CHAPTER 5

RESULTS AND DISCUSSIONS

In this chapter, we will present the influence of plasma conditions such as SF_6 pressure, RF power and treatment time to the improvement of hydrophobicity properties of the fabric. Then, the change of fabric surface morphology and surface roughness after SF_6 plasma treatment will be presented in both of SEM and AFM results. Finally, the atomic species in SF_6 plasma and chemical composition on fabric surface will be presented.

5.1 Effect of RF Power and SF_6 Pressure on Hydrophobicity Properties of Fabrics

In this work, the fabrics are treated under different operating conditions. The SF_6 pressure is in the range of 0.005-1 Torr and the RF power is in the range of 25-75 watts. The treatment time was fixed at 1 and 5 minutes. The operating conditions are shown in Table 4.1. All treated fabrics with SF_6 plasma demonstrate increasing of hydrophobicity. Fig. 5.1 - 5.2 and Fig. 5.3 - 5.4 show the results of absorption time measurement of treated fabrics as a function of pressure at different RF power with treatment time of 1 minute and 5 minutes, respectively.

For 1 minute treatment, the best improvement in absorption time was obtained at RF power of 50 watts in all samples. At a fixed RF power and treatment time, the data shows that treatment at pressure higher than 0.5 Torr will maximize the absorption time for mixed Thai silk and cotton. Similar result was found

for PET and Thai silk, but rapid improvement would be obtained at the operating pressure higher than 0.05 Torr. It can be seen that only at low SF_6 pressure (0.005 and 0.05 Torr), the measured absorption time depends on the RF power. However, at RF power of 75 watts, the absorption time decreases. This may be because plasma is confined in small area less than 3 cm in radial distance from the center of fabric under 75 watts conditions while we obtained the absorption time from droplets placed 3 cm from center. It should be noted that at higher pressure, all fabrics achieved high absorption time, regardless of RF power because amounts of active species increase as SF_6 pressure is increased. The suitable condition is at the pressure of 0.5 Torr and RF power of 50 watts.

For 5 minutes SF_6 plasma treatment, PET, Thai silk and cotton fabrics show approximately the same absorption time regardless of the RF power and SF_6 pressure of the treatment. In contrast, the absorption time of mixed Thai silk fabric still depends on RF power and SF_6 pressure. However, we found that the treatment time longer than 5 minutes or the treatment with higher RF power (more than 75 watts) and higher SF_6 pressure (more than 1 Torr), the fabrics are damaged and burned near the center resulted in decrease of absorption time. These changes are believed to be the effect of etching at the fiber [34].

The contact angle and the surface energy resulted in Fig. 5.5 - 5.6 show a dramatic increase of hydrophobicity in all PET, mixed Thai silk, Thai silk and cotton samples. It can be seen that the contact angle of treated sample increase up to about 145^o resulted in the surface energy down to about 20 dynes/cm (0.02 N/m). The measured contact angle of treated fabric, varying from 135^o-145^o of which the contact angle does not depend on different operating condition or the type of fabrics. These results agree with reported by Selli et al. [12] and Chaivan et al. [13]. As a result, any clear trend of contact angle and surface energy as a function of plasma condition are not obtained.

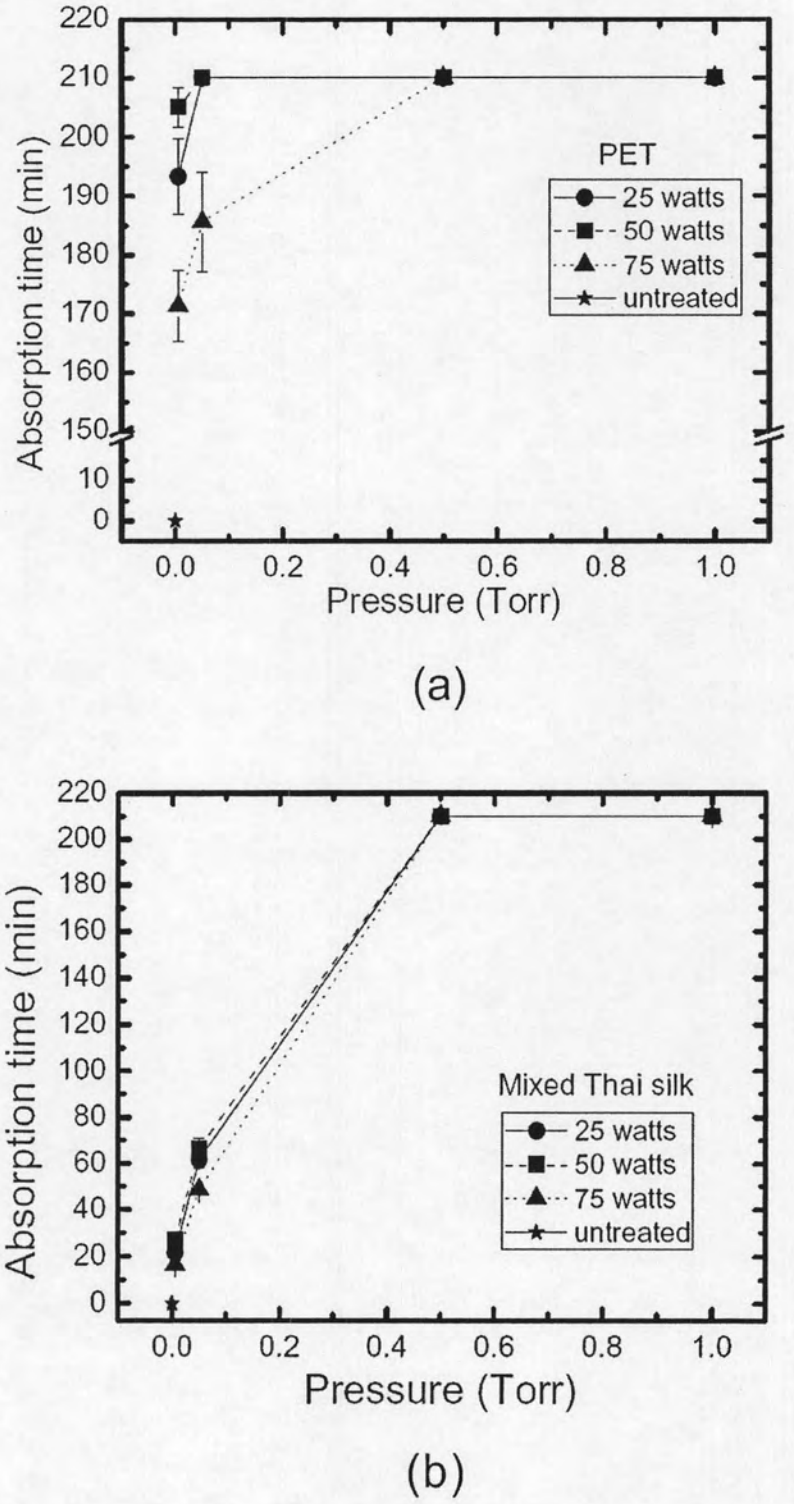
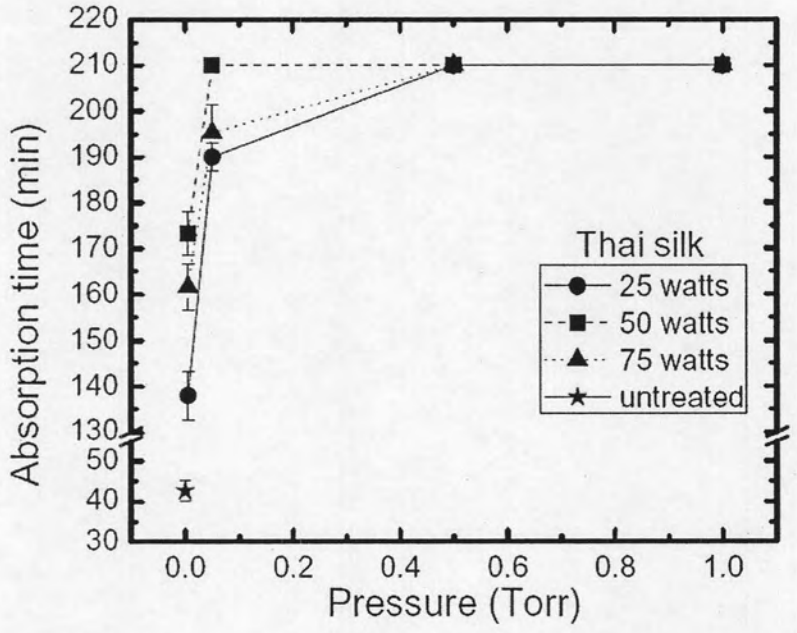
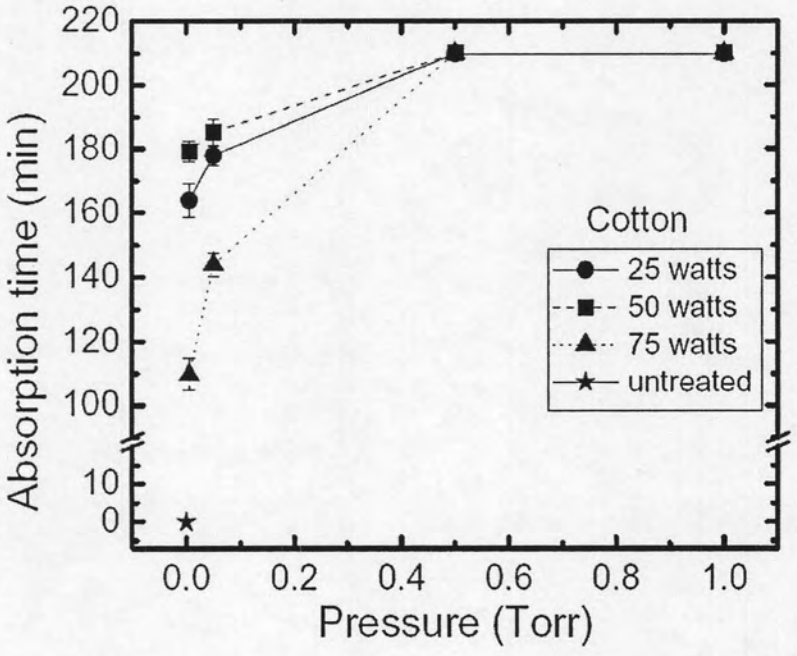


Figure 5.1: Water droplet absorption time on PET (a) and mixed Thai silk (b) fabrics which were treated for 1 min as a function of pressure at different RF powers.



(c)



(d)

Figure 5.2: Water droplet absorption time on Thai silk (c) and cotton (d) fabrics which were treated for 1 min as a function of pressure at different RF powers.

