Effect of SF_6 plasma treatment on hydrophobicity improvement of fabrics

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(Received 2 May 2007)

We report the improvement of the hydrophobicity in fabrics treated by radio-frequency (RF) inductively coupled SF_6 plasma. The plasma was generated in the pressure range of 0.005-1 torr and with the RF power range of 25-75 watts. A set of fabrics including polyethylene terephthalate (PET), silk, cotton and mixed cotton-silk woven fabrics are treated under different operating conditions. Treated fabrics were characterized by scanning electron microscopy, water contact angle and absorption time measurement as a function of storage time after treatment. The atomic species in SF_6 plasma were analyzed by optical emission spectroscopy (OES), while the chemical compositions on fabric surface were also investigated by x-ray photoelectron spectroscopy (XPS). The OES and XPS results show spectrum lines of F I in SF_6 plasma and peaks of F 1s on sample surface, respectively. We expected that the change of fabric hydrophobicity is resulted from both surface etching and deposition of C-F residue on the fabrics fibers.

I. INTRODUCTION

To improve fabrics characteristics, conventional finishing processes usually include wet chemical treatments. On this regards, the finishing of fabrics by plasma processes are proposed to advantageously replaced many of such chemical treatments. This is due to the minimal contamination and the high acquiring speed in the plasma processes. Moreover, most plasma process only produces minimal gases exhaust, hence, more environmentally friendly. There are several possible activations during the plasma treatment i.e. surface deposition, polymerization, grafting, and etching. These activations can modify surface properties of the material while leave the bulk characteristics of the fabrics unaffected. Studies show that characteristics improvement can be imparted to the fabrics through low temperature plasma treatment employing various types of gas [1-6]. In this work, SF_6 is used as the plasma gas media and the source of fluorine atoms producing fluorination on the sample surface. The main aim of this study is to optimize plasma conditions to improve the hydrophobicity of PET, silk, cotton and mixed cotton-silk woven fabrics.

II. EXPERIMENTAL DETAILS

IIa. Plasma Reactor

The schematic diagram of the homemade radio-frequency inductively coupled plasma (RF-ICP) reactor is shown in Fig. 1. The major components of the system are the reactor chamber, the RF generator, the impedance matching network, the gas and pressure handling components and the plasma diagnostic system. In this work, the plasma source is powered by a 1000-Watt 13.56-MHz RF generator (Dressler model CESAR-1310) with output impedance of 50 Ω.

The matching network, used in the system, is placed inside a perforated aluminum cylinder, which acts as a Faraday cage protecting the electronic instruments from the effect of stray RF fields. The matching network is designed based on the LC resonant circuit, which consists of a variable vacuum capacitor and an 8-10 turns planar coil with maximum diameter of 150 mm as the inductor. The variable vacuum capacitor can be varied in the range of 80 pF to 1000 pF. The calculation and detail of the matching network coupling circuit has been given in previous work [7].

The reactor chamber is made of stainless steel in a cylindrical form, which is covered by two stainless steel plates at the top and bottom flanges. The top plate has a 20-cm diameter circular opening, which is covered by a quartz circular plate to isolate the vacuum and still let the RF field from the planar coil placed above the quartz plate to couple into the plasma.

The base pressure at 2×10^{-5} torr can be achieved using the vacuum system consists of a turbo molecular pump backed by a rotary vane pump. The pressure inside the system is measured by Penning type pressure gauge, which mounted at the port on the sided flange of the chamber. During plasma operation, the operation gas enters the chamber via mass flow controllers (Allborg model GFC-17). An automated pressure controller (Edward model 1800) is utilized to control the pressure inside the reactor chamber to the desired values.

