CHAPTER IV
RESULTS AND DISCUSSION

4.1 Raw Silk and Conventional Degumming

The properties of raw silk and conventional degummed silk fiber in term of average % weight loss, breaking strength, elongation and color strength are presented in Table 4.1. The average % weight loss by the conventional degumming method was 24.05 ± 1.06. The breaking strength and elongation of conventional degummed silk were lower than the raw silk because sericin which acts as a binder to fibroin was removed. For the direct dye staining test, the raw silk was stained by dark red color while conventional degummed silk was appeared almost white. Color strength of raw silk and conventional degummed silk were 2.85 and 0.07 respectively.

Table 4.1 Properties of raw silk and conventional degumming silk

Property	Raw silk	Degumming silk with conventional method
Average weight loss (%)	-	24.05 ± 1.06
Breaking strength (N)	7.114 ± 0.270	5.523 ± 0.197
Elongation (%)	31.10 ± 1.50	21.9 ± 1.10
Color strength	2.85	0.07
Staining color	Dark red	White

Surface morphology of raw silk and conventional degummed silk was investigated by a scanning electron microscope as shown in Figure 4.1. Micrograph (a) in Figure 4.1 shows the surface of raw silk fibers that was coated with large amount of sericin on fibroin. In micrograph (b) shows surface morphology of degummed silk fiber that was degummed by conventional method. In this condition, sericin was completely removed from fibers, presenting a uniform removal of sericin.

The entire morphology of longitudinal individual stands was clearly observed and no sign of destruction and damage to the surface of silk fibers.

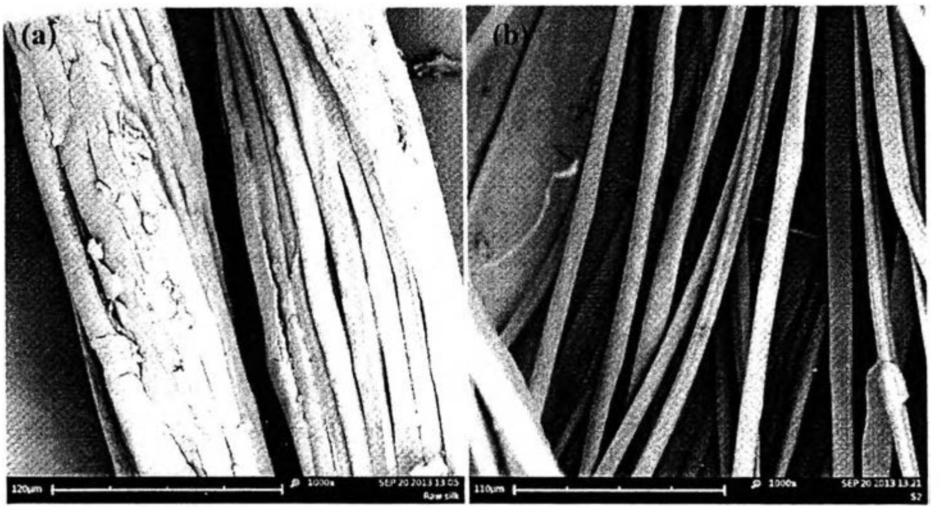

Figure 4.1 SEM micrographs of (a) raw silk fibers and (b) conventional degummed silk.

X-ray diffraction patterns were measured to evaluate the changes in crystalline structure and crystallinity of silk fibers. Figure 4.2 shows x-ray diffraction patterns of raw silk fibers and conventional degummed silk fibers. The 2θ angle of characteristic diffraction peak of fibers is around 20° which correspond to crystalline spacing of 4.41 Å. The result showed that the crystalline structure of raw silk fibers with oriented β crystals remained unaffected by the degumming. However, the relative intensity of the peak of the degummed silk was lower than the raw silk, which indicated that the degummed silk had lower crystallinity than the raw silk.

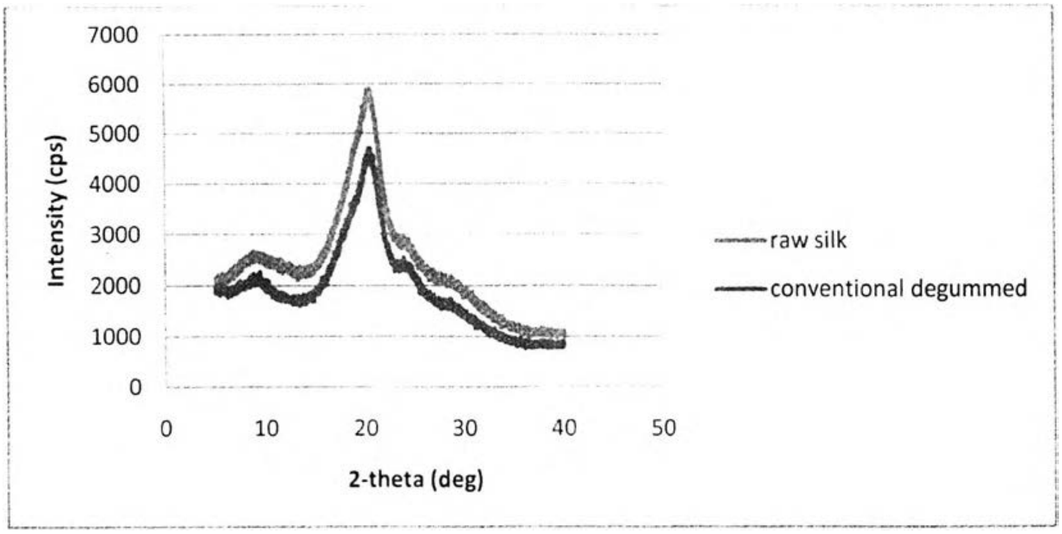

Figure 4.2 X-ray diffraction patterns of raw silk fibers and conventional degummed silk fibers.