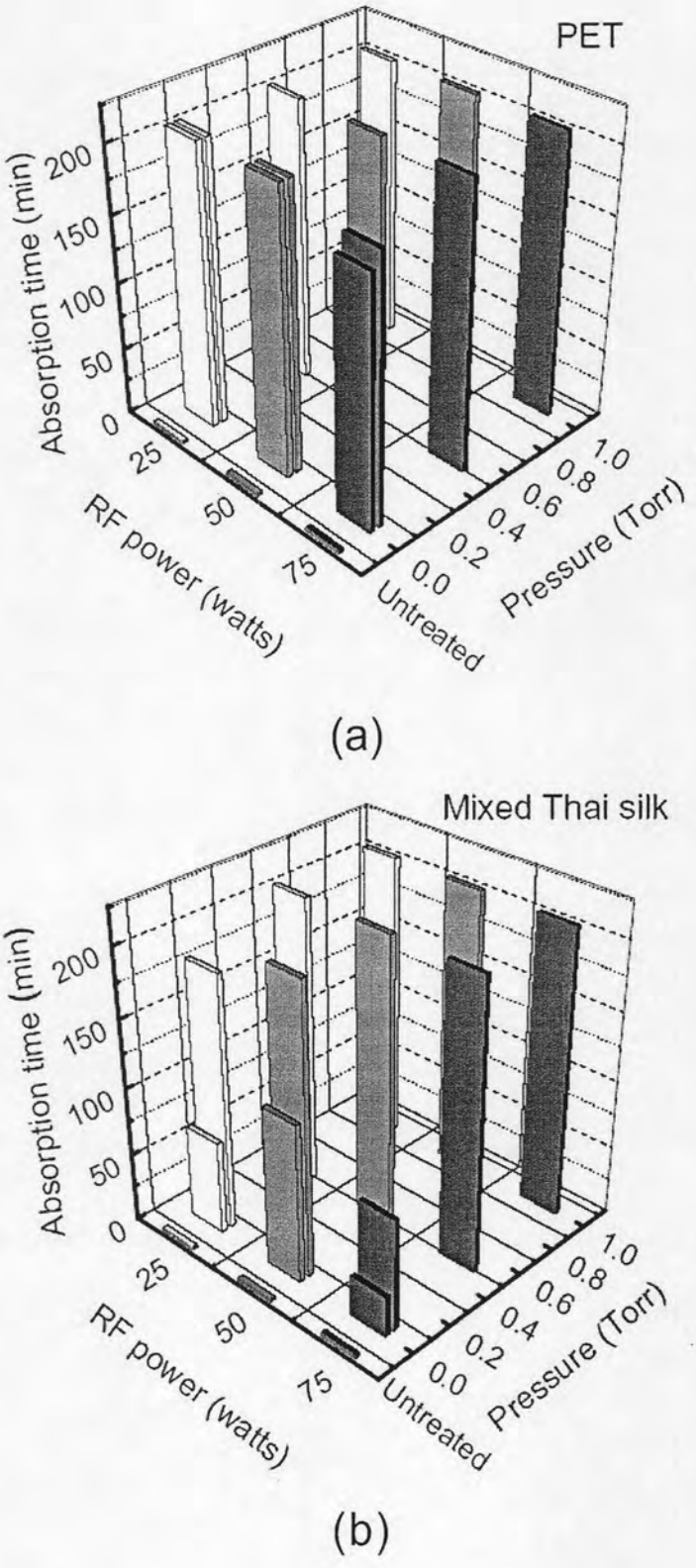
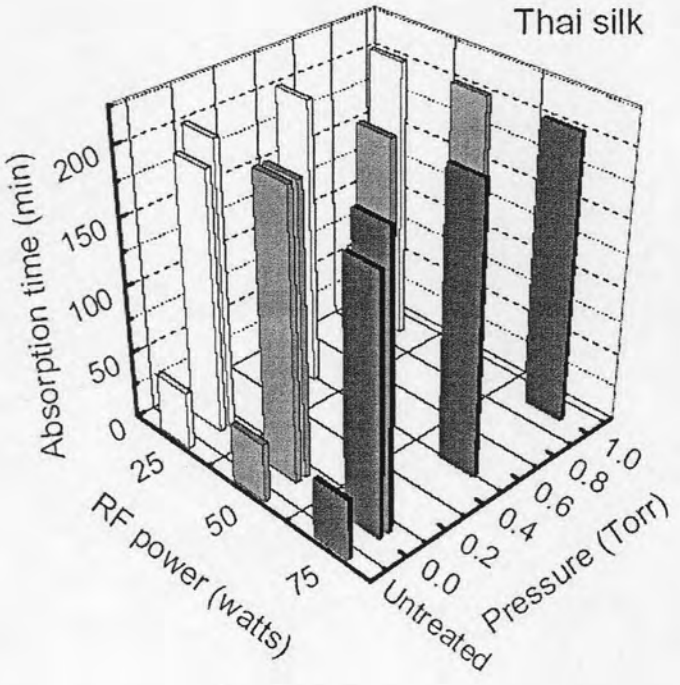
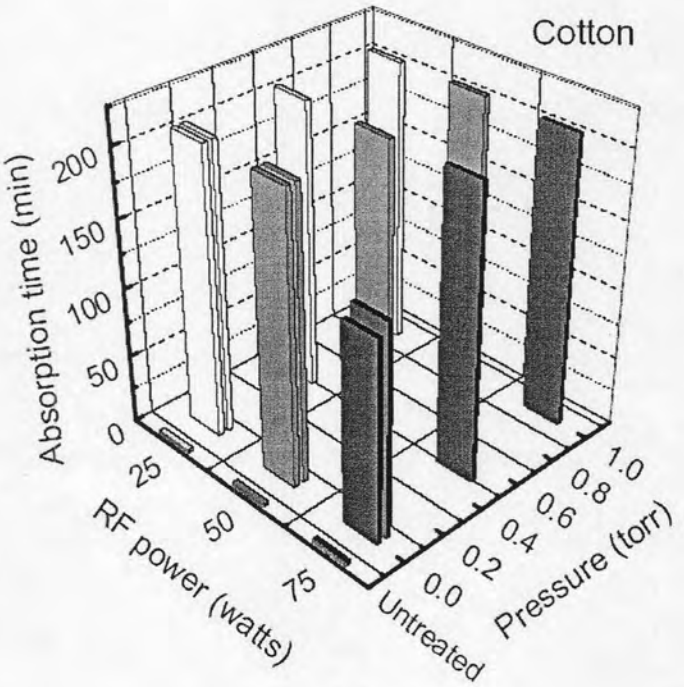


Figure 5.3: Water droplet absorption time on PET (a) and mixed Thai silk (b) fabric which were treated for 5 min as a function of pressure at different RF powers.



(c)



(d)

Figure 5.4: Water droplet absorption time on Thai silk (c) and cotton (d) fabrics which were treated for 5 min as a function of pressure at different RF powers.

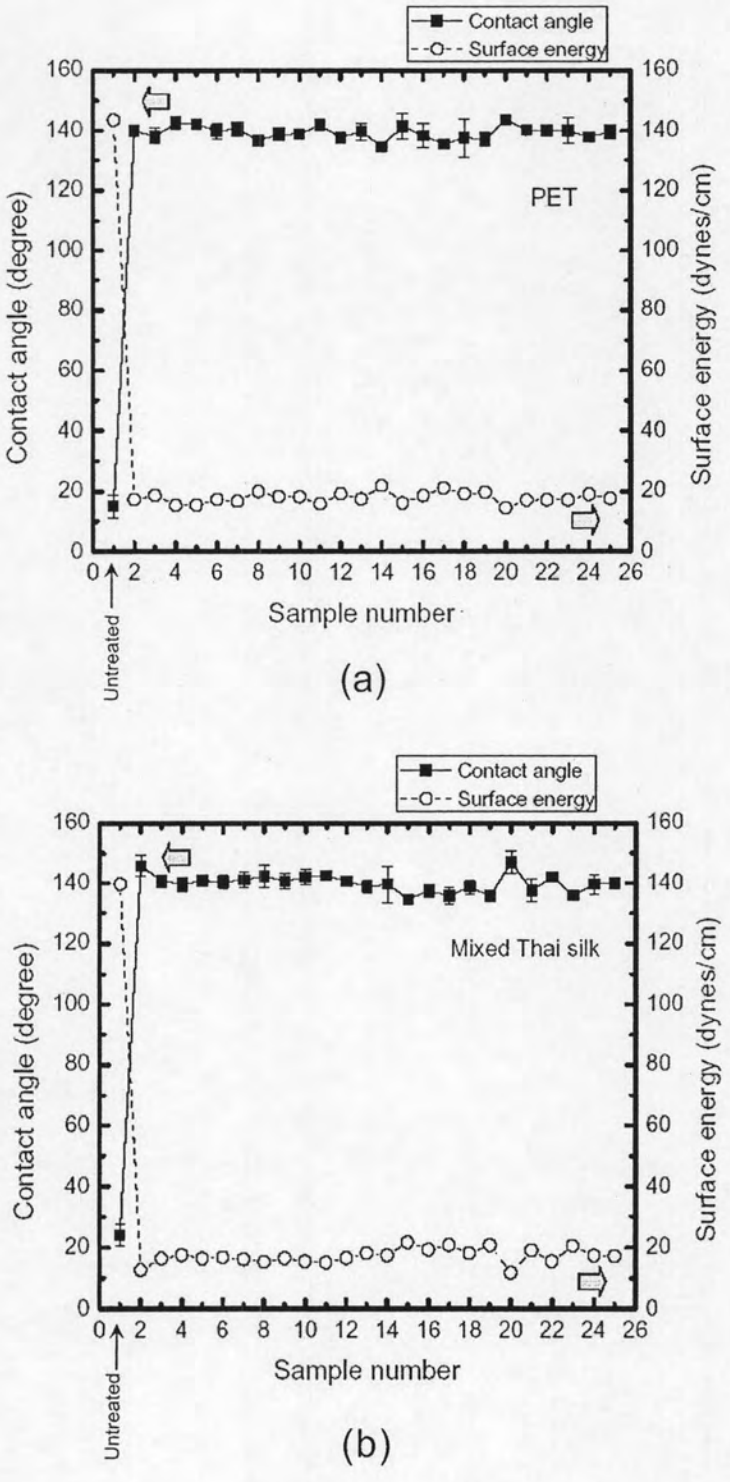


Figure 5.5: Water contact angle and surface energy of untreated and treated PET (a) and mixed Thai silk (b) fabrics as a function of sample number (different operating condition).

