

CHAPTER VII
SURFACE CHARACTERIZATION OF COTON COATED BY
A THIN FILM OF POLYSTYRENE WITH AND WITHOUT
A CROSS-LINKING AGENT

ABSTRACT

Thin polystyrene film coated on cotton was successfully formed by admicellar polymerization. Divinyl benzene (DVB) was used as cross-linking agent to form networked polystyrene to improve film coverage. Wettability test and XPS analysis were used to characterize the coated surface. The optimum amount of DVB was 1%. At this amount of addition, the film coverage was most complete as judged by the reduction of O1s signal.

Key Words:

Polystyrene film, cross-linking agent, divinyl benzene, XPS, admicellar polymerization, wettability

INTRODUCTION

Thin film coatings are widely used technique for modification of a substrate surface. Common methods for applying thin film coatings include chemical vapor deposition, plasma polymerization, physical vapor deposition, and electrochemical deposition. Admicellar polymerization is a method that can be used to create a thin polymeric film on a substrate surface.¹⁻⁹ The method makes use of the formation of a surfactant bilayer on a substrate surface at a surfactant concentration just below the CMC. In the surfactant layer, the amphiphilic molecules are oriented with their ionic head groups pointing outward while the long hydrophobic tails interact to form a hydrophobic inner core (Fig. 1a). The surfactant bilayer formed on a substrate surface has been called an "admicelle". When an organic monomer is added into the

solution, it will be preferentially adsorbed in the core of the admicelle in a process called “adsolubilization” (Fig 1b), and when an initiator is added, the monomer in the admicelle will undergo polymerization reaction to form a polymeric layer on the substrate surface (Fig 1c). After the polymerization, surfactant in the upper layer may be removed by washing to expose the polymeric layer on the substrate surface.

Admicellar polymerization has been successfully used to coat a thin film of a variety of polymers on various kinds of substrate. Recently, the method has been used to form a thin polystyrene film on cotton.^{1,2} The resulting cotton shows good water repellency property. Water repellent cotton has wide application in tentage material, canvas, rain coats, and furnishing textiles. Polystyrene is known to form a cross-linking polymer with divinyl benzene (DVB)¹⁰ as shown in reaction scheme in Fig 2. Many studies have been carried out on various aspects of the reaction.¹¹⁻¹⁶ In this work, the effect of adding DVB to the styrene monomer in the admicellar polymerization process on cotton was studied. After the polymerization, the wettability of the treated cotton surface as determined by the Wilhelmy microbalance technique was correlated to the surface coverage of the polymer as determined by XPS.

XPS is a powerful technique that is widely used for characterization of a substrate surface.¹⁷⁻²² It provides information about the chemical state and concentration of elements comprising the outermost surface layers of a solid. The sample depth of this technique is generally less than 10 nm.²³ In this work, it was used to characterize films of polystyrene coated on cotton in both qualitative and quantitative analysis. The peak C(1s) was qualitatively used to differentiate characteristic peaks between cotton and polystyrene and confirm that cotton fabric modified by admicellar polymerization was coated with polystyrene. The coverage and film thickness of polystyrene on cotton were quantitatively determined by XPS using the peak of O(1s) that has no signal for pure polystyrene, but does occur in cellulose of cotton. The coverage and thickness of film were used to comparatively explain wettability of different cotton samples prepared using various amounts of DVB.

EXPERIMENTAL

Materials

A plain weave, medium-weight (150 g/m^2), bleached cotton fabric was purchased from Boonchaury Co. Ltd. Prior to use, the fabric was washed in a washing machine at 95°C several times until it was free from any remaining surfactant as checked by the UV absorption of the last washing liquid at the wavelength of 225 nm.

Styrene monomer and divinyl benzene were purchased from Aldrich Co.Ltd. The inhibitors in both chemicals were removed by washing with 10% NaOH according to the method described by Collins, et al.²⁴

Dodecylbenzene sulfonate (DBS) used as the surfactant was purchased from Aldrich Co.Ltd.

Sodium persulfate used as initiator was purchased from BHD Laboratory Supplies CO.Ltd. Hydrochloric acid and sodium chloride were purchased from Merck and Alex Chemicals Co.Ltd., respectively.

Admicellar polymerization process

The admicelle polymerization was carried out at DBS concentration just at or below the CMC as determined from the adsorption isotherm of DBS-cotton system as shown in Fig 3. The concentration of DBS in solution was determined by Cecil UV spectrophotometer model CE 2040 at the wavelength of 225 nm.

From the adsorption isotherm, the CMC was found at $1,050 \mu\text{M}$ and so a DBS concentration of $1,000 \mu\text{M}$ was chosen for the admicellar polymerization process. The solution was adjusted to pH 4 and to a concentration of 0.15 M NaCl to enhance surfactant adsorption.

To carry out the admicellar polymerization, a 20 mL aliquot of DBS solution was pipetted into a 24 mL glass vial and 0.5 g piece of cotton fabric in the square shape of $1.5 \times 1.5 \text{ in}^2$ was placed in the vial in the vertical position with no folding or overlapping. The styrene monomer with varying amount of divinyl benzene as

cross-linking agent of 0, 1, 2, and 5 mole % was pipetted into the vial to give a DBS:monomer ratio of 1:5. Initiator at a DBS:monomer ratio of 1:1 was then injected into the vial. The vials were sealed and maintained at 30 °C in a shaker bath for 8 h to allow for admicelle formation and adsolubilization of the monomer in the admicelle. After that, the temperature of the system was raised to and maintained at 80 °C for 2 h to effect the polymerization reaction.

After that, the fabric was taken from the vial and washed 5 times with hot distilled water at 80 °C for 1 h each time using a water:cotton ratio of 200:1 by weight to make sure that the outer layer of DBS was completely removed. The fabric was then dried in an oven at 110 °C to 5 h before it was taken out for further test.

Water repellency test by the drop test

An initial characterization of the treated surface was by the drop test. A distilled water droplet of 10 μL was placed on the cotton fabric surface with a 20 μL syringe. The drop was carefully placed on the fabric with no impact force. The fabric was judged water repellent when the droplet remains spherical on the fabric with no wetting after 30 min.