IIb. Samples Preparations

Commercially available polyethylene terephthalate (PET), silk, cotton and mixed cotton-silk (cotton 25% silk 75%) woven fabrics were used as the samples in this study. Prior to plasma treatment, fabrics were washed

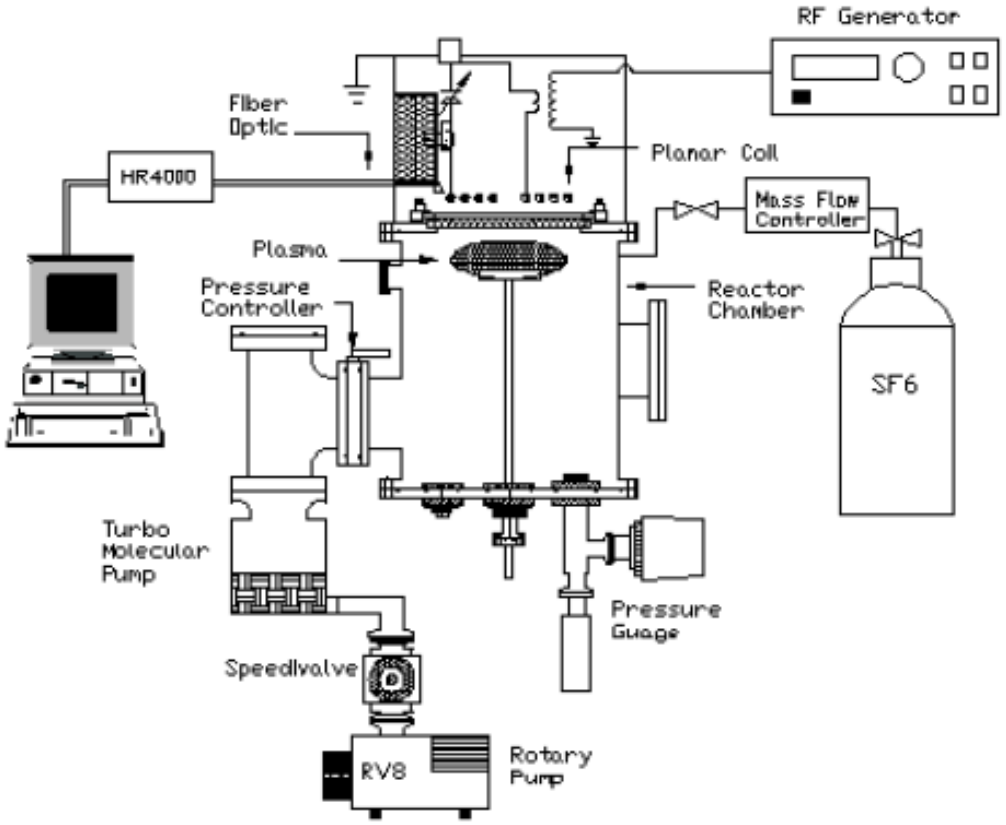


FIG. 1. Schematic diagram of the RF-ICP system.

twice in ultrasonic bath for 10 minutes at room temperature. The first washes were performed with a water solution containing 5 percent by weight of non-ionic non-residue detergent. The second washes were performed with only de-ionized water. Samples were then dried in a muffle at 80°C for 60 minutes.

All samples were cut to the dimensions of 10×10 cm. The samples were secured in a horizontal plane with a sample stretch holder and placed along the center axis of the chamber 4 cm below the quartz plate which is 6 cm below the planar coil. The stretch holder is circular in shape and having the treatment area of 200 cm^2. The SF6 gas used in all experiment has the purity of 99.99%.

The plasma operating conditions were set at the pressure of 0.005, 0.05, 0.5 and 1 torr with RF power of 25, 50 and 75 watts. The treatment times was fixed at 1 minute. It was observed that at RF power higher than 75 watts, the plasma was unstable while at pressure higher than 1 torr, the fabrics are usually damaged.

IIc. Characterization Of The Treated Samples

In order to investigate the hydrophobicity or the ability to repel the water from the surface of material, different measurements can be performed such as contact angle measurement [1-3,8-10], rolling-off angle measurement [1], liquid wicking rate measurement [11], capillary rise measurement [12], and absorption time measurement [1-3]. However, one of the simplest and reliable method to measure the wettability which opposes to the ability to repel water, is the measurement of water contact angle (θ) as illustrated in Fig. 2.