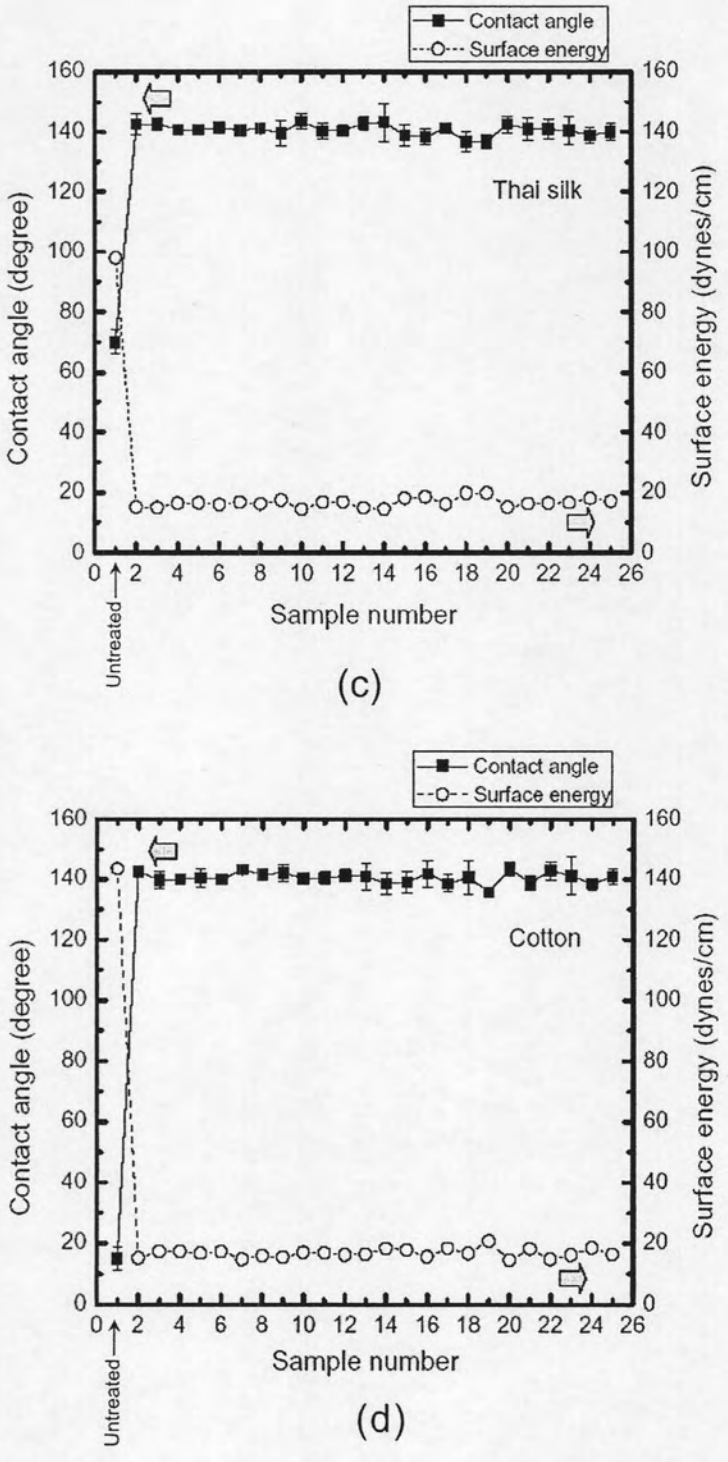


Figure 5.6: Water contact angle and surface energy of untreated and treated Thai silk (b) and cotton (d) fabrics as a function of sample number (different operating condition).

5.2 Effect of Type of Fabric on Hydrophobicity Improvement

Fig. 5.7 shows a comparison of absorption time on PET, cotton, Thai silk and mixed Thai silk as a function of RF power at the pressure of 0.05 Torr and the treatment time of 1 minutes. Prior to the treatment by SF_6 plasma process, the water droplet on PET, cotton and mixed Thai silk sample is rapidly absorbed into the fabric surface. So, the absorption time on these untreated samples could not be measured. The result of untreated Thai silk absorption time is about 40 minutes. We found that the best hydrophobic property improvement is obtained in PET sample, while longer treatment time is necessary for hydrophobicity improvement in the case of mixed Thai silk, especially when operating at higher RF power and higher SF_6 pressure. However, the relation between absorption time and amount of fluorine on each of fabric will be discussed in detail in section 5.6.

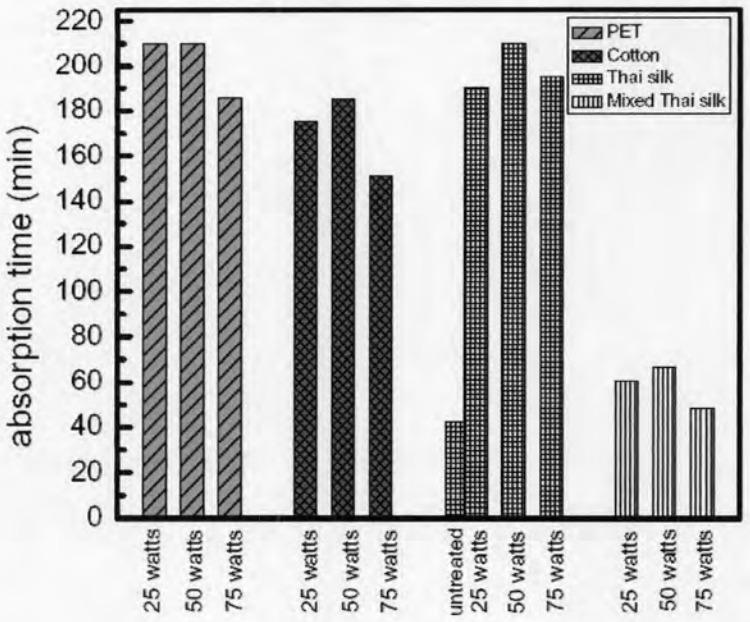
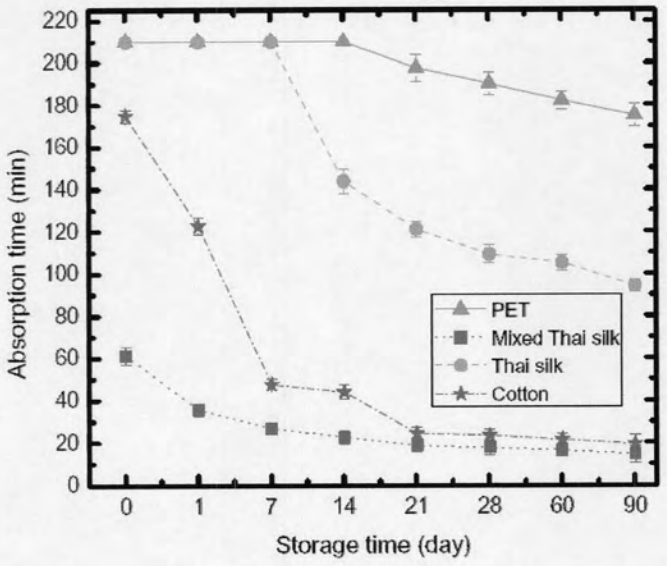


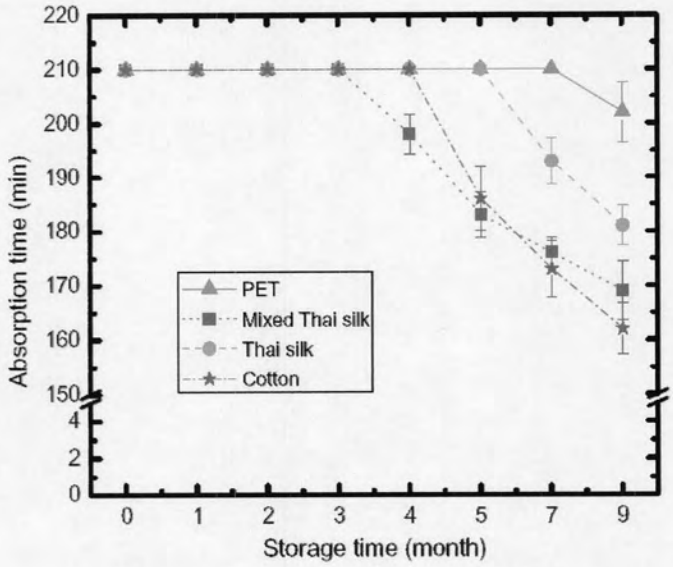
Figure 5.7: Absorption time of PET, cotton, Thai silk and mixed Thai silk as a function of RF power. Plasma pressure and treatment time are 0.05 Torr and 1 minutes, respectively.

5.3 Effect of Storage Time on Hydrophobicity Properties of Fabrics

In this work, the treated fabrics at plasma condition at the pressure of 0.5 Torr, the RF power of 50 watts and the treatment time of 5 min (best treatment condition for hydrophobicity property improvement) and at plasma condition at the pressure of 0.05 Torr, the RF power of 25 watts and the treatment time of 1 min (bad treatment condition for hydrophobicity property improvement) are chosen as example of condition to compare effect of storage time on hydrophobicity property. All treated fabrics were kept in a humidity controlled carbinet which allow the measurement of the absorption time to be performed again at different time after treatment. It can be seen that the hydrophobicity properties of fabric decrease at increasing storage time. Selli et al. [12] reported that decreasing hydrophobicity is due to fluorine hidden within fibers during storage time but is not due to the removal of fluorine from sample surface. However, we found that hydrophobicity stability after the exposure of SF_6 plasma depends on the type of fabric and the plasma condition. Compared with treated fabrics at bad plasma treatment (Fig. 5.8(a)), the treated fabrics at the best plasma treatment (Fig. 5.8(b)) have an obvious longer hydrophobicity stability. This result can be attributed to the higher SF_6 pressure and higher RF power representing greater density of active species as well as the longer treatment time which indicates the greater amount of active species bombarding the sample surface. We observed that the best hydrophobicity stability was obtained in PET samples.



(a)

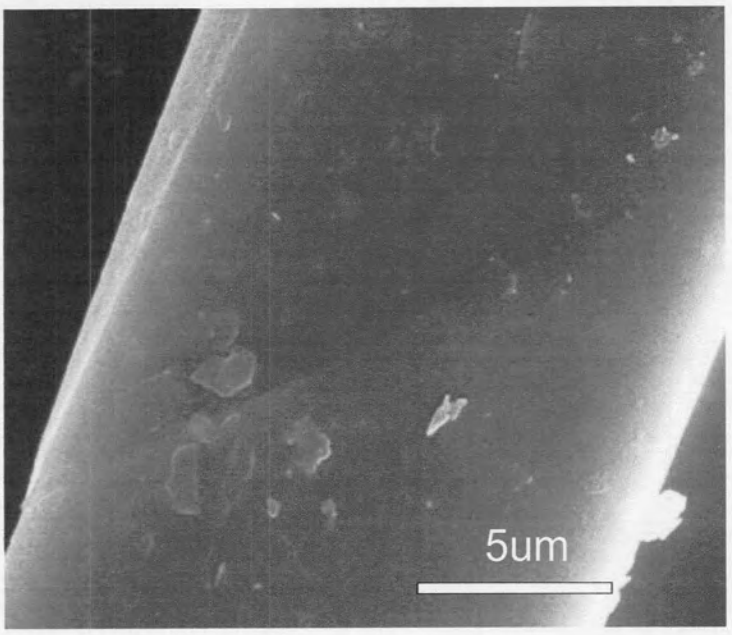


(b)

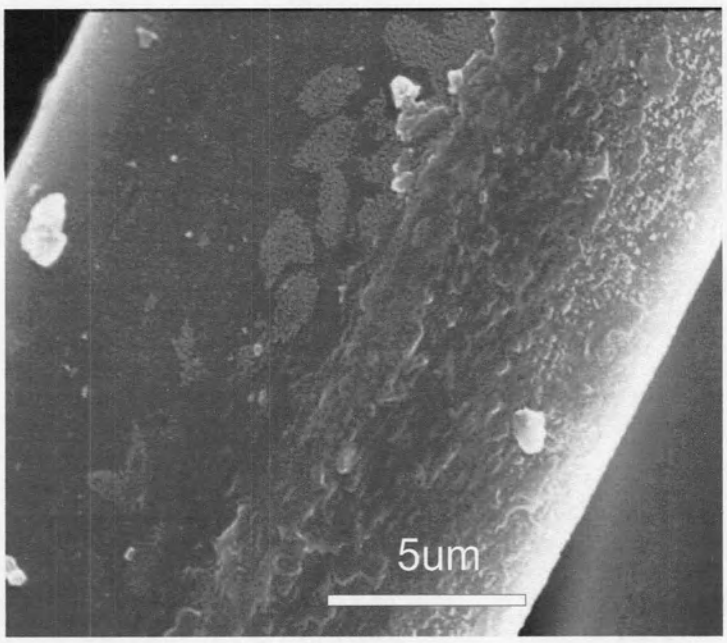
Figure 5.8: Absorption time of PET, cotton, Thai silk and mixed Thai silk, (a) treated for 1 min at pressure of 0.05 torr and RF power of 25 watts, (b) treated for 5 min at pressure of 0.5 torr and RF power of 50 watts, measured at different times after treatment.

