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Measurement of the adhesion between single melamine formaldehyde micro-particles and a flat fabric surface using AFM

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Abstract

Understanding adhesion of micro-particles particularly microcapsules containing a functional active on fabric surface is crucial to effective delivery of the active to the latter. Fabric surface is very rough, and direct measurement of the adhesion of single micro-particles on surfaces with roughnesses greater than the particle diameter can be difficult. In this work cotton films were successfully generated by dissolving cotton powder in an organic solvent and their properties including surface roughness, thickness, contact angle and purity were characterised. The adhesive forces between single melamine formaldehyde (MF) micro-particles and a cotton film under ambient condition with a relative humidity (RH) above 40% were measured using atomic force microscopy (AFM), which was considered to be dominated by capillary forces. It was also found that there was little adhesion between MF micro-particle and cotton film in aqueous solution of surfactant sodium dodecylbenzenesulfonate (SDBS). Instead, repulsion between them was observed and reduced with the increase of surfactant concentration and the decrease in solution pH. The repulsion contributions are thought to originate mainly from electrostatic repulsion. It is believed that the studies on the adhesion between single MF micro-particles and a cotton film under ambient conditions or in the surfactant solutions are beneficial in attempts to enhance the adhesion of microcapsules on fabric surface via modification of their surface composition and morphology.

Key words: micro-particle, atomic force microscopy, melamine formaldehyde, fabric, cotton, adhesion, repulsion

1. Introduction

Microcapsules with a core-wall structure confer the unique characteristics of masking the core material to reduce unnecessary reaction with outside agents. Hence, microcapsules have been widely applied in a large number of industrial sectors including pharmaceutical [1], food [2], agriculture [3], construction [4], household and personal cares [5]. In the use of household care products such as detergents, microcapsules containing perfume constituents were introduced into the softeners and detergent powder to minimise the loss of perfume in the successive rinses of laundry process, and to deliver it to the surface of fabrics, both woven and non-woven [6]. Of particular interest in this work are melamine formaldehyde (MF) microcapsules containing perfume oil, which may be included in liquid detergents for their end-use applications. As such, understanding the mechanical strength and adhesion of MF microcapsules on fabric surface becomes extremely critical, since microcapsules need to be strong enough to withstand a series of processes, such as preparation, transportation, mixing, washing and drying, adhere to the fabrics during washing and drying, and to be ruptured to release perfume when required (e.g. by rubbing and friction). This paper focuses on studying the adhesion of single MF micro-particles to mimic MF microcapsules on a fabric surface under an ambient condition as well as in solutions with a model surfactant of different pH values and concentrations.

Atomic force microscopy (AFM) allows accurate measurement of surface and intermolecular forces. Tipless AFM cantilevers are available for attaching single micro-particles of interest to them to measure their adhesion on another surface, which is known as the colloidal probe technique [7], and has been used by researchers to study the interaction force between specific particles and surfaces of interest in air or a liquid [7-13]. To the authors' best knowledge, however, there is no published research on direct measurement of adhesion between single MF micro-particles and a fabric surface under an ambient condition or in surfactant solution. Although single MF micro-particles were attached to tipless cantilevers [14], only the adhesion between MF micro-particles (10 μ m in diameter) coated with human serum proteins and macrophage was investigated. Therefore, this work aims to measure the adhesion between single MF micro-particles and a fabric surface under an ambient condition or in surfactant solutions using AFM.

However, it is not desirable to conduct AFM experiments on real fibres due to their rough morphology [13]. It is even more difficult to study the adhesion of single micro-particles on a single fibre under an ambient condition or in a liquid environment. Therefore it is desirable to create a flat surface which can mimic fabric. A new method has been reported for preparation of thin cellulose films by dissolving wood pulps in an organic solvent, NMMO (N-methylmorpholine-N-oxide) [15]. The model cellulose surface, which is flat, enables consistent results to be obtained between experiments [13, 16]. It was reported that different materials, such as cotton, paper grade pulp, unbleached chemical pulp, rayon fibres and waste paper, can be dissolved in NMMO [17]. The work presented in this paper aims to adapt the method initially used to dissolve wood pulps [15] to dissolve cotton powder, in order to generate a flat cotton film for reliably measuring the adhesion of single MF micro-particles on it to mimic the adhesion of MF microcapsules on the fabric surface.

2. Materials and methods

2.1 Materials

Cotton films were prepared using the following ingredients: cotton linter cellulose powders, also called cotton powders (Sigma-Aldrich, UK), 50 wt.% N-methylmorpholine-N-oxide (NMMO) solution (Sigma-Aldrich, UK), dimethyl sulfoxide (DMSO) (ACS spectrophotometric grade, $\geq 99.9\%$, Sigma-Aldrich, UK) and 50% (w/v) poly(ethyleneimine) (PEI) in water solution (Sigma-Aldrich, UK), general purpose grade sodium hydroxide powder (Sigma-Aldrich, UK) and water for gradient analysis of High Performance Liquid Chromatography (HPLC) (Fisher Scientific, UK). Silicon wafers with a thickness of $381 \pm 25 \mu\text{m}$ (Type N <100> Phos, IDB Technologies Ltd, UK) were employed as substrates for cotton films to be deposited on. Monodispersed MF micro-particles with a diameter in the range of 9.2-12.5 μm (Microparticles GmbH, Germany) were used. The MF micro-particles, produced by hydro-thermal acid-catalyzed polycondensation of methylol mela-mines in the temperature range 70-100 °C without any surfactants, have superior mechanical properties and high temperature resistant up to 300°C, and their density is 1.51 g/cm³ and its refractive index 1.68 [18]. The physical appearance of MF micro-particles (mean diameter = 12.5 μm) is shown by an ESEM image in Figure 1, where the MF micro-particles possess smooth surfaces and uniform sizes. Anionic surfactant sodium dodecylbenzenesulfonate (SDBS) powder (Sigma-Aldrich, UK), which contributed to 5 wt.% of a normal household detergent, was diluted in HPLC water to act as liquid media for the adhesion measurements. The amount of SDBS in its made-up solution had a concentration ranging from 0.2 mM to 14.4 mM. The pH of SDBS solutions was varied from 3 to 11 in order to study the effect of pH on the adhesion, which was adjusted by gradually adding acetic acid or 10 wt.% NaOH solution until the desired pH was reached.

