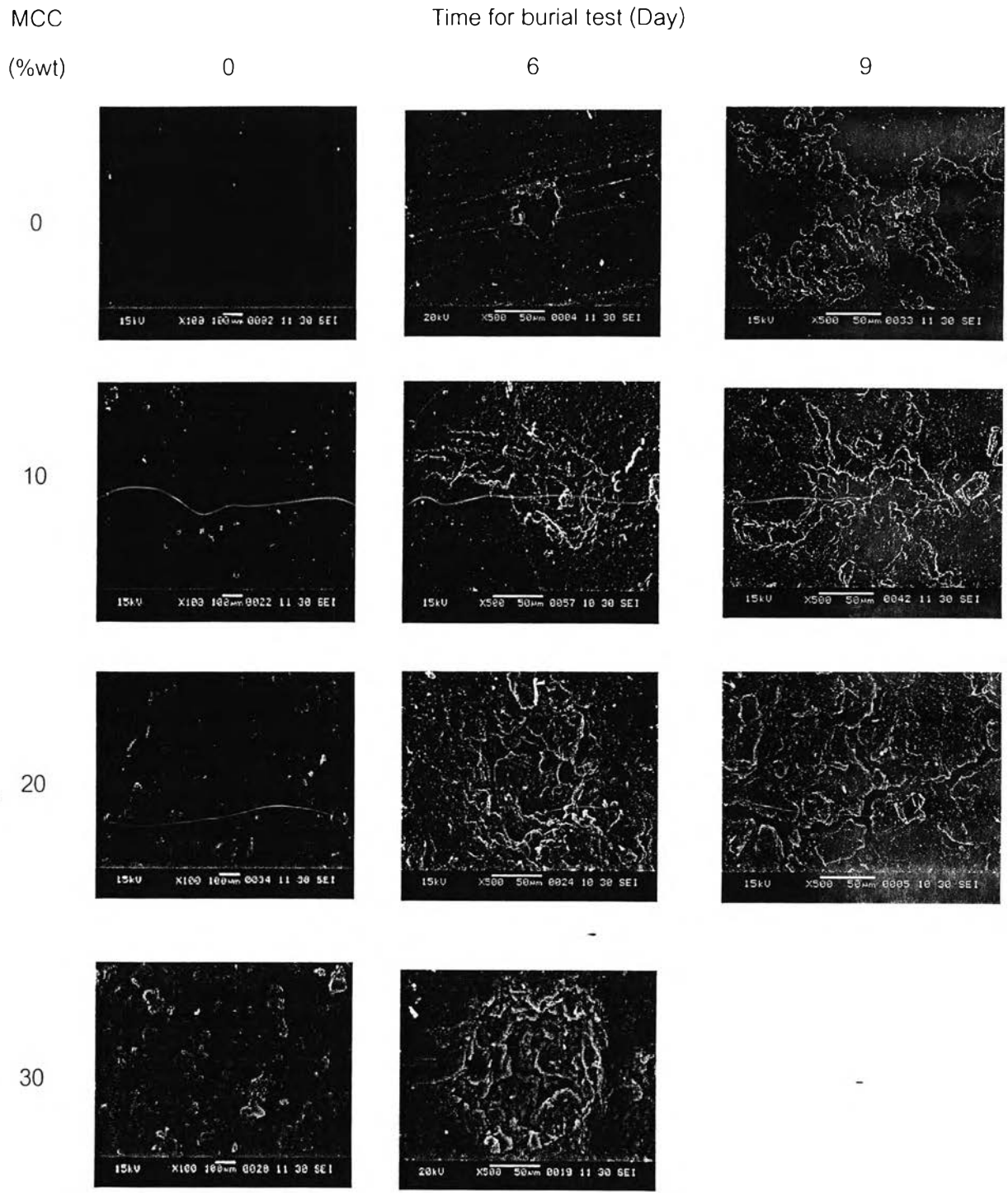

Figure 4.46 SEM micrographs of the surface of biocomposite films reinforcing with H_2SO_4-BG microcrystalline cellulose after soil burial test for 6 days