4.2 Degumming by Plasma

4.2.1 Effect of Discharge Power

In this study, four different discharge powers were used, which were 60, 250, 1000 and 2000 W and the average weight losses of plasma treated silk fibers were 2.63 ± 0.24, 3.38 ± 0.20, 5.25 ± 0.23 and 6.31 ± 0.10 % respectively. Figure 4.2 shows that the silk fiber weight loss increases significantly with increase of discharge power. Theoretically, discharge power is actually a direct control to the plasma etching efficiency. The higher etching efficiency, the higher silk fiber weight loss possibly remove higher amount of sericin from the silk fiber. The higher discharge power means more energetic or active species generated during the plasma process and results in more effective physical bombardment or chemical etching on the surface of silk fiber.

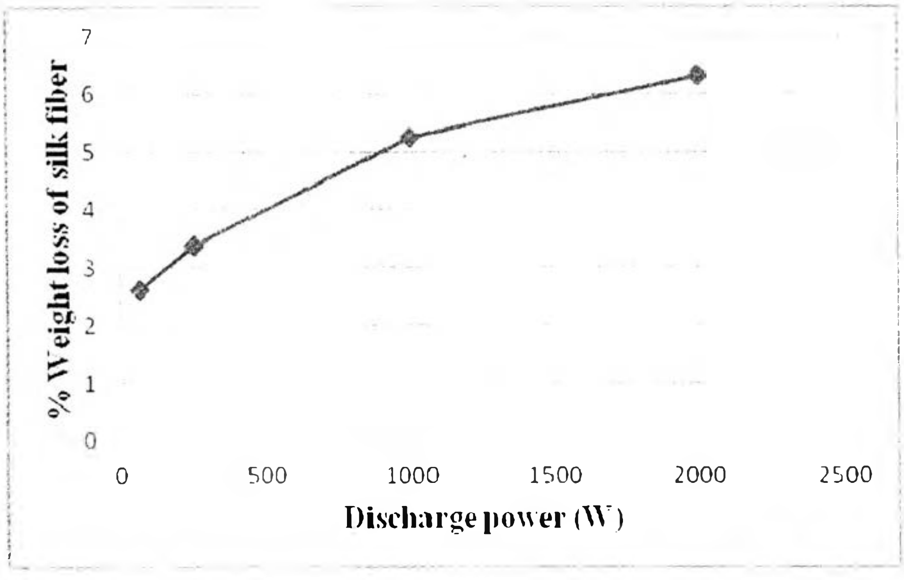

Figure 4.3 Effect of discharge power on silk fiber weight loss. Exposure time at 5 min, oxygen flow rate at 500 cc/min and temperature at 25 °C.

Effect of discharge power on breaking strength, elongation and color strength are shown in Table 4.2. The breaking strength of degummed silk fiber slightly decreases when discharge power increases. In the same way, the elongation of degummed silk fiber also decreases when discharge power increases. When compared the breaking strength and elongation of the plasma degummed silk with the raw silk and the conventional degumming method, it was found that the breaking strength and elongation of the plasma degummed silk was lower than the raw silk and higher than the degummed silk by the conventional method. The breaking strength of silk fiber can be indicating the efficiency of the silk degumming process because sericin acts as reinforcement material for silk fiber when it is removed so the breaking strength decreases. The breaking strength of the degummed silk by plasma was higher than the degummed silk by conventional method because the lower amount of sericin was removed from the silk fiber.

For the direct dye staining test, the direct dye used was Hirus Supra Red 3BL 140 % indicating sericin remaining. Silk containing sericin is dyed dark red and silk without sericin is un-dyed. The raw silk was stained dark red color because a large amount of sericin in the fibers. Meanwhile, the conventional degummed silk was appeared almost white as a result of sericin residue. The color of plasma degummed silks were appeared light dark red color paler than the raw silk one. Color strength (K/S value) of raw silk, plasma degummed silk when the discharge power increased from 60, 250, 1000 and 2000 W and conventional degummed silk were 2.85, 2.81, 2.69, 2.60, 2.51 and 0.07 respectively. The results from both the mechanical properties and the direct dye staining test correspond to the results of silk fiber weight loss. The higher silk weight loss, the lower breaking strength, elongation and the lower color strength.

Table 4.2 Effect of discharge power on properties of silk fiber. Exposure time at 5 min, oxygen flow rate at 500 cc/min and temperature at 25 °C

Property	Raw silk	Degummed silk				
		Conventional method	Plasma discharge power (W)			
			60	250	1000	2000
Weight loss (%)	-	24.05 ± 1.06	2.63 ± 0.24	3.38 ± 0.20	5.25 ± 0.23	6.31 ± 0.10
Breaking strength (N)	7.114 ±0.270	5.523 ±0.197	6.913 ±0.231	6.882 ±0.242	6.760 ±0.243	6.748 ±0.411
Elongation (%)	31.10 ±1.50	21.90 ±1.10	28.50 ±1.40	27.50 ±1.80	27.10 ±1.80	26.80 ±1.50
Color strength	2.85	0.07	2.81	2.69	2.60	2.51
Staining color	Dark red	White	Dark red	Dark red	Dark red	Dark red

Figure 4.4 shows the effect of discharge power on surface morphology of the degummed silk fibers. Micrographs (a-c) show the surface morphologies of the silk fiber that was treated with difference discharge powers which were 60 W, 250 W

and 1000 W were not significantly changed from the raw silk. sericin still appear as a non-uniform coating on the surface of the fibers. Micrograph (d). in some parts of the fiber, sericin layers break away from the main fiber, leaving the clean fibroin fiber surface appear.