2.2 Methods

Generation of Cotton Films

Silicon wafer surface normally has a native layer of silicon oxide, of which the thickness is approximately between 1-2 nm [19]. A silicon wafer was dipped into 10 wt.% NaOH solution for 30 seconds [13], and then rinsed with copious amount of HPLC water before being dried with a constant flow of nitrogen gas. The silicon wafer was subsequently immersed in 1 g l⁻¹ PEI solution for 10 min [16], and then rinsed with copious amount of water and again dried with a constant flow of nitrogen gas. 0.5 g of cotton powders were added into 25 g 50 wt.% NMMO in water solution, which was heated to 115 °C for about 2 hours using a magnetic stirrer with hotplate (RCT basic, IKA, Germany). The mixture was contained in a 200 mL beaker (*Diameter* (D) = 73 mm, *Height* (H) = 90 mm), which was placed in a glass oil bath (*D* = 112 mm, *H* = 63 mm) containing paraffin liquid oil (Fisher Scientific, UK), and the level of paraffin oil in the bath was always kept higher than the mixture in the beaker to ensure a full submersion of such mixture. A contact thermometer with a Proportional-Integral-Derivative (PID) controller (ETS-D5, IKA, Germany) connected to the hotplate was employed to control the temperature of paraffin oil at 115.0 ± 0.2 °C; this was achieved by immersing a stainless steel sensor of the contact thermometer in the oil bath. As a result, the temperature of the mixture of cotton powders and NMMO solution was always maintained at 115.0 °C. Once cotton powders were completely dissolved, 75 g of DMSO solvent was then gradually added to control the viscosity of the mixture. This produced 0.5% w/w cotton solution that was ready for spin-coating. The cotton solution was spin-coated at 3500 rpm using a spin coater (WS-400B-6NPP/LITE, Laurell Technologies Corporation, US) for 30 seconds onto a silicon wafer with an anchoring layer of PEI polymer, followed by precipitation in HPLC water. The cotton film was then immersed in a fresh batch of HPLC water for 1 hour and another 3 hours in another fresh batch of HPLC water. It was finally dried in a desiccator and ready for the measurements of the adhesion of single MF micro-particles on its surface.

Ellipsometry

A spectroscopic ellipsometer (UVISEL, Horiba Jobin Yvon Ltd., UK) was employed to measure the thicknesses of the silicon oxide layer on a silicon wafer, PEI polymer film and cotton film. The experimental data obtained were processed by DeltaPsi2 v2.0.8 software to obtain the thicknesses of films. The mean thickness of each film was based on the measurements of 5 separate locations.

Contact Angle Measurement

The wetting behaviour of water on a cotton film was characterised using a contact angle measurement apparatus equipped with a charge-coupled-device camera (KP-M1E/K, Hitachi). The experiments were performed at room temperature of 25.0 ± 0.1 °C. A drop of HPLC water, approximately 1 μ L in volume, was placed on the centre of a piece of cotton film. The profile of the water drop on the cotton film was visualised with a side view camera within 1 minute in order to obtain the equilibrium contact angle. The image was subsequently analysed with First Ten Angstroms video analysis software v1.96 to determine the contact angle.

X-ray Photoelectron Spectroscopy (XPS)

The cotton films were also analysed using an X-ray photoelectron spectrometer (Escalab 250 system, Thermo VG Scientific, UK) to ensure the cotton film was free from the solvent (NMMO). It operates under a pressure of $\sim 5 \times 10^{-9}$ mbar. An Al K α X-ray source was used, which provided a monochromatic X-ray beam with an incident energy of 1486.68 eV. A pass energy of 20 eV over a binding energy range of 22 eV and centring on the binding energy of the element being examined was applied to obtain a high resolution spectrum with an increment of 0.1 eV. Each spectrum acquired was based on the average of three scans. The recorded XPS peaks were analysed using the XPS software (Avantage v1.85 software). In case solvent residues were present on the cotton film, the individual peaks would appear within the binding energy range in the photoelectron spectrum, which represent the specific elements originated from the solvent.

Zeta Potential Measurement

The zeta potentials of cotton powders in surfactant SDBS solutions of a given concentration (0.2 mM) but different pH values (3-12) were characterised using a Zetamaster (ZEM 5004, Malvern Instruments Ltd., UK) at a room temperature of 25.0 ± 0.1 °C. Zeta potential is the potential at a shear plane which is at some distance from the particle of interest, based on the particle and liquid medium as a joint system. The measurement of zeta potential of cotton powder in surfactant solution was repeated 10 times at each pH.

Atomic Force Microscopy

A D3100 AFM (Digital Instruments, Santa Barbara, CA), which has a wide horizontal stage movement range, was employed for force measurement under an ambient condition between single MF micro-particles and a cotton film as well as imaging the surface of the latter. A MultiMode AFM (Digital Instruments, Santa Barbara, CA) was applied to measure the adhesive force between single MF micro-particles and a cotton film in SDBS surfactant solutions with different concentrations and pH values. Both AFMs were operated using a NanoScope III controller.

Imaging Cotton Films

The scan rate applied for imaging was 1.0 Hz at all times and the images obtained had a resolution of 256×256 pixels. Under the tapping mode, phosphorus (n) doped silicon cantilevers with a spring constant of 40 Nm⁻¹ (Model RTESP, Veeco, France) were used to obtain the topographic view and RMS roughness of cotton films.

Attachment of Single MF Micro-particle onto Cantilever

Two types of cantilevers were used for the adhesive force measurements: tipless rectangular silicon cantilever (Length 90 μm; Width 35 μm) (Model NSC12, MikroMasch, Estonia) and silicon nitride V-shape cantilever (Length 315 μm; Width 18 μm) (Model MLCT, Veeco, France). The NSC12 cantilevers were much stiffer in comparison with the MLCT cantilevers; hence, the latter were more sensitive and offered a higher force resolution. A colloid probe was formed when a single MF micro-particle was attached to a tipless cantilever with a two-component epoxy glue (Araldite Rapid, Bostik Findley Ltd., UK). The above procedure was completed with an aid of the D3100 AFM. A little drop of mixed components of epoxy glue was placed on an empty location of a glass slide with MF micro-particles. By varying the horizontal movement setting of the stepping motor in the D3100 AFM, a tipless cantilever held by a piezo was positioned on top of the epoxy glue, and lowered down gradually to come into contact with the glue. The cantilever was then moved to above a MF micro-particle and then lowered down slowly until it touched the top surface of the micro-particle, which was normally indicated by a change in output signal of the piezo. Furthermore, the contact between the micro-particle and cantilever could also be indicated by the total distance the stepping motor had moved in the downward direction, which should be approximately equal to the focusing distance between the cantilever and the glass slide (~1 mm) minus the micro-particle's diameter.

Figure 2 is an ESEM image showing a MF micro-particle of 11.9 μm in diameter attached to a tipless cantilever, which also confirms that there was no glue spreading over the surface of the micro-particle.

Calibration of Cantilevers

After a single micro-particle was attached to the tipless cantilever of rectangular shape (NSC12), the spring constant of this cantilever was calibrated using a reference cantilever method [20]. This method is not suitable for calibration of soft cantilevers, because it requires a cantilever under test to be measured against a hard surface to generate a force curve so as to determine a deflection sensitivity. A soft cantilever had a too small spring constant to generate a force curve against a hard surface. As such, a thermal noise method [21] was used to calibrate the spring constant of MLCT cantilevers. The calibrated spring constants of cantilevers were obtained by averaging three calibration results.

