Improvement of the Water Absorbency of Softener-treated Fabric: Addition of a New Hydrophilic Surface

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Abstract: Softening agents, when applied in appropriate amounts, can impart softness to fabrics, particularly cotton towels, such that improved comfort and feel can be achieved when using the fabrics. On the other hand, water absorbency, which is commonly regarded as the mark of high-quality cotton products, significantly decreases when any of the currently existing softeners is used. To date, when a softener is used on cotton fabrics, there is a trade-off between excellent softness and high-water absorbency. In our research, we introduced a new sensory evaluation indicator called the “water wiping-off feeling ratio” which looks primitive but shows high correlation with our actual feel over any other existing indicators. Furthermore, we developed a new method and model to overcome the above-mentioned trade-off, involving the use of small particles with a hydrophilic surface together with the softener. Inspired by the theory of fractal geometry and the combination of models/eqations by Cassie, Baxter, and Wenzel, the idea of adding new convex hydrophilic domains onto the surface of cotton fibers along with the softening agent was conceived. Finally, we successfully improved the wiping-off feel without decreasing the softness, i.e., we developed a strategy to overcome the above-mentioned trade-off in softener-treated fabrics that has proven challenging thus far.

Key words: softener, water absorbency, Cassie–Baxter equation, convex domain

1 Introduction

It is well known that softener can easily impart softness to fabrics, such as cotton towels, causing them to have discernible comfortable or pleasant feel. In our previous reports [1, 2], we proposed a new theory regarding the softening mechanism of softeners: the softening phenomenon of cotton is caused by the inhibition of the formation of cross-linkages between fibers by the non-freezing-type bound water of the softener via hydrogen bonding; as such, gradation occurs, where the fibers located in the outer surface of the yarn are more affected by the softener molecules than those in the inner part. Through this mechanism, a softener can certainly impart excellent softness. However, the water absorbency of cotton fabrics, which is generally higher than those of other fabrics, decreases when a softener is used [3]. The current softening agents in the global market have a particular chemical structure, including two long hydrophobic alkyl chains. Therefore, the surfaces of softener-treated yarns and cloth easily become hydrophobic, in which case water cannot quickly be absorbed between the fibers. This is why the water absorbency of cotton fabrics reduces in a short time frame, e.g., during wiping-off, when a softener is used. A decrease in the water absorbency of softener-treated towels causes skin irritation because small droplets remain on the surface of the cloth even after wiping; this results in a never-ending incomplete wiping feel or a tactual cold feel when wiping water off the body after bathing [11]. This "tack phenomenon" is caused by liquid bridging or the formation of a water layer between the softener-treated towel and human skin. In addition, cotton fluffs cling to the skin in this situation, adding to the frustration.

Since softeners were introduced to the US in 1955, di-octadecyl dimethyl ammonium chloride (DODAC) has been widely used as a softening agent. The problems associated with this material, including low water absorbency of treated fabrics and environmental safety issues such as low biodegradability, have been debated as social issues. To overcome these problems, various new softening agents have been developed. In particular, around 1980 in the
Japanese market, the low water-absorbency problem was widely discussed among consumers. In Japan, it is usual to use a towel after taking a bath. This is contrary to the case in western countries where people wear bathrobes after bathing to absorb the water over a relatively long time. Many Japanese people use a small towel to remove the water by “wiping” it off. The Japanese word used to refer to the towel is “Tenugui,” which refers to a cotton cloth for rubbing and wiping, which was replaced with “towel” under the influence of the European culture. During this relatively rapid rubbing motion, Japanese consumers feel significant difference in the rates of water absorption between an ordinary cotton towel and a softener-treated one. In other words, the Japanese are habitually more sensitive about the water-wiping efficacy of towels than people of other cultures.

Through these trials, new softening agents with improved water absorbency have been proposed. One of them is dioleyl dimethyl ammonium chloride (DOE), which is a cationic surfactant with long unsaturated alkyl chains\(^{12,13}\). Ohbu\(^4\) reported that DOE not only effectively improved the water absorbency of fabrics but also had high moisture-evaporation characteristics.

