

CHAPTER VI

WETTABILITY OF COTTON MODIFIED BY ADMICELLAR POLYMERIZATION*

ABSTRACT

The wettability of yarns from plain cotton fabric and from polystyrene-coated fabric modified by admicellar polymerization was examined by transient force measurements with a microbalance. Analysis of observed time scales and forces suggests that water transport in cotton yarn proceeds by an initial rapid, capillary-driven axial flow over the exterior, followed by a radial flow between fibers, and is completed by a slow diffusion of water into the individual fibers. Both the initial and final forces indicated a significant reduction in the affinity of the modified fabric for water. Admicellar polymerization after optimization yielded coated cotton yarn that absorbed only 3% of the water retained by the unmodified yarn.

INTRODUCTION

Wettability is an important characteristic of materials, indicating the hydrophobic or hydrophilic nature of the surface. To quantify wettability, one typically examines the contact angle value by any of several techniques.¹ The dynamic contact angle measurement, for example, couples slow movement of the three-phase line with a Wilhelmy plate system which uses a highly sensitive balance to determine the interaction forces between the surfaces of a solid and a liquid from which the contact angle can be found. The structure and scale of many porous materials poses a particular challenge to evaluating wettability.

There are a wide variety of traditional methods to measure the wettability of textiles. These methods aim at determining the extent to which the material is water-repellent or the degree to which water is not adsorbed, with hydrophilicity mainly

* The content of this Chapter has appeared previously (T. Pongprayoon, E. A. O'Rear, N. Yanumet, and W. Yuan, *Langmuir*, 19, 3770-3778, 2003)

determined by the competitive effects of spreading among the fibers and adsorption within fibers. Illustrating these techniques are the vertical wicking test, measurement of the so-called “Saturated Value”, and the determination of the time required for adsorption of a certain volume or the drop test, three methods studied by J. J. De Boer.² Alternatively, water adsorption by fabric can be observed by photographing the area wetted as liquid spreads from a water droplet placed on the surface.³

In textile fabric, the most important factor affecting physiological comfort is moisture transport. Water transport is closely related to wettability. A fabric that rapidly moves water away from the human body makes the wearer feel more comfortable by keeping him dry, while a fabric impermeable to bulk water may be desirable for external wear. Among textile materials, cotton stands out as the best fabric for transporting water.

Moisture transportation in textiles and porous materials has been extensively studied.²⁻³ The wicking in fibers is the displacement of a fiber-air interface with a fiber-liquid interface by the spontaneous flow of a liquid into the porous substrate, driven by capillary force.⁴ Capillary flow in textile and other porous substrates has been examined by several techniques⁵⁻⁷ and a mathematical model of capillary flow has been applied to help interpret the effects of geometrical and material parameters.⁸ The kinetics of capillary rise usually follow the Lucas-Washburn equation⁹ which can be used to calculate the contact angle by observing the relationship between wicking rate and the distance traveled by the liquid. The Lucas-Washburn equation is shown below:

$$dh/dt = r\gamma_L \cos\theta / 4\eta h + r^2 \rho g \cos\beta / 8\eta \quad (1)$$

where h is the distance traveled by the liquid from the reservoir, r is the effective pore radius, η is the viscosity of liquid, β is the angle between the direction of flow and the gravitational acceleration g . When penetration is horizontal ($\beta = 90^\circ$) or when r is very small, the second term drops out, leaving:

$$dh/dt = r\gamma_L \cos\theta / 4\eta h \quad (2)$$

The integration subject to the initial conditions in which $h = 0$ at $t = 0$ gives:

$$h^2 = (r\gamma_L \cos\theta / 2\eta).t \quad (3)$$

The contact angle from the Lucas-Washburn equation relates to the phenomenon of wetting and spreading of solid-liquid interfaces. The contact angle by using Wilhelmy weighting balance is another well-known approach typically applied to the study of contact angles on nonporous solid surfaces¹⁰⁻¹¹ and to the study of wicking rate for porous materials.¹²⁻¹³ The equation to calculate the contact angle from Wilhelmy technique is:

$$\cos \theta = F/\gamma P \quad (4)$$

where F is the vertical force balance that shows the weight of the meniscus that must be equal to the upward force provided by the suspended substrate, γ is surface tension of liquid, and P is the wetted perimeter. For non-porous single fibers, F must be found with an electrobalance. This approach measures the contact angle in a force balance, much like hydrostatic pressure counters surface tension in the sessile drop technique.¹⁴

In the present work hydrophobic cotton was formed by using admicellar polymerization. The aim was to produce hydrophobic cotton that would repel water, while, at the same time, allow water vapor to be transported through the fabric. Admicellar polymerization has successfully been used to form very thin films of a wide variety of different polymers on various substrates.¹⁵⁻²⁴ The method involves a multi-step process based on the formation of admicelle aggregates comprised of physically adsorbed surfactants at a solid-solution interface and on the partitioning of monomers into the adsorbed surfactant aggregate. Polymerization of adsolubilized monomer leads to the formation of a thin film on the solid substrate. The mechanism of polymerization in the admicelle is similar to that in the micelle during emulsion polymerization.^{16, 25} After the polymerization reaction is complete, labile surfactant on polymer film can be removed by washing with distilled water. By using this

technique, the final hydrophobic cotton fabric retains water transportation between fibers in yarn so that molecular water can pass through the fabric. In this work, the wettability of admicellar-treated cotton was studied by using Wilhelmy method.

EXPERIMENTAL

Materials

A plain weave, medium-weight (150 g/m²), cotton fabric was purchased from Boonchaury Co. Ltd. The fabric was desized, scoured, and bleached from the factory. 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.

The commercial hydrophobic, fluorochemical treated cotton, was purchased from Thanapaisan Co., Ltd.

Styrene monomer was purchased from Aldrich Co.Ltd. The inhibitor in styrene monomer was removed by washing with 10% NaOH aqueous solution according to the method described by Collins, et al.²⁶

Dodecylbenzene sulfonate, LAS anionic surfactant, was purchased from Aldrich Co.Ltd. Sodium persulfate used as initiator was purchased from BHD Laboratory Supplies. Hydrochloric acid and sodium chloride were purchased from Merck and Alex Chemicals Co.Ltd., respectively.

Structure of cotton yarn pictured by electron microscope

Geometry of cotton yarn was examined by electron microscopy and optical microscopy (Nikon OPTIPHON-2). Digital images were captured on CCD camera of Hamamatsu C2400 and analyzed with OPTIMAS-5 software. For picturing their cross-section and counting the number of fibers in each yarn, the yarns were fixed with cured polyester and polished until smooth. The surface was then observed by electron microscope.

Admicellar polymerization to prepare the hydrophobic cotton

The admicellar polymerization of styrene on cotton was carried out using 1000 μM aqueous LAS solution at pH 4 and 0.15 M of NaCl with varying LAS:styrene and initiator:styrene ratios. At the start of the experiment, a piece of cotton fabric weighing 0.5 g was placed in a 24 mL vial containing 20 mL LAS solution. Styrene and initiator were injected by syringe into the vial. The sealed vials were shaken at 30°C for 8 h to allow time for admicelle formation and adsolubilization of monomer into the admicelle. After that, the temperature of the system was raised to and maintained at 80°C for 2 h to initiate the polymerization reaction.

The fabric was then taken out 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 labile LAS was completely removed. The fabrics were then dried in an oven at 110 °C for 5 h before characterization.

Hydrophobicity testing by the drop test

Hydrophobicity of the fabric was evaluated initially by placing a drop of water on the cotton surface by injecting 30 μL of distilled water with a syringe. The drop was carefully placed on fabric with no impact force as shown in Fig 1. Time taken for the droplet to disappear was taken. The fabric was judged hydrophobic when the time taken for the droplet to disappear was greater than 30 min. A drop adsorbed in less than a second on unmodified fabric.