Force Measurement

The contact mode was used for force measurements. For the experiments performed under an ambient condition, the room temperature and air relative humidity (RH) were recorded using a thermo-hygrometer (DT-615, ATP Instrumentation Ltd., UK). A typical scan rate used in the AFM force measurement is 0.1-2.0 Hz [22]. In this work, a scan rate of 0.5 Hz was used for all the force measurements in both D3100 AFM and MultiMode AFM, except for scan rates that were varied in the cases to study the effect of probe approach/separation speed on the adhesion. Since it also depends on the use of ramp size, the speed could be different when employing D3100 AFM and MultiMode AFM, even though the same scan rate of 0.5 Hz was used, vice versa. The force measurement in the liquid environment was always performed 0.5 hr to 1 hr after the fluid cell of MultiMode AFM was filled with a liquid medium, in order to allow the liquid system to be stabilised, which can be indicated by the end of flashing signal of its photo detector.

3. Results and Discussion

Film Topography & Roughness

The RMS surface roughness of a silicon wafer, silicon wafer treated by 10% NaOH solution and PEI film is 0.3 nm, 0.3 nm and 0.4 nm respectively, based on a scan area of $5\ \mu\text{m} \times 5\ \mu\text{m}$ by AFM (images not shown). The experiments demonstrated that elimination of either NaOH treatment or anchoring PEI polymer layer resulted in the cotton film not being able to adhere to the silicon substrate. It may be because that the silicon wafer has a native silicon oxide layer on the surface and the high pH value of NaOH solution converts the Si-OH bond on silicon surface to Si-O⁻, or the Si-O-Si bond to Si-O⁻ and Si-O⁻, enabling the silicon oxide to adsorb more polymers. The importance of including an anchoring polymer layer to attach the cotton film to the wafer was also emphasised in [15]. The method reported in [15] was adapted and applied in this work to successfully prepare a thin cotton film by dissolving cotton powder. The cotton films were characterised using AFM to study the material distribution of cotton on the film surfaces and to measure their roughness. Figure 3 gives typical topography and 3-D surface images of a cotton film from a scan area of $5\ \mu\text{m} \times 5\ \mu\text{m}$, generated from cotton powders; the RMS roughness of the cotton film is 5.2 nm.

Film Thickness

Ellipsometry was employed to measure the thickness of respective layers of films during generation of a cotton film. The film thickness was obtained by measuring 5 individual and visibly defect-free locations across the film, and the mean thickness of each film and the twice standard errors are presented in Table 1. The mean thicknesses of the native silicon oxide layer on the silicon wafer surface (after being treated with 10% NaOH solution), PEI polymer film and cotton film are 2.5 ± 0.4 nm, 0.9 ± 0.2 nm and 13.1 ± 2.5 nm, respectively. The thickness of a cotton film generated from dissolving pulp and using the same type of PEI polymer was reported to be around 30 nm [16], which is approximately twice of that of the cotton film generated from cotton powder solution. The thickness of cellulose film increases with the concentration of cellulose solution [23]. As the concentration of the dissolved pulp solution was not specified in [16], the thickness of the cellulose film prepared from wood pulp and that of the cotton film prepared from cotton powders are therefore not directly comparable.

Table 1 Thicknesses of the silicon oxide layer on a bare silicon wafer (after being treated with 10% NaOH solution), PEI polymer film and cotton film.

Location	SiO ₂	PEI	Cotton
1	2.1	0.7	13.5
2	2.8	0.7	15.7
3	2.9	0.9	15.4
4	2.5	1.2	10.4
5	2.0	0.9	10.7
Mean (nm)	2.5 ± 0.4	0.9 ± 0.2	13.1 ± 2.5

Hydrophilic Property

The results of contact angle measurement show that the contact angle, θ , between a drop of water and cotton film is 33° (image not shown). It is comparable with the contact angles (24° - 33°) suggested in [15] for pure cellulose. Since the contact angle between the water droplet and cotton film is less than 90° ; the cotton film is considered to be hydrophilic, which implies that in an ambient environment with a relatively high RH, the adhesive force between a cotton film and another hydrophilic surface could be mainly due to capillary forces [24].

Presence of Solvent (NMMO) on the Cotton Film Surface

In order to ensure there is no solvent residue (NMMO) on the film, the detailed XPS scan of its surface was undertaken and concentrated on the binding energy of the element originated from the solvent. NMMO solvent consists of N element with a binding energy of 402 eV. The binding energy ranging from 390 eV to 412 eV was scanned for N 1s and the results are presented in

Figure 4. No visibly distinctive N 1s peaks can be observed in the range of this binding energy except the baseline noise. This indicates there is no presence of NMMO solvent on the surface of the cotton film [15]. If there were any NMMO residue on the cotton film surface, the spectra would look similar to those of the PEI film (

Figure 5) in which a distinctive N 1s peak can be identified, as the PEI polymer consists of N element.

Adhesion between Single MF Micro-particles and a Cotton Film under Ambient Condition

The experiments were performed to study the adhesion between a MF micro-particle and a cotton film under an ambient condition; at the same time, the effect of piezo separation speed on the adhesion was also investigated. In

Figure 6, the measurement results of the MF micro-particle are based on measurements at 14 different locations on the cotton film at each speed of 276 nm/s, 2.76 $\mu\text{m/s}$ and 12.85 $\mu\text{m/s}$; 5 repeated measurements were conducted at each location. The NSC12 cantilever used had a calibrated spring constant of 14.8 N.m^{-1} . A t statistical test [25] shows that the speeds have no significant effect on the adhesion between the MF micro-particle and cotton film, with 95% confidence. This agrees with the suggestion in [24] that there was no evidence that varying the speed significantly affected the pull-off force for relatively hard materials, such as the MF micro-particle and cotton film studied here. As the experiments were conducted at an air RH of 43%, and MF is of a hydrophilic nature, it is likely that the main mechanism of adhesion between them is via capillary force rather than that described by JKR contact mechanics theory, the latter of which is normally applicable to interpret dry contact at very low air RH. Corresponding to the separation speeds shown in Figure, the contact time varies from 0.01 to 0.4s. It has been reported that the time for water vapour condensation to reach equilibrium is 1ms [26], which is an order of magnitude smaller than the shortest contact time and explains that the obtained adhesive force did not change with the separation speed or contact time in this range. Eriksson et al [27] have found the increase in relative humidity resulted in larger adhesion between a cross-linked poly(dimethylsiloxane) film and cellulose film. This was probably because such cellulose film had a semi-crystalline structure increasing the mobility of surface molecules to easily take up water to form a strong joint [13, 27].