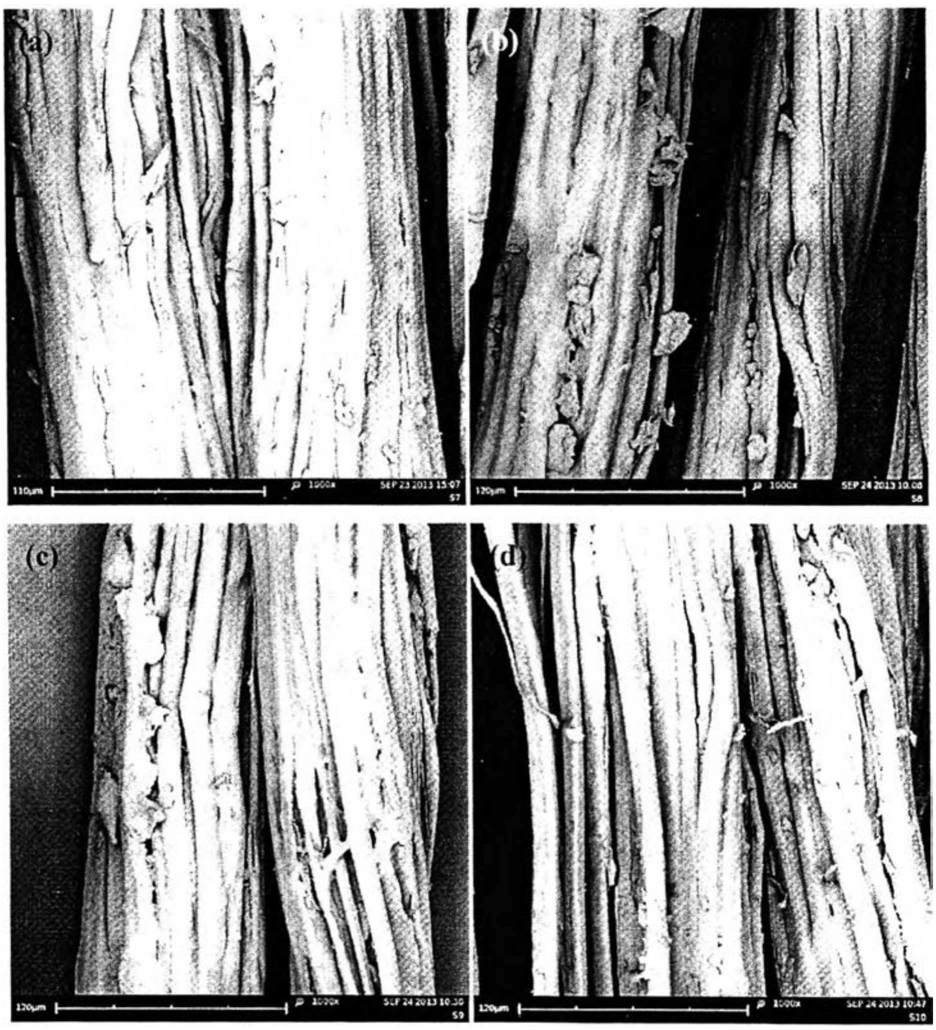

Figure 4.4 SEM micrographs of silk fibers treated by plasma. Condition: exposure time at 5 min, oxygen flow rate at 500 cc/min and temperature at 25 °C and varying discharge power. (a) 60 W, (b) 250 W, (c) 1000 W and (d) 2000 W.

Figure 4.5 shows x-ray diffraction patterns of raw silk fibers and conventional degummed silk fibers and plasma treated silk which the discharge power was varied. The characteristic diffraction peak of silk fibers still exists after being treated with the plasma. It indicates that the crystalline structure of the fibers with oriented β crystals remains unaffected. When considered the relative intensity between the raw silk and the silk treated by plasma, it was not significantly changed because the plasma species can bombard and penetrate only the external surface where it is exposed to, while the conventional degummed silk has ability to penetrate into internal area.

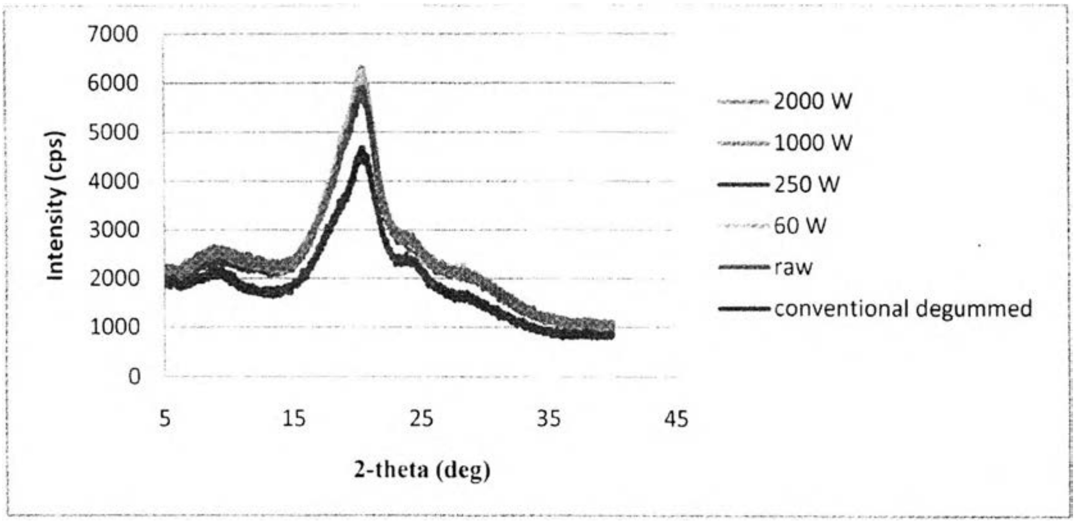

Figure 4.5 Effect of discharge power and x-ray diffraction patterns of raw silk fibers, conventional degummed silk fibers and plasma treated silk fibers.

4.2.2 Effect of Exposure Time

The discharge power of 1000 W and 2000 W were selected for studying the effect of time because it gave high % weight loss. The silk fiber weight loss was increased when degumming time increased as the results shown in Figure 4.6. The longer exposure time prolongs the physical bombardment and plasma chemical etching on the surface of silk (sericin layer), resulting in more sericin chain broken and sericin layer removed.