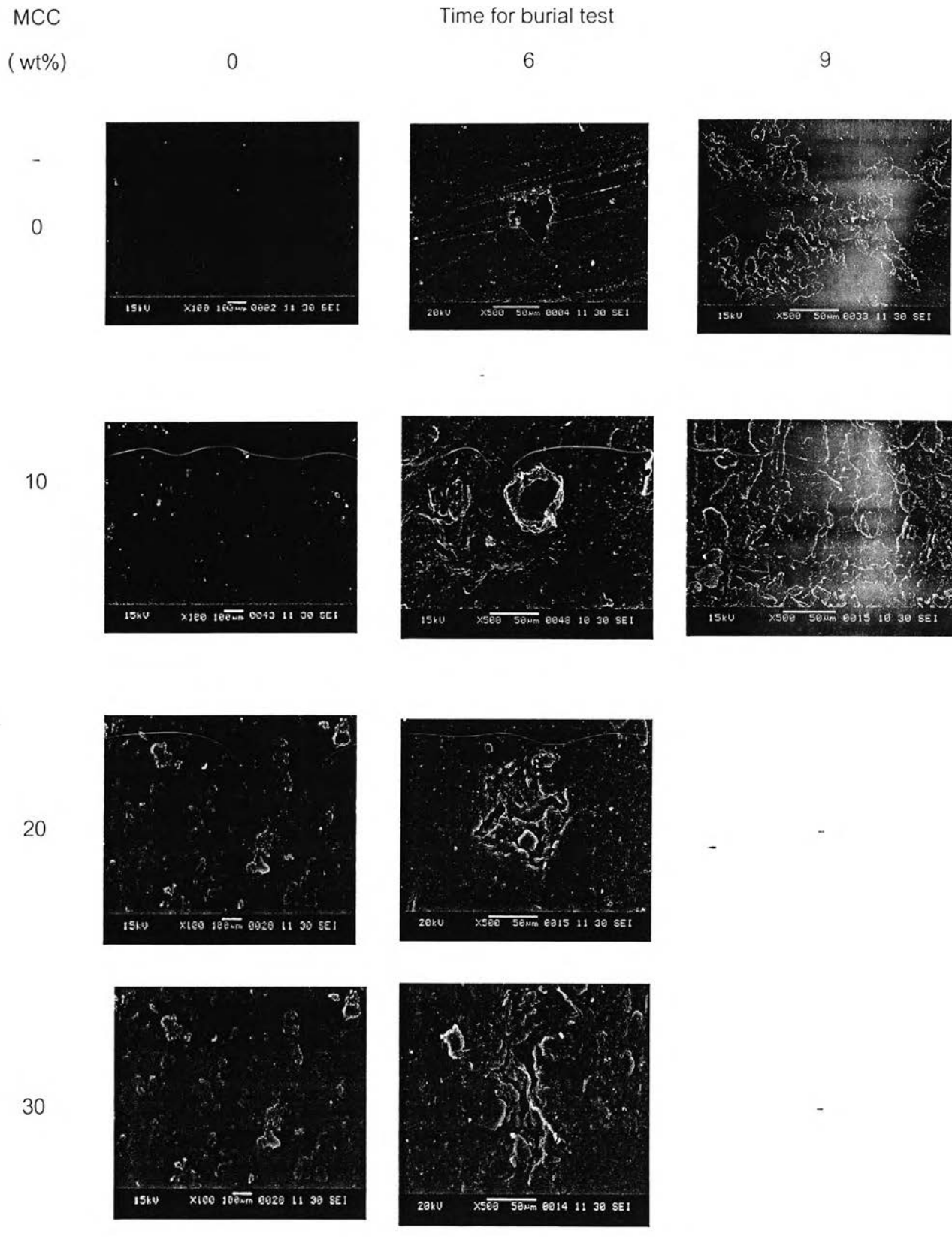

Figure 4.47 SEM micrographs of the surface of biocomposite films reinforcing with HCl-BS microcrystalline cellulose after soil burial test for 6 days