Wettability test by the Wilhelmy microbalance technique

Individual yarns were taken from the fabric and cut into 8 mm lengths for testing. Each yarn was attached with wire and hung from the Wilhelmy microbalance (Cahn model DCA-322). The machine was set as shown in Fig 4. With the machine in operating under microcomputer control, the yarn was slowly lowered to touch the water surface in the beaker and then held still for 5 min before being withdrawn to the previous position. After that it was taken up to the previous position. The curves of force and position shown in Fig 5, and of force and time shown in Fig 6 were recorded by the machine. From the curve of force and time in Fig 6, it can be seen that, as soon as the yarn touches the water surface, the force jumps up due to the wetting of the yarn. This is termed the “initial force” and it is taken to indicate the

wettability of the yarn. After a time of 5 minutes, the yarn is lifted above the liquid surface, with a sudden drop of the force occurring at this point(Fig. 5). However, it was found that the force did not return to zero indicating that some water is retained inside the yarn structure after it was lifted off the water surface. The force remaining is termed the “absorption force”.

Surface characterization by XPS

The cotton fabric sample was cut to be a small piece and placed onto the sample holder of XPS characterization. X-ray photoelectron spectroscopy (XPS), a Physical Electronics PHI 5800 ESCA system with a concentric hemispherical analyzer and a monochromatic Al K α X-ray source (1486 eV) was used to analyze them. The C1s and O1s spectra of the cotton sample were obtained for qualification and quantification of polystyrene film.

RESULTS AND DISCUSSION

Water repellency test by the drop test

Fig 7 shows the results of the drop test on unmodified and admicellar-modified cotton by the drop test. In the case of unmodified cotton (Fig 7(a)), the water droplet was found to disappear immediately with water spreading over a wide area. In the case of admicellar-modified cotton both with and without divinyl benzene cross-linking agent (Fig 7(b)), the droplet remains spherical even after 30 min with no spreading indicating that all modified fabrics are hydrophobic with good water repellency.

Wettability test by Wilhelmy microbalance technique

The initial force and the adsorption force of unmodified and admicellar-modified cotton were compared in Fig 8 and 9. The initial force and the force from water absorption were used to determine the optimum amount of cross-linking agent.

As shown by the data of Fig 8, the initial force differed significantly between unmodified and modified cotton. The initial force of unmodified cotton was 7.81 mg while the initial force of all modified cotton samples was lower than that depended on amount of cross-linking agent. Addition of 1% of DVB was found to give the lowest initial force, although statistically indistinguishable from the 0 or 2% levels. From the adsorption curve in Fig 9, it can be seen that all modified cotton adsorbed very small amount of water, while the yarn of unmodified cotton absorbed about 1.5629 mg of water. The difference in the absorption force of modified cotton with varying amounts of DVB is shown in Fig 10. Again, the sample prepared with 1% DVB shows the lowest absorption force. From the results it appears that the optimum amount of DVB is at 1%.

Surface characterization of modified cotton by XPS

Qualitative analysis

XPS was used to characterize the surface of modified cotton covered with polystyrene film. XPS peak shows the characteristic binding energy (eV) of elements. Polystyrene standard peak of XPS was used to compare unmodified cotton, and modified cotton prepared with increased cross-linking agent.

Cotton and polystyrene are hydrocarbon compounds that can show the C(1s) peak of XPS. Fig 11a shows the C(1s) peak of polystyrene. The pristine polystyrene is fitted with two components centered at 284.5 eV corresponding to the C-C and C-H bonds, and the smaller peak at 291.3 eV corresponds to a shake-up satellite of pi to pi* of aromatic ring. The C(1s) peak of cotton is shown in Fig 11b. It combines three peaks at 284.4 eV of C-C and C-H bonds, 286 eV of C-O bond, and 287.5 eV of O-C-O bond. Both peaks of polystyrene and cotton are clearly different. To confirm polystyrene coating on cotton, cotton modified by varying amount of DVB was also characterized with XPS as shown in Fig 11c to 11f. Both C(1s) peaks of polystyrene and cotton were presented in all cotton samples, with the main peak in all occurring at 284.4eV; importantly, each sample exhibited the peak of aromatic ring at around

291.3 eV. The results confirm that polystyrene has been successfully coated on the cotton surface of all treated cotton.

Quantitative analysis

The polystyrene film coated on cotton was characterized by XPS in two directions, the wide direction, or termed “coverage”, and the deep direction or “thickness”. This study was used to understand the improvement of film coating from the effect of cross-linking agent.

Polystyrene film coverage on cotton was calculated from the signal of oxygen that is one of the main elements of the cellulose molecule of cotton. The other two primary elements are carbon and hydrogen. The main elements of polystyrene are carbon and hydrogen. For this work, the signal of oxygen in cotton was used to estimate the extent of polymer coverage on modified cotton. If cotton is coated by polystyrene, the strength of the oxygen signal should be reduced. From the results in Table 1, all treated cotton fabrics have reduced oxygen signal, but to a different degree depending on the amount of cross-linking. A control sample with LAS indicates that surfactant adsorption alone cannot explain the signal reduction. All treated cotton was found to be hydrophobic by the drop test, but the amount of coverage was not the same. The treated cotton with 1% to 2% cross-linking agent gave higher coverage than that with no cross-linking agent and higher than that with 5% cross-linking agent. The results are consistent with the wettability tests which show that the samples with 1-2 % DVB have the lowest wettability or highest hydrophobicity. The results indicate that there is a direct correlation between the wettability of the surface and the oxygen signal obtained from XPS as shown Fig 12.

The thickness of polystyrene film was calculated by using the ratio of cotton and polystyrene intensity. The thickness measurement of coated film by XPS has been applied in previous works.²⁵⁻²⁶ The results in Table 2 show that all treated cotton with DVB gave thicker films than that without DVB. This is attributed to the formation of a cross-linking network on addition of DVB. The apparent film thickness of all samples was less than 1.5 nm., which is the approximate length of the hydrocarbon tail group of DBS used to form admicelle on cotton. This suggests that

styrene monomer and DVB polymerization took place within the very confined space of the admicelle as shown in Fig 13. Polystyrene apparently covers the surfaces of individual fibers that comprise the cotton yarn of threads in the fabric. This high level of integration of polystyrene and cotton can explain the great reduction in water absorption. It is also consistent with the small thicknesses of the film as the polystyrene is dispersed throughout the porous cotton yarn. Both wettability measurements and XPS data indicate an increase in polystyrene coverage of cellulose as cross-linking agent is added at 1-2% and a decrease in coverage at 5%. Thus, changes in molecular structure with cross-linking causes both improvement and degradation of water repellency. Addition of DVB should increase molecular weight and tend toward a two dimensional network structure. Attempts to confirm increased molecular weight using GPC were inconclusive. Polystyrene becomes insoluble after cross-linking, so only lower molecular weight species could be extracted. However, indirect evidence came from the observation that the amount of extractable sample was less with higher amounts of DVB. Grady recently confirmed the problems in extracting polymer from a surface after admicellar polymerization²⁷.