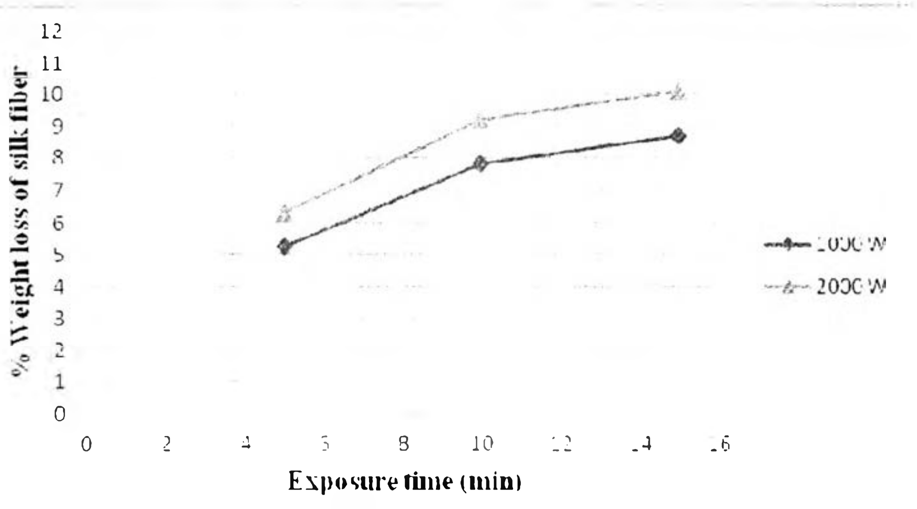

Figure 4.6 Effect of exposure time on silk fiber weight loss. Discharge power at 1000 and 2000 Watt, oxygen flow rate at 500 cc/min and temperature at 25 °C.

The properties of degummed silk fiber, breaking strength, elongation and color strength are shown in Table 4.3. The breaking strength of degummed silk fiber slightly decreases when exposure time increases. However, the elongation of degummed silk fiber significantly decreases when discharge power increases especially at 15 min. For 1000 W and 15 min, the elongation is almost equal to that of the conventional degummed silk. For 2000 W and 15 min the elongation of degummed silk fiber is lower than conventional degummed silk. It may be due to the too long plasma etching which may damage to the fibroin layer. The Elongation is significantly decreases while the breaking strength slightly decreases because when the sericin was removed, the amorphous part was removed. Normally, amorphous part has ability to elongate, when this part is removed fiber become more striffness result in the significantly decrease of the elongation.

The staining test performed with the degummed silks obtained from the three conditions, which were 1000 W and 5 min, 1000 W and 10 min and 2000 W and 5 min was stained light dark red. Meanwhile, For 1000 W and 15 min, 2000W and 10 min and 2000W and 15 min were appeared pale pink, which indicates that a smaller amount of sericin remaining.

Table 4.3 Effect of exposure time on properties of silk fiber. Discharge power at 1000 and 2000 Watt, flow rate at 500 cc/min and temperature at 25 °C

Property	Raw Silk	Degumming of silk						
		conventional method	Plasma					
			1000 Watt			2000 Watt		
			Plasma exposure time (min)			Plasma exposure time (min)		
			5	10	15	5	10	15
Weight loss (%)	-	24.05 ± 1.06	5.25 ± 0.23	7.80 ± 0.34	8.61 ± 0.40	6.31 ± 0.10	9.17 ± 0.29	10.08 ± 0.11
Breaking strength (N)	7.114 ±0.270	5.523 ±0.197	6.760 ±0.243	6.738 ±0.259	6.631 ±0.234	6.748 ±0.411	6.719 ±0.309	6.602 ±0.386
Elongation (%)	31.10 ±1.50	21.90 ±1.10	27.10 ±1.80	24.40 ±1.80	21.50 ±1.60	26.80 ±1.50	23.00 ±1.60	19.50 ±1.82
Color strength	2.85	0.07	2.60	2.19	1.43	2.51	1.74	0.96
Staining color	Dark red	White	Dark red	Dark red	Pale pink	Dark red	Pale pink	Pale pink

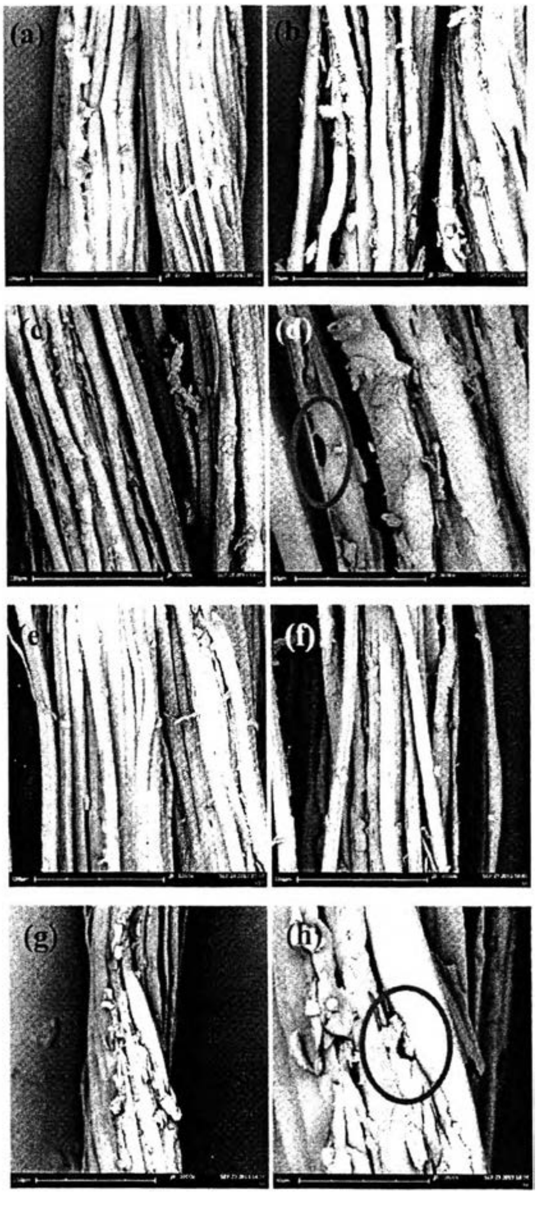

Figure 4.7 SEM micrographs of silk fibers treated by plasma. Condition: oxygen flow rate at 500 cc/min and temperature at 25 °C. (a) 1000 W at 5 min, (b) 1000 W at 10 min, (c) 1000 W at 15 min (1000X), (d) 1000 W at 15 min (3000 X), (e) 2000 W at 5 min, (f) 2000 W at 10 min, (g) 2000 W at 15 min (1000X) and (h) 2000 W at 15 min (3000X).