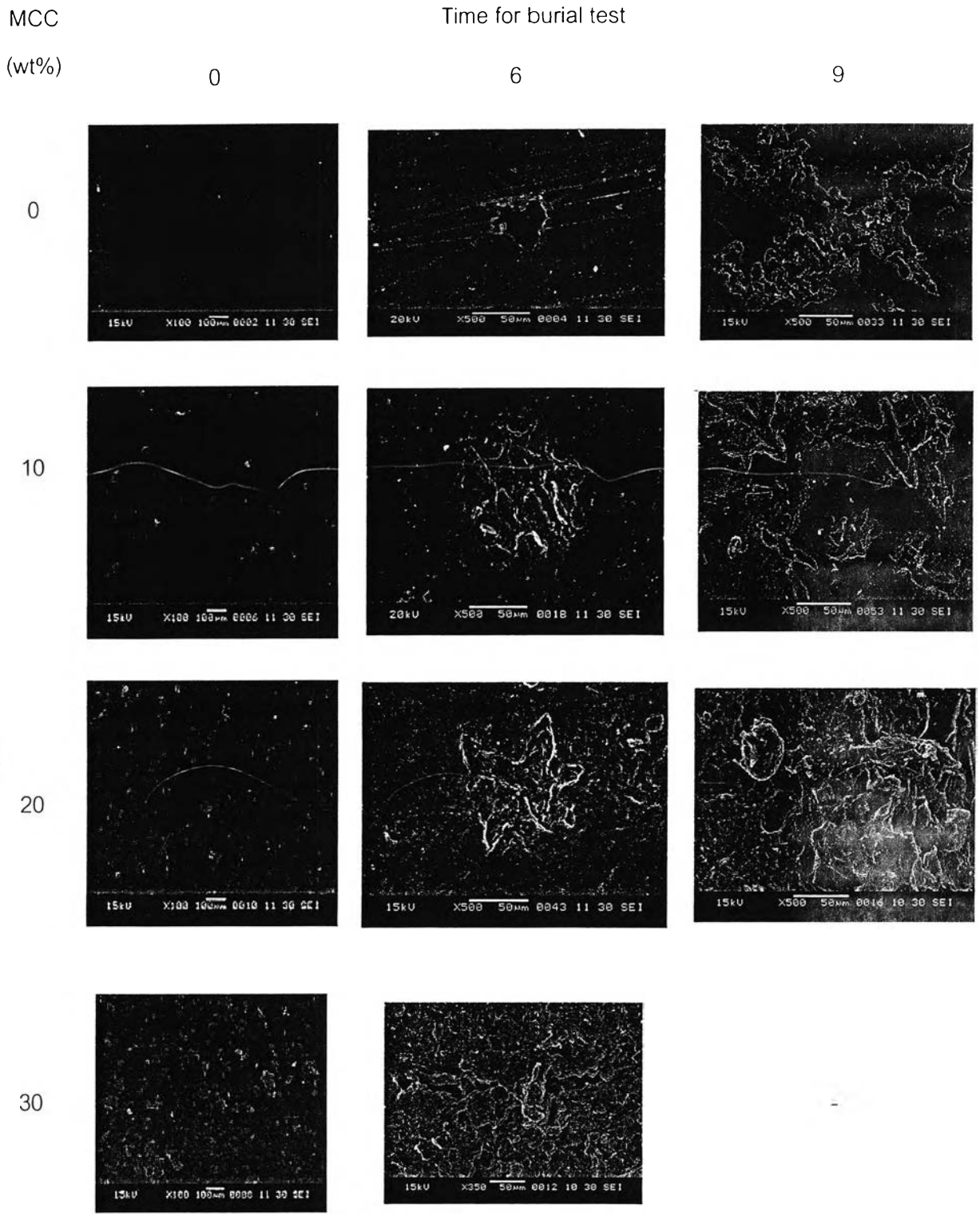

Figure 4.48 SEM micrographs of the surface of biocomposite films reinforcing with H_2SO_4 –BS microcrystalline cellulose after soil burial test for 9 days