Well-known properties can help explain the observed effects of cross-linking in this study. Molecular interactions between polar cellulose and nonpolar polystyrene should not be strongly attractive. Surfactant helps to bridge these two species as polymer is forming and then after admicellar polymerization, but it must compete with the tendency of a linear polymer to coil and attain a zero end-to-end distance. Coiling will cause polymer to pull up from the substrate. Creation of cross-links ties polystyrene to adjacent polymer molecules in a two dimensional network that should reduce its ability to retract from the cotton surface. The decrease in coverage at 5% DVB can be understood by the volume change associated with polymerization. Material density increases as monomer converts to polymer, an effect that is even greater with cross-linking. The combined effects of reduced retraction and contraction with the latter dominating at 5%DVB can explain the observed trends in polystyrene coverage.

CONCLUSIONS

The addition of cross-linking agent leads to better coverage of the polymer on the fiber surface resulting in fiber with improvement in wettability. The optimum amount of cross-linking agent is 1%. Above this both the coverage and wettability begin to decrease.

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List of Tables

Table 1. : Coverage results from XPS

Table 2. : Polystyrene film thickness analyzed from XPS

Table 1.

Sample	Oxygen Signal; O(1s)	Surface Coverage (%)
Cotton	35.94	0.00
Cotton-Surfactant	32.18	10.46
Cotton-PS-0%DVB	23.98	33.28
Cotton-PS-1%DVB	16.70	53.53
Cotton-PS-2%DVB	17.00	52.70
Cotton-PS-5%DVB	27.51	23.46

Table 2.

Sample	Thickness (nm)
Cotton-PS-0%DVB	0.53
Cotton-PS-1%DVB	1.23
Cotton-PS-2%DVB	1.00
Cotton-PS-5%DVB	0.81

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- Figure 12. Relationship between oxygen signal from XPS and initial force
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 (● : styrene, ◐ : DVB)

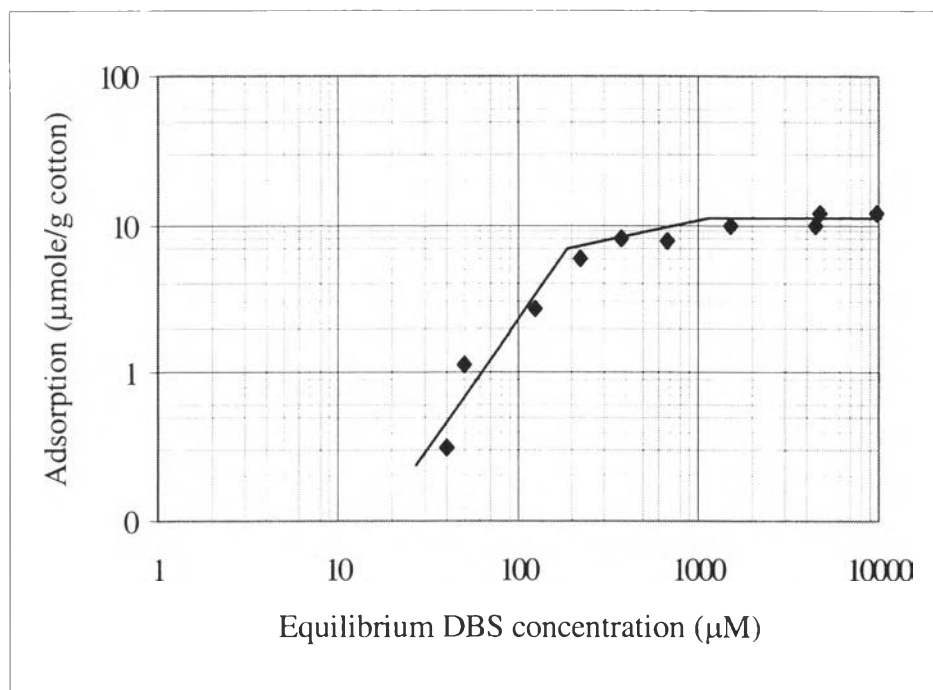


Fig 3

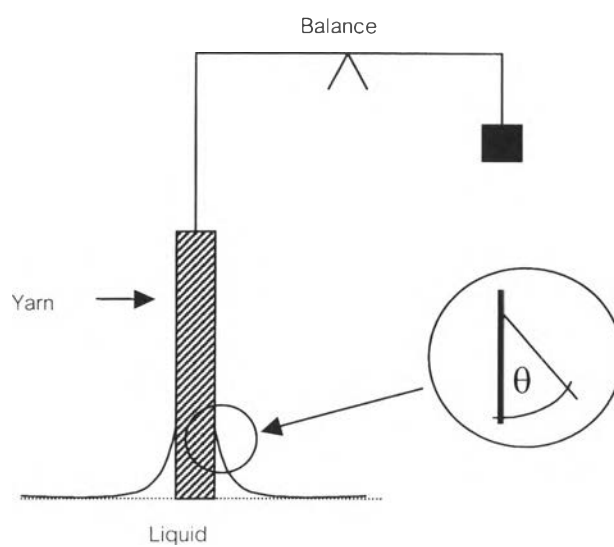
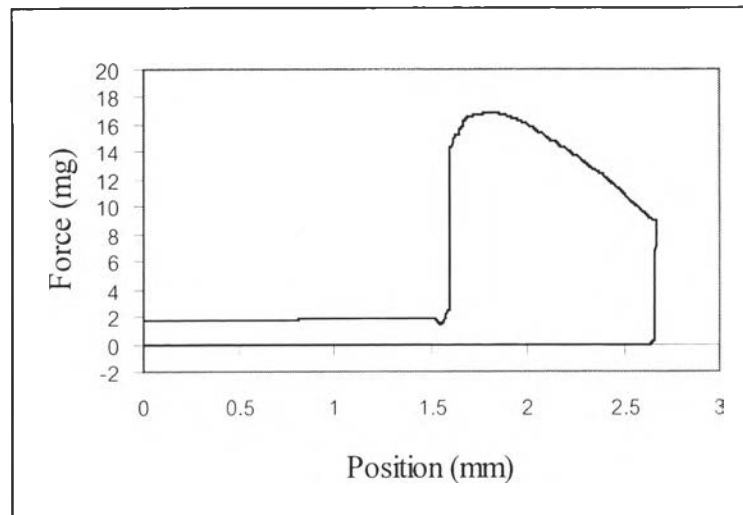
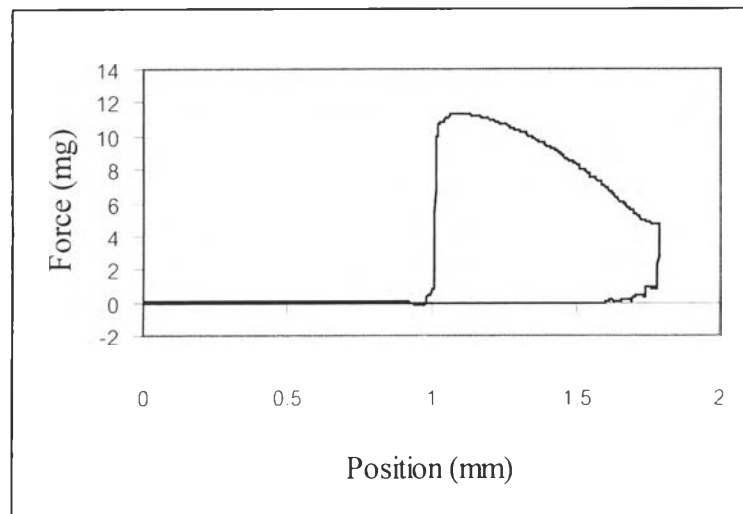