Figure 4.7 shows the effect of exposure time on surface morphology of the degummed silk fibers. Both 1000 W (Micrographs, a-d) and 2000 W (Micrographs, e-h) show the longer exposure time, more sericin layers break away from the main fiber but still incomplete removal of sericin. However, at 15 min both 1000 W (Micrographs, c-d) and 2000 W (Micrographs, g-h) show sign of destruction and damage to the surface of silk fibers.

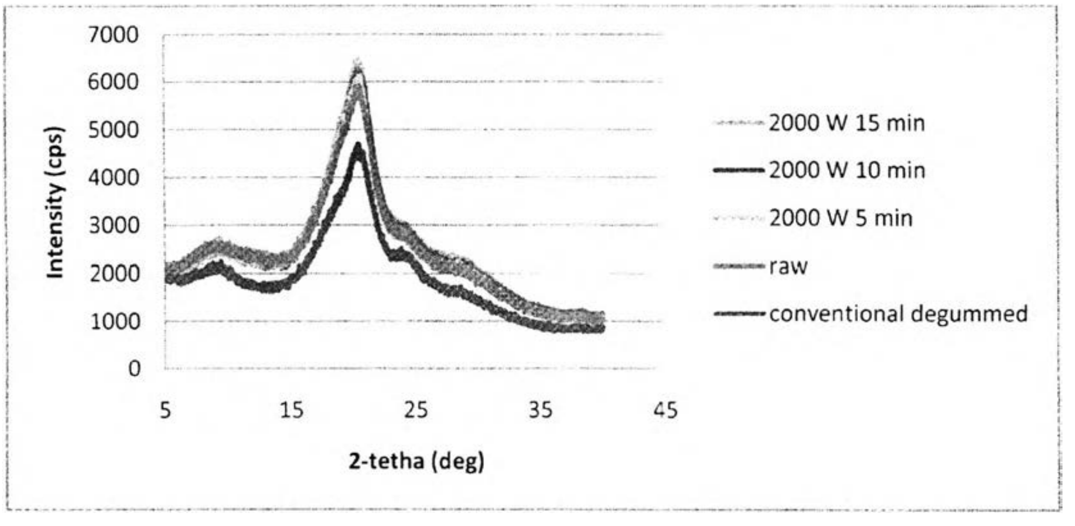

Figure 4.8 Effect of exposure time and x-ray diffraction patterns of raw silk fibers, conventional degummed silk fibers and plasma treated silk fibers.

Figure 4.8 shows x-ray diffraction patterns of raw silk fibers, conventional degummed silk fibers and plasma treated silk which the exposure time was varied. The effect of exposure time on the crystalline structure and crystallinity was the same as that of the discharge power. After the silk fibers were treated with the plasma, the characteristic diffraction peak of silk fibers still exists and the crystallinity was not significantly changed compared to the raw silk.

4.2.3 Effect of Flow Rate

The optimum power of 2000 W and exposure time of 10 min was used to study the effect of flow rate of plasma gas. Three oxygen flow rates, 250, 500 and 1000 cc/min were varied. Figure 4.9 shows that the silk fiber weight loss increased significantly from 250 to 500 cc/min and insignificantly change from 500 to 1000 cc/min. For 250 cc/min, it gave the low % weight loss of silk fiber possibly due to an inadequate supply of oxygen gas. For 500 cc/min and 1000 cc/min, the % weight loss was not significantly change which indicated maximum etching condition.

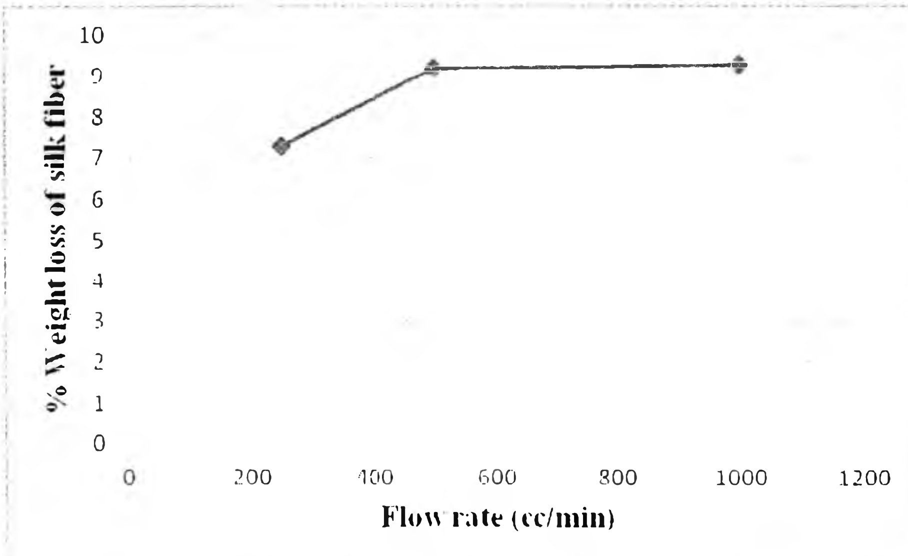

Figure 4.9 Effect of oxygen flow rate on silk fiber weight loss. Discharge power at 2000 Watt, exposure time at 10 min and temperature at 25 °C.