5.4 Fiber Surface Morphology and Surface Roughness

SEM images of PET, mixed Thai silk, Thai silk and cotton are shown in Fig. 5.9 - Fig. 5.12, respectively. All SF_6 plasma treated fabrics present similar behavior in the extent that, all treated fabrics are rougher than untreated fabrics. However, SEM experiments are needed in connection with AFM measurement to confirm the increased roughness of treated fabric by root-mean-square (rms) surface roughness analysis. Fig. 5.13 shows 2D (top) and 3D (bottom) AFM image of the untreated and SF_6 plasma treated PET fabrics. We found that the surface roughness of PET fabric was increased from 28 nm to 45 nm after plasma treatment. Similar result was also found for Thai silk and cotton fabric. The surface roughness of Thai silk fabric was increased from 10 nm to 32 nm, as illustrated in Fig. 5.14 while the roughness of cotton fabric was increased from 3 nm to 23 nm, as illustrated in Fig. 5.15. The increased roughness of treated fabric could due to both etching process from high energy species generated in plasma and depositing process of residue on the sample surface [12, 36]. The increased surface roughness also support to improve hydrophobicity property of fabric. This is so usually known as "lotus effect" which can be observed on a lotus leaf. The sharp characteristic of the surface reduces a contact surface between water surface and sample surface, minimizing the surface energy [1, 37]. It should be noted that the rms surface roughness of all sample in this thesis is in the same order of magnitude as reported by Poletti et.al. [38] and Gupta et. al. [39]. Wagner et al. reported that the height of papilla and distance between the top of papilla on surface in the order of micrometer range can reduce contact area between water surface and sample surface [46]. For our treated fabrics, the increased nanoroughness is very small compared to the size of water droplet (40 μl in volume) used in the experiment. The increased nanoroughness is not sufficient to support the bulk volume of water droplet and reducing contact area between water surface and sample surface. So, the increase of roughness on treated fabric surface is not the main reason to improve hydrophobicity.



(a)



(b)

Figure 5.9: SEM micrographs of PET fabrics with magnification of 5000. (a) before plasma treatment (b) after plasma treatment at the pressure of 0.5 Torr, RF power of 50 watts, and treatment time of 5 min.

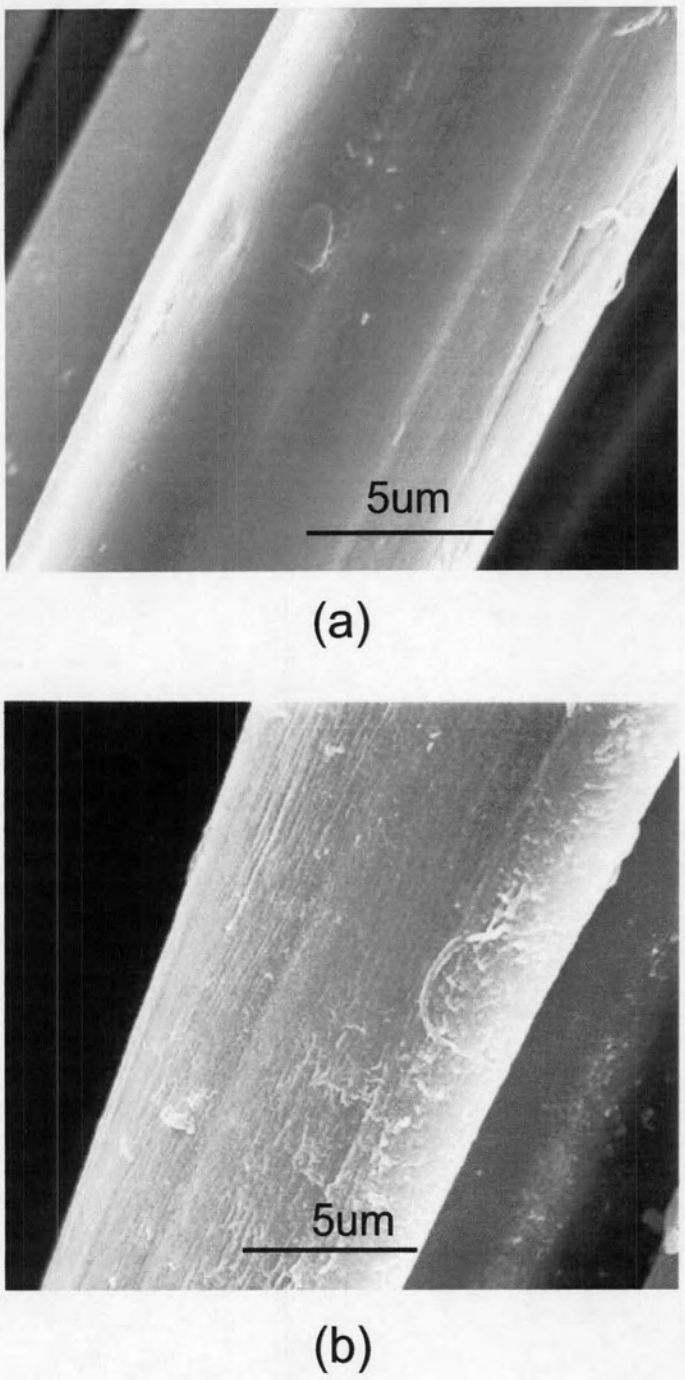
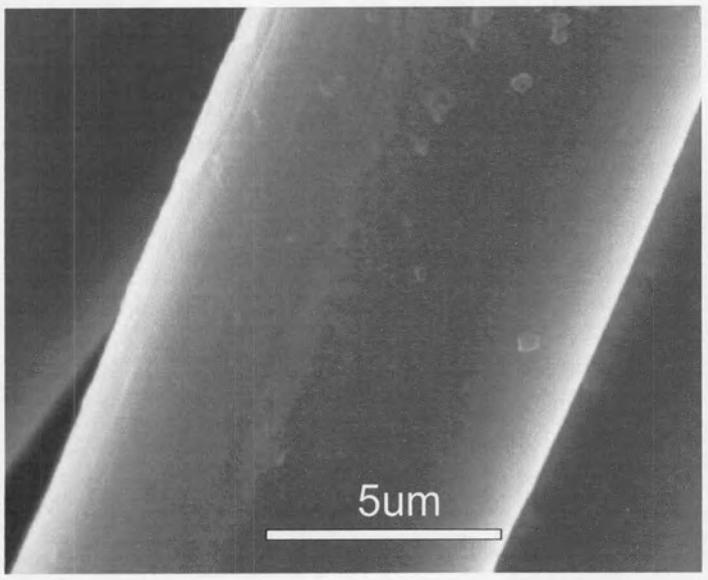
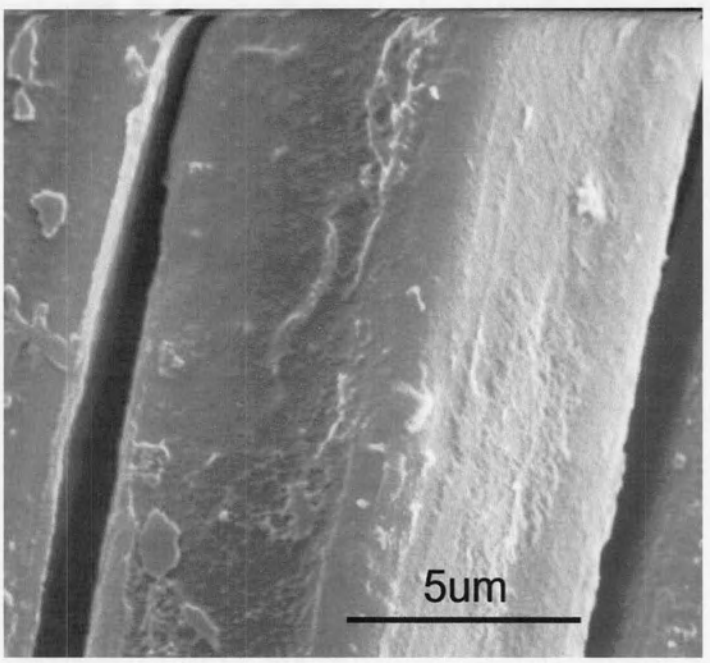


Figure 5.10: SEM micrographs of mixed Thai silk fabrics with magnification of 5000. (a) before plasma treatment (b) after plasma treatment at the pressure of 0.5 Torr, RF power of 50 watts, and treatment time of 5 min.

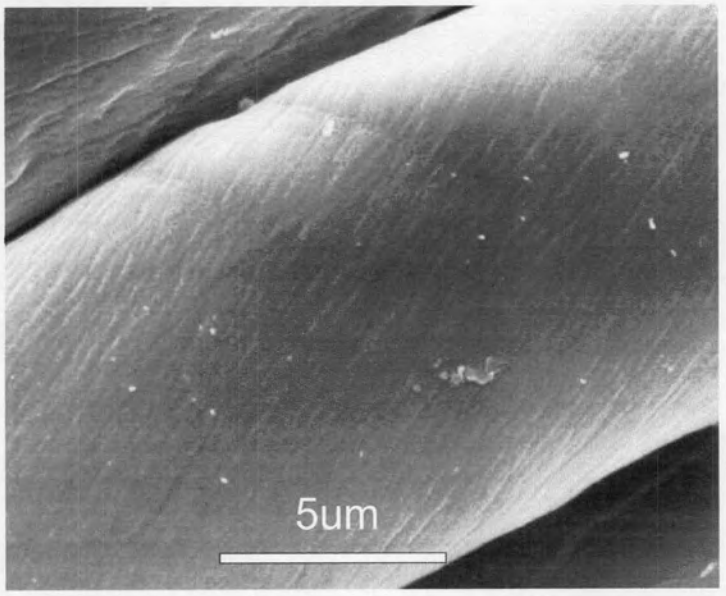


(a)

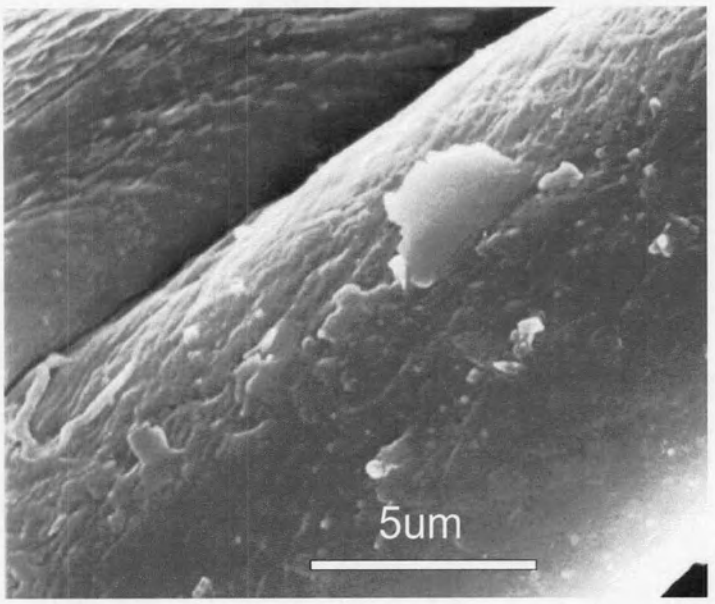


(b)

Figure 5.11: SEM micrographs of Thai silk fabrics with magnification of 5000. (a) before plasma treatment (b) after plasma treatment at the pressure of 0.5 Torr, RF power of 50 watts, and treatment time of 5 min.