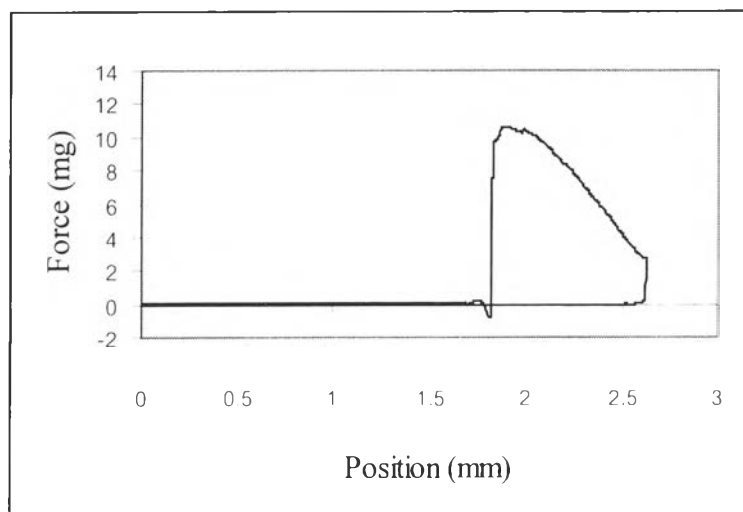
Fig 4



(a)

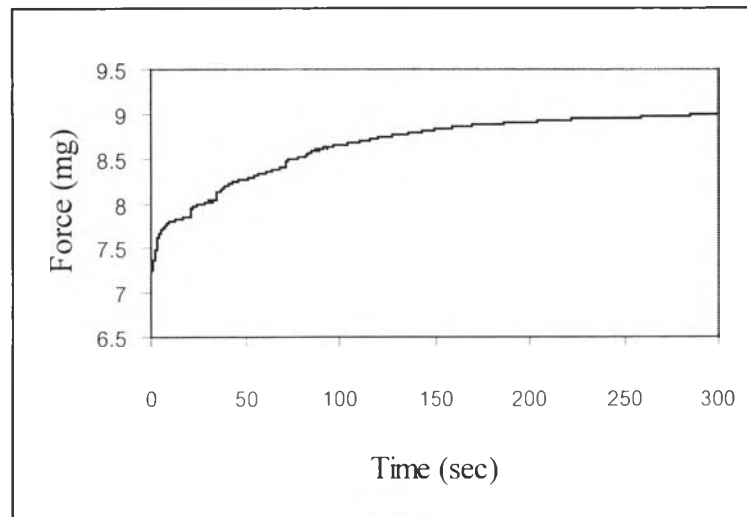


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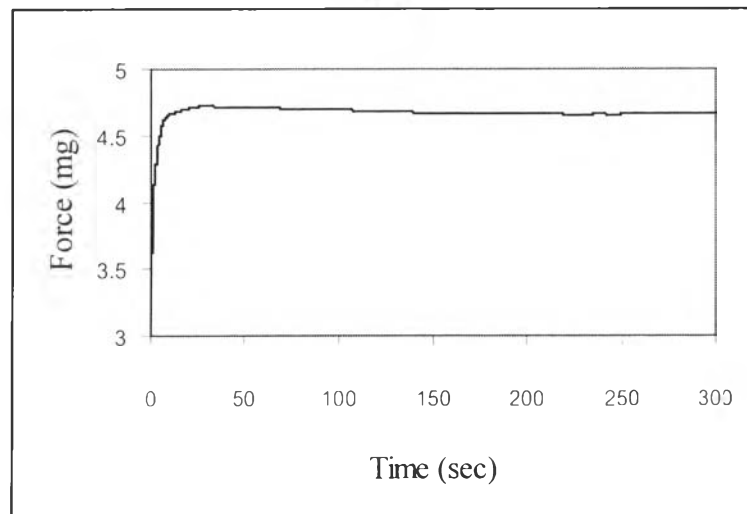