Effect of flow rate on breaking strength, elongation and color strength are presented in Table 4.4. The breaking strength of 500 and 1000 cc/min were 6.719 ± 0.214 and 6.705 ±0.313 and the elongations were 23.00 ± 1.58 and 22.90 ± 1.40 respectively, the breaking strength and elongation of degummed silk fiber were not significantly changed. At 250 cc/min, the breaking strength was 24.30 ± 1.50 and elongation was 6.760 ± 0.411 which were higher than that of 500 and 1000 cc/min corresponding to the higher % weight loss. For the staining test, the flow 250 cc/min showed stained dark red while 500 and 1000 cc/min appeared pale pink and had color strength almost equal.

Table 4.4 Effect of flow rate on properties of silk fiber. Discharge power at 2000 Watt. exposure time at 10 min and temperature at 25 °C

Property	Raw silk	Degumming of silk			
		Conventional method	Plasma		
			Flow rate of oxygen gas (cc/min)		
			250	500	1000
Weight loss (%)	-	24.05 ± 1.06	7.29 ± 0.21	9.17 ± 0.29	9.28 ± 0.20
Breaking strength (N)	7.114 ±0.270	5.523 ±0.197	6.760 ±0.411	6.719 ±0.214	6.705 ±0.313
Elongation (%)	31.10 ±1.50	21.90 ±1.10	24.30 ±1.50	23.00 ±1.58	22.90 ±1.40
Color strength	2.85	0.07	2.06	1.74	1.71
Staining color	Dark red	White	Dark red	Pale pink	Pale pink

Figure 4.10 shows the effect of oxygen flow rate on surface morphology of the degummed silk fibers. Micrograph (a) show the lower seriin removal compare to micrographs (b and c). Micrographs (b and c) present the higher sericin removal from interlacing region of fibers indicating by more individual fibers seperated from each other.

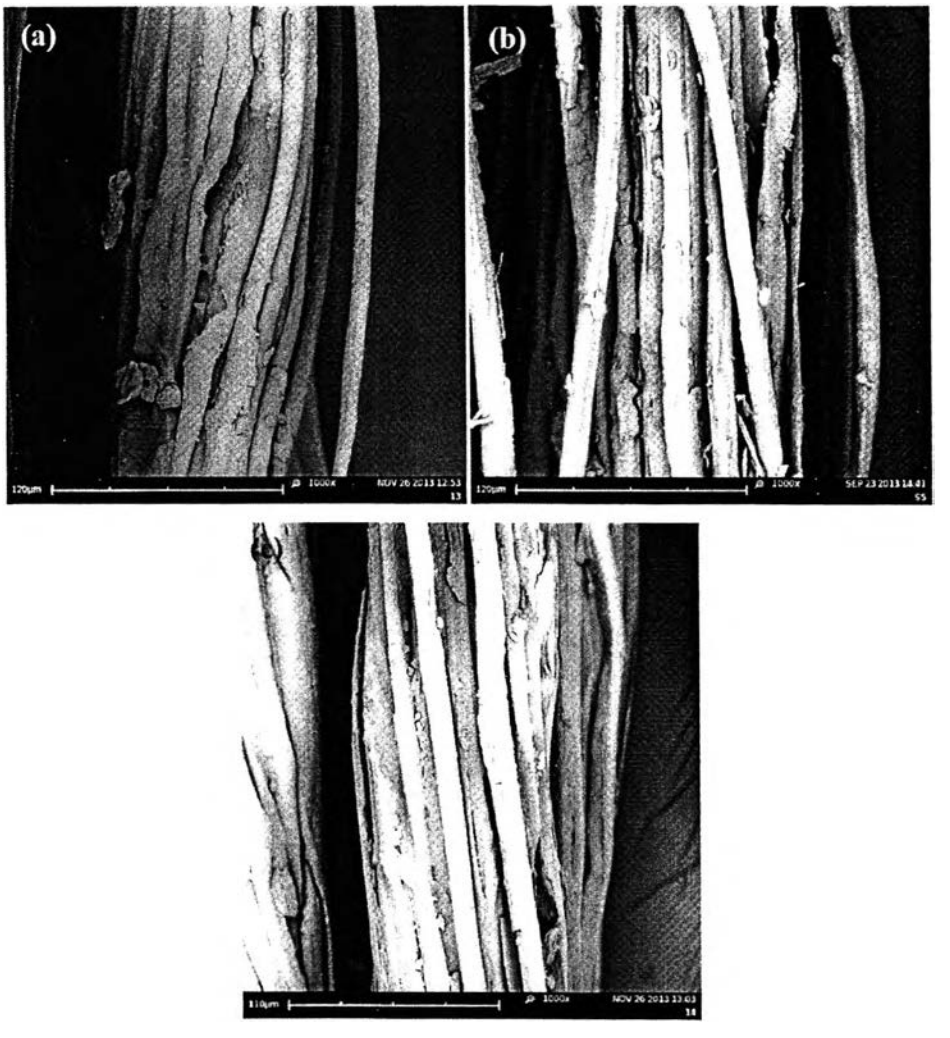

Figure 4.10 SEM micrographs of silk fibers treated by plasma. Condition: discharge power at 2000 Watt, exposure time at 10 min and temperature at 25 °C and varying oxygen flow rate. (a) 250 cc/min, (b) 500 cc/min and (c) 1000 cc/min.