Wettability test by Wilhelmy microbalance technique

Individual yarns were taken from the fabric and cut into short segments 8 mm in length for testing. The wettability was evaluated further by contact angle measurement using the Wilhelmy microbalance technique (Cahn model DCA-322). The cotton yarn was attached to wire and hung on the balance in a vertical

orientation to determine the force during testing. The method is illustrated by Fig 2. After calibrating the instrument, the wicking method¹²⁻¹³ was applied for yarn characterization. The yarn was slowly lowered to touch the water surface in the beaker and was held still for 5 min. After that it was taken up to the previous position. Software on the unit controlled this test and collected data continuously. Relative curves of force and position and of force and time were shown in real time and stored for later analysis. Typical curves from these experiments are shown in the results. Adsorbed water, contact angle, and mode of wettability (water transport) were determined from these curves.

Characterization of the coated surface of cotton

A piece of fiber was removed from the cotton yarn and stuck on a mica plate by melted polymer to image its surface by AFM (NanoScope III, Multimode Scanning Probe, Digital Instruments). The instrument was operated in 'height' mode under ambient condition with a standard silicon nitride tip.

RESULTS AND DISCUSSION

Analyzing the structure of cotton yarn

The structure and size of cotton yarn were observed with electron microscope. Typical images are shown in Fig 3. Yarn diameter was approximately $228 \pm 22 \mu\text{m}$ as averaged from 10 yarn samples. The cross section of the yarn shows that the cotton yarn has a porous structure of roughly circular shape. A yarn consists of about 100–150 fibers that appear closely packed as shown in the cross section micrograph (Fig 3b). Each fiber was about 15-20 μm in diameter.

Conditions of admicellar polymerization for hydrophobic cotton

The drop test provides a quick and simple method to evaluate the reaction

conditions for admicellar polymerization. After modification, rinsing and drying, hydrophobic cotton fabric was arbitrarily defined as supporting a water droplet for more than 30 min. Results from this initial test were used to evaluate the optimal amount of styrene monomer and initiator to produce hydrophobic cotton by admicellar polymerization. The results in Table 1 show that the ratio of LAS to styrene monomer that resulted in hydrophobic character was 1:5 and higher while the ratio of water-soluble initiator to styrene was 1:1 using the 1:5 LAS:styrene ratio. Yarns from these fabrics were further characterized by the Wilhelmy method.

Transient force measurements and water transport in unmodified cotton yarn

The drop test could not detect any difference in hydrophobicity and wettability of cotton treated by admicellar polymerization of those samples deemed “hydrophobic.” A more sensitive method was applied to study the wettability or hydrophobicity of a surface by determination of the contact angle. The Cahn microbalance yields curves showing the relationship between force and position and the relationship between force and time. In this case, Fig. 4a shows the change in force for a typical experiment on yarn taken from plain cotton fabric. Results are recorded as the microbalance operates from the moment the yarn is contacted with the water surface, while the yarn is then held at the same position for 5 min, and then finally as it is being lifted up to the previous position. The near instantaneous step changes and slower increases in force with time complicate interpretation of these curves.

Normally, the force reading is automatically zeroed at initiation of the test. The reading rises sharply after the cotton yarn first touches the water surface (Fig. 4b) because water is transferred suddenly onto the yarn. Over the next several minutes, the force increases more gradually. After 5 min, the yarn is raised from the original water surface with the force increasing continuously until the attached film of water around the yarn breaks free (Fig. 4a). As the yarn separates from the bulk water, the force decreases rapidly. Residual force upon completion of the cycle indicates the weight of water adsorbed by and adhered to the yarn. This is termed

water adsorption. The initial force and water adsorption of 11 samples of unmodified yarn are shown in Figure 5.

These experiments, coupled with analysis, provide interesting insights into water transport during wicking of a single yarn. We considered in the analysis of the data the separate processes that might occur during different phases of the test cycle. For the curve showing the relationship between the force and time (Fig. 4b), the force was first measured after the yarn touched the water and monitored for 5 min while the yarn was held on the water surface. Typically, the force increased rapidly in a step change once the yarn touched the water. That initial force can be attributed to capillary flow. However, as the yarn touches the liquid surface, water might be drawn up axially over the exterior surface as well as between the fibers of the yarn. Thus, there is some uncertainty in the wetted perimeter P that applies. We calculated P from the Wilhelmy Equation (Eq. 4) using the observed step change in force with an assumed contact angle for untreated cotton ($\theta = 0$) and compared the result to the dimensions found by electron microscopy. The value obtained of $P_{\text{H}_2\text{O}} = 1.2$ mm compares favorably to an estimate for the yarn from the geometric approximation of a circular cross-section. The circumference yields $P_y = \pi D_{\text{yarn}} = 0.7$ mm with $D_{\text{yarn}} = 230$ μm . In contrast, the wetted perimeter should be on the order of $P_f = N\pi D_{\text{fiber}} = (125)\pi(17\mu\text{m}) = 7$ mm for a significant contribution from capillary flow between the fibers. This suggests the initial wetting by water is primarily limited to flow over the exterior surface of the yarn. Undoubtedly, flow starts between fibers at the end dipped in water, only at a much lower rate.

The force-time data as well as the residual force clearly indicate the fiber becomes saturated from slower processes with time scales on the order of seconds to hundreds of seconds. In this time period, the observed value of the force for the unmodified cotton sample rises from about 8.6 mg to about 10.2 mg (Fig. 4b), reasonably matching the final water uptake of about 1.8 mg. Further insight into these transient processes was obtained from solution of the diffusion equation:

$$\partial C_{\text{H}_2\text{O}}/\partial t = D \nabla^2 C_{\text{H}_2\text{O}} \quad (5)$$

where C_{H_2O} is the concentration of water in the cellulose and D is the diffusivity of water in the cellulose.

Water diffusion in a cotton yarn that consists of about 100 fibers and which is porous in nature was considered to study the transportation of water from the surface of the yarn into the interior. The calculation of diffusion into the yarn was carried out to evaluate possible modes of transient water transfer fitting the observed time scales. Two cases of radial diffusion in cylindrical geometry, diffusion into the entire yarn and diffusion into a single fiber, were considered and the diffusion equation was solved using the “Gurney-Lurie” charts for cylindrical geometry.²⁷ For molecular diffusion, the chart is in terms of four dimensionless ratios:

Y = unaccomplished concentration change

$$= (C_{A,s} - C_A) / (C_{A,s} - C_{A,0})$$

$$X_D = \text{relative time} = D_{AB}t/x_1^2$$

$$n = \text{relative position} = x/x_1$$

$$m = \text{relative resistance} = D_{AB}/k_c x_1$$

Time, t , and position, x , are the temporal and spatial points of interest. The characteristic length, x_1 , is the dimension from the point of symmetry (i.e. the radius or centerline to the surface) so that n corresponds to the spatial position of interest in terms of the fractional distance from the center to the outer surface. The relative resistance, m , is the ratio of convective mass transfer resistance ($1/k_c x_1$) to the internal molecular mass transfer resistance ($1/D_{AB}$). The assumptions in this analysis were that water was transported only in the radial direction at each part along the yarn length; that there was no convective mass transfer ($m = 0$) of water in the yarn; that negligible water was present initially throughout ($C_{A,0} = 0$ % water saturation); and that the yarn was saturated at the surface ($C_{A,s} = 100$ %). When water adsorbs completely, C_A at the center ($n = 0$) approaches 100% and Y goes to zero. The yarn is implicitly treated as a pseudo-homogeneous solid and swelling is neglected. From the “Gurney-Lurie” chart, $X_D = 1.3$. The analysis was repeated with single fiber dimensions using the radius of a single fiber in the yarn as equal to 8×10^{-6} m as observed by SEM. The mass diffusion coefficient of water in cellulose was taken as 4.8×10^{-13} m²/s.²⁸

From these calculations, the time for diffusion of water into single cotton fibers should be about 200 sec. Applying the calculation to the whole yarn yields a time period for diffusion of many thousands of seconds. The observed time scale (Fig. 4) matches the value calculated from single fiber diffusion. One may conclude that a likely explanation for the later transients in force is water penetration into the individual fibers. Combining this diffusion result with conclusion above for the initial force, we suggest the dominant mechanism for water transport in this yarn involves a very rapid initial axial flow over the exterior surface, a subsequent capillary-driven radial flow between fibers into the interior of the yarn in a few seconds, and then finally transport by radial diffusion into the individual fibers on a time frame of hundreds of seconds, leading to greater swelling. Cotton fibers are known to swell by as much as 20% in its diameter on adsorption of water.²⁹ Figure 6 depicts the various steps in the proposed mechanism.