We can consider a water droplet in equilibrium due to the balance surface tensions at the interfaces between solid/liquid (γ_{SL}), between solid/vapor (γ_{SV}), and between liquid/vapor (γ_{LV}). The relation between contact angle and surface tension is given by Young-Dupre equation [8,9].

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}. \quad (1)$$

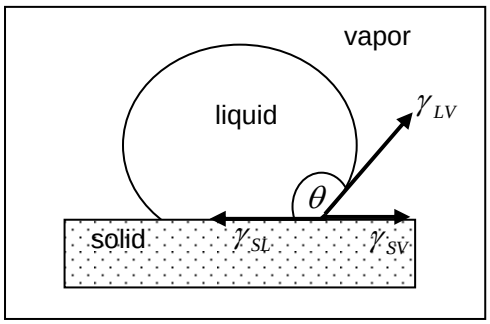


FIG. 2. Schematic diagram of contact angle, showing the balance of surface tension forces.

In addition, the work of adhesion (W_a) is defined as work required to separate a unit area of interface between liquid and solid of a surface. The work of adhesion is then

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} . \quad (2)$$

This gives the correlation between contact angle and work of adhesion as

$$W_a = \gamma_{LV}(1 + \cos\theta) \quad (3)$$

where, surface tension of water in air (γ_{LV}) equal to 73 dynes/cm. According to Eq. (3), higher contact angle represents lower work of adhesion, in other words, more ability to repel water. In this work, the water droplets contact angles were measured by Tantac CAM-PLUS contact angle meter.

It is sometime possible that large deviation in contact angle result could occur even in the same set of measurement. This is due to the roughness and the irregularity of the fabric surfaces. Hence, another method to measure the hydrophobicity, the absorption time measurement, was also implemented to correlate the result with the other parameters.

The water droplets (40 μl in volume) were dripped on the sample surface using a micropipette at three random positions of each sample fabrics. The data of the absorption time were obtained by averaging the time results of these three droplets. The absorption time was restricted to a maximum of 210 minutes. After this, the water volume lost is considered mostly due to the evaporation and the fabric is considered unwettable.

III. RESULTS AND DISCUSSION

Fig. 3 shows an example of the dramatic improvement in the hydrophobicity of the fabrics after SF_6 plasma treatment. The contact angle results in Table I show the abrupt increases of hydrophobicity in all PET, cotton and mixed cotton-silk samples. Prior to the treatment by plasma process, the water droplets on these fabrics were rapidly absorbed into the fabric surface, while after treatment, the water droplet could be observed on the surface with contact angles between 135º − 145º. In case of silk, a contact angle after treatment increased from 101º to 144º. Our study shows that these improvements in hydrophobicity do not particularly depend on the operating condition or the types of fabrics. No clear trend of the hydrophobicity as a function of the plasma conditions was obtained.

All tested fabrics demonstrate the increasing of hydrophobicity after the plasma treatment. Figs. 4 and 5 show the results of absorption time measurement of water droplets on cotton and silk as a function of pressure at different RF power. The measurement was

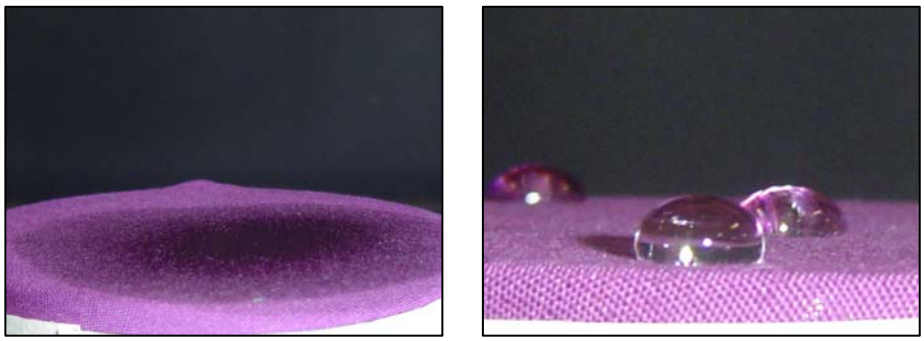


FIG. 3. The PET sample (a) before and (b) after the SF6 plasma treatment. The water droplet is instantly absorbed into the untreated fabric while stay unabsorbed on the treated fabric surface.