An ion-complex softener consists of a cationic surfactant and an anionic surfactant with a branched alkyl chain. This type of softeners has been shown to effectively improve the water absorbency of fabrics\(^5-18\). Imidazole-salt softeners, which are synthesized from low-cost materials such as fatty acids and diethylenetriamine, are also well known\(^19\) because they result in a soft feel but still with some decrease of the water absorbency. The improvement in the water absorbency by these softening agents is explained by the mobility of the softener agent molecules on/in the fabrics after drying.

Yamamura\(^20-22\) reported that the flexibility of the alkyl groups of DODAC with different alkyl chains (C12, C14, C18) dramatically changes the molecular mobility over the gel transition temperature (Tc), which results in increased water absorbency and improved wettability. Ohbu and Tanaka\(^4\) also proposed an interpretation based on the concept of molecular mobility, that DOE can build lamellar liquid-crystal structures at room temperature. An ion-complex softener has also been shown to have better water-flow dynamics based on the same reasoning\(^23\).

However, when we evaluated the performance of these softeners according to the “feel,” i.e., the ease of wiping water off the surface of the skin with a cotton towel, the water absorbency still reduced with increasing softener concentration as was expected\(^4\). Interestingly however, we were unable to find studies on the correlation between the water absorbency values measured by the AATCC/ASTM Test method or JIS methods, which include the dropping method (AATCC/ASTM Test method TS-018; the water absorbency of textiles is determined by measuring the time it takes a drop of water placed on the fabric surface to be completely absorbed by the fabric), the Byreck method (JIS Test method JIS L1907; the water absorbency of textiles is determined by measuring the height with capillary force between the fibers), and the wipe-off feel on skin method.*

In general, there is an apparent gap between the water absorbency value measured by previous methods and the actual ease of wiping water off the surface of the skin with a cotton towel. These confusing results are well known in this research field\(^24\). These results indicate that the “wiping-off efficacy” is not a simple parameter and should be understood as a multivariate phenomenon composed of complex elements in the skin and the muscles. This explains the difficulty of measuring the water-wiping efficacy, particularly using a method that only measures the water absorbency. For these reasons, we introduced a new sensory evaluation system, which is primitive but close to the actual wiping-off behavior, and created a new technology to overcome the above-mentioned trade-off between high softness and high-water absorbency for softener-treated fabrics.

The core of this new technology is the combined use of the softener with very small particles having hydrophilic surfaces.

2 Experimental Section
2.1 Samples
2.1.1 Preparation methods for softener-treated towels
Cotton towels (TW-220, Takei Corporation, Japan) were pre-washed using a fully automatic washing machine. Twenty-four cotton towels and 52.22 g of nonionic detergents (Emulgen108, Kao Corp., Japan, 10% aqueous solution) were loaded into the washing machine (NA-F702P, Panasonic Corp., Japan) with 47 L of water. The samples were washed for 9 min (with water containing the aforementioned nonionic detergent), rinsed twice with water (tap water in Wakayama city), and spin-dried for 3 min. This step was repeated three times. Thereafter, the

*As researchers for softening-agent manufacturers, we aim to improve the products by properly correlating the sensory evaluation of consumers. To achieve this, a suitable method is required; however, all the existing methods we tested failed. It is known that the cutaneous receptors in the human skin, including the Ruffini’s ending, Meissner’s corpuscles, Merkel cell, and Pacinian corpuscles, play a role in the sensory evaluation; in addition, the “wiping motion” had to be considered.

Considering the multivariate nature of human sensation, it was difficult to find a simple mechanical measurement method. This explains why softening-agent formulators still obtain sensory evaluations for products from employed well-trained panelists.
samples were washed for 9 min (with water only), rinsed twice with water, and spin-dried for 3 min. This step was repeated twice.

Ester amide (2-[N-[3-alkanoyl(C16-18) amino propyl]-N-methylamino] ethylalkanoate, hydrochloride (EA), Kao Corporation, Japan), hereinafter referred to as EA\(^{20}\), was used as a softener without further purification. EA is a tertiary ammonium salt and a highly biodegradable type of softener manufactured by Kao Corporation. In general, tertiary ammonium salts are considered to exhibit lower performance than quaternary ammonium salts. However, for EA, the amide functional group introduced into the molecular structure results in a higher softness than DODAC\(^{20}\). The softener treatment concentrations were set to 0, 0.05, and 0.1 o.w.f. (abbr: on the weight of fabric) each. The standard concentration in this field is 0.1% o.w.f.