Transient force measurements in hydrophobic yarn

Microbalance measurements on 16 samples of yarn which are judged hydrophobic by the drop test were studied. These are samples which were prepared using an LAS:styrene ratio of 1:7 and an initiator:styrene ratio of 1:1. The initial and adsorption forces of the 16 samples are shown in Fig 7. The typical force and position and force and time curves of the samples are shown in Fig. 8. It can be seen that, compared with the curves for the unmodified cotton, the initial force of the hydrophobic cotton was much lower at around 1.8 mg, and unlike the unmodified cotton, the force vs time curve remained unchanged after the initial water uptake. In line with the model proposed for the unmodified cotton above, this is taken to show that, after the rapid initial axial flow over the exterior surface, the flow of the liquid stops due to the hydrophobicity of the coated fibers.

Water uptake measurement

The final amount of absorbed and adhered water in a cotton yarn was known from the magnitude of the force after a sample was lifted from water. From the

results in Fig 5, the average force after removal from the bulk water of 11 untreated cotton samples was approximately 1.563 ± 0.437 mg. This showed that they absorbed water very well because the yarns were hydrophilic, porous materials. From the proposed model, it can be envisaged that water is retained in the spaces between fibers as well as within the water-swollen fibers. For the treated, hydrophobic cotton, the average residual force of 16 samples was about 0.0504 ± 0.0222 mg as shown in Fig 7. Thus, water uptake by modified yarn amounted to only 3% of that by yarn from the unmodified fabric. This confirms the conclusion that there was no radial flow of water into the spaces between fibers after the initial rapid axial flow. These results showed that the cotton treated by admicellar polymerization had significant increase in hydrophobicity as compared to the natural cotton which is highly hydrophilic.

The effect of the amount of styrene on contact angle and water adsorption

Contact angles indicate the hydrophobicity or hydrophilicity of the solid surface. As the effect from capillary flow is usually very fast,⁸ the initial force on the fiber was assumed to be due only to capillary flow so that θ might be calculated by Wilhelmy equation,

$$\cos \theta = F/\gamma P = mg/\gamma P$$

with g equal to 980.665 cm/s^2 and surface tension γ equal to 72.600 dyns/cm for water. The P value was found from the F value for unmodified cotton with contact angle taken to be zero.³⁰ Thus, contact angles were found and values for the hydrophobic cottons compared and contrasted with the result for untreated cotton. Increase in hydrophobicity leads to an increase in contact angle.

The dependence of contact angle of treated cotton on varying amount of styrene and initiator is shown in Table 2 and 3. From the results, it can be seen that this approach can discern differences in the hydrophobicity of treated cotton surfaces beyond the capability of the drop test as shown in the data for the effect of styrene

and initiator amounts. This technique was not only easier and faster than other methods, but it also can be used to compare and identify differences that might not otherwise be easily quantified.

The amount of styrene was investigated to determine the optimum condition for making hydrophobic cotton by admicellar polymerization. The contact angle and water adsorption were used to identify the differences in the hydrophobicity of the treated surface. The results are shown in Fig 9 and 10. From Figure 9, the optimum amount of styrene was found at surfactant to styrene ratio of 1:5. The contact angle increased generally with the amount of styrene and more dramatically from a surfactant to styrene ratio of 1:4 to 1:5. The contact angle continued to increase when higher ratios of styrene were used. Similarly, water adsorption decreased sharply in the yarn from the ratio of 1:4 to 1:5. The optimum amount of initiator is shown in Figure 10. All conditions were prepared by using 1:5 surfactant to styrene ratio. It was found that 1:1 initiator to styrene ratio was the optimum condition that showed the hydrophobic character. It is interesting to note that, in a study of the effect of the contact angle on capillary penetration, it has been concluded that spontaneous penetration is arrested for contact angle higher than about 60° .³¹ In this work, the change to a hydrophobic cotton also occurred at the contact angle (using P_{H_2O}) greater than 60° .

Atomic Force Microscopy (AFM) images

AFM images show the morphology of untreated cotton and admicellar-treated cottons in Fig 11 and 12. From both, their surfaces look similar; however the contact angles and water adsorption in yarns are clearly different as seen from results above. These images show that the coated polystyrene film on cotton using the ratio 1:7 of LAS:styrene was an ultrathin film. The morphology changes significantly when the styrene becomes supersaturated, that is, as the ratios of LAS:styrene approaches 1:50 (Fig 13a). Coated polystyrene films in this case were very thick compared with 1:7 ratio of LAS:styrene. These results were similar to the yarn of the commercial hydrophobic cotton. These yarns also exhibit a distinct chemical coating on the cotton surface in the AFM image (Fig 13b). In the fabrics modified by the

supersaturated styrene and by the commercial method, water uptake in yarn and contact angle could not be measured by dynamic contact angle instrument because the yarns floated on the water surface.

CONCLUSIONS

The Wilhelmy technique has been used to study the wettability and transport in cotton yarn. The process of water transport in unmodified cotton yarn may be described by the sequence of capillary-driven convection over the external surface, radial flow between the fibers along the length, and diffusion into the individual fibers. Yarn modified with a thin film of polystyrene applied by admicellar polymerization exhibits higher contact angles and takes up about 2 orders of magnitude less water. The amount of styrene and initiator used for admicellar polymerization affects the wettability of the coated fabric.

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- Table 3. Initial force, water adsorption, and contact angle of cotton treated with varying initiator:styrene ratio.

Table 1.

1.a

Sample	Surfactant:styrene	Wetting time (min)
1	1:2	0
2	1:3	0.27
3	1:4	4.56
4	1:5	>30
5	1:6	>30
6	1:7	>30

* Initiator:styrene ratio = 1:1

1.b

Sample	Initiator:styrene	Wetting time (min)
1	1:1	>30
2	1:2	28.50
3	1:3	1.25
4	1:4	0

* LAS:styrene ratio = 1:5

Table 2.

LAS: Styrene Ratio	Initial Force (mg)		Water Absorption (mg)		Contact Angle	
	Average	STD	Average	STD	Average	STD
1:2*	7.70	1.94	1.38	0.42	10.3	24.6
1:3*	6.44	0.81	1.26	0.22	34.6	10.0
1:4*	4.98	1.33	0.46	0.45	50.5	14.6
1:5	3.75	0.95	0.06	0.02	61.4	8.1
1:6	3.60	1.06	0.05	0.02	62.6	7.9
1:7	2.69	0.74	0.05	0.02	69.9	5.8

*Hydrophilic by drop test

Table 3.