It was suggested that capillary force between particle and surface becomes the dominant adhesive force above $\sim 40\%$ relative humidity (RH) [24]. The equation for capillary force, F_C , describing “sphere-on-flat” geometry can be expressed in Equation 1 [24] as:

$$F_C = 4\pi R \gamma_L \cos \theta_c \quad (1)$$

where θ_c is the contact angle of water on the two surfaces of sphere and substrate, which is assumed to be identical θ_c since the contact angle on a flat MF film was 34° [28] and that on the cellulose film was 33° from this work. R denotes radius of sphere; γ_L is surface tension of liquid, 72 mN.m^{-1} . This equation neglects (i) any contribution to adhesion from the solid-solid interaction across the liquid bridge; (ii) any existing condensed liquid film before the surfaces is brought into contact. Therefore, the capillary force ($\theta_c = 33.5^\circ$) after being normalized with the radius of micro-particle, i.e. F_C/R , was predicted to be 754 mN.m^{-1} . The measured normalised adhesive force for the MF micro-particle at the speed of 2760 nms^{-1} is $218 \pm 19 \text{ mN.m}^{-1}$ on average. The measured adhesion falling well below the prediction of liquid bridge theory was also observed by others [24; 29]. It was interpreted that the adhesion resulting from liquid bridge depends on a complex interplay of many effects, notably the geometry of surface asperities, meniscus radii (the radii of adsorbed water film), contact angles and the thickness of adsorbed water film. Furthermore, the contact angles and the adsorbed water layer are also very sensitive to the surface chemical conditions. As such, besides capillary force, surface chemistry and surface roughness are also two factors contributing to the adhesive force.

The adhesive forces measured at 4 random locations on the cotton film are shown in Figure 7. It is apparent that the adhesive force is the lowest at location 3 ($121 \pm 4 \text{ mN.m}^{-1}$) and is the greatest at location 4 ($180 \pm 1 \text{ mN.m}^{-1}$). Such variation might result from different roughness at each location, as shown in Figure 3(a). As discussed above, the main adhesive force at RH greater than 40% is attributed to capillary force which also depends on factors such as surface roughness [24].

Interaction between Single MF Micro-particles and a Cotton Film in SDBS Surfactant Solution

Single MF micro-particles were attached to MLCT cantilevers as colloidal probes, and their detailed calibrated spring constants are specified below. According to the working principle of AFM, the

deflection of a cantilever is sensed by the means of reflecting laser beam on top of the cantilever, which is immersed in the fluid, to the position-sensitive photodiode. The noise that is present in raw data is therefore suppressed if laser beam is reflected in a clear fluid instead of more complex liquid medium. As a result, a dodecylbenzenesulfonate (SDBS) surfactant solution was used instead of a detergent solution, in which the interaction between a MF micro-particle (diameter = 9.2 μm) and cotton film was studied. SDBS surfactant itself is one of the main components in detergent solutions. It was found that the obtained approach and separation curves overlap, as those described in [30]. Therefore, only the approach (extending) curves are presented for clarity. Unless otherwise stated, the results below are based on experiments performed on at least 5 locations on a cotton film (5 measurements per location). The piezo separation speed of 250 $\text{nm}\cdot\text{s}^{-1}$ corresponding to a scan rate of 0.5 Hz was used to study the interaction between MF micro-particles and a cotton film in SDBS solutions.

The concentrations of SDBS solutions used were 0.2 mM, 1.4 mM and 14.4 mM, in which the amount of SDBS was equivalent to that in 0.15 wt.%, 1.0 wt.% and 10 wt.% detergent solution, respectively. The calibrated spring constant of the cantilever was 0.13 $\text{N}\cdot\text{m}^{-1}$. It is apparent from Figure 8 that the interaction between the MF micro-particle and cotton film is influenced by the concentration of SDBS solution. At 0.2 mM, the repulsion started when the two surfaces were approximately 60 nm apart; the magnitude of maximum repulsive force was around 4.5 nN. At 14.4 mM, the repulsion commenced when two surfaces were at a much closer distance of approximately 20 nm away from each other; the magnitude of maximum repulsive force dropped to around 1.5 nN. However, in any case, there was no significant adhesion (separation curve not shown). The force resolution of the interaction curves is generally limited by the thermal fluctuation and spring constant of cantilever, and it is 0.02 nN for the interaction curves in Figure 8, which is determined by following the method reported in [31].

It is evident that the repulsion becomes less pronounced with increasing concentration of SDBS solution. Both electrostatic and steric repulsion forces are dependent on ionic strength of liquid medium; the former is generated by surface charges, and the later results from a few chains extending away from the surface [13]. In order to determine the dominant mechanism here, Figure 9 was plotted by applying a logarithmic scale to the force data in Figure 8. Each force curve shows an approximately exponential decay, suggesting the electrostatic force was dominant in this case [30]. The decrease in repulsive force with increasing SDBS concentration is likely to be due to the reduction in the extent of the electrical double layer with the increased effective electrolyte concentration in solution. This is further validated as the surfactant SDBS is non-adsorbing and anionic, and both the surfaces (MF and cellulose) are of anionic nature [18, 24].

The interaction between a MF micro-particle (diameter = 9.2 μm) and a cotton film in 0.2 mM SDBS solution as a function of its pH is shown in Figure 10. The calibrated spring constant of the cantilever employed was 0.09 $\text{N}\cdot\text{m}^{-1}$. At pH 11, repulsion occurred when the MF micro-particle was 70 nm away from the cotton film. At pH 3, the repulsion began whilst two surfaces were 20 nm away. The results indicate that the distance at which repulsion occurs increases with increase of the pH. This is probably due to the surface charges of cotton films increasing with increasing solution pH [32]. The amount of SDBS in 0.2 mM surfactant solution is equivalent to that in 0.15 wt.% detergent solution which is the typical concentration used for washing machine. The results in

Figure 10 show that the interaction becomes more repulsive with increasing pH.

In order to interpret

Figure 10, zeta potentials of cotton powders with the particle diameter of 20 μm in 0.2 mM SDBS surfactant solution with varying pH were measured. The mean value of 10 measurements at each pH is presented in

Figure 11. Overall, the zeta potentials of cotton powders in the solutions became more negative as pH increased. Previous work also showed that the zeta potential of MF micro-particles in aqueous solution with pH values in the range of 6.7 to 12 was also negative, and became more negative with increasing pH [18]. The AFM measurement results in

Figure 10 also indicate that repulsion between the MF micro-particle and cotton film increases with increasing pH. Qualitatively, the AFM results are consistent with the zeta potential measurements. This suggests again electrostatic repulsion could be one of mechanisms for the interaction of MF micro-particle and cotton film in the surfactant solution.

However, there has been evidence to demonstrate some MF microcapsules after being mixed with woven cotton bundles attached to them [33]. The data presented above show that there was negligible adhesion between a MF micro-particle and cotton film in a simulated detergent liquid. The MF microcapsules were produced by an in-situ polymerisation of melamine-formaldehyde pre-condensate crosslinked with acrylamide/acrylic acid [34]. Although the MF microcapsules might have slightly different surface composition from MF micro-particles used in this work, the zeta potential data of MF microcapsules in SDBS surfactant solution at varying pH [33] give similar trend to that of MF micro-particles [18]. As such, the MF micro-particles are considered to be good representative of MF microcapsules. This implies that the physical structure of woven cotton bundles could in fact entrap the microcapsules to promote their retention on them. Therefore, the main mechanism of microcapsule attachment to fibre surface is probably through physical entrapment rather than adhesion.