TABLE I. Contact angle of water on PET, cotton, silk and cotton-silk fabrics before and after the SF_6 plasma treatment.

Type of fabrics	Contact angle (degree)	
	Before treatment	After treatment
PET	**	139 ± 1
Cotton	**	140 ± 1
Silk	101 ± 5	144 ± 3
Mixed cotton-silk	**	142 ± 3

** Fabric absorbed water rapidly.

performed instantly after 1 minute treatment of SF_6 plasma. In both cotton and silk, best improvement in absorption time was obtained in the samples treated at the RF power of 50 watts. At a fixed RF power and treatment time, it was observed in cotton samples that the absorption time increased with increasing operating pressure and reached the maximum observation time limit of 210 min when the operating pressure was 0.5 torr. Similar result was also found in silk, but more rapid improvement was obtained when the operating pressure was higher than 0.05 torr. As can be seen from Figs. 4 and 5, an optimum condition for plasma treatment for cotton and silk can be achieved at the operating pressure of 0.5 torr and the RF power of 50 watts.

Fig. 6 shows a comparison of absorption time on PET, cotton, silk and mixed cotton-silk as a function of RF power at operating pressure of 0.05 torr and treatment time of 1 min. Again, due to the rapid absorption of water droplet on untreated PET, cotton and mixed cotton-silk, the absorption time on these samples could not be measured. The result of untreated silk absorption time is approximately 40 min. Among the fabrics tested, best improvement of hydrophobicity was obtained in PET samples.

We have measured the storage time effect on hydrophobic property of all fabrics, as shown in Fig. 7. The results indicate that the hydrophobic durability after the exposure of SF_6 plasma depend on the type of fabrics. The best hydrophobic durability was obtained in PET samples in which the maximum observation absorption time limit of 210 min. was still obtained after 14 days. On the contrary, for cotton, the hydrophobicity gradually decreased to a minimum in 21 days.

The OES spectra of plasma during the sample treatments were obtained using a commercial optical spectrometer and software (Ocean Optics model

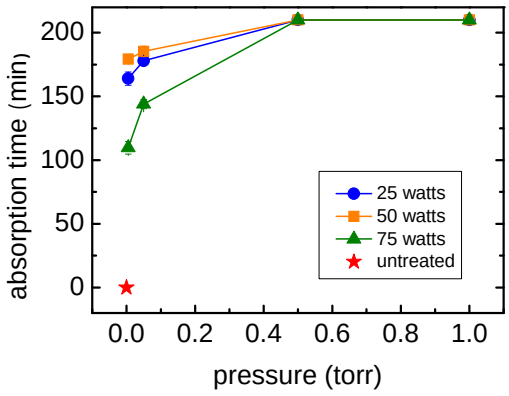


FIG. 4. Water droplet absorption time on cotton which were treated for 1 min at different pressures and RF powers. Untreated cotton absorbed water rapidly

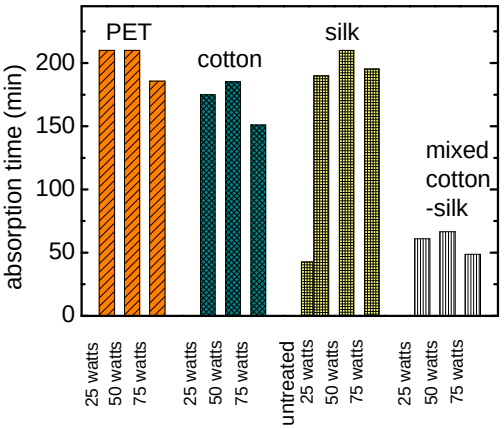


FIG. 6. Water droplet absorption time on PET, cotton, silk and mixed cotton-silk as a function of RF power. Plasma pressure and treatment time are 0.05 torr and 1 min, respectively.

