



CHAPTER III EXPERIMENTAL

3.1 Materials

Carbon black with a supplier provided specific surface area of $96 \text{ m}^2/\text{g}$ and an average diameter of $0.24 \mu\text{m}$ was obtained from Cabot company, Inc. Ferric oxide with a purity of more than 99% was obtained from Sigma-Aldrich, which has a specific surface area of $13.98 \text{ m}^2/\text{g}$ determined by a BET surface area analyser with nitrogen adsorption, and the diameter in the range of 0.23 to $1.00 \mu\text{m}$. Kaolinite (purum) was supplied by ITALMAR Co., Ltd. (BKK, Thailand). Kaolinite was found to have a median particle size of $14.4 \mu\text{m}$ with the size distribution in the range of about 0.1 – $20 \mu\text{m}$.

The surfactants used in this study were sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and octyl phenol ethoxylate with an average of 10 ethylene oxides per molecule (OP(EO)10-tradename Triton X-100) with a purity of more than 99% which were all purchased from Sigma-Aldrich. Methyl ester sulfonated (MES, 89% purity) and alcohol ethoxylate with nine ethoxyl groups (AE9, 99% purity) were obtained from PTT Co., Ltd., Linear alkylbenzene sulfonate (LAS, 80% purity) was purchased from The East Asiatic (Thailand) Public Co., Ltd. Commercial detergent (Breeze excel) from Unilever Company was purchased from a supermarket in Bangkok. Three types of studied fabrics, pure cotton, pure polyester and polyester/cotton blended (65/35) were purchased from Test Fabric Co. (Middlesex, NJ, USA).

For other chemicals, sodium hydroxide (NaOH, analytical purity grade), hydrochloric acid (HCl, analytical purity grade) and nitric acid (HNO_3 , analytical purity grade) were supplied by Lab-Scan analytical sciences (BKK, Thailand). Hydrofluoric acid was purchased from Sigma-Aldrich (BKK, Thailand).

3.2 Experimental Procedures

3.2.1 Determination of Specific Surface Area

For studied particulate soils, carbon black was degassed at 150°C overnight, ferric oxide and kaolinite were degassed at 200°C overnight. For studied fabrics, pure cotton and pure polyester cut into a very small pieces weighting 1 g were degassed at 100°C overnight. Their specific surface areas were determined by nitrogen adsorption BET measurement using a surface area analyzer (Quanta Chrome, Autosorb-1)

3.2.2 Point of Zero Charge (PZC) Measurement

The samples were added into deionized water having different solution pH. The solution pH was adjusted by using a 1 M HCl or 1 M NaOH solution. The solution was then stirred at 30°C for 24 h. After that, the initial and the final pH value of this solution were measured with the pH meter (Ultra basic DENVER Instrument). PZC could be found from the plot between final pH in y-axis and initial pH in x-axis, the pH that no change in the initial and final pH was reported as the PZC of those samples.

3.2.3 Zeta Potential Measurement

Each of studied solid samples was added into a surfactant solution having different pH values, and then the mixture was stirred at 30°C for 24 hours. After that the solution was transferred to an electrophoretic cell of a zeta meter (Zeta Meter 3.0+ unit) equipped with a microscope module. After applying a suitable voltage, the charged particles move towards to the electrode until attaining a steady state (the particles move with a constant velocity). The velocity was then measured and referred as its electrophoretic mobility, which automatically calculates the zeta potential in millivolt unit by using the Helmholtz-Smoluchowski equation. For a given data set, at least 20 particles were monitored and the average zeta potential value was reported.

3.2.4 Adsorption Isotherm Experiments

The surfactant adsorption isotherm experiments were carried out in order to find the amount of surfactant adsorbed on the solid surface and on fiber as a function of surfactant concentration and pH solution. A surfactant stock solution was diluted with distilled water to obtain various surfactant concentrations. The prepared surfactant solution with a known volume and a solid sample with a proper weight were mixed in a vial with a screw cap. The initial pH was adjusted at different values by adding a 1 M NaOH or a 1 M HCl solution. The filled vials were allowed to equilibrate at 30 °C for 4 days to achieve the steady state. After equilibrium, the supernatant was separated from the mixture by the centrifugation method at 12,000 rpm for 30 min. The supernatants were analyzed for bulk phase concentrations of surfactant by using a total organic carbon analyzer (TOC) (Shimadzu, TOC 5000). All experiments were conducted with three replicates at a constant temperature of 30°C and the averaged data were used to calculate the amount of surfactant adsorbed by the concentration difference method.

3.2.5 Dispersion Stability Measurement

The dispersion stability of the studied particulates in the presence and absence of any studied surfactant was investigated using a UV-VIS spectrophotometer (Shimadzu, UV-1800). The light wavelength was found to insignificantly affect the light absorbance for the two particulates and surfactants. Thus, in this present study, the wavelength was fixed at 500 nm (visible light region). The series of dispersed particle systems were prepared at a particulate concentration of 0.2 %w/v in the presence and absence of studied surfactants with the pH range of 5-11. The solution pH was adjusted by adding either a 1 M NaOH or a 1 M HCl solution. After being well mixed, the prepared solution was transferred to a cuvette of the spectrophotometer and the particulate-free solution for each system was transferred to the other cuvette as a blank. Then the absorbance (at the position of $\frac{3}{4}$ from the top or $\frac{1}{4}$ of the way from the bottom of the cuvette) was measured as a function of time at room temperature. A high absorbance indicates high dispersion stability, whereas a low absorbance indicates low dispersion stability or a high degree of coagulation.