4. Conclusions

The method proposed in [15] has been successfully adapted to generate flat cotton films using cotton powders as a raw material instead of wood pulps. As a result, measurement of adhesive force between single micro-particles and a flat cotton film could be performed to overcome the inconsistent topography of fibre bundles. The cotton film was characterised using techniques including AFM, ellipsometry, contact angle measurement and XPS and it was concluded that such film was thin and possessed a relatively smooth surface. In addition, the cotton film was of hydrophilic nature and free of the used solvent. The obtained adhesive force between a MF micro-particle and cotton film under an ambient condition (air with RH > 40%) was suggested to be mainly capillary force, which plays an important role between hydrophilic surfaces at high air RH. It was demonstrated that the measured adhesive force agrees well with that predicted by the capillary force theory, taking the surface roughness, contact angle and meniscus radius into consideration.

It was revealed that there was little adhesion between single MF micro-particles and a cotton film in the SDBS surfactant solution, which is one of main components of detergent. It was also found that there was mainly repulsion between the MF micro-particle and cotton film in the surfactant solution, and the repulsion tended to reduce with increasing concentration of the surfactant from 0.2 mM to 14.4 mM. This might be due to the electrostatic repulsion which arises when two surfaces with same charges are approached together in an electrolyte solution. It was also found that the repulsion between MF micro-particle and cotton film reduced with decreasing pH of the surfactant solution.

The zeta potential of cotton powders in SDBS solution was negative when pH of the solution was in a range of 3 to 12, and reduced with the decreasing pH, which combined with the negative zeta potential of MF micro-particles supports the AFM finding that the repulsion between MF micro-particle and cotton film reduced with decreasing pH of the SDBS solution. The obtained results for the interaction between MF micro-particle and cotton film in SDBS solution implied that no significant adhesion existed between them, and that the main mechanism of microcapsule retention on the woven cotton fabric is probably due to physical entrapment. Future work will investigate physical and chemical modifications of the surface of MF micro-capsules in order to change their charge and morphology to enhance their adhesion on fabric surfaces and physical entrapment into fabric bundles.

References

1. B. B. C. Youan, T. L. Jackson, L. Dickens, C. Hernandez and G. Owusu-Ababio, *Journal of Controlled Release*, 76, 313 (2001)
2. H. C. Greenblatt, M. Dombroski, W. Klishevich, J. Kirkpatrick, I. Bajwa, W. Garrison and B. K. Redding, *Encapsulation and Controlled Release*, D. R. Karsa & R. A. Stephenson, eds., The Royal Society of Chemistry, Cambridge (1993).
3. P. Chamberlain, K. C. Symes, *Encapsulation and Controlled Release*, D. R. Karsa & R. A. Stephenson, eds., The Royal Society of Chemistry, Cambridge (1993).
4. R. Q. F. Janssen, G. J. W. Derks, A. M. Van Herk and A. L. German, *Encapsulation and Controlled Release*, D. R. Karsa & R. A. Stephenson, eds., The Royal Society of Chemistry, Cambridge (1993).
5. B. Turner, L. Levey, *Encapsulation and Controlled Release*, D. R. Karsa & R. A. Stephenson, eds., The Royal Society of Chemistry, Cambridge (1993).
6. L. T. T. Ho, *Formulating Detergents and Personal Care Products* AOCS Press, Champaign, Illinois (2000).
7. W. A. Ducker, T. J. Senden and R. M. Pashley, *Nature*, 353, 239 (1991).
8. S. Biggs, *Journal of the Chemical Society-Faraday Transactions*, 92, 2783 (1996).
9. W. R. Bowen, N. Hilal, R. W. Lovitt and C. J. Wright, *Journal of Membrane Science*, 154, 205 (1999).
10. W. R. Bowen, R. W. Lovitt and C. J. Wright, *Journal of Materials Science*, 36, 623 (2001).
11. W. R. Bowen, R. W. Lovitt and C. J. Wright, *Journal of Colloid and Interface Science*, 237, 54 (2001).
12. X. Li and B. E. Logan, *Langmuir*, 20, 8817 (2004).
13. S. M. Notley, M., Eriksson, L. Wagberg, S. Beck and D. G. Gray, *Langmuir*, 22, 3154 (2006).
14. S. Leporatti, A. Gerth, G. Kohler, B. Kohlstrunk, S. Hauschildt and E. Donath, *Febs Letters*, 580, 450 (2006).
15. S. Gunnars, L. Wagberg and M. A. C. Stuart, *Cellulose*, 9, 239 (2002).
16. C. Aulin, A. Shchukarev, J. Lindqvist, E. Malmstrom, L. Wagberg and T. Lindstrom, *Journal of Colloid and Interface Science*, 317, 556 (2008)
17. T. Rosenau, A. Potthast, H. Sixta and P. Kosma, *Progress in Polymer Science*, 26, 1763 (2001).
18. H. Fiedler, *Synthesis and Properties of Monodisperse Melamine Resin Particles*, Micro-particles GmbH, Germany (2008).
19. E. A. Taft, *Journal of the Electrochemical Society*, 135, 1022 (1988).
20. M. Tortonese and M. Kirk, *Micromachining and Imaging*, 3009, 53 (1997).
21. J. L. Hutter and J. Bechhoefer, *Review of Scientific Instruments*, 64, 1868 (1993).
22. J. Fritz, D. Anselmetti, J. Jarchow and X. FernandezBusquets, *Journal of Structural Biology*, 119, 165 (1997).
23. S. Falt, L. Wagberg, E. L. Vesterlind and P. T. Larsson, *Cellulose*, 11, 151 (2004).
24. R. Jones, H. M. Pollock, J. A. S. Cleaver and C. S. Hodges, *Langmuir*, 18, 8045 (2002).
25. D. C. Montgomery, G. C. Runger and N. F. Hubele, *Engineering Statistics*, 2nd Edition, John Wiley & Sons, Inc. (2001).
26. Z. Wei, Y.-P. Zhao, *Journal of Physics D-Applied Physics*, 40, 4368 (2007).
27. M. Eriksson, S. M. Notley and L. Wagberg, *Biomacromolecules*, 8, 912 (2007).
28. C. R. Crick, I. P. Parkin, *Thin Solid Films*, 519, 2181 (2011).
29. C. S. Hodges, J. A. S. Cleaver, M. Ghadiri, R. Jones, R. and H. M. Pollock, *Langmuir*, 18, 5741 (2002).
30. A. Carambassis and M. W. Rutland, *Langmuir*, 15, 5584 (1999).

31. R. Owen, *A Practical Guide to AFM Force Microscopy and Data Analysis*, JPK Instruments AG, Germany (2002).
32. T. A. Camesano and B. E. Logan, *Environmental Science & Technology*, 34, 3354 (2000).
33. M. Liu, *Understanding the Mechanical Strength of Microcapsules and Their Adhesion on Fabric Surfaces*, PhD Thesis, University of Birmingham, UK (2010).
34. G. Sun and Z. Zhang, *Journal of Microencapsulation*, 18, 593 (2001).

Figures

Figure 1 An ESEM image of MF micro-particles with a mean diameter of 12.5 μm .