(a)



(b)

Figure 5.12: SEM micrographs of cotton fabrics with magnification of 5000. (a) before plasma treatment (b) after plasma treatment at the pressure of 0.5 Torr, RF power of 50 watts, and treatment time of 5 min.

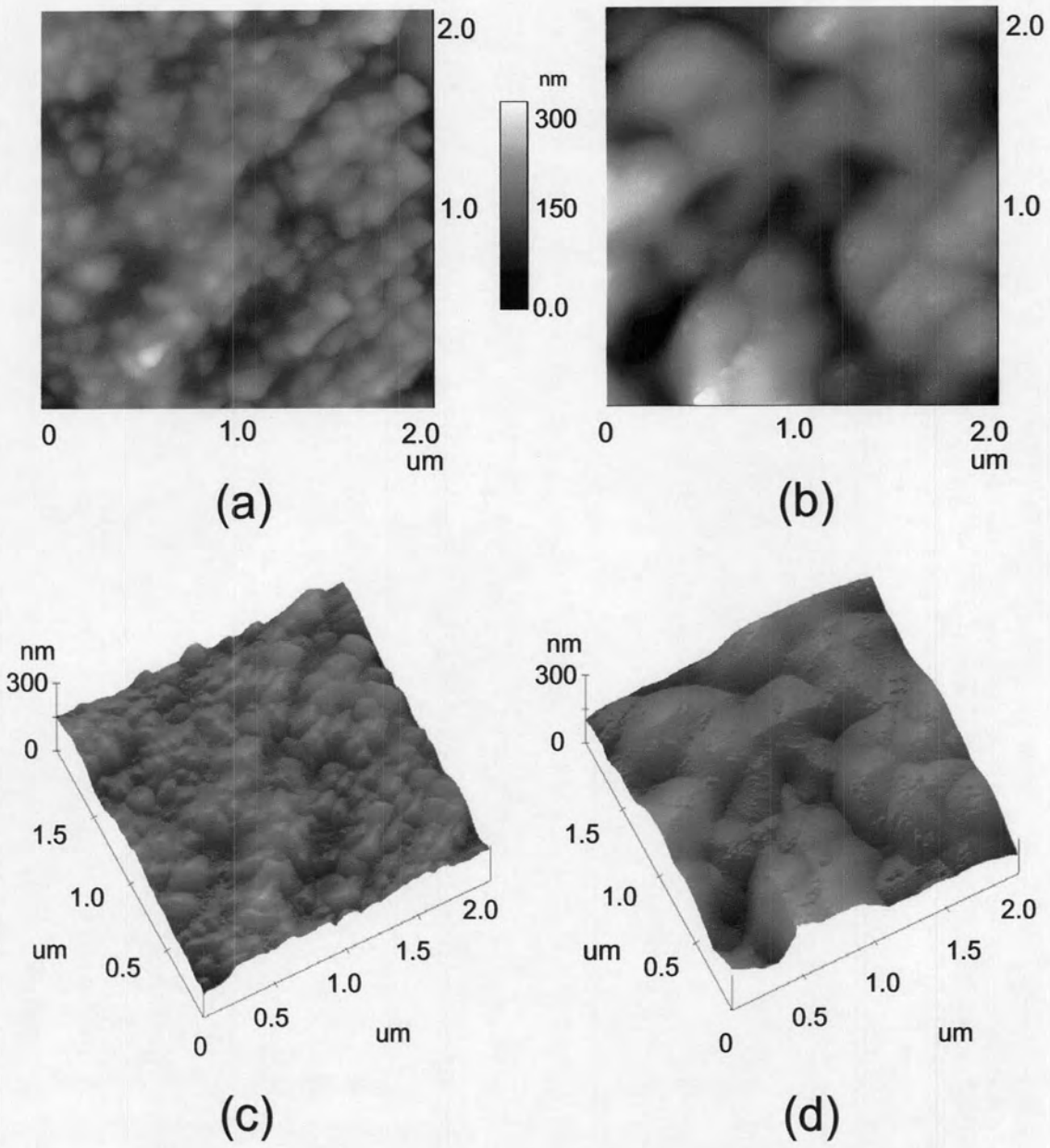


Figure 5.13: AFM images 2×2 μm^2 of PET fabrics. (a) and (c) before plasma treatment, (b) and (d) after plasma treatment at the pressure of 0.5 Torr, RF power of 50 watts, and treatment time of 5 min.

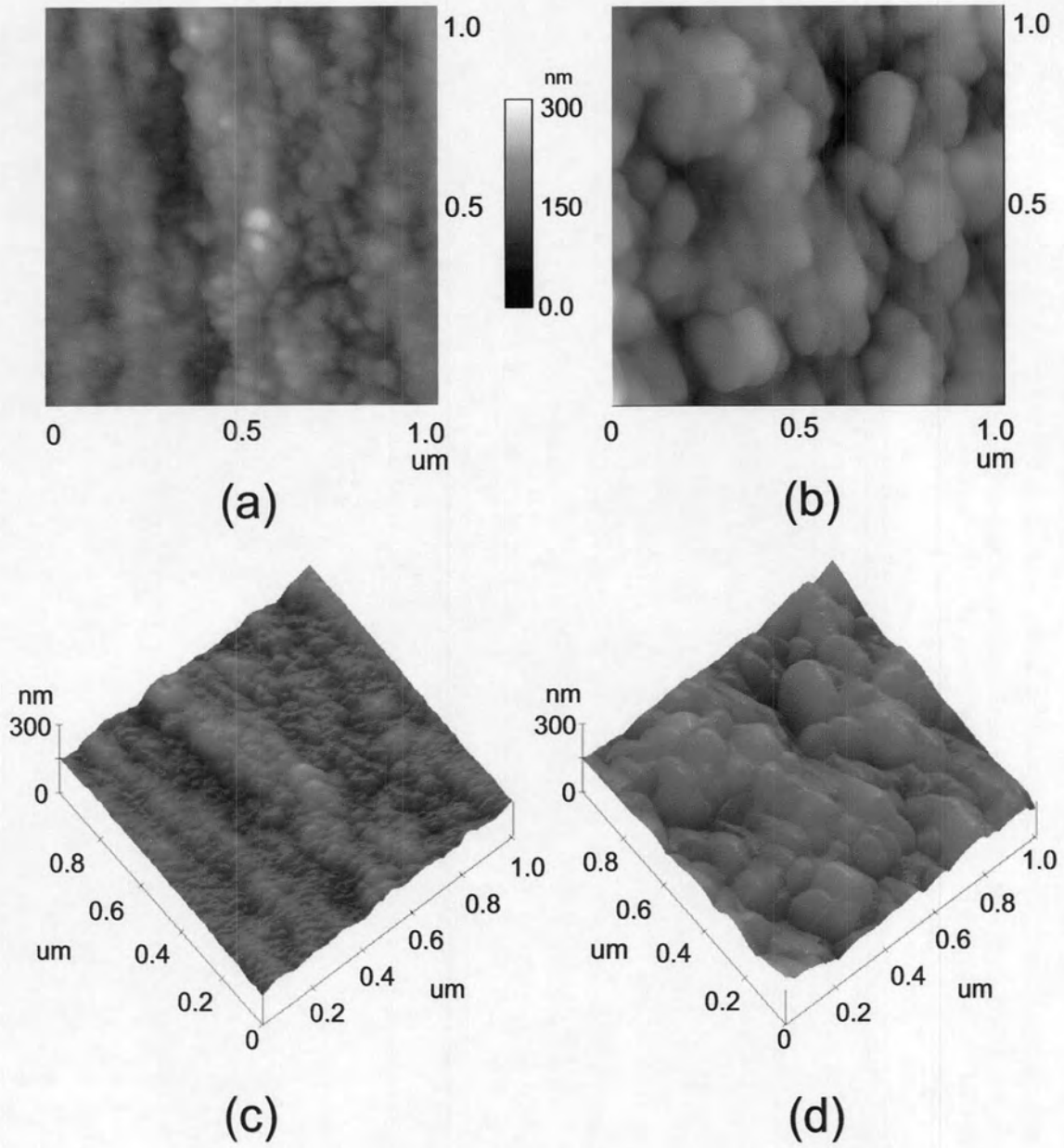


Figure 5.14: AFM images 1×1 μm^2 of Thai silk fabrics. (a) and (c) before plasma treatment, (b) and (d) after plasma treatment at the pressure of 0.5 Torr, RF power of 50 watts, and treatment time of 5 min.