Initiator: styrene Ratio	Initial Force (mg)		Water Absorption (mg)		Contact Angle	
	Average	STD	Average	STD	Average	STD
1:1	3.75	0.95	0.06	0.02	61.4	8.1
1:2*	4.61	1.24	0.51	0.37	53.9	17.1
1:3*	5.75	1.19	0.95	0.33	42.7	8.8
1:4*	7.47	1.77	1.18	0.59	17.3	2.1

*Hydrophilic by drop test

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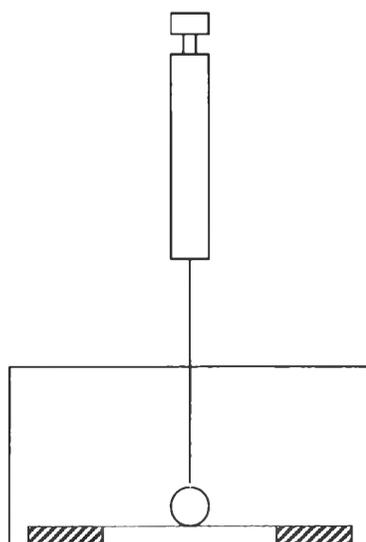


Figure 1.

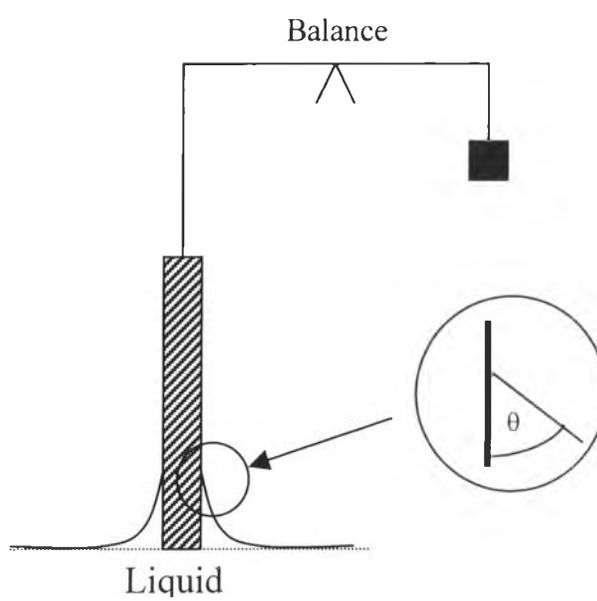
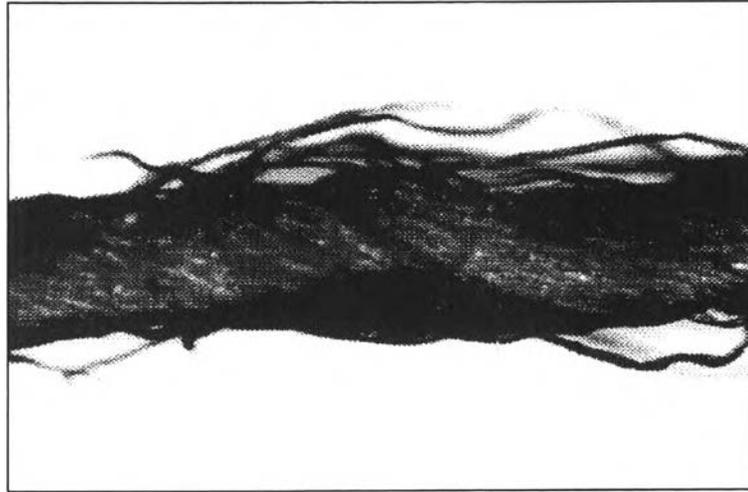
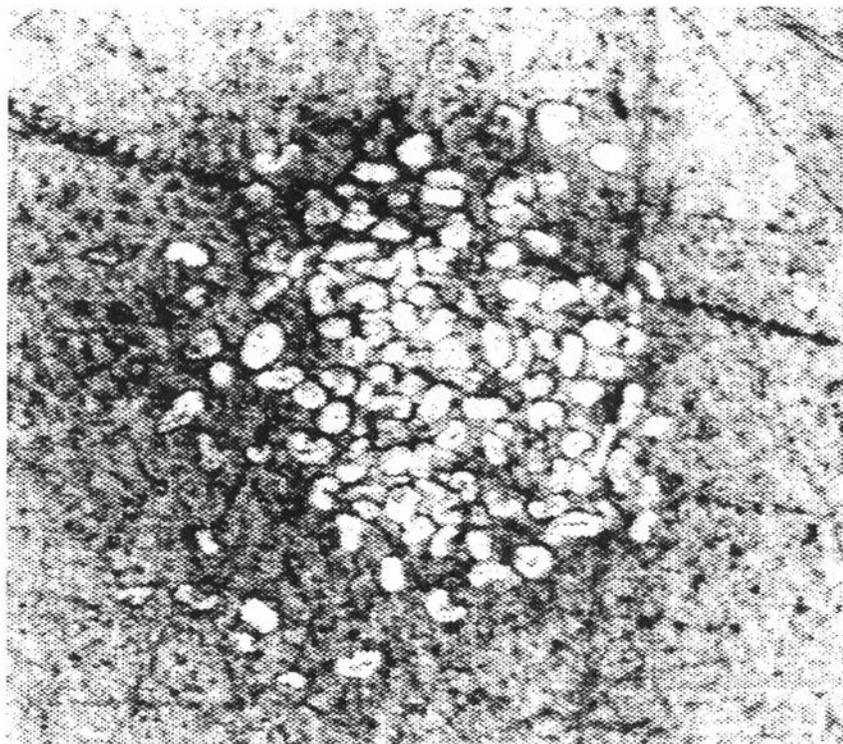


Figure 2

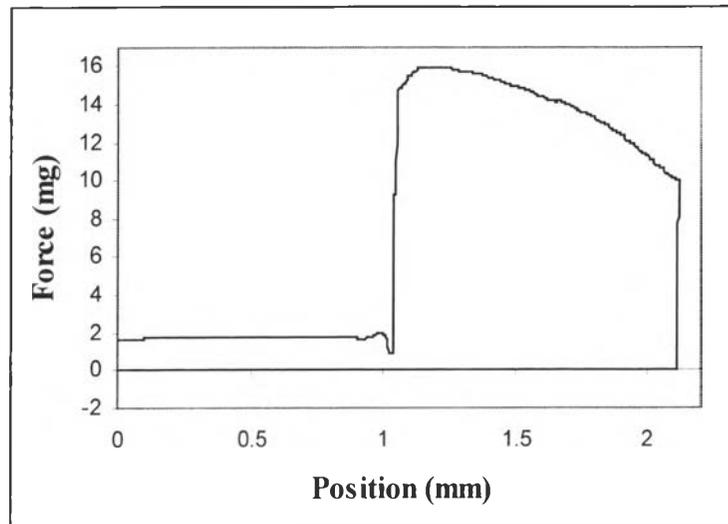


(a)

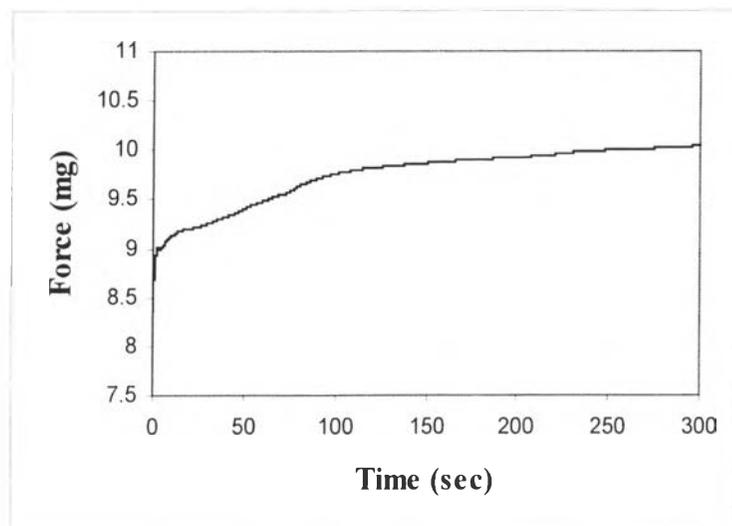


(b)

Figure 3



(a)



(b)

Figure 4.