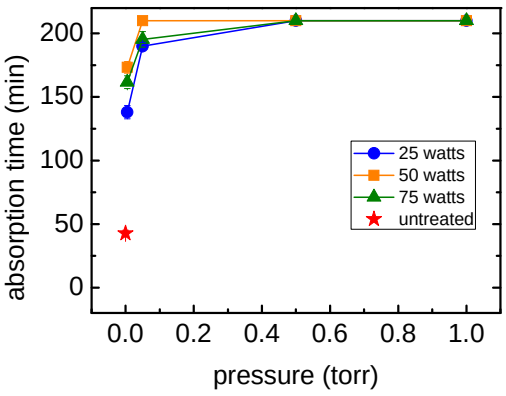


FIG. 5. Water droplet absorption time on silk which were treated for 1 min at different pressures and RF powers.

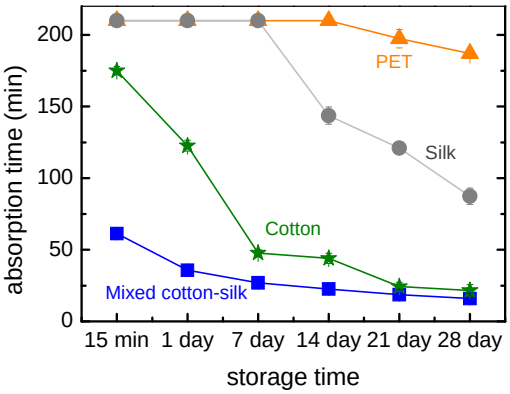


FIG. 7. Water droplet absorption time on PET, cotton, silk and mixed cotton-silk, treated for 1 min at pressure of 0.05 torr and RF power of 25 watts, measured at different times after treatment.

HR4000 and OOIBase32). The OES spectrum of SF_6 plasma in Fig. 8 features the spectra lines of F I (excited fluorine) [13] which is believed to be the source of hydrogen abstracting and attached with carbon composite in the fiber lead to C-F bonds [14]. This result is in good agreement with the XPS measurement (Kratos Analytical model AMICUS). Fig. 9 shows the XPS survey scans of untreated (a) and treated (b) silk surface.

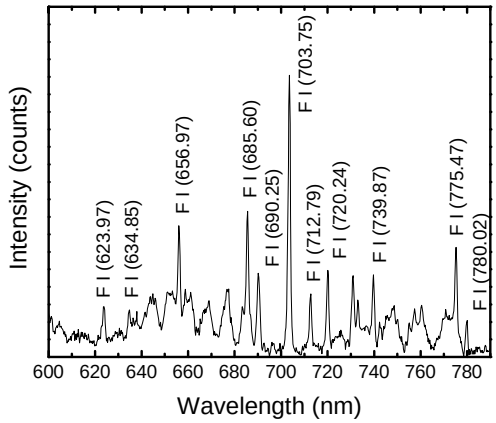


FIG. 8. OES spectrum of SF_6 plasma at the pressure of 0.05 torr and the RF power of 25 watts. The spectrum was identified using the NIST atomic wavelength table which indicated F I peaks in the spectrum.

An increase in the intensity of the peak for F 1s is observed after SF_6 plasma treatment. We expect that the change of sample hydrophobicity is resulted from the deposition of such C-F residue on the fabrics fibers. Previous studies show that the hydrophobic properties can also be achieved when fabrics were treated by plasma which contain other fluorinated compound such as tetrafluoromethane (CF_4) [15] and tetrahydro-perfluorodecyl acrylate (AC8) [16].