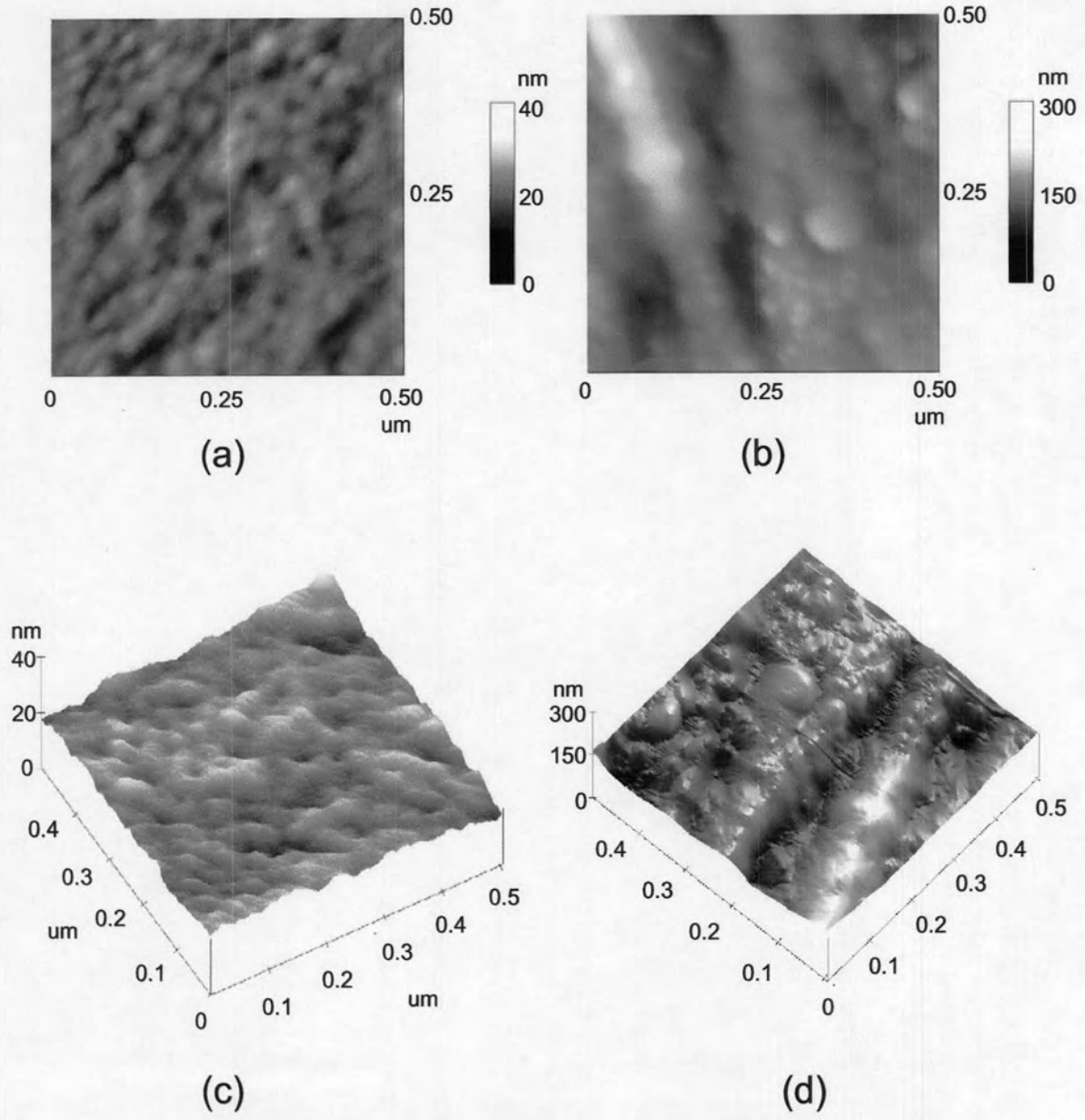


Figure 5.15: AFM images 0.5×0.5 μm^2 of cotton fabrics. (a) and (c) before plasma treatment, (b) and (d) after plasma treatment at the pressure of 0.5 Torr, RF power of 50 watts, and treatment time of 5 min.

5.5 Atomic Species in SF_6 Plasma

The optical spectra of SF_6 plasma as illustrated in Fig. 5.16 presents spectral lines of FI (excited fluorine) in the range of 600-800 nm.

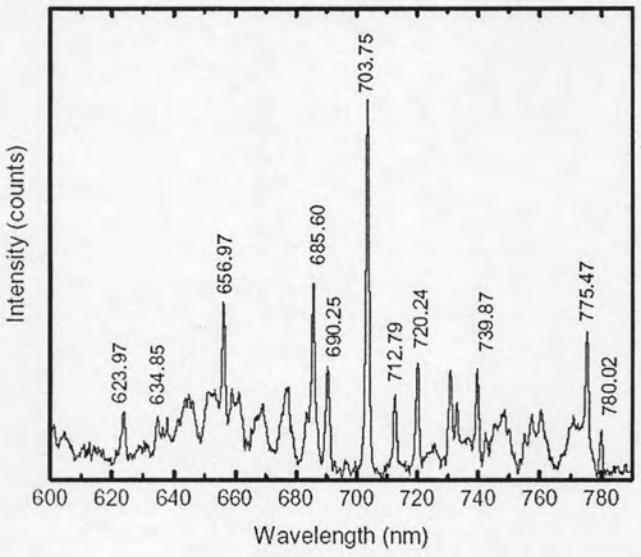


Figure 5.16: Optical emission spectra of SF_6 plasma at pressure of 0.05 torr and the RF power of 25 watt.

We found two dominant intensity lines at 703.75 nm and 685.60 nm which indicated the important processes producing fluorine atom [34], described by equation below,

$$e^- + SF_6 \rightarrow e^- + SF_5 + F^*, \tag{5.1}$$

$$e^- + F \rightarrow e^- + F^*, \tag{5.2}$$

where F* is fluorine at excited state.

The F* atoms are active species that can be bounded with carbon composite of each fabric to improve the hydrophobicity, the details of chemical bounds will be presented in section 5.6.

5.6 Chemical Composition on Surface Fabrics

In this work, treated fabrics at plasma condition at the pressure of 1 Torr and the RF power of 75 watts are not chosen for XPS analysis because fabrics are damaged from plasma. Here, we have chosen the treated fabrics at plasma condition at the pressure of 0.5 Torr, the RF power of 50 watts and the treatment time of 5 min (best treatment condition for hydrophobicity property improvement) and at plasma condition at the pressure of 0.05 Torr, the RF power of 25 watts and the treatment time of 1 min (bad treatment condition for hydrophobicity property improvement) to be the case study on the effect of plasma conditions to the amount of fluorine on fabric sample. Fig. 5.17 - 5.18 show survey spectrum for untreated and SF_6 plasma treated PET, mixed Thai silk, Thai silk and cotton surfaces, respectively. It is clearly seen that the peak of F 1s is observed on all samples after SF_6 plasma treatment. The intensity of peak for F 1s increases as plasma condition is increased. In contrast, the intensity of peak for C 1s and O 1s decreases as plasma condition is increased. However, the peak of sulfur with the binding energy in the rage of 160-170 eV [41, 42] could not be observed on our samples. That is, after plasma treatment there are no sulfer atoms bounded to carbon and oxygen atoms in the fabrics. The high-resolution XPS scan is used to obtain the information on the actual chemical bounding of fluorine on the treated surface. Fig. 5.19 shows high resolution scan of the C 1s for untreated and SF_6 plasma treated PET fabric. The method of curve fitting to obtain resolving overlapping peaks is presented in appendix A. Line-shape analysis by peak deconvolution shows that the C 1s spectrum for untreated PET contains three distinct peaks which corresponds to three different type of carbon atom in the PET structure as showed in Fig. 5.20. These peaks can be assigned as follows; C1 (at 284.7 eV) corresponding to carbon bonding in aromatic ring (C-C/C-H), C2 (at 286.6 eV) assigned to methylene carbons singly bonded to oxygen atom (C-O), and C3 (at 288.5 eV) corresponding to carbon atoms in ester group (C=O)[12, 38, 39, 26, 40]. After the plasma treatment with SF_6, the C 1s spectrum as showed in Fig. 5.19(b) -

5.19(c) shows six distinct peaks, which all three peaks (C1, C2, C3) for untreated remained evident, three new peaks can be seen at 289.1, 291, and 293 eV. These peaks can be assigned to CF, CF_2, and CF_3, respectively [12, 36, 38, 39, 26, 40]. The summary of functional groups and their binding energies are showed in Table A.1. These new peaks are attributed to the wider peak of C1s spectrum. This result indicates interaction between SF_6 plasma and PET fiber. It has been reported [12, 36] that the F atoms in SF_6 plasma are the only active species which can interact with fiber. The mechanism of fluorine implantation in PET fiber can be described in a reaction scheme as follows,

$$-C-H- \xrightarrow{e^-,I^+,F^\bullet} -C^\bullet \xrightarrow{F^\bullet} -C-F-, \tag{5.3}$$

for aromatic ring and

$$-CH_2-CH_2- \xrightarrow{e^-,I^+,F^\bullet} -CH^\bullet CH_2 \xrightarrow{F^\bullet} -CFH-CH_2-, \tag{5.4}$$

for methylene carbon, which $C^\bullet$ is a radical of carbon atom and $F^\bullet$ is a radical of fluorine atom.

Two above reactions can be explained as F atoms are source of hydrogen abstracting and attached with carbon composite in the fiber lead to C-CF_x bound which increase the hydrophobicity of the fabric [12, 36]. However, we found that the intensity of the new peaks depends on the plasma condition, namely, the intensity of peak for CF, CF_2, and CF_3 increased as the plasma condition is increased.

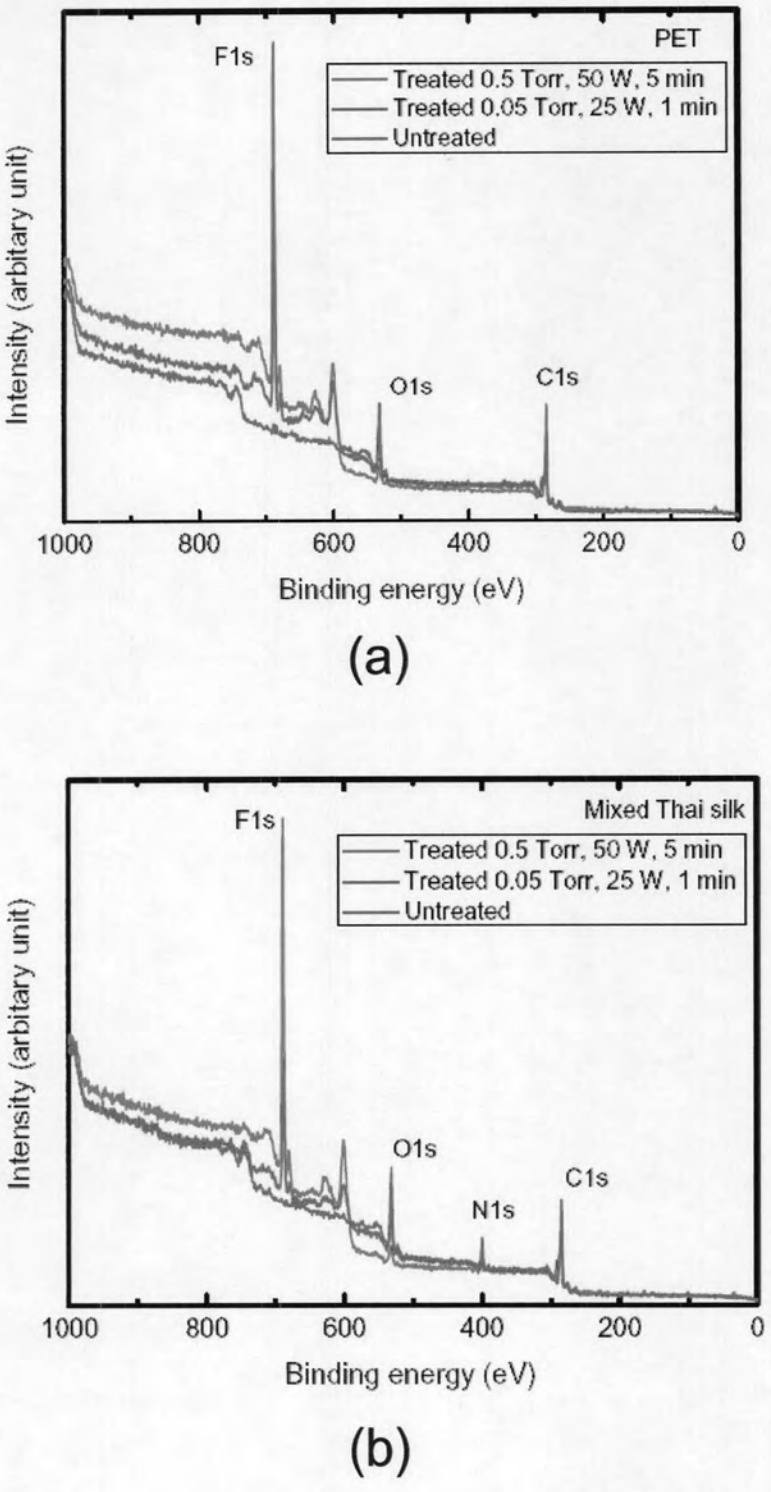
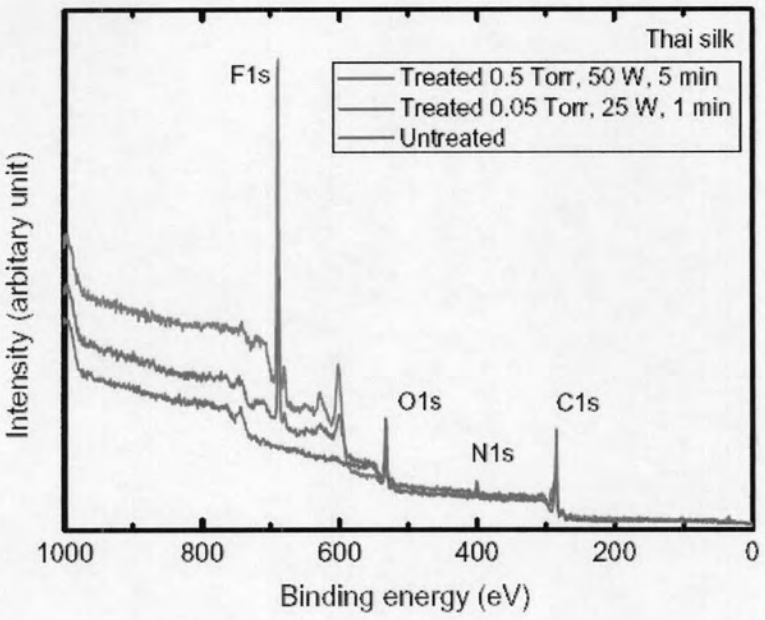
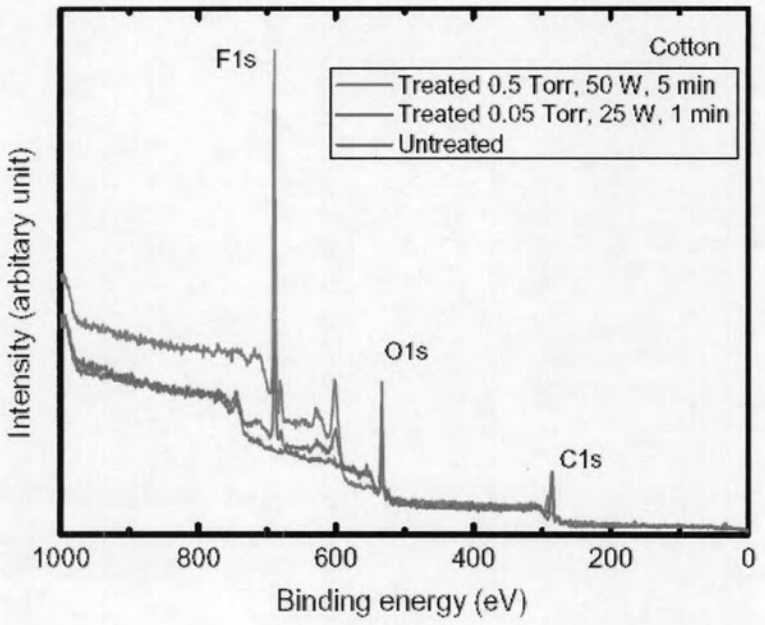