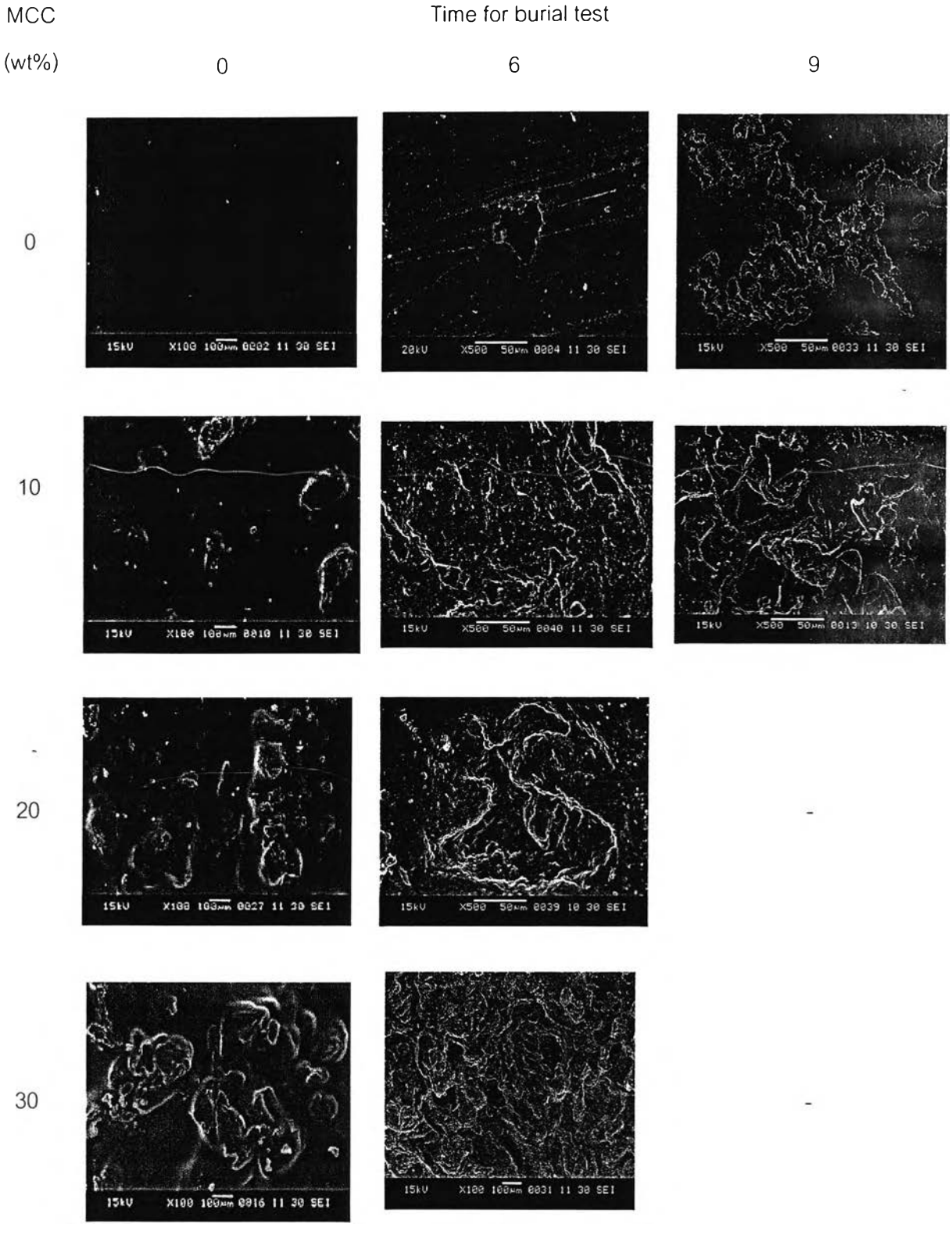

Figure 4.49 SEM micrographs of the surface of biocomposite films reinforcing with CM microcrystalline cellulose after soil burial test for 9 days

4.3.5.1.3 Weight loss

The biodegradation of biocomposite film was tested by soil burial method. It is an outdoor experiment. All of the tested specimens had the same shape and size to avoid the effects of the film's shape on its biodegradability.

Considering on the effect of time, The Figure of all biocomsite films illustrate that the percent weight loss of all the films increased as a function of time and mount of microcrystalline. Moreover, the biocomposite film samples can be not weighed, when the time was over than 16 days, since most of the films became small fracments and were difficult to collect every parts of them.