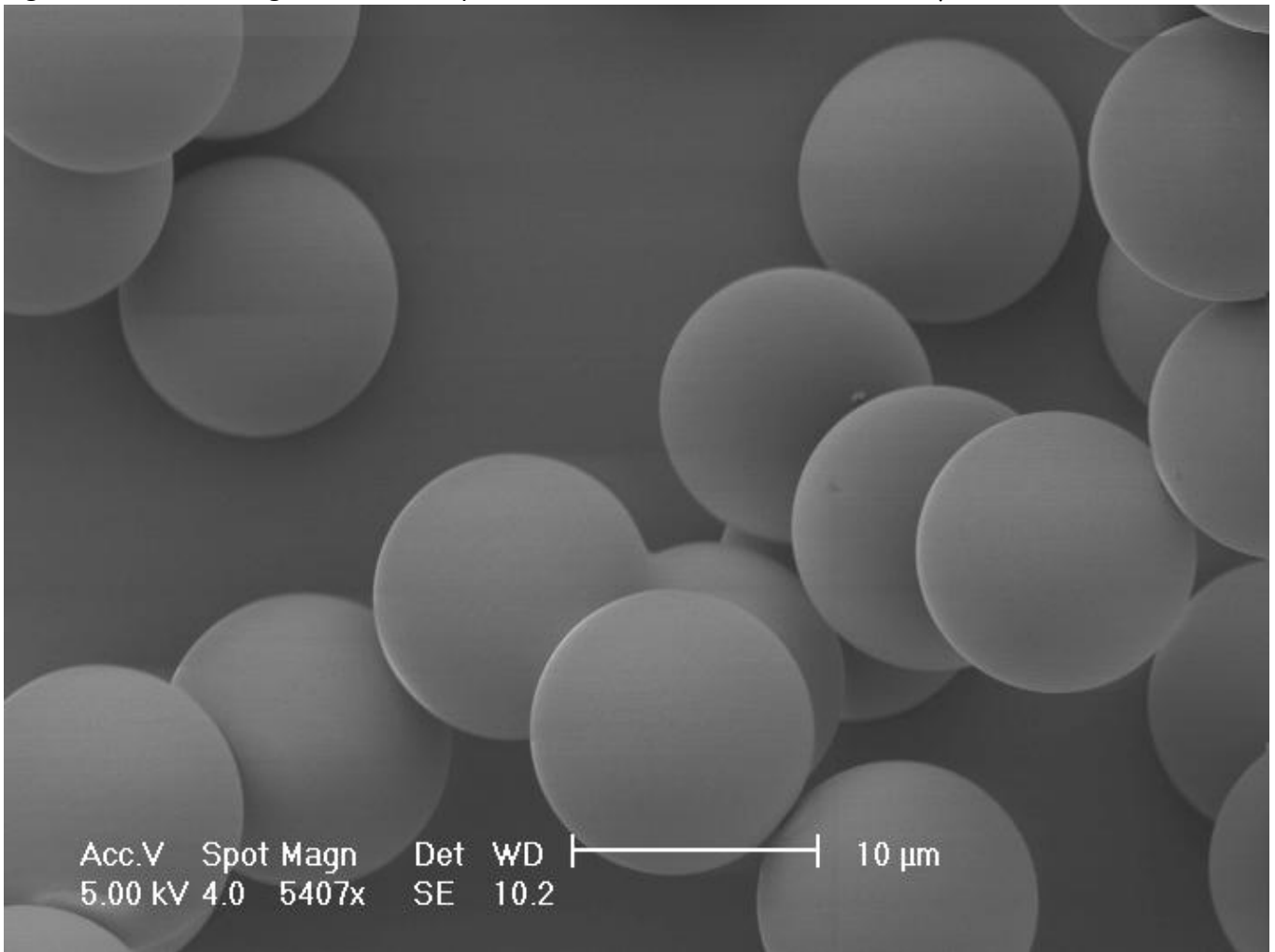


Figure 2 An ESEM image showing a micro-particle (diameter=11.9 μm) attached to a tipless cantilever.

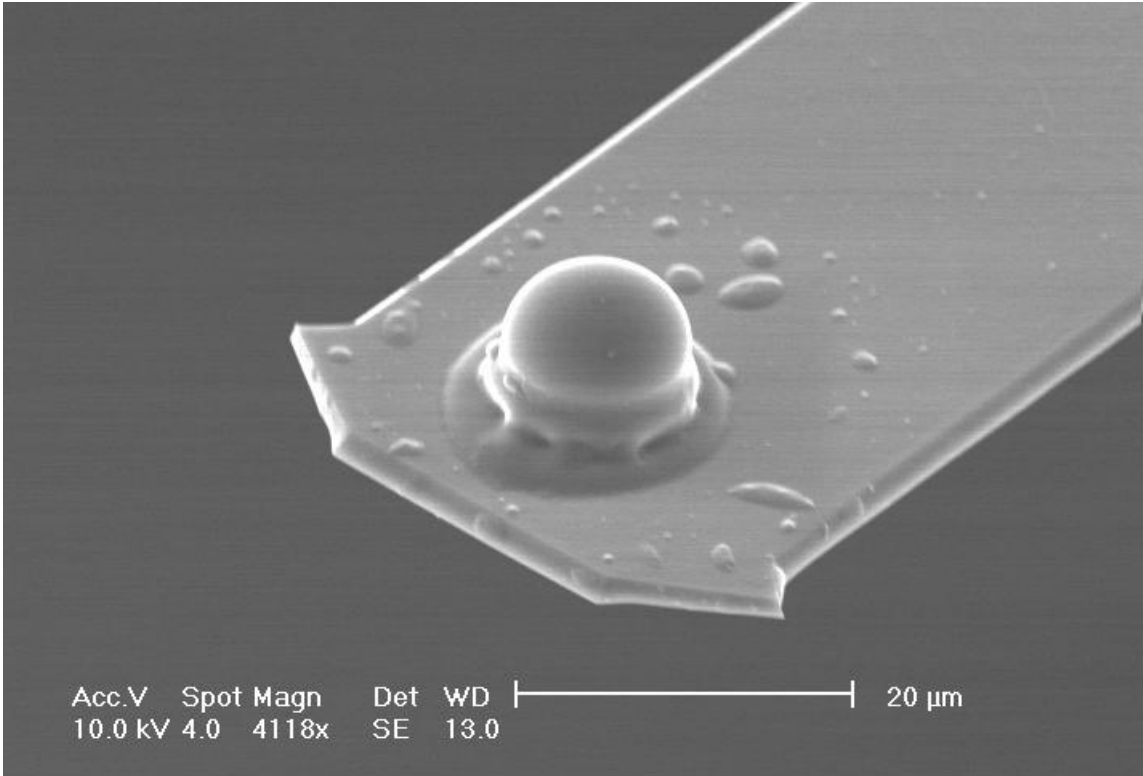


Figure 3 AFM (a) topography image (b) 3-D surface view of a dry cotton film generated from cotton powders (scan area $5\mu\text{m}\times 5\mu\text{m}$). The cotton concentration in the solution is 0.5wt.%. The RMS roughness of the film shown here is 5.2 nm.