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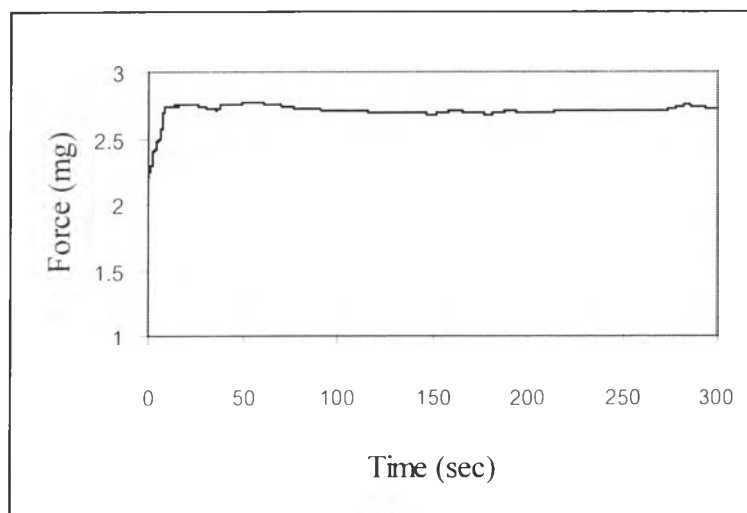
Fig 5



(a)

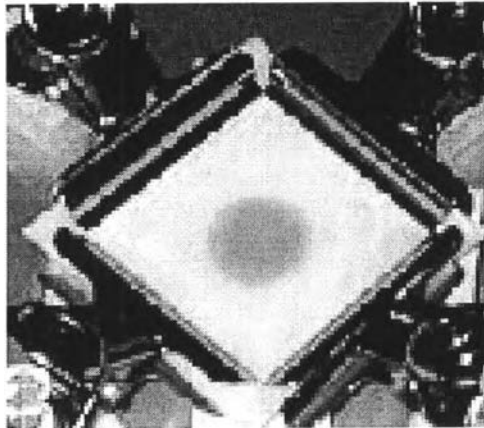


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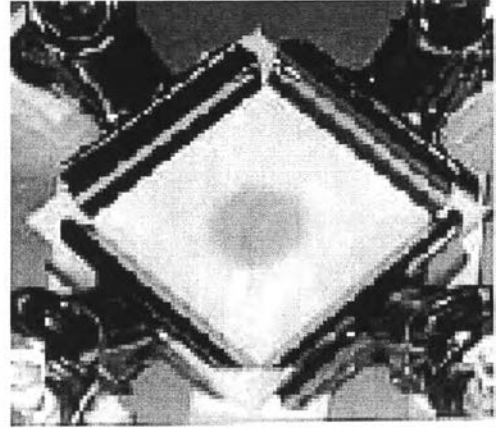


(c)

Fig 6

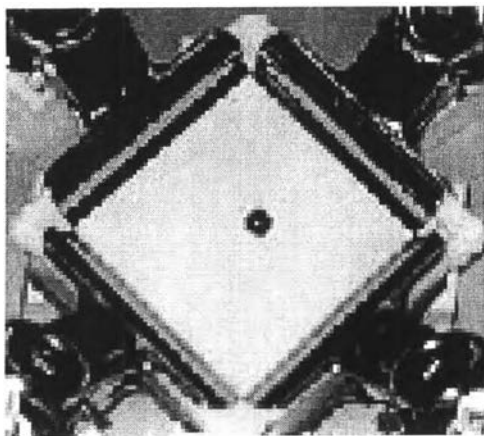


Water droplet after 1 sec

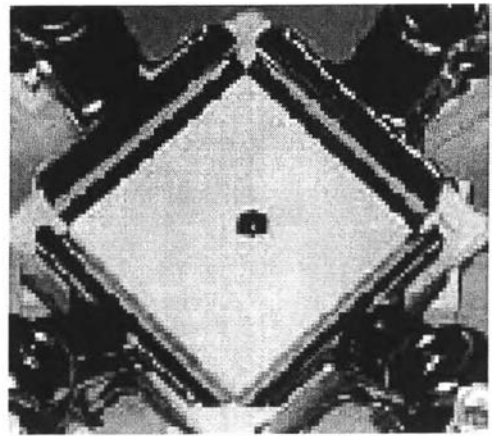


Water droplet after 30 min

(a)



Water droplet after 1 sec



Water droplet after 30 min

(b)