Fig. 10 shows the SEM images of silk sample fibers. It can be seen that the surface of treated silk fiber (b) is rougher compared to that of untreated silk fiber (a). The similar results of rough fibers surface after plasma treatment was also observed in PET and cotton samples. This rougher surface resulted from C-F residue deposition. The etching of the fiber surface could as well contribute to the roughening and the improvement of the fabrics hydrophobicity. This phenomenon is known as the "lotus effect" [17,18]. Essentially, the water droplets can achieve a smaller contact area by being supported on top of the sharp features of the surface lowering the interaction energy and hence increasing the hydrophobicity.

IV. CONCLUSIONS

The improvement in hydrophobicity of PET, silk cotton and cotton-silk fabrics were observed with the applications of SF_6 plasma treatments. The suitable

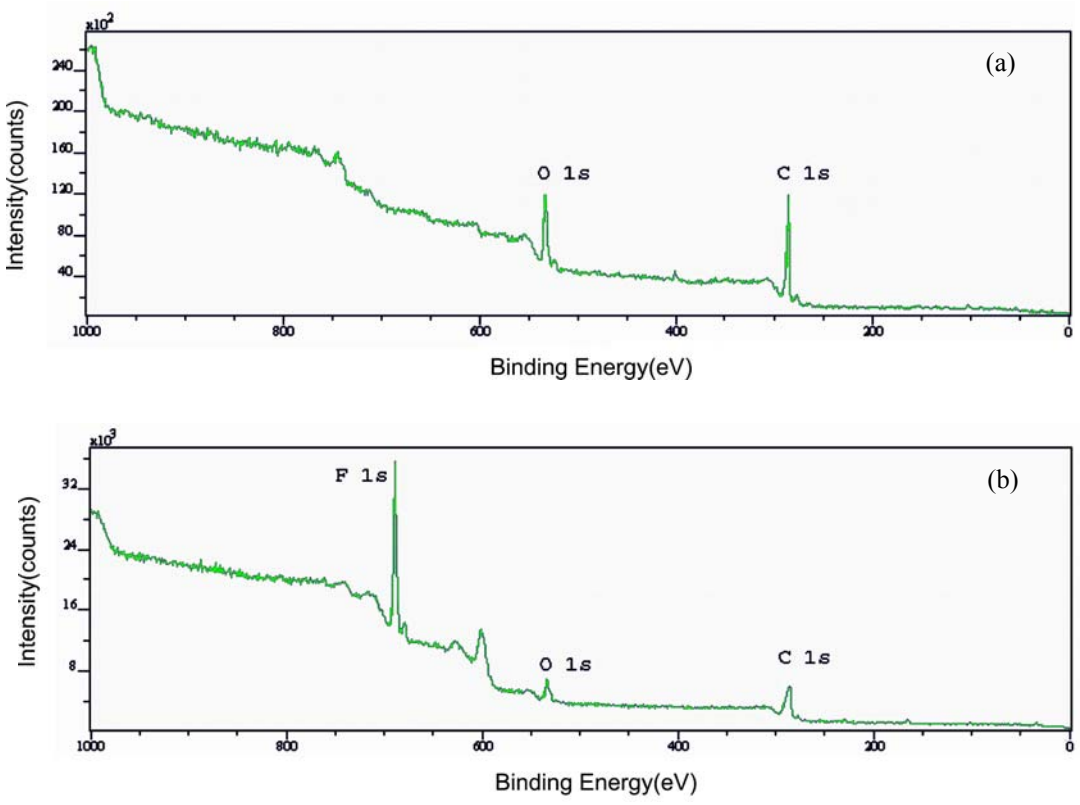
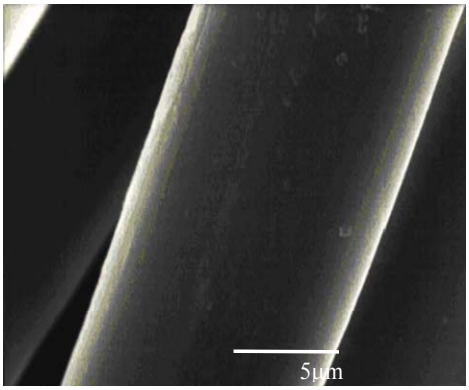
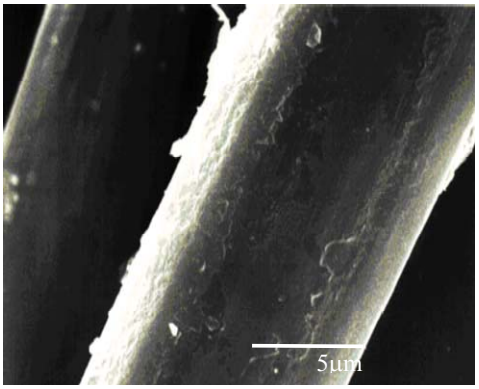