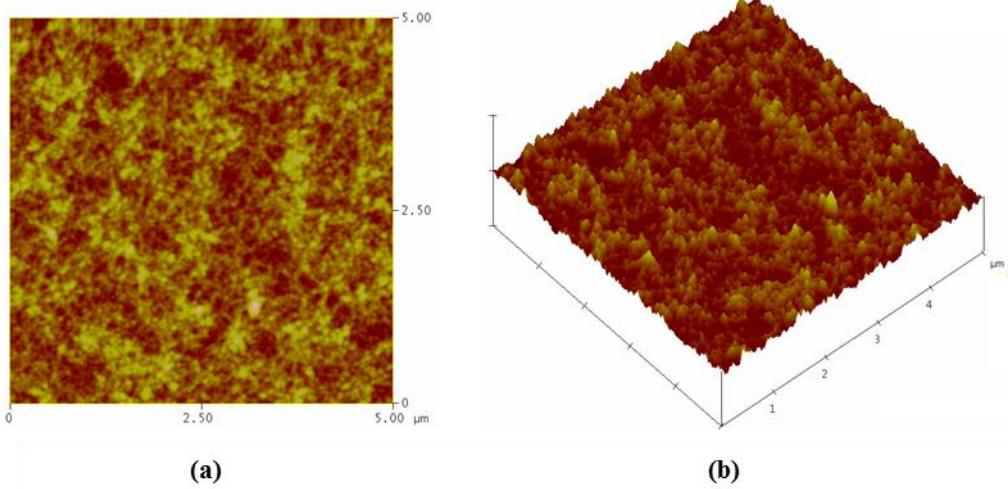


Figure 4 XPS spectra of N 1s for a cotton film.

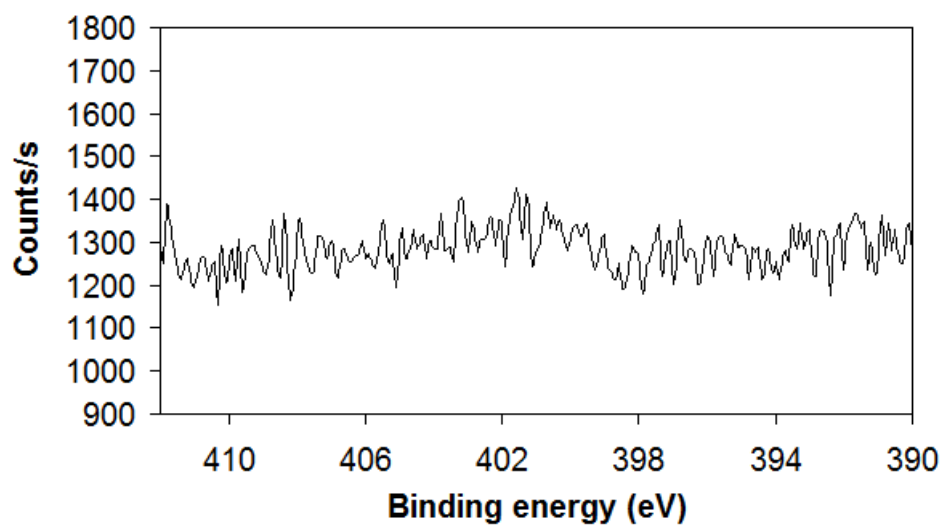


Figure 5 XPS spectra of N 1s for a PEI film.

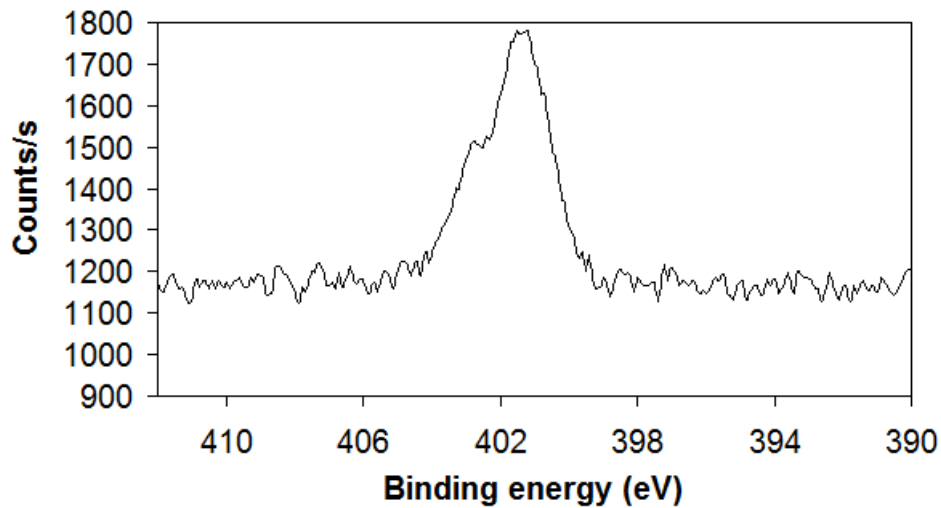


Figure 6 The adhesive forces (normalised with micro-particle radius) between a MF micro-particle (diameter = 11.9 μm) and a cotton film under the ambient condition (air RH 43%), measured at piezo separation speeds of 276 nm/s, 2760 nm/s and 12850 nm/s; the contact time was 0.4, 0.04 and 0.01seconds, respectively. The compression load applied was 740 nN. The error bars represent two standard errors of the mean.

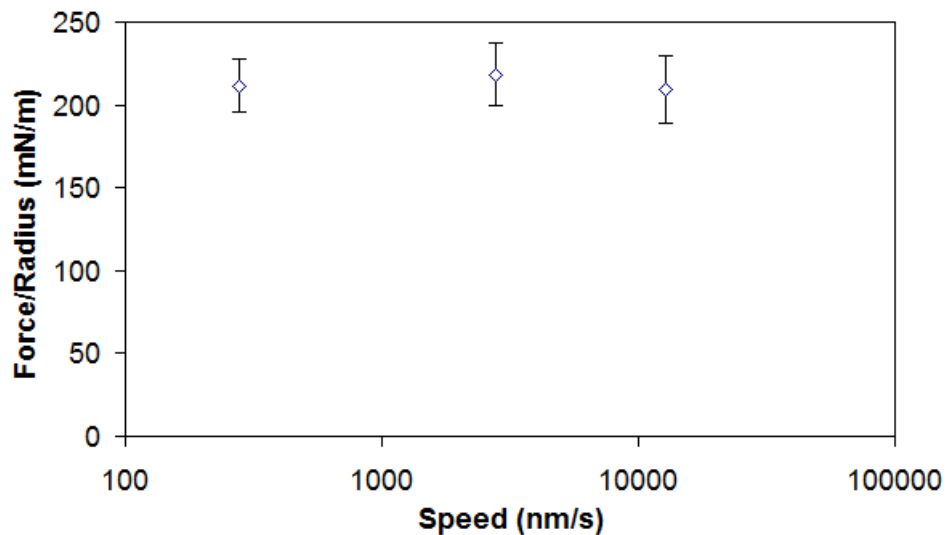


Figure 7 The adhesive forces (normalised with micro-particle radius) between a MF micro-particle (diameter=11.9 μm) and cotton film under the ambient condition (air RH 43%), measured at the piezo separation speed of 2760 nm/s; the contact time was 0.04 seconds and the compression load applied was 740 nN. The error bars represent two standard errors of the mean.