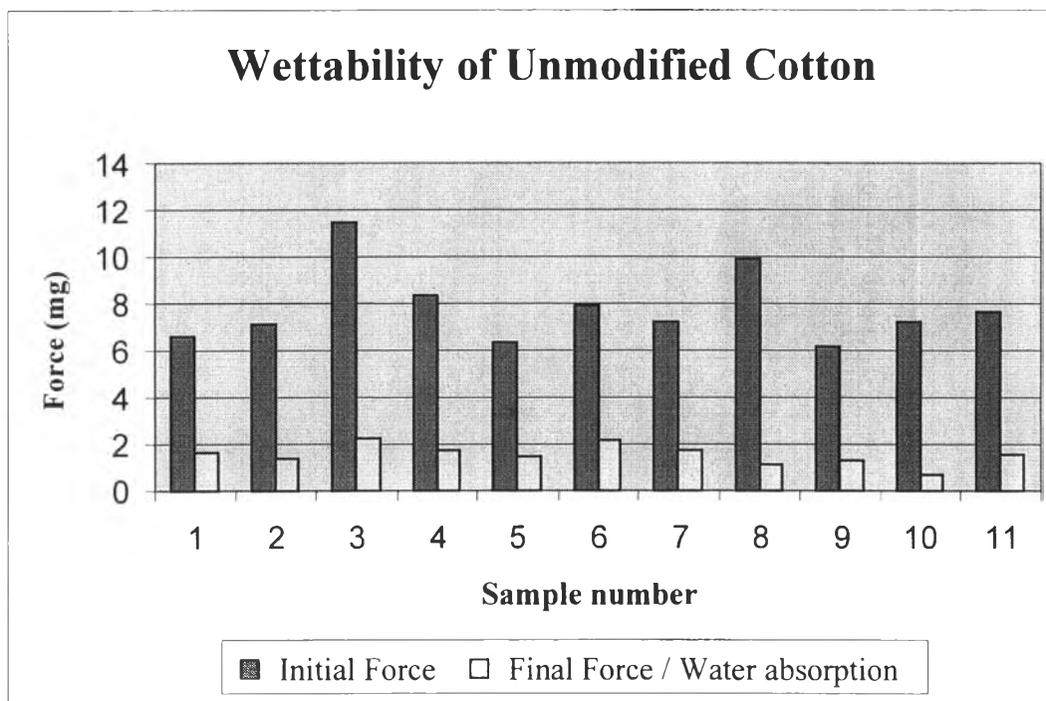


Figure 5.

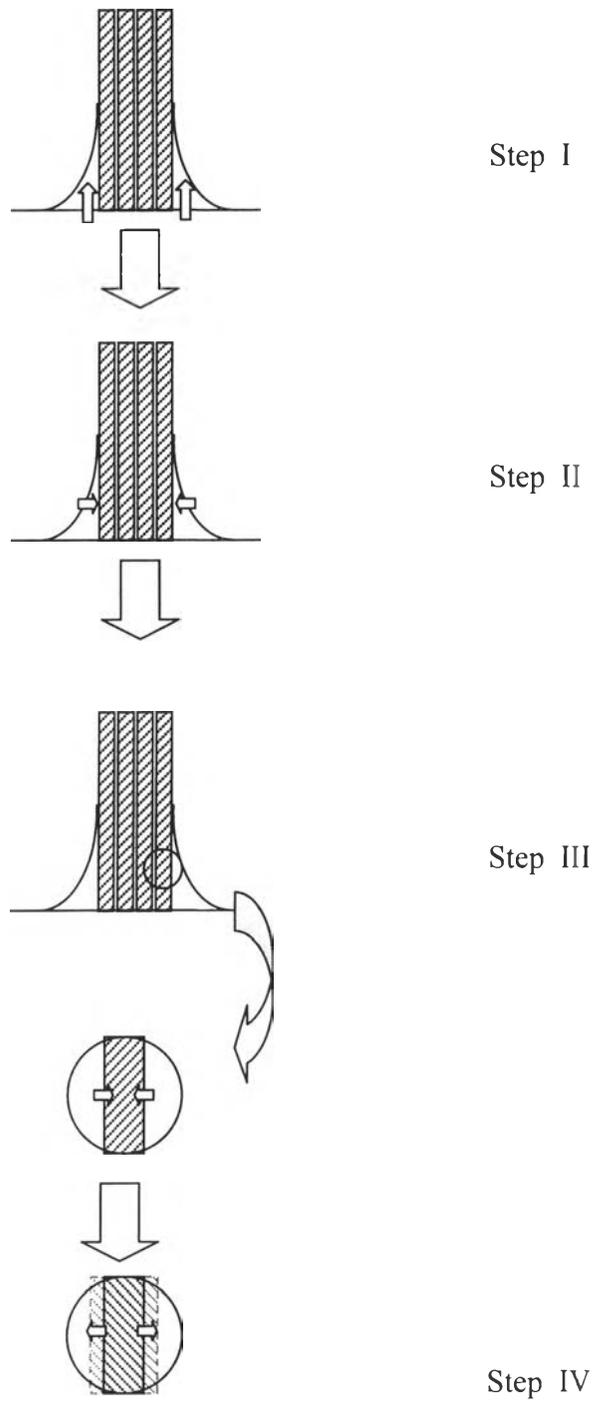


Figure 6.