Figure 5.17: XPS survey spectrum for untreated and SF_6 plasma treated PET (a); mixed Thai silk (b).



(a)



(b)

Figure 5.18: XPS survey spectrum for untreated and SF_6 plasma treated Thai silk (a); cotton (b).

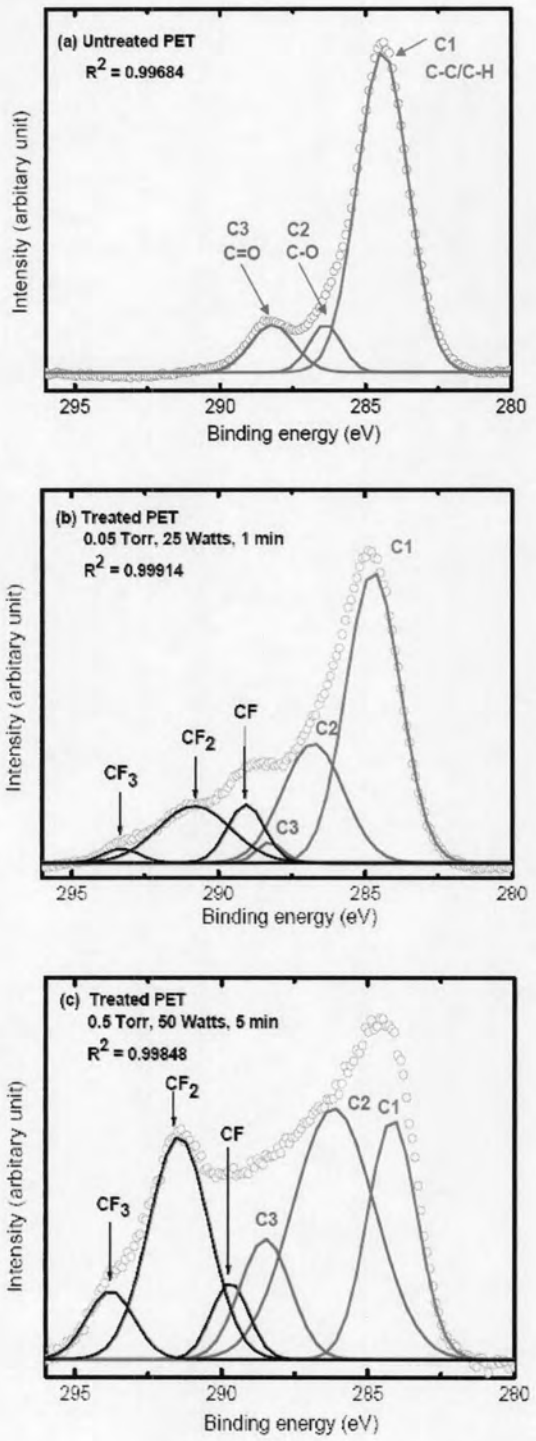


Figure 5.19: Line-shape analysis of the high-resolution C 1s XPS spectra for PET fabric surface. (a) untreated fabric, (b) treated at pressure of 0.05 Torr, the RF power of 25 watts, and treatment time of 1 min, (c) treated at pressure of 0.5 Torr, the RF power of 50 watts, and treatment time of 5 min.

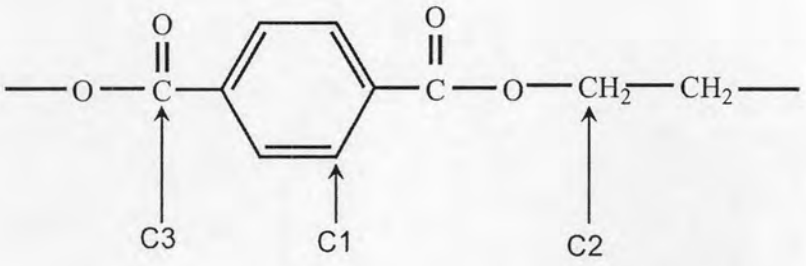


Figure 5.20: The structure of PET fabric [1].

Fig. 5.21 - 5.22 show C 1s XPS spectra of mixed Thai silk and Thai silk fabric surface, respectively. The C 1s spectrum for both of untreated mixed Thai silk and Thai silk contains three distinct peaks. These peaks correspond to three different types of carbon atom in the structure of silk as illustrated in Fig. 5.23. These peaks can be assigned as follows; C4 (at 284.7 eV) corresponding to carbon atom bounded only to carbon or hydrogen (C-C/C-H), C5 (at 286 eV) can be assigned to carbon atom singly bounded to nitrogen (C-N), and C6 (at 288.5 eV) corresponding to carbon atom doubled bounded to oxygen (C=O) [14]. After SF_6 treatment at pressure of 0.5 Torr, RF power of 50 watts and treatment time of 5 min, three new peaks at 289.1, 291, and 293 eV appear in the spectrum. This is due to presence of CF, CF_2, and CF_3, respectively [14]. However, the treated fabric at the pressure of 0.05 Torr with the RF power of 25 watts and the treatment time of 1 min, the peak at binding energy of 293 eV associating to CF_3 is not observed in both of fabrics. This is due to CF_3 group on the fabric requires more energy to break bounded between carbon atom and hydrogen or oxygen atom than CF_2 and CF group.

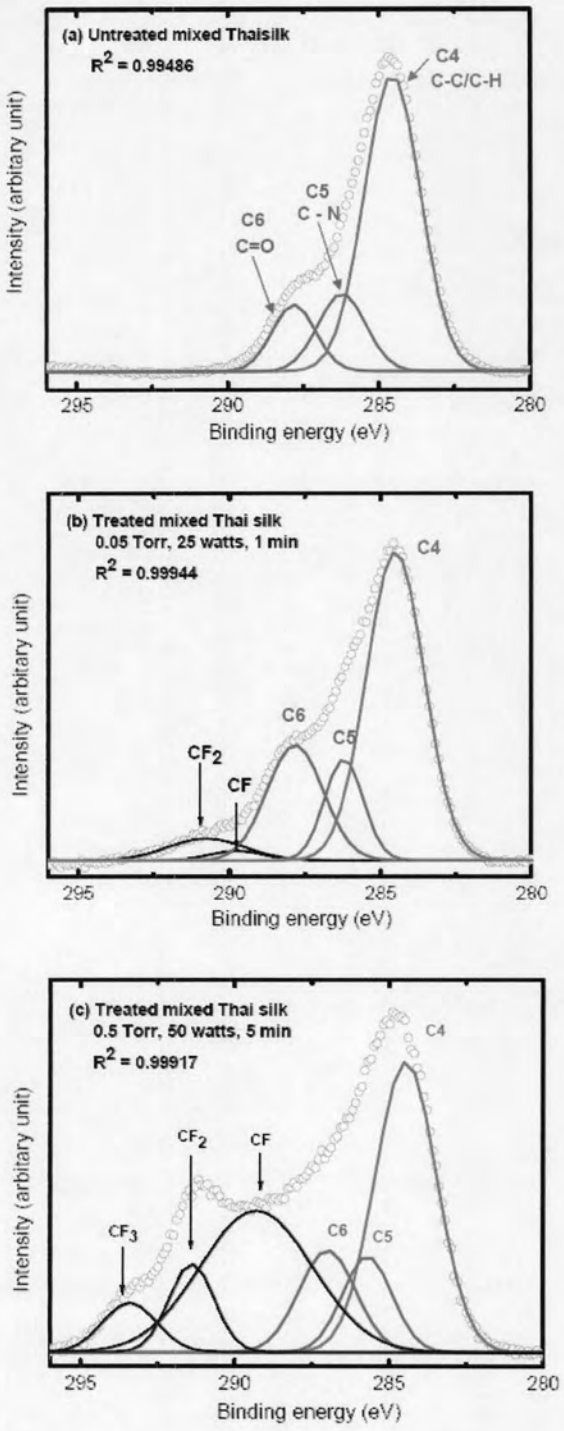


Figure 5.21: Line-shape analysis of the high-resolution C 1s XPS spectra for mixed Thai silk fabric surface. (a) untreated fabric, (b) treated at pressure of 0.05 Torr, the RF power of 25 watts, and treatment time of 1 min, (c) treated at pressure of 0.5 Torr, the RF power of 50 watts, and treatment time of 5 min.