FIG. 9. Survey scans of XPS on silk samples; (a) untreated, and (b) treated sample. The treated sample was exposed to SF_6 plasma for 1 min at the pressure of 0.5 torr and the RF power of 50 watts.



(a)



(b)

FIG. 10. SEM photographs of the silk samples at 5000×; (a) untreated, and (b) treated sample. The treated sample was exposed to SF_6 plasma for 1 min at the pressure of 0.05 torr and the RF power of 25 watts.

operating condition in our RF-ICP system to yield good improvement of hydrophobicity is obtained at the operating pressure of 0.5 torr and RF power of 50 watts. We expected that the change of fabric hydrophobicity is resulted from both surface etching and deposition of C-F residue on the fabrics fibers.

ACKNOWLEDGEMENT

We thank C. S. Wong for the discussion on the setup of RF-ICP plasma reactors; S. Tungasmita and V. Pavarajarn for SEM and XPS analysis. This research is supported by the National Research Council of Thailand.

REFERENCES

[1] E. Selli, *et al*., J. Mater. Chem., **11**, 1985-1991 (2001).
[2] E. Selli, *et al*., Macromol. Chem. Phy., **202**, 1672-1678 (2001).
[3] E. C. Rangel, *et al*., Surf. Interface Anal., **35**, 179-183 (2003).
[4] F. Hochart, *et al*., Surf. Coat Technol.**, 165**, 201-210 (2003).
[5] P. Chanvan, *et al*., Surf. Coat Technol.**, 193**, 356-360 (2005).
[6] V. Castelvetro, *et al*., Plasma Processes and Polymers, **3**, 48-57 (2006)
[7] B. Paosawatyanyong, J. Sci. Res Chula. Univ., **29**, 198-211 (2004).
[8] E. L. Decker, *et al*., Coll. Surf. A, **156**, 177- 189 (1999)
[9] A. W. Adamson, *Physical Chemistry of Surfaces*, chapters 10 and 13, 4th edition, Wiley, New York, 1982.
[10] C. M. Weikart, *et al*., J. Coll Interface Sci., **211**, 18-27 (1999)
[11] E. Temmerman and C. Leys, Surf. Coat Technol.**, 200**, 686-689 (2005).
[12] F. Ferrero, Polymer Testing, **22**, 571-578 (2003)
[13] National Institute of Standard and Technology, *NIST Atomic Spectra Database* (2003), Available from http://www.physics.nist.gov/cgi-bin/ASD/line1.pl.
[14] C. Riccardi, *et al*., Plasma Sources Sci. Technol., **10**, 92-98 (2001).
[15] G. Poletti, *et al*., Applied Surface Science, **219**, 311–316 (2003)
[16] F. Hochart, *et al*., Surf. Coat Technol.**, 165**, 201-210 (2003).
[17] N. Shirtcliffe, *et al*., Surface and Coatings Technology, **142-144**, 1121-1128 (2001).
[18] H Höcker, Pure Appl. Chem., **74**, 423–427 (2002).