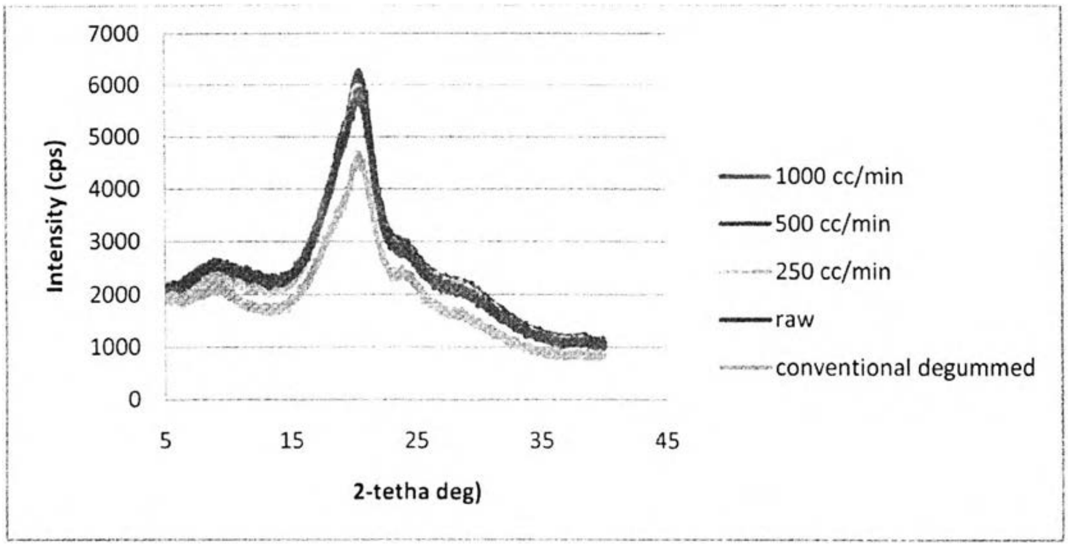

Figure 4.11 Effect of flow rate and x-ray diffraction patterns of raw silk fibers, conventional degummed silk fibers and plasma treated silk fibers.

Figure 4.11 shows x-ray diffraction pattern of raw silk fibers, conventional degummed silk fibers and plasma treated silk which the flow rate was varied. The treated silk fibers by plasma still have the characteristic diffraction peak. The relative intensity of treated silk fiber was not significantly changed compared to the raw silk fiber.

4.2.4 <u>Effect of Temperature</u>

The optimum etching condition which was 2000 W, 10 min and 500 cc/min oxygen gas flow rate. was selected for studying the effect of chamber temperature. Figure 4.12 shows that the silk fiber weight loss decreased with temperature from 25 to 50 °C, while form 50 to 75 °C the % weight loss of silk fiber increase. At, 75 °C the silk fiber burn damaged.

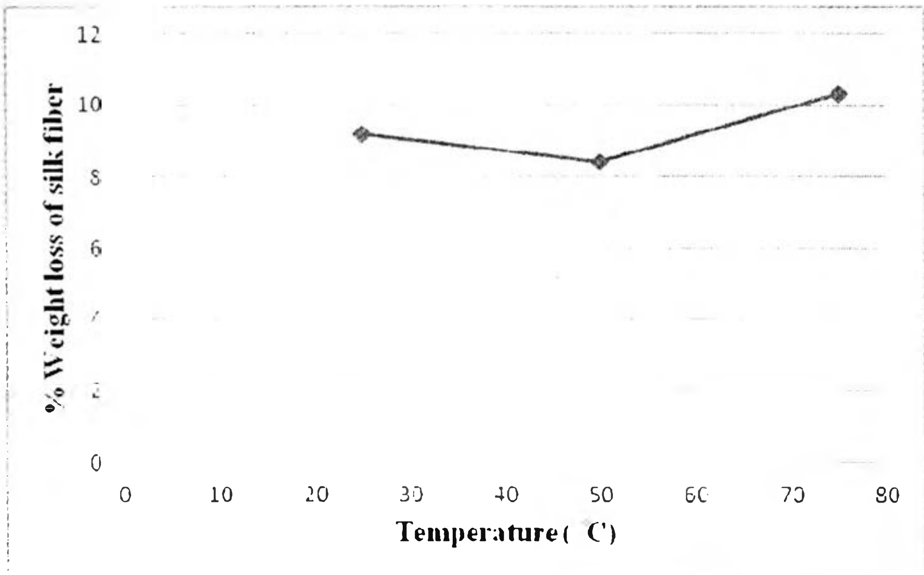

Figure 4.12 Effect of temperature on silk fiber weight loss. Discharge power at 2000 Watt, exposure time at 10 min and oxygen flow rate at 500 cc/min.

Table 4.5 shows the properties of silk fiber. The breaking strength and elonation of degummed silk decrease as the temperature increase from 25 °C to 75 °C. Possibly, because the increase of temperature could make silk fiber brittle, so the elonation and breaking strength are decrease. The staining test shows that the degummed silk by plasma at 50 °C was appeared dark red while 25°C and 75 °C were appeared pale pink. Color strength of 50°C was higher than 25 °C due to its low % wight loss.

Table 4.5 Effect of chamber temperature on properties of silk fiber. Discharge power at 2000 Watt, exposure time at 10 min and oxygen flow rate at 500 cc/min

Property	Raw silk	Degumming of silk			
		Conventional method	Plasma		
			Chamber temperature (°C)		
			25	50	75
Weight loss (%)	-	24.05 ± 1.06	9.17 ± 0.29	8.42 ± 0.25	10.32 ± 0.26
Breaking strength (N)	7.114 ±0.270	5.523 ±0.197	6.719 ±0.411	6.519 ±0.219	5.997 ±0.274
Elongation (%)	31.10 ±1.50	21.90 ±1.10	23.00 ±1.50	21.90 ±1.69	17.9 ±1.90
Color strength	2.85	0.07	1.74	2.53	2.20
Staining color	Dark red	White	Pale pink	Dark red	Dark red