The Figure 4.51 and 4.52 show the percent are weight loss of biocomposite films reinforcing with HCl-BG and H_2SO_4 –BG. These Figures shown at the same microcrystalline content, the % weight loss of biocomposite film reinforcing with HCl-BG microcrystalline cellulose presents were had higher than that of the biocomposite film reinforcing H_2SO_4 –BG microcrystalline cellulose. Similarly, the biocomposite film reinforcing with HCl-BS microcrystalline cellulose had greater % weight loss than the biocomposite film reinforcing with H_2SO_4-BS at the same microcrystalline content. These results can be attributed to the water absorption properties of biocomposite film. The water absorbed on the material leads to the microorganisms to grow and utilize the materials as energy source. The result in 4.3.4 shows the hydrophilic of the biocomposite film increased; while the microcrystalline cellulose increased. This behavior caused an increasing in the % weigh loss of the the biocomposite film increased. In addition, the results from 4.3.4 showed that the biocomposite film reinforcing with HCl-BG microcrystalline had more hydrophilicity than the biocomposite film reinforcing with H_2SO_4-BG microcrystalline cellulose at the same microcrystalline content that is attributed to the affect of the average particle size and dispersion of the microcrystalline cellulose. Similarly, at the same of microcrystalline content, the biocomposite film reinforcing HCl-BS microcrystalline cellulose had greater hydrophilicity than the biocomposite film reinforcing with H_2SO_4 –BS microcrystalline

cellulose because the HCl-BS microcrystalline cellulose had larger particle size and low dispersion in the starch matrix. Therefore, the biocomposite film reinforcing with HCl-BS microcrystalline cellulose had higher the percent weight loss than the biocomposite film reinforcing with H_2SO_4-BS at the same microcrystalline content.

Regardingly, the effect of cellulose source, the Figure 4.51 and 4.53 display that the biocomposite film reinforcing with HCl-BG MCC had more percent weight loss than the biocomposite film reinforcing with HCl-BS MCC at the same microcrystalline content. This result can be described that this behavior can be described by DSC and water absorption result in 4.3.3.2 and 4.3.4, respectively. The degree of crystallinity of biocomosite film reinforcing with HCl-BG microcrystalline cellulose seemed to have higher than that of biocomposite films reinforcing with HCl-BS microcrystalline cellulose. Therefore, the biocomosite films reinforcing with HCl-BG microcrystalline cellulose is influences on the water absorption than that of the biopcomposite film reinforcing with HCl-BS. Furthermore, it contributed to higher percent water absorption. Accordingly, percent weight loss of the biocomposite film reinforcing with HCl-BG microcrystalline cellulose was higher than the biocomposite film reinforcing with HCl-BS microcrystalline cellulose

In case of H_2SO_4-BG and H_2SO_4-BS, this result can be described by DSC and water absorption similar to previous discuss. The degree of crystallinity of biocomosite film reinforcing with H_2SO_4-BG microcrystalline cellulose seemed to have higher than that of biocomposite films reinforcing with H_2SO_4-BS microcrystalline cellulose. Therefore, the biocomosite films reinforcing with H_2SO_4-BG microcrystalline cellulose is influences on the water absorption than that of the biopcomposite film reinforcing with H_2SO_4-BS. Therefore, the percent weight loss of the biocomposite film reinforcing H_2SO_4-BS higher than the biocomposite film reinforcing H_2SO_4-BG at the same microcrystalline content.

commercial microcrystalline cellulose had increased when the time increased. The percent weight loss of biocomposite film reinforcing commercial microcrystalline cellulose had higher than the biocomposite reinforcing with bagasse and banana stem microcrystalline cellulose at the same microcrystalline content because the biocomposite reinforcing with microcrystalline present the more hydrophilic than the biocomposite reinforcing with bagasse and banana stem. This phenomena is attributed to affect of the average particle size and dispersion of microcrystalline cellulose in the starch matrix.