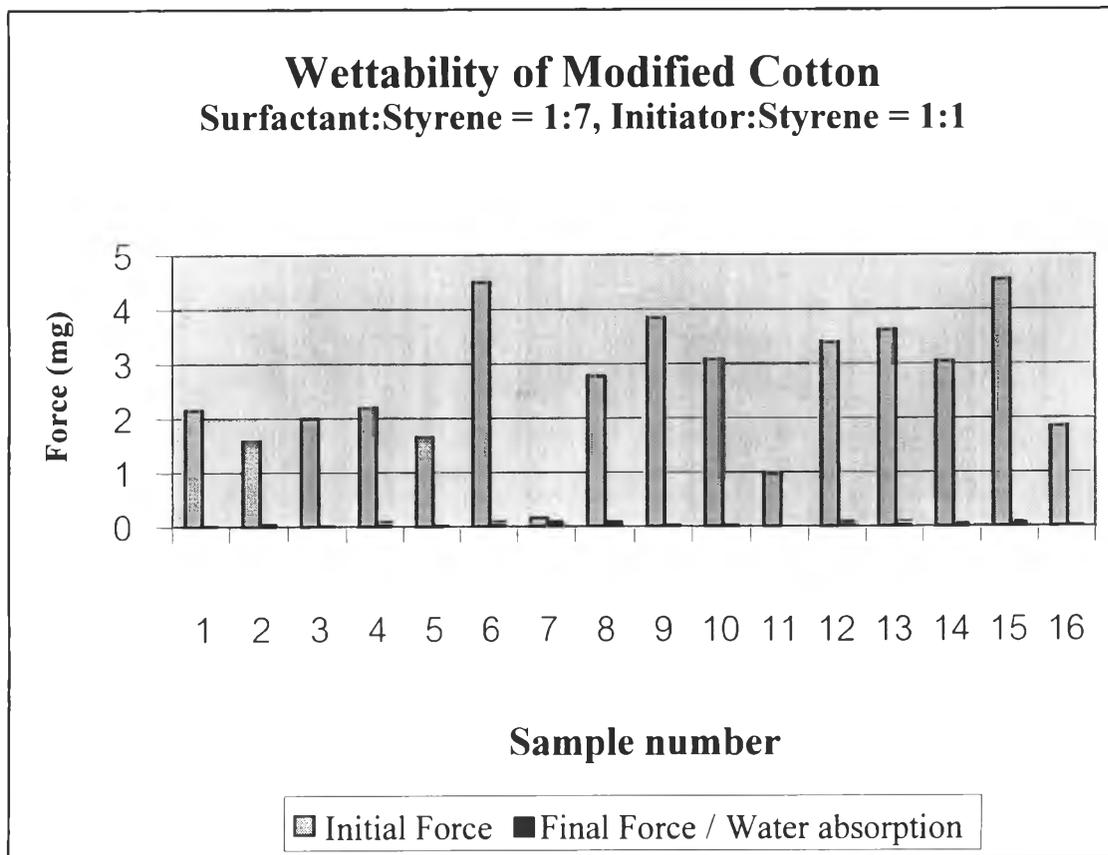
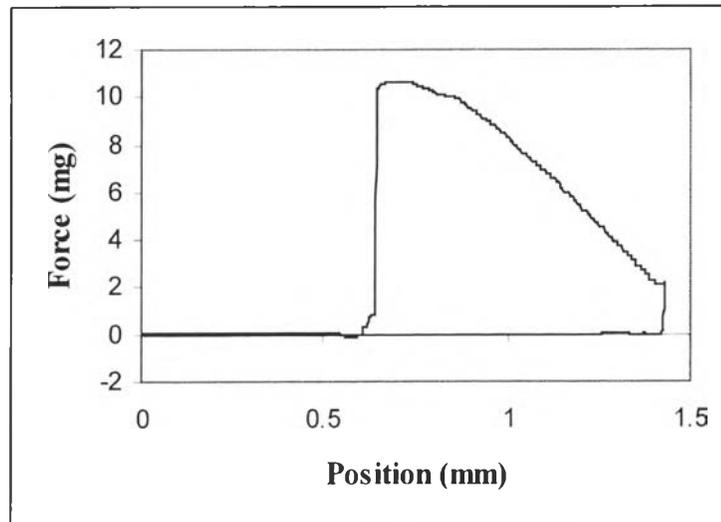
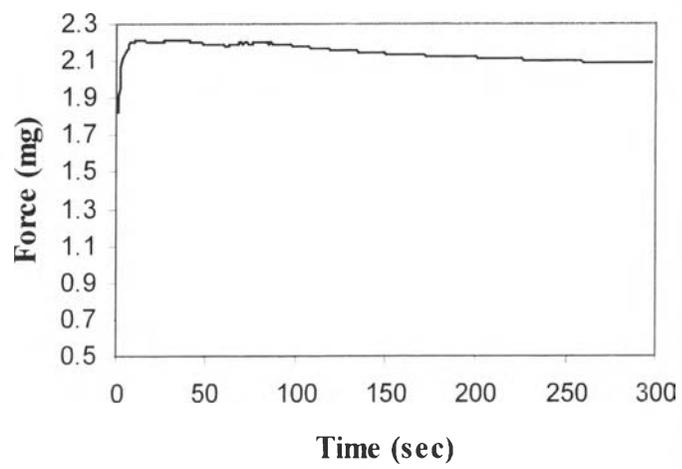


Figure 7

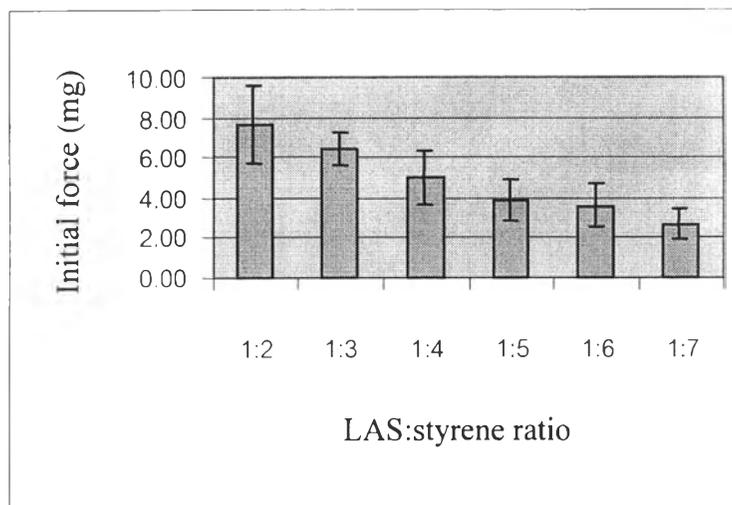


(a)

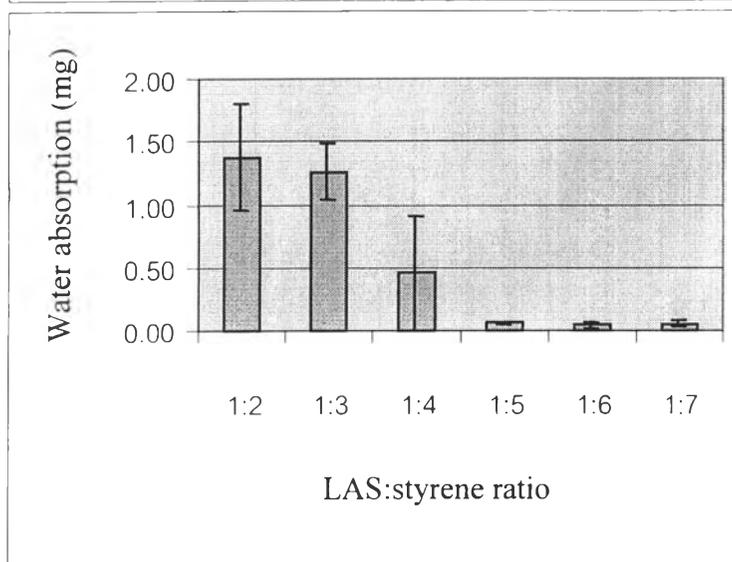


(b)

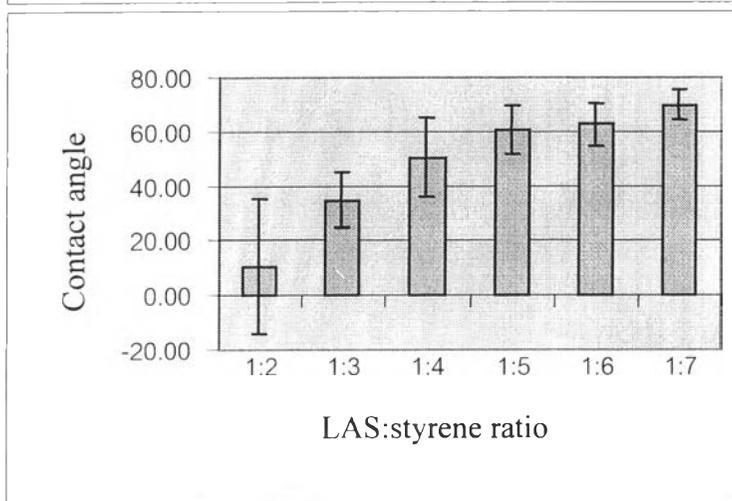
Figure 8.