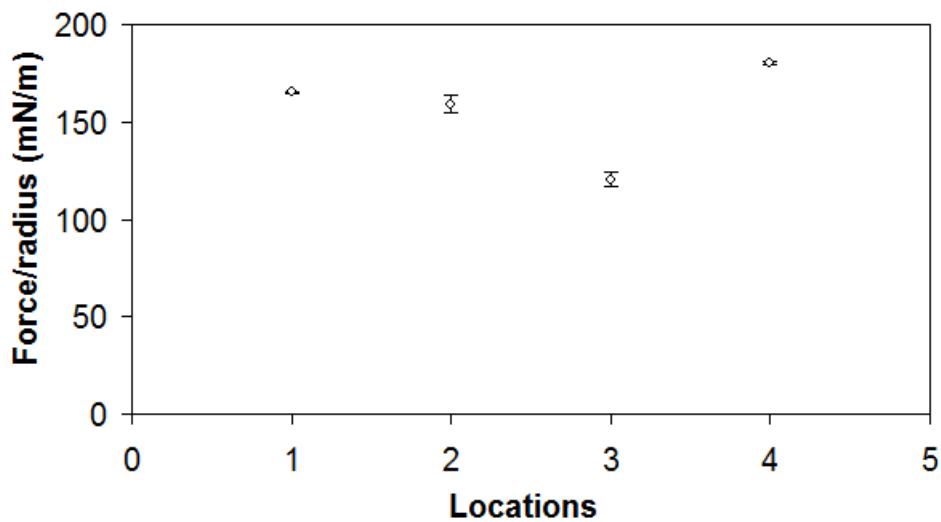


Figure 8 The interaction between a MF micro-particle (diameter = 9.2 μm) and a cotton film immersed in SDBS surfactant solution of various concentration at pH 7.

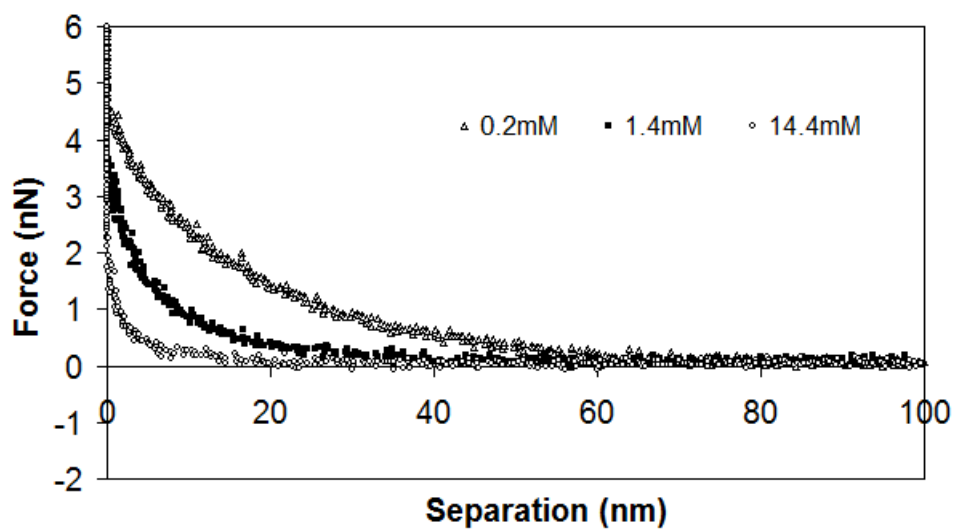


Figure 9 The interaction between a MF micro-particle (diameter = 9.2 μm) and a cotton film immersed in SDBS surfactant solution of various concentration at pH 7. (This figure applies a logarithmic scale to the force data in Figure 8)

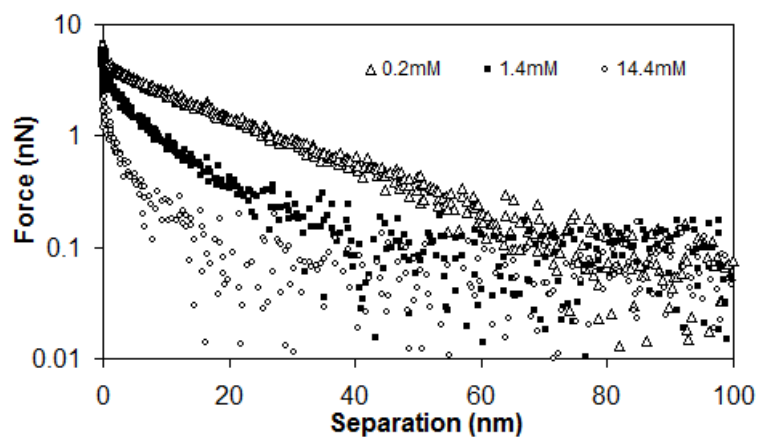


Figure 10 The interaction between a MF micro-particle (diameter = 9.2 μm) and a cotton film immersed in 0.2 mM SDBS surfactant solution with varying pH.

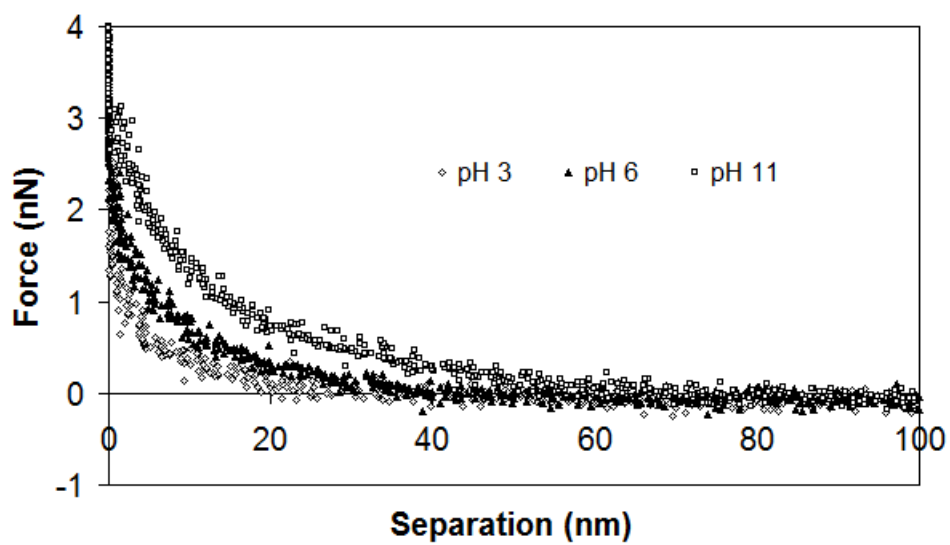


Figure 11 Zeta potential of cotton powders (mean particle size=20 μm) in 0.2 mM SDBS surfactant solution with varying pH.