3.2.6 Contact Angle Measurement

The contact angle measurement was carried out using the sessile drop technique by a contact angle measuring instrument (Krüss, DSA 10 Mk2). The carbon black powder or fabric was first compressed into a smooth sheet. The fabric samples were cut in 0.5 cm × 0.5 cm and put into 22 mm diameter circular molding then compressed at 140 kg/cm² and 270 °C for 5 min by using a compression molding unit (LAB Tech, LP20) to obtain a fused fabric. After that, the fused fabric surface was cleaned by deionized water and then dried at 80 °C for 30 min in an oven. A 5 µL drop of the surfactant solution, which contained different surfactant concentrations, was then placed onto the fused sheet by using a micro-syringe and the contact angle was measured after 20 s. During the measurement, the sample chamber was kept at 30 °C and saturated with water vapor to prevent drop evaporation.

3.2.7 Surface Tension Measurement

The surface tensions of studied surfactant solutions containing different surfactant concentrations were conducted by using a bubble pressure tensiometer (Krüss, BP2). The rate of bubble generation was varied during measurement of the bubble pressure to ensure that this rate was low enough for attainment of equilibrium. The maximum value of the bubble pressure obtained from the plot of the bubble pressure vs. time was used to calculate the equilibrium surface tension.

3.2.8 Detergency Experiments

3.2.8.1 *Fabric Preparation*

The test fabrics; pure cotton and pure polyester were pre-washed with distilled water before use to eliminate residues of mill finishing agents and then dried at room temperature for a day. The pre-washing method followed the ASTM standard guide D4265-98 (Annual Book of ASTM Standards, 2000). Finally, the pre-washed fabrics were cut in the warp and weft directions.

3.2.8.2 *Soiling Procedure*

An amount of 0.02 g of carbon black was added into 80 g of distilled water and mixed by using a magnetic stirrer before pouring on the test fabric specimen which was placed in a plastic container and kept in a shaker bath for 1 h. A

0.2 g/L ferric oxide liquid dispersion was prepared by ultrasonic treatment for 30 min while a 5 g/L kaolinite one was dispersed by using a Terg-O-Tometer (Copley Scientific, DIS 8000) for 30 min with an agitation speed of 120 rpm. Twenty pieces of the prewashed fabric were added to either prepared ferric oxide or kaolinite solution. Soiling time for both systems was 20 min in the Terg-O-Tometer at a constant temperature of 30°C with an agitation speed of 120 rpm. After that, the soiled fabric swatches were dried at room temperature for 1 d. The dried soiled fabric samples were kept in a desiccator until use.

3.2.8.3 Laundry Procedure

The Laundry experiments were carried out in the Terg-O-Tometer, which is a standard testing unit for detergency. The experiments were conducted in a 1000 mL washing solution having different surfactant types and concentrations and solution pHs. The testing conditions were 20 min washing, 3 min first rinse and 2 min second rinse with de-ionized water and an agitation speed of 120 rpm. Temperatures of both washing solution and rinsing water were held at 30 °C. Three soiled swatches were washed in each bucket in one cycle as replication, and one unsoiled swatch was used for redeposition testing.

3.2.8.4 Determination of Detergency Efficiency

The detergency performance of carbon black and ferric oxide was determined by the refraction method. The reflectance measurement was conducted using a calorimetric spectrophotometer (Hunter Lab, Color Flex). The color change of pre-washed and post-washed swatches was quantified by the lightness parameter (L^*), which was reported in the range of 0 (completely black) to 100 (completely white). The calorimeter was calibrated against standard black and white plates before each actual measurement with at a minimum of 3 different positions for each sample. The detergency performance was quantified in terms of the percentage of detergency (%D) by using the following equation:

$$\%D = \text{Detergency (\%)} = [(A-B)/(C_0-B)] \times 100$$

where A is the average reflectance of the soiled swatches after washing, B is the average reflectance of the soiled swatches before washing and C_0 is the average reflectance of the unsoiled swatches before washing.

For kaolinite, the detergency performance was accessed by using the quantitative analysis. The pre and post-washed swatches were digested with a concentrated hydrofluoric acid. After the digestion step, the obtained filtrates were diluted with deionized water. The concentrations of silicon (Si) were analyzed by using atomic absorption spectroscopy (Varian, SpectrAA300) at a wavelength of 251.6 nm. The differences in the amounts of the studied particulates on pre and post-washed swatches were used to calculate the detergency performance and redeposition. The detergency efficiency was calculated from the set of three washed swatches as replicates and the results were reported as a mean value with the standard deviation; i.e., the square root of the variance.

3.2.9 Surface Morphology Examination

The study of surface morphology of the fabric samples before and after washing at different studied conditions was investigated by using a scanning electron microscope, SEM (JEOL, 5200-2AE). The samples were coated by a thin film of platinum for 2 min prior to examination.