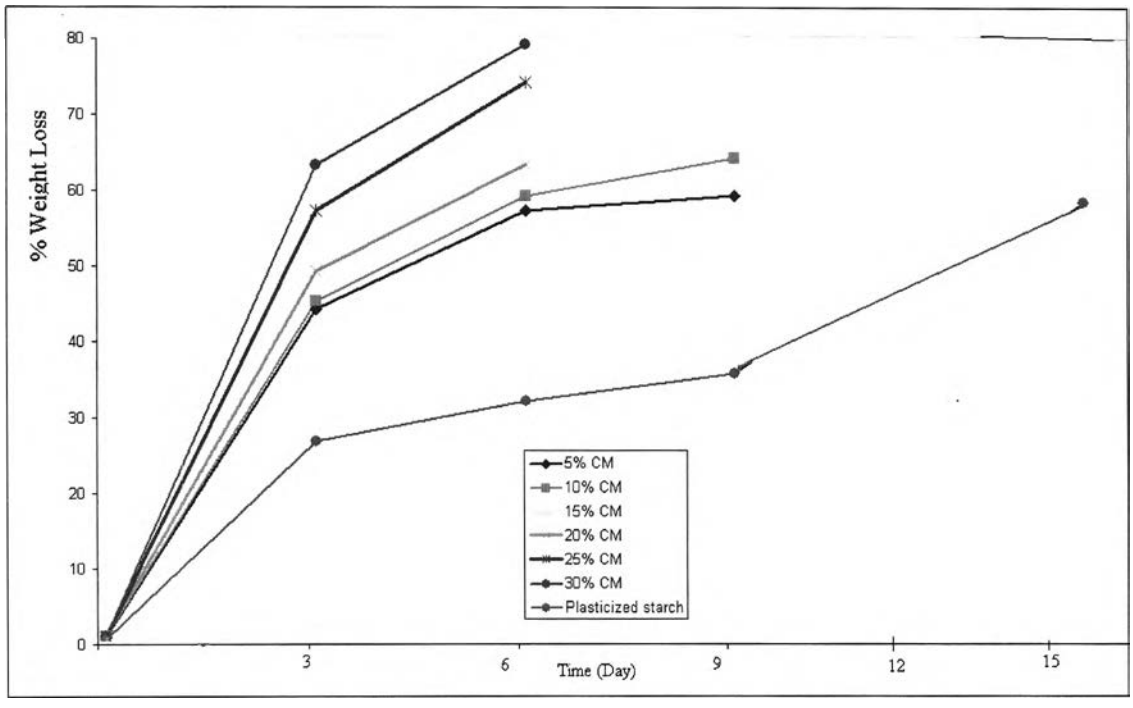

Figure 4.50 %weight loss of biocomposite film reinforcing with commercial microcrystalline cellulose

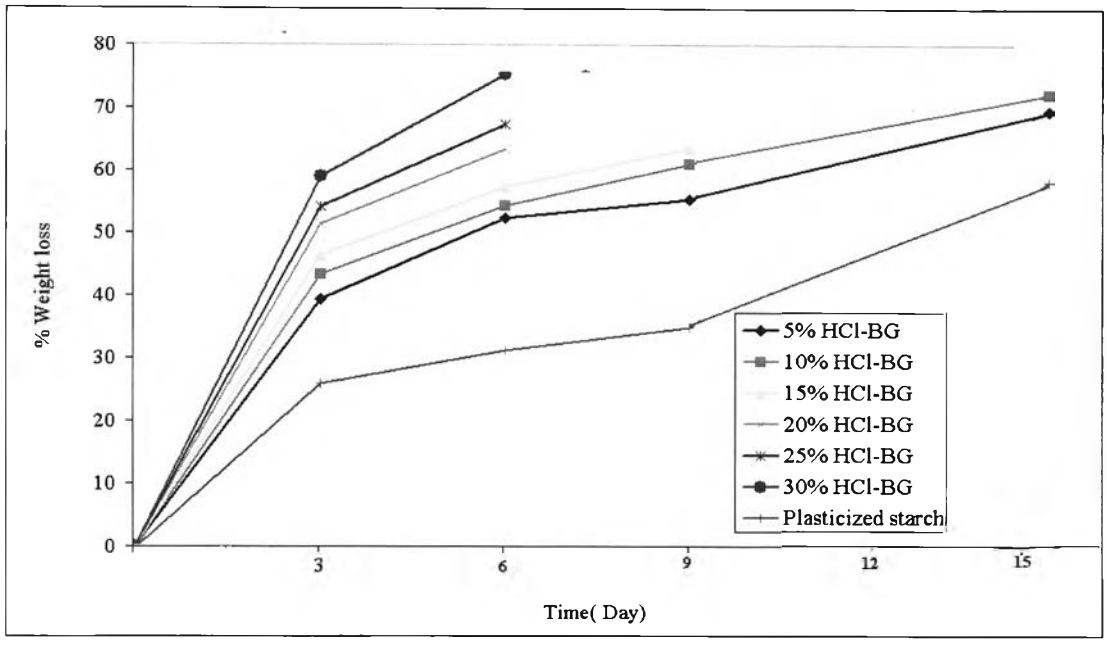

Figure 4.51 %weight loss of biocomposite film reinforcing with HCl-BG microcrystalline cellulose