Fig 7

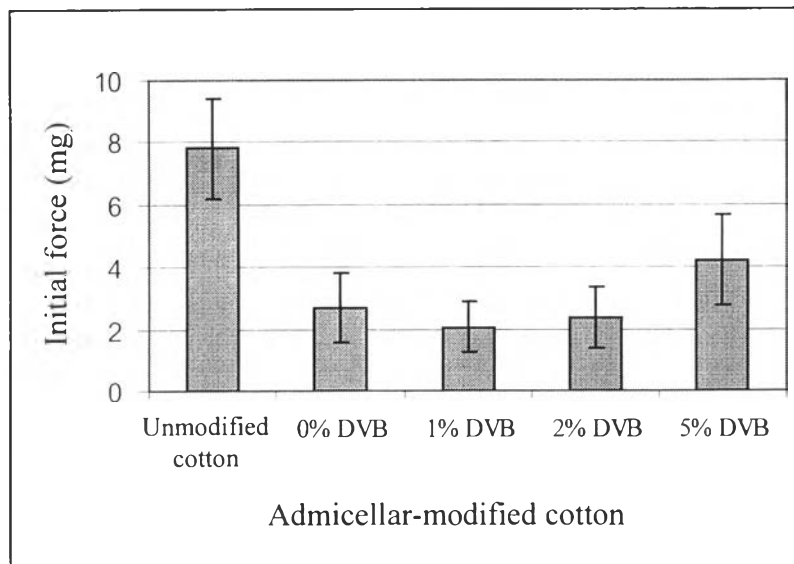


Fig 8

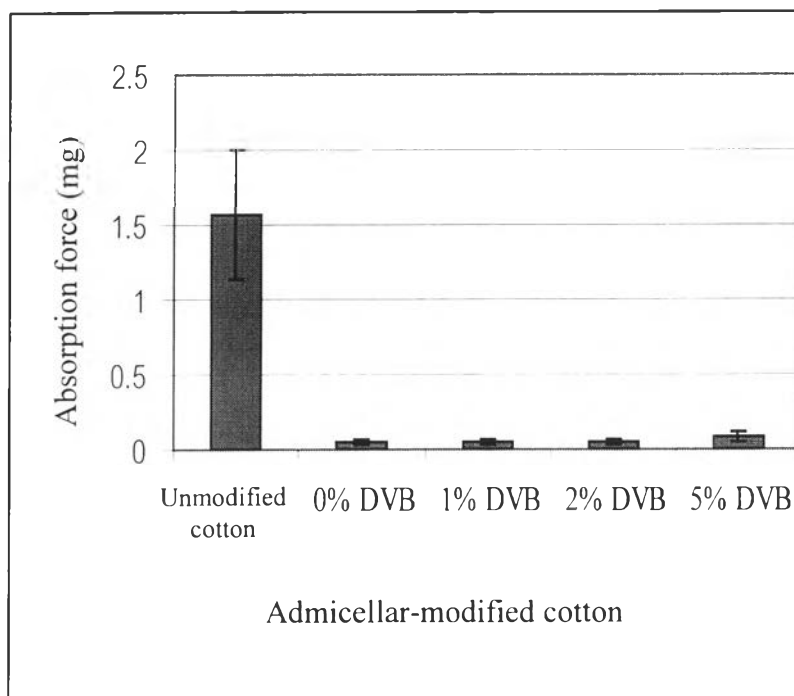


Fig 9

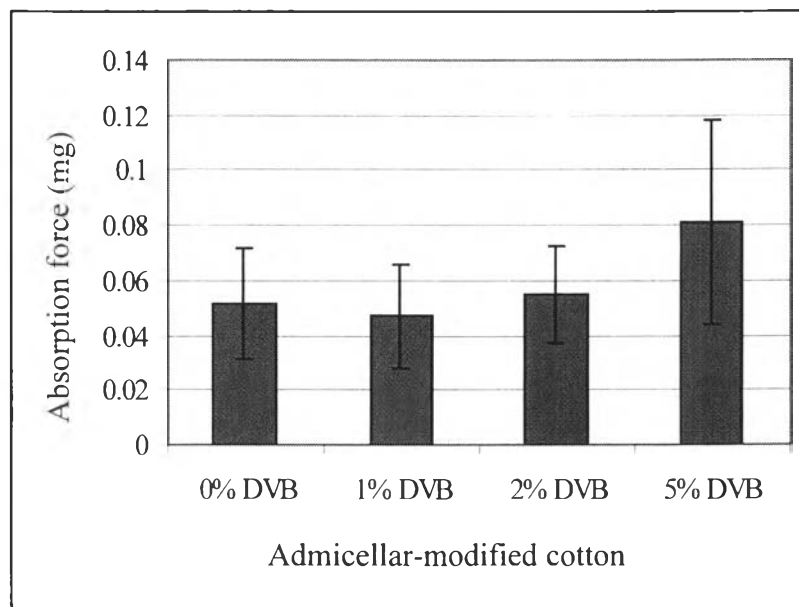
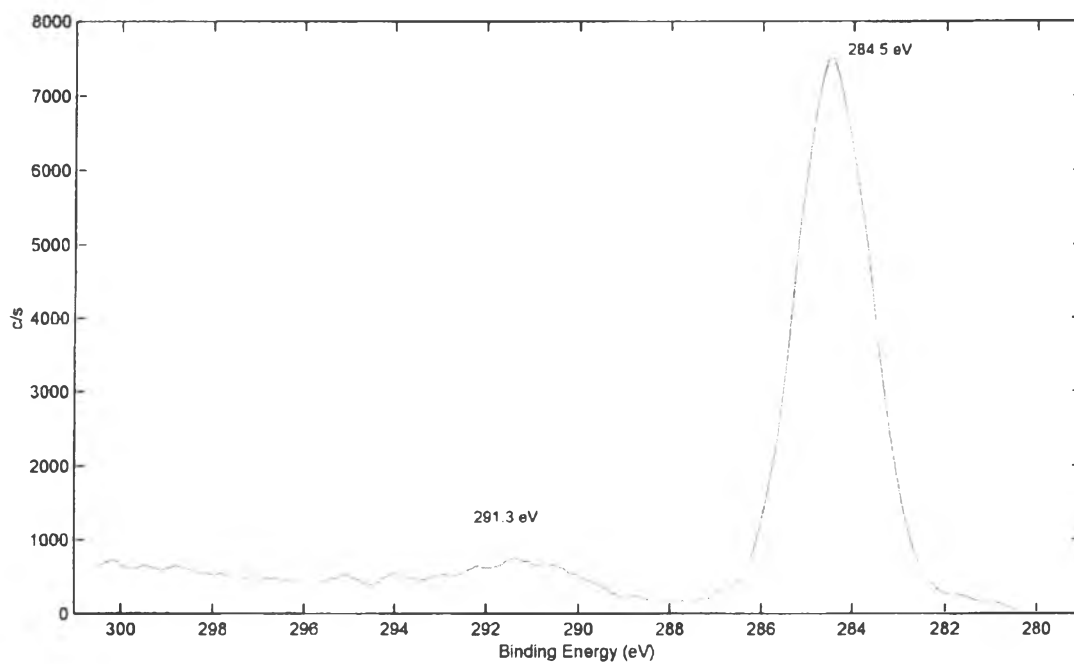
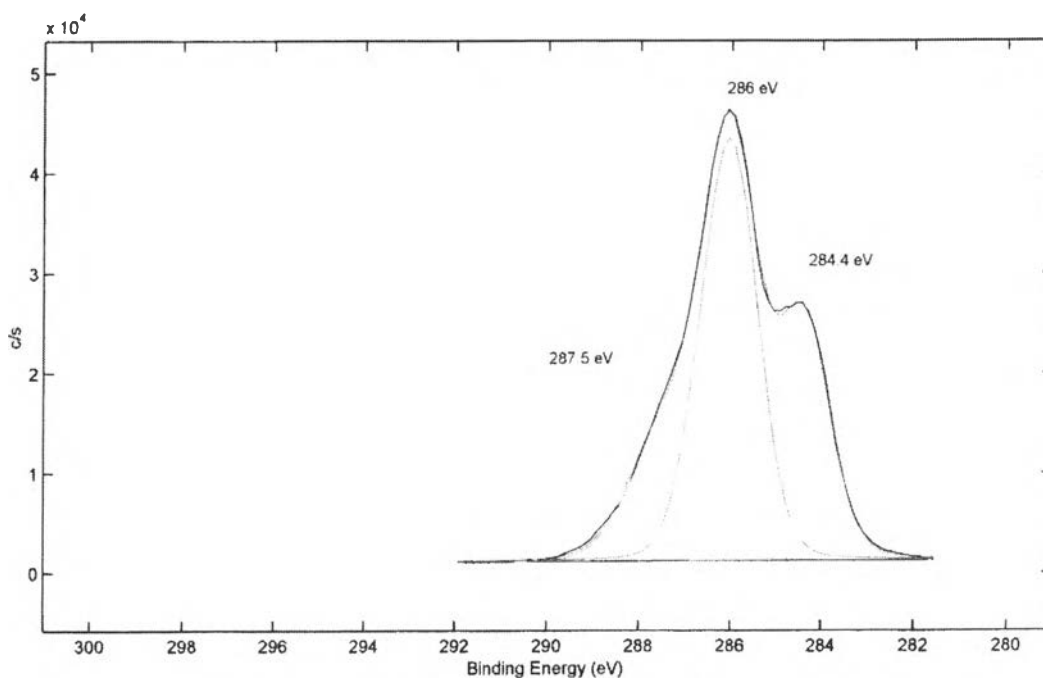