(a)



(b)



(c)

Figure 9

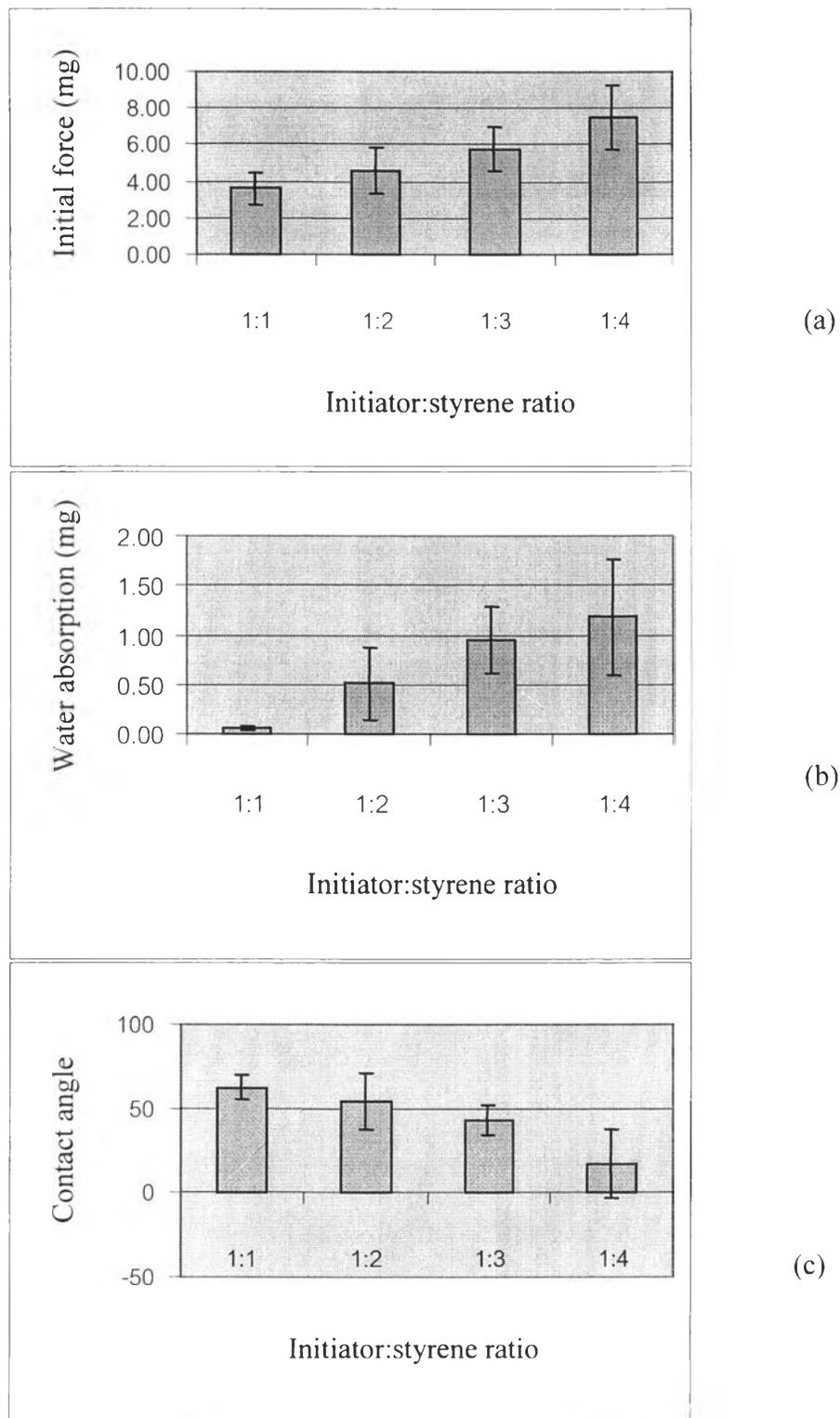
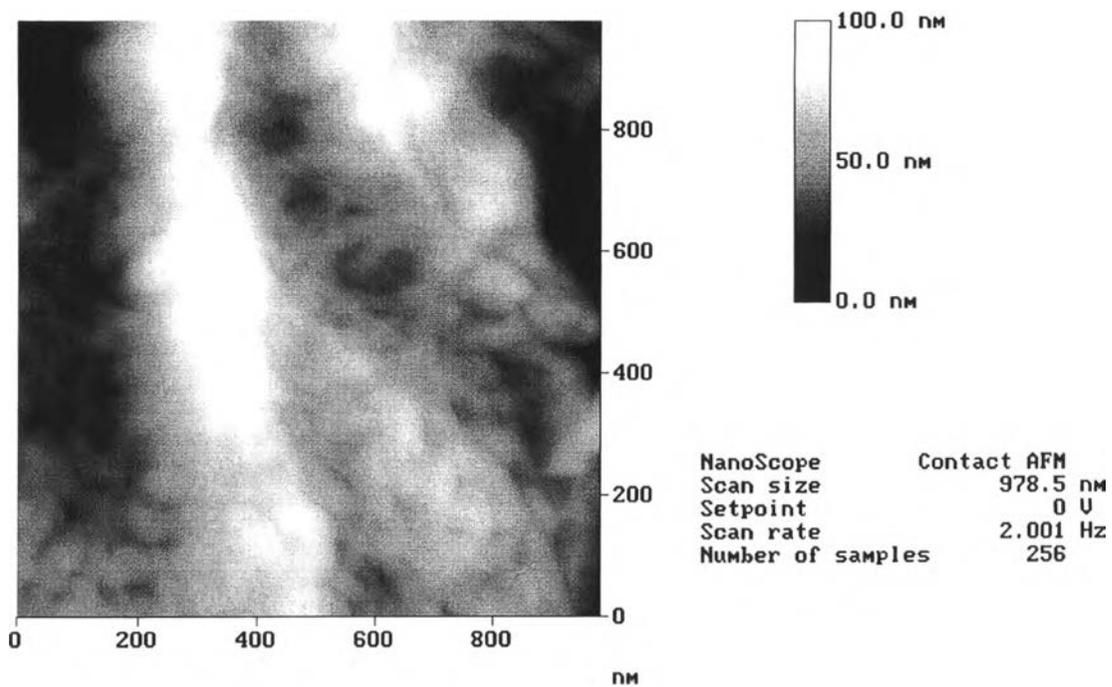
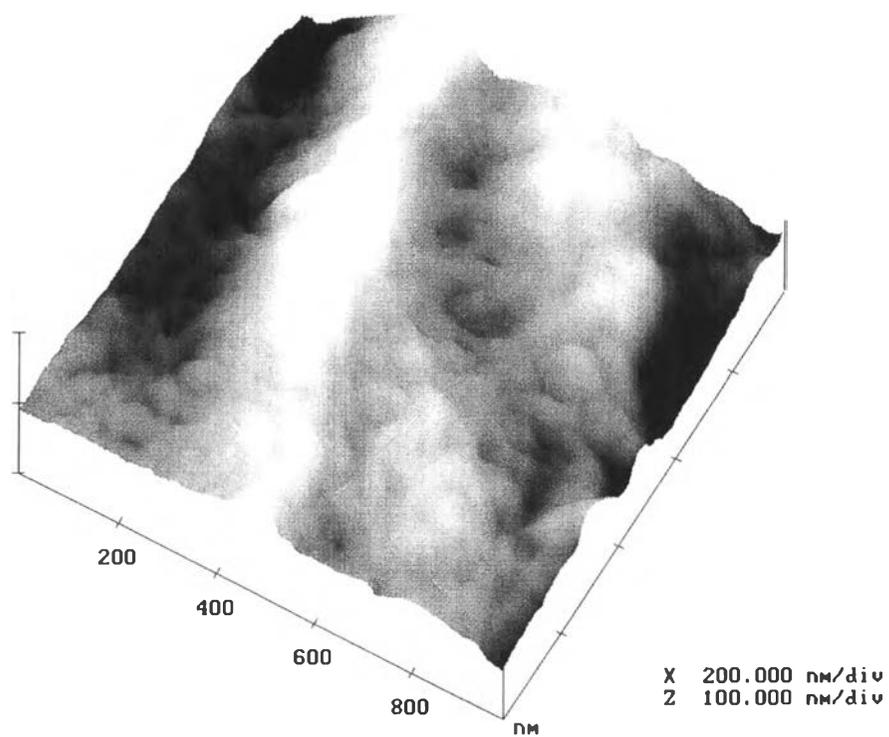