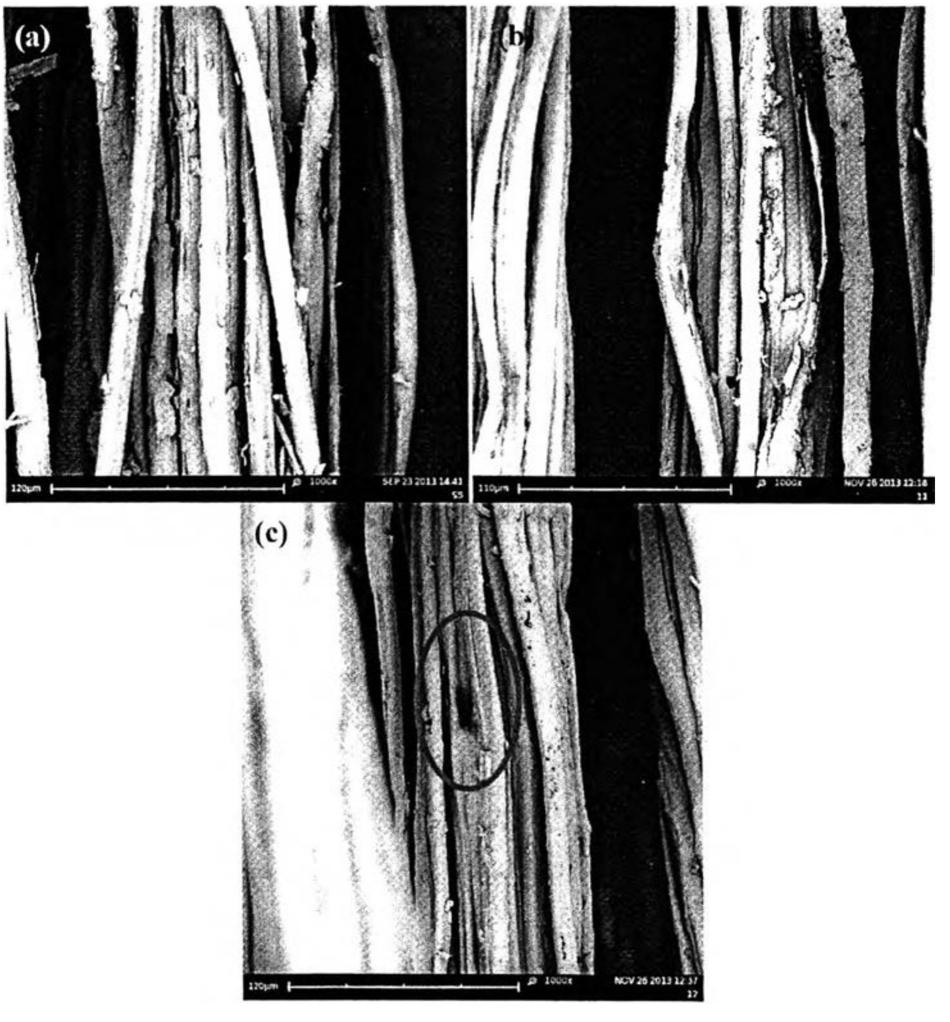

Figure 4.13 SEM micrographs of silk fibers treated by plasma. Condition: discharge power at 2000 Watt, exposure time at 10 min and oxygen flow rate at 500 cc/min. and varying chamber temperature (a) 25 °C, (b) 50 °C and (c) 75 °C

Figure 4.13 shows the surface morphology of silk degummed by plasma in diferrent chamber temperature. All of micrographs (a-c) show a non-uniform removal of gum from interlacing region of fibers but micrograph (c) shows a black spot on the silk fiber which was burn damaged because too high chamber temperature.

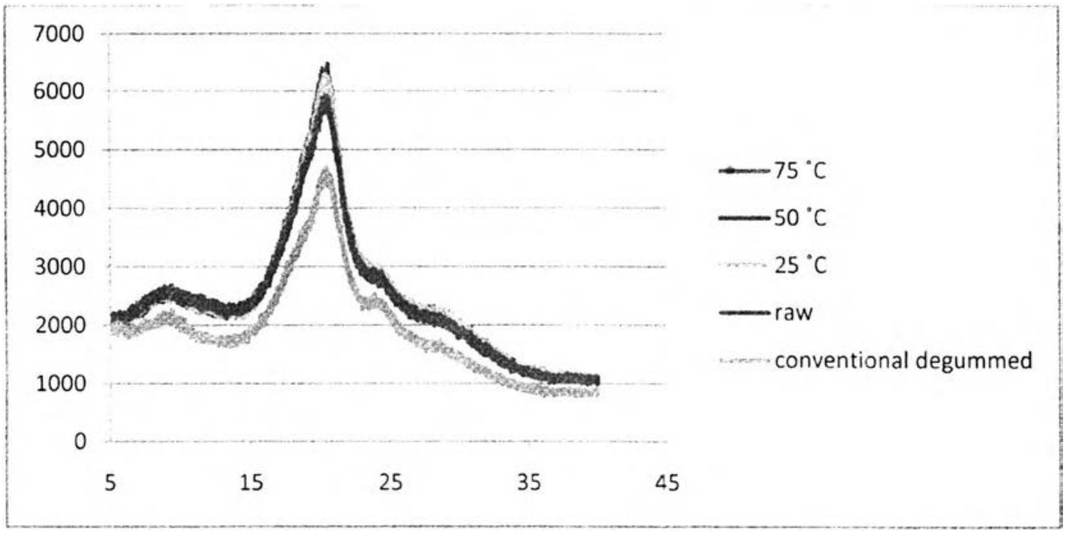

Figure 4.14 Effect of temperature and x-ray diffraction patterns of raw silk fibers, conventional degummed silk fibers and plasma treated silk fibers

Figure 4.14 shows x-ray diffraction patterns of raw silk fibers, conventional degummed silks fiber and plasma treated silk fibers which the chamber temperature was varied from 25 °C to 75 °C. The crystalline structure of the plasma treated silk fibers remains unaffected because the characteristic diffraction peak for the silk fiber still exists. The relative intensity of the plasma treated silk fibers was not significantly changed compared with the raw silk fibers.