Fig 10

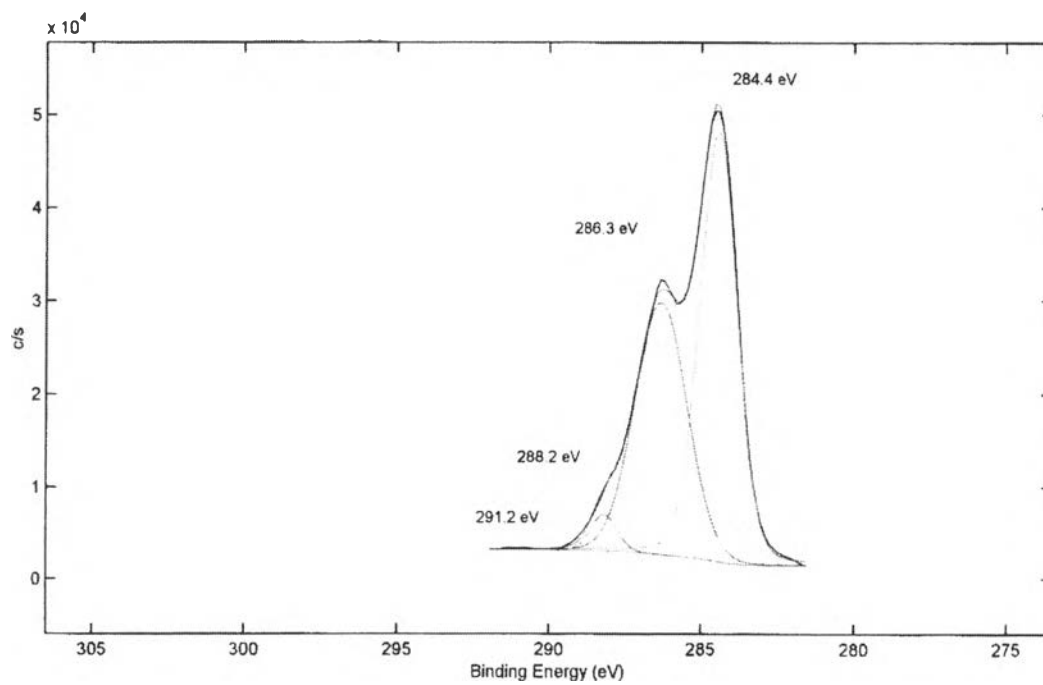


(a)

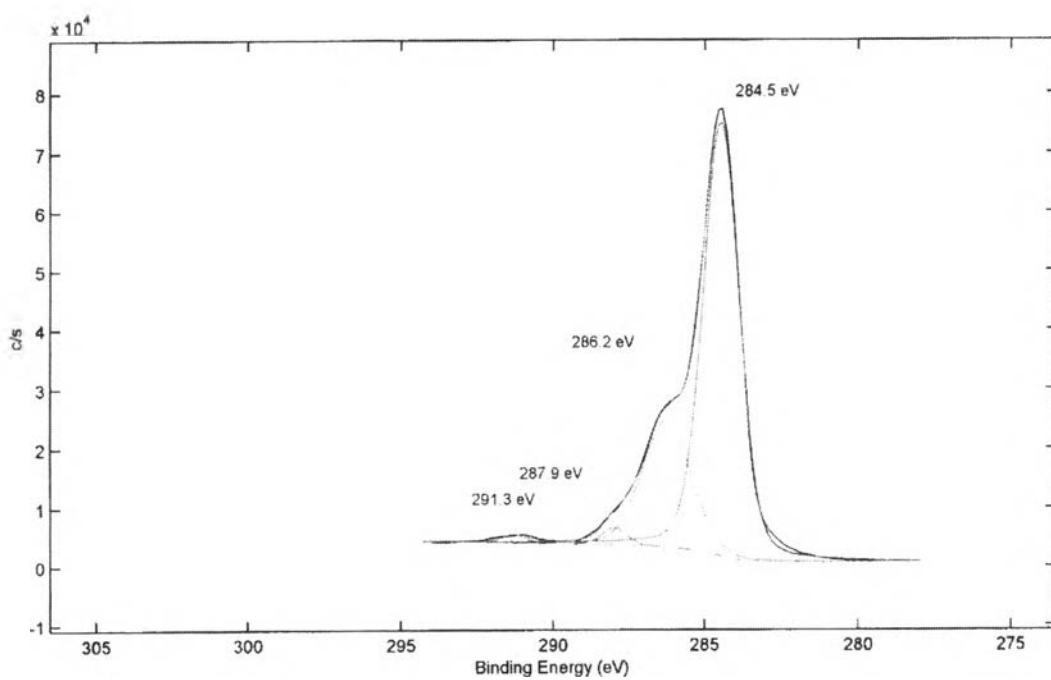


(b)