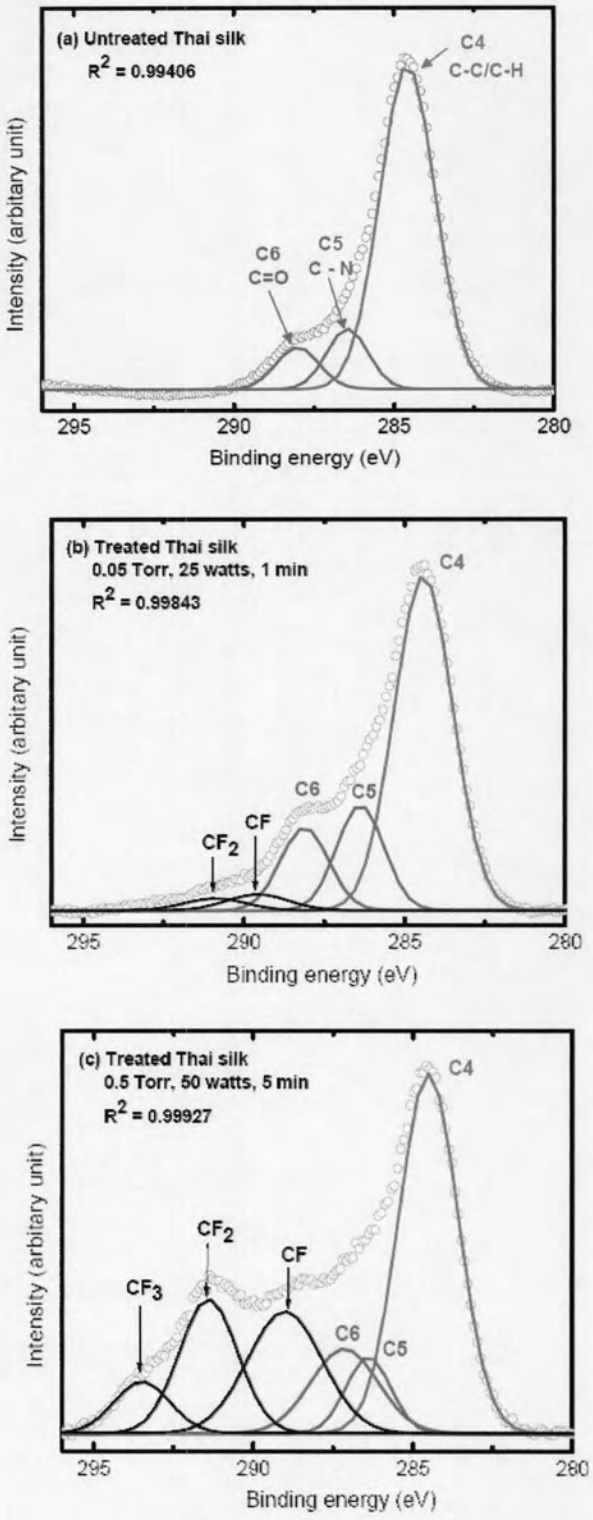


Figure 5.22: Line-shape analysis of the high-resolution C 1s XPS spectra for Thai silk fabric surface. (a) untreated fabric, (b) treated at pressure of 0.05 Torr, the RF power of 25 watts, and treatment time of 1 min, (c) treated at pressure of 0.5 Torr, the RF power of 50 watts, and treatment time of 5 min.

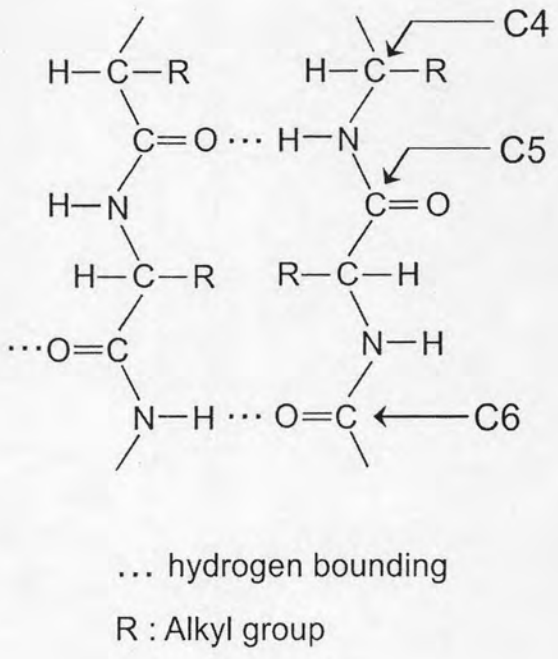


Figure 5.23: The structure of fibroin polymer in silk fabric [43].

Fig. 5.24 shows high resolution scan of C 1s for untreated and treated cotton fabric with SF_6 plasma. According to the structure of cotton as shown in Fig. 5.25 which contains three different types of carbon atoms. These carbon atoms correspond to three distinct peaks in XPS spectra as illustrated in Fig. 5.24(a). The assignment of signals are as follows; C7 (at 284.7 eV) can be assigned to C-C/C-H, C8 (at 286.2 eV) corresponding to -COH, and C9 (at 287.2 eV) assigned to C-O-C [10]. After treated fabrics with SF_6 plasma at the pressure of 0.5 Torr with the RF power of 50 watts and the treatment time of 5 min, XPS spectra exhibit three new peaks at 289.1, 291, and 293 eV which correspond to CF, CF_2, and CF_3, respectively [10]. Similar result can be seen in mixed Thai silk and Thai silk fabrics, after treated cotton at the pressure of 0.05 Torr the with RF power of 25 watts and the treatment time of 1 min, there is no peak that exhibits the binding energy of 293 eV which associating to CF_3.

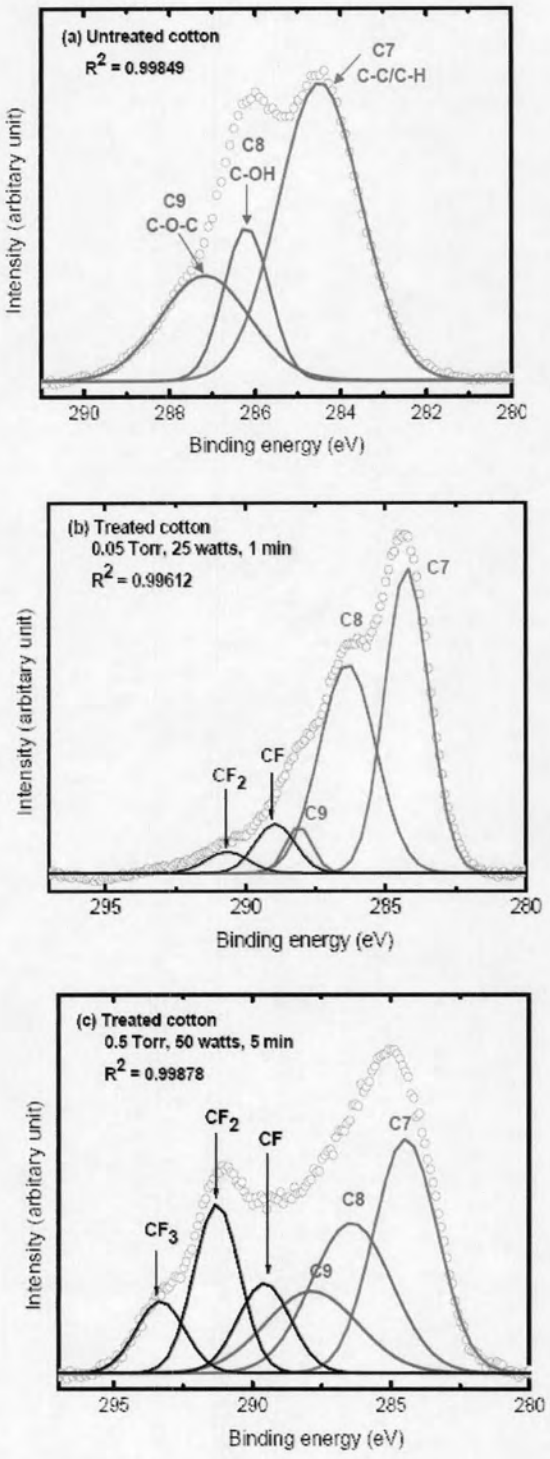


Figure 5.24: Line-shape analysis of the high-resolution C 1s XPS spectra for cotton fabric surface. (a) untreated fabric, (b) treated at pressure of 0.05 Torr, the RF power of 25 watts, and treatment time of 1 min, (c) treated at pressure of 0.5 Torr, the RF power of 50 watts, and treatment time of 5 min.

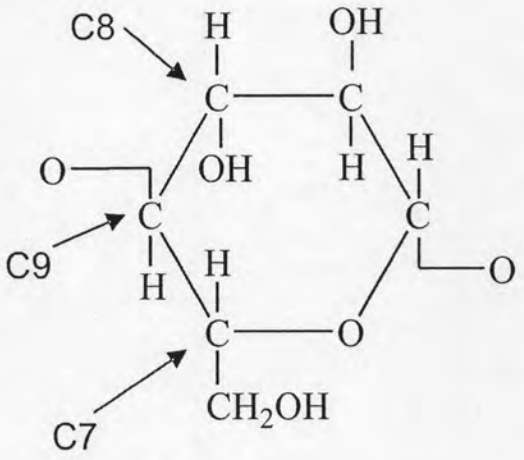


Figure 5.25: The structure of cotton fabric [44].

Due to the presence of fluorine-containing groups (CF, CF_2, and CF_3) in all sample structure after the treatment, the amount of fluorine is determined by intergrated area of these peaks. Table 5.1 shows the relative condition of plasma treatment and atomic ratio for PET, mixed Thai silk, Thai silk and cotton fabrics treated by SF_6 plasma. All fabrics show similar trend, the ratio of fluorine to carbon (F/C) increases while the ratio of oxygen to carbon (O/C) decreases with increasing RF power and SF_6 pressure or increasing treatment time. We noted that the absorption time is directly related to the amount of fluorine on sample surface. The amount of fluorine implanted on PET for treatment at the pressure of 0.05 Torr with the RF power of 25 watts and the treatment time of 1 min is higher than one that implanted on mixed Thai silk, Thai silk and cotton fabrics. This result agrees with the best hydrophobicity properties improvement which could be achieved for PET sample. However, the optimum condition for the treatment (pressure of 0.5 Torr, RF power of 50 watts and treatment time of 5 min) shows the closed value of F/C atomic ratio (0.45-0.49) of C2 in Table 5.1, regardless of the type of fabrics .

Table 5.1: The F/C and O/C atomic ratio of untreated and treated samples.

Conditions	PET			Mixed Thai silk			Thai silk			Cotton		
	AT	F/C	O/C	AT	F/C	O/C	AT	F/C	O/C	AT	F/C	O/C
Untreated	-	0.00	0.34	-	0.00	0.33	40	0.00	0.30	-	0.00	0.45
C1	210	0.34	0.25	67.7	0.15	0.30	190	0.25	0.27	170	0.21	0.41
C2	210	0.49	0.11	210	0.45	0.15	210	0.48	0.12	210	0.47	0.13

AT : Absorption time

C1 : Pressure of 0.05 Torr, RF power of 25 W, and treatment time of 1 min

C2 : Pressure of 0.5 Torr, RF power of 50 W, and treatment time of 5 min

- : Fabric absorbs water immediately

We emphasized that the hydrophobicity of fabrics can be controlled by varying plasma conditions in our RF-ICP system.