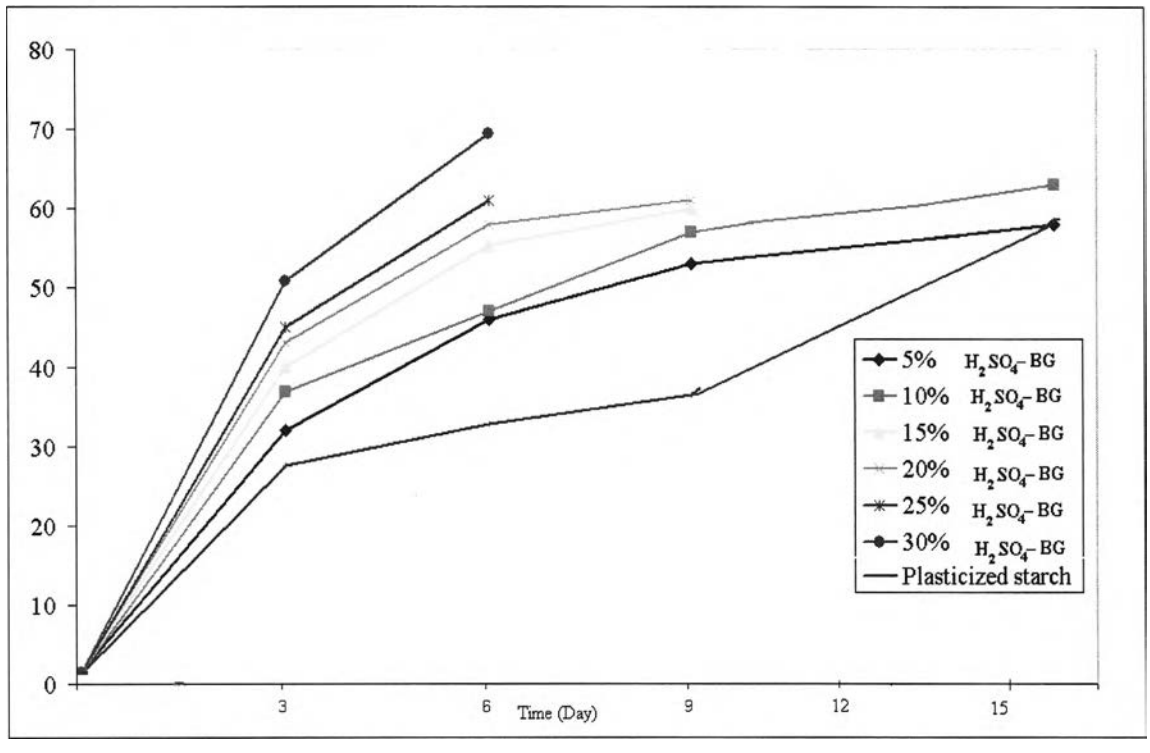

Figure 4.52 %weight loss of biocomposite film reinforcing with H_2SO_4-BG microcrystalline cellulose