Fig 11

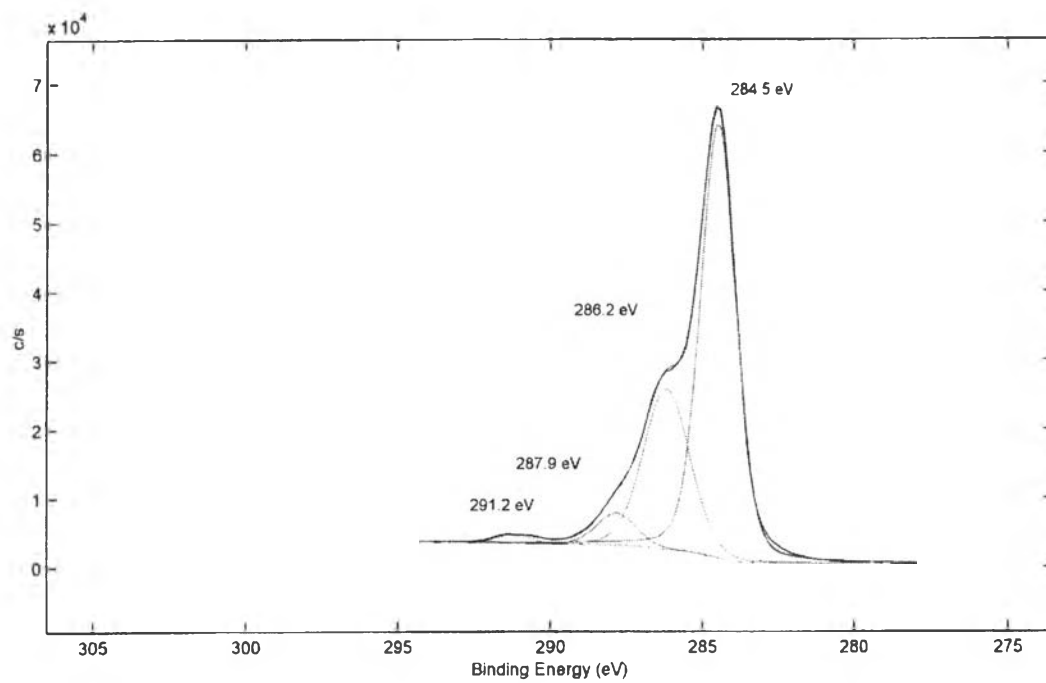


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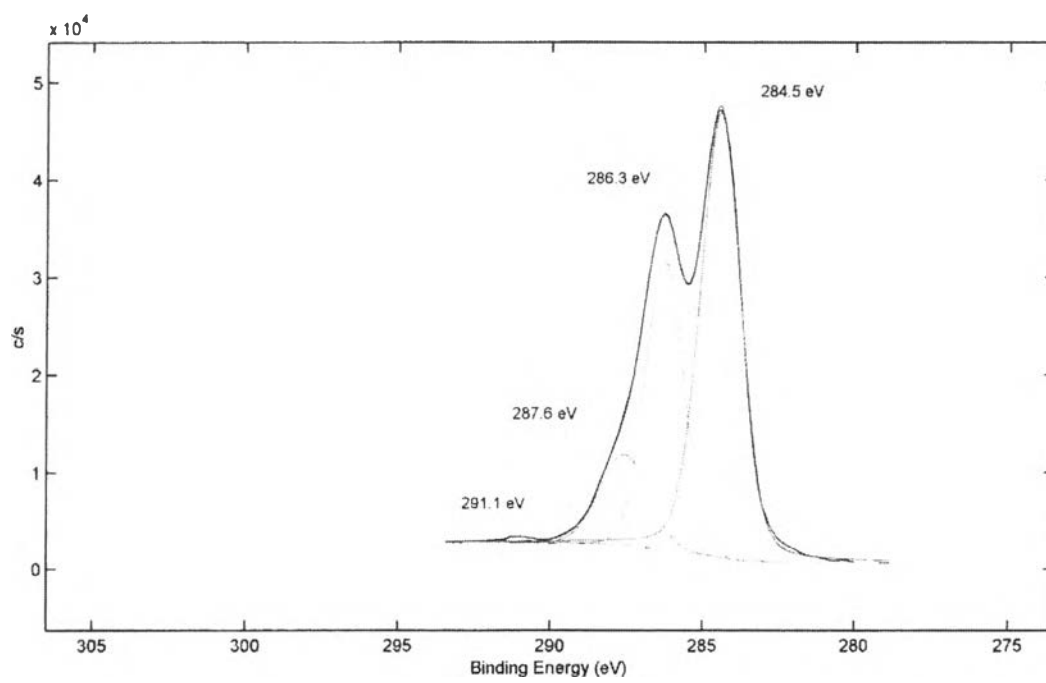


(d)

Fig 11 (cont.)



(e)



(f)

Fig 11 (cont.)

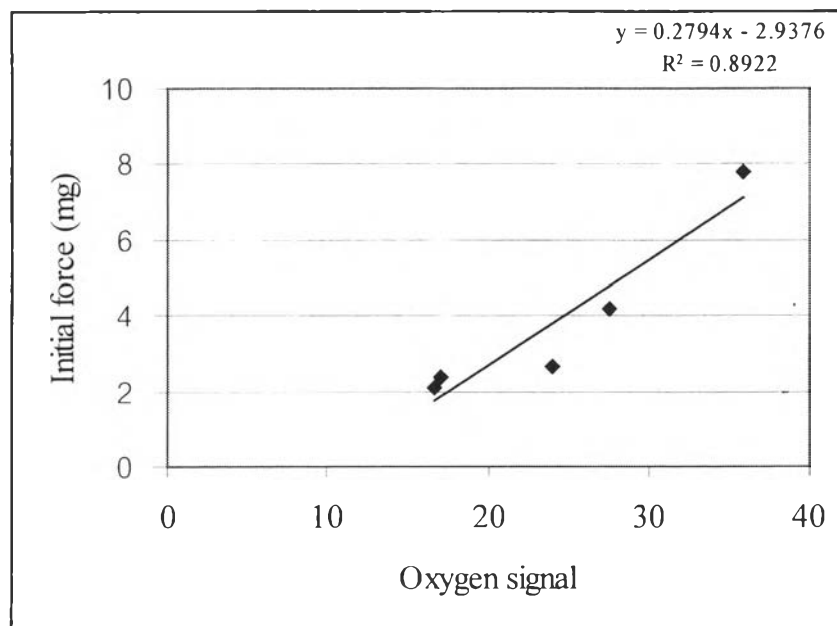


Fig 12

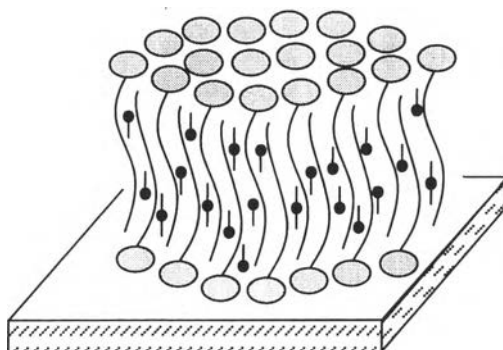


Fig 13