Figure 10

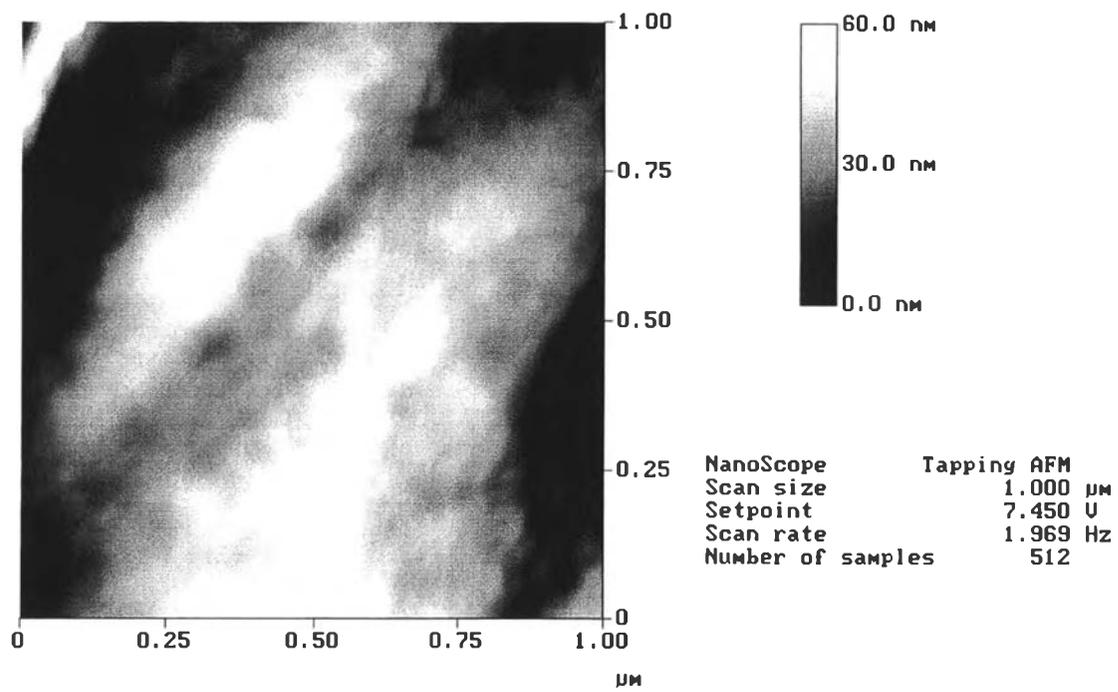


(a)

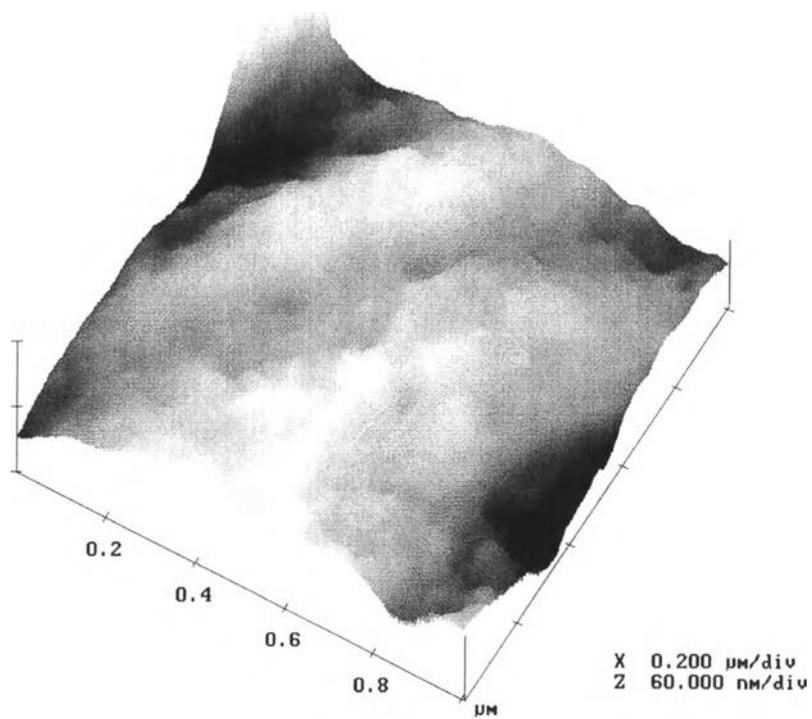


(b)

Figure 11



(a)



(b)

Figure 12

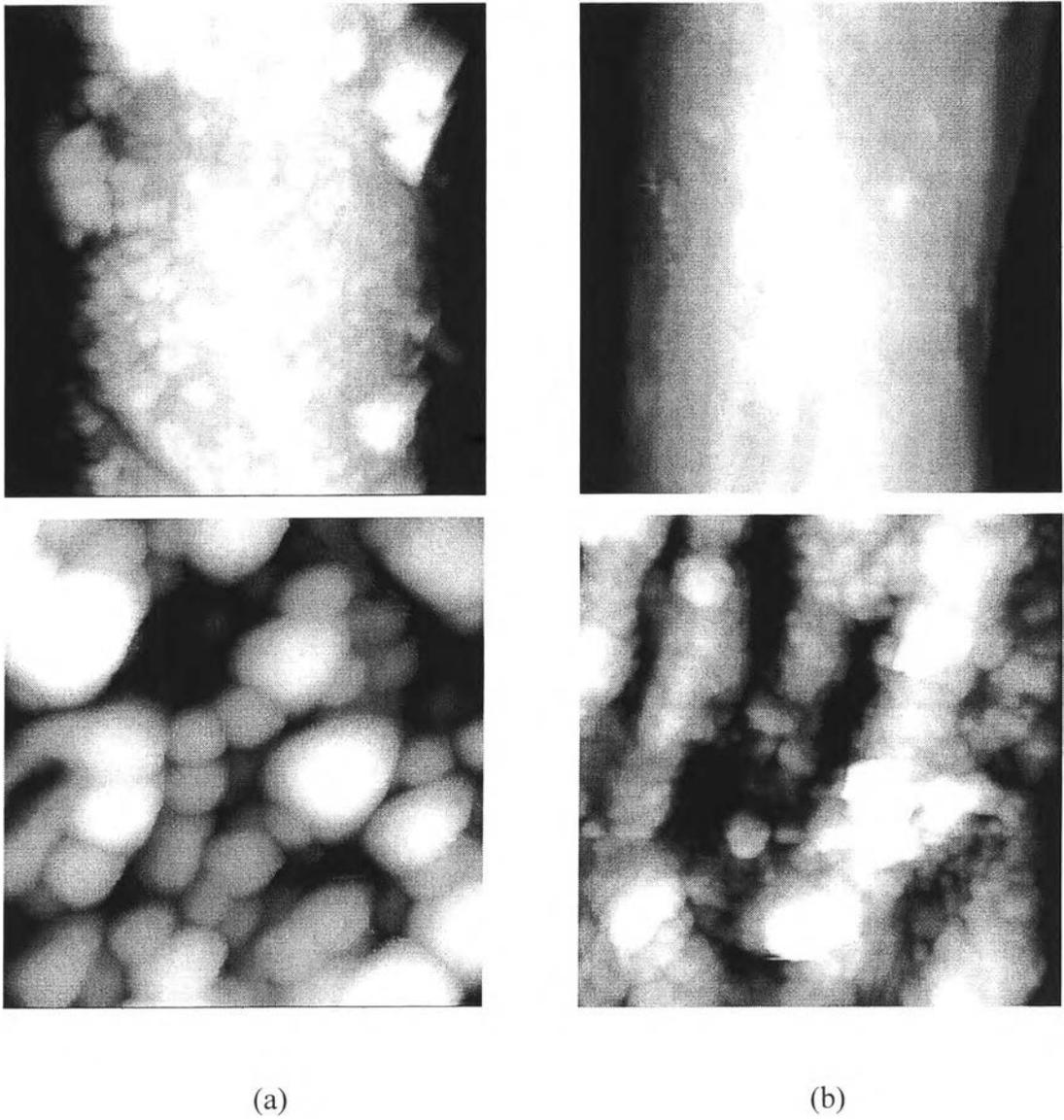


Figure 13