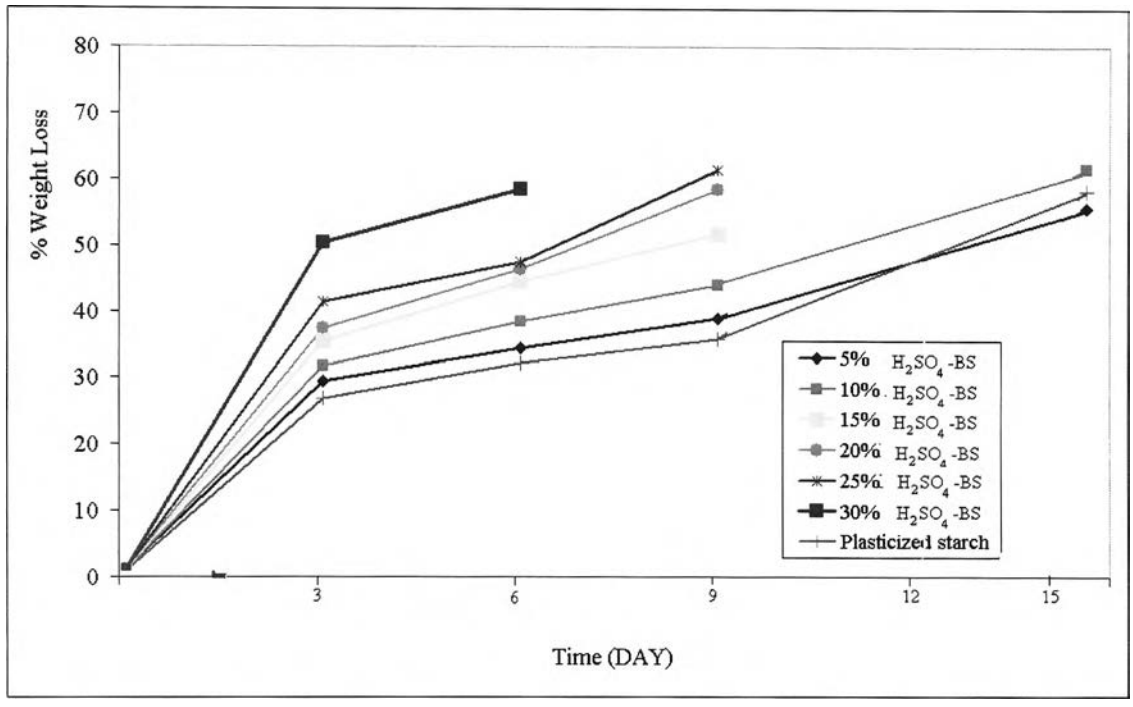

Figure 4.53 %weight loss of biocomposite film reinforcing with HCl-BS microcrystalline cellulose

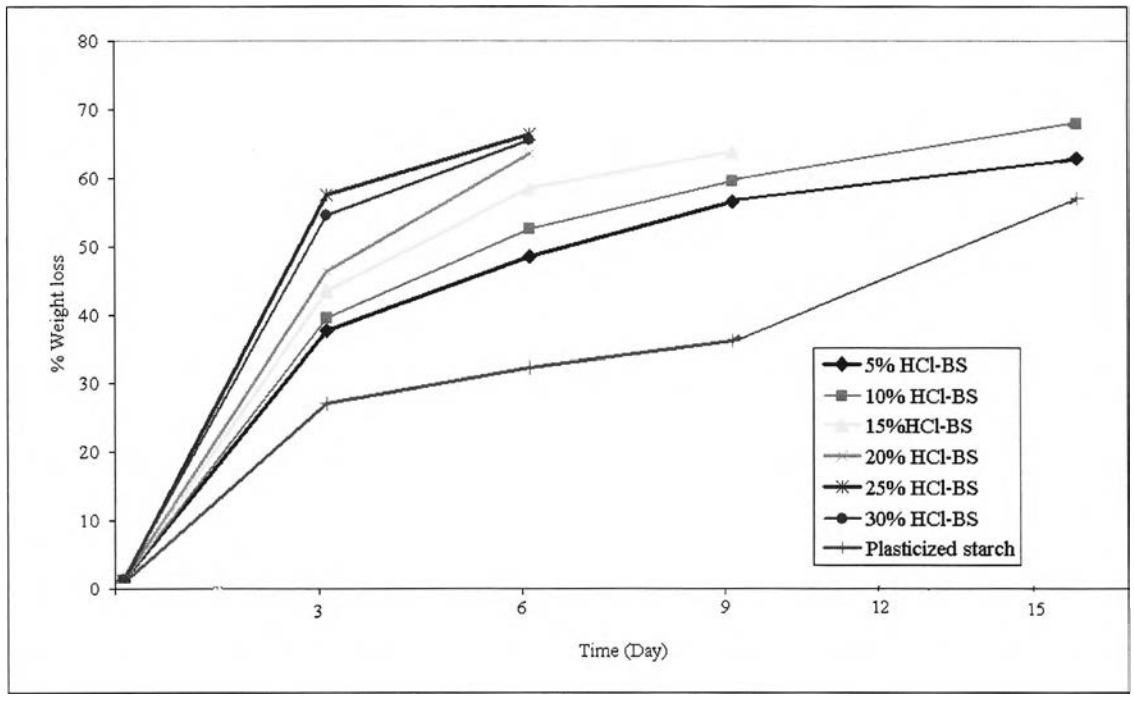

Figure 4.54 %weight loss of biocomposite film reinforcing with H_2SO_4-BS microcrystalline cellulose