The cationic linear polymer used was a cationic starch (Kanta-ta MX-2075, Kao Corporation, Japan), with a viscosity of 130–470 mPa\(\cdot\)s in a 3% water solution at 30°C, and poly-dimethylamino ethyl methacrylate (PQDM, KP Polymer, Kao Corporation, Japan), with a viscosity of 1600–3700 mPa\(\cdot\)s in a 10% solution at 25°C. The treatment concentrations of the cationic polymer samples ranged from 0.1 to 1.0% o.w.f., with 0.1% o.w.f. of the softener (EA).

The small hydrophilic particles, which were synthesized by the method described below, were also used. The treatment concentrations of these particles ranged from 0.1 to 1.0% o.w.f., with 0.1% o.w.f. of the softener (EA).

2.1.2 Synthesis of small hydrophilic particles

Hydrophilic particles\(^{25}\) were synthesized via emulsification polymerization. Ion-exchange water (325 g), 7.4 g of cationic starch (synthesized from cornstarch and 3-N,N,N-trimethylammonium chloride-1,2-propylenoxide) (Wako Pure Chemical Industries Ltd, Japan), 1.2 g of polyvinyl alcohol (Gohsenol GL-05, Nippon Gohsei, Japan), 5.5 g of a 20 wt.% aqueous solution of polyoxyethylene dodecyl ether (Emulgen 150, the number of ethylene oxides per molecule is 50, Kao Corp, Japan), and 10.0 g of a 3.7 wt.% sodium phosphate buffer solution (Wako Pure Chemical Industries Ltd, Japan) were added to a 1 L separable flask equipped with a stirrer, thermometer, reflux condenser, and nitrogen introduction pipe. The atmosphere was replaced by N\(_2\) gas for 20 min, following which the temperature was increased to 60°C and the solution was stirred for 1 h. Subsequently, 2.82 g of vinyl acetate (Wako Pure Chemical Industries Ltd, Japan) and 0.25 g of V-50 azo-initiator (Wako Pure Chemical Industries Ltd, Japan), dissolved in 8.0 g of ion-exchange water, were added, and the temperature was increased to 75°C. Following this step, 17.1 g of vinyl acetate (Wako Pure Chemical Industries Ltd, Japan), 0.18 g of methacrylic acid (Wako Pure Chemical Industries Ltd, Japan), and 0.034 g of V-50 azo-initiator (Wako Pure Chemical Industries Ltd, Japan) dissolved in 12.0 g of ion-exchange water were added dropwise into the separable flask for 1 h. The mixture was stirred for 6 h for the polymerization reaction to occur. After this treatment, the emulsion was cooled to room temperature (around 20°C) and filtered with a nylon mesh (255 mesh).

2.1.3 Measurement of the particle diameter

The above-mentioned emulsion was diluted to 0.3% by weight with ion-exchange water. The particle diameter was measured using a dynamic light scattering measurement instrument (Zeta-Sizer Nano, Malvern Corporation, England). The measured diameter of the particles was 140 nm.

2.2 Evaluation

Since no adequate machine-based method was found to measure the water-wiping efficacy or softness, we devised a primitive manual method, which was most correlative to skin sensation or feel.

2.2.1 Number of wiping actions

Cotton towels treated with the EA softener were placed on hangers and used by trained 5 panelists to wipe the water off their hands (pressure was from 5 to 10 g/cm\(^2\), velocity was 0.2-0.3 sec/20 cm). The number of repeated motions was counted visually until the panelist was satisfied (eight panelists participated in the experiment; n = 8). The treatment concentrations of EA were 0, 0.1, or 0.3% o.w.f.

2.2.2 Residual water on the skin after wiping

Here, 300 mL of ion-exchange water was poured on the entire right arm of 5 female trained panelists. The water was wiped off with a cotton towel treated with a softener of various concentrations under constant loading conditions (1.0 g/cm\(^2\)). The loading condition was standardized by training manually. After this activity, the residual water on the skin was collected using filtering paper, and the water content was measured. The following equation was used to calculate the residual water on the skin: residual water on the skin (wt.%) = \(100 \times \frac{(water\ weight\ in\ towel + water\ weight\ in\ filter\ paper)}{(water\ weight\ in\ filter\ paper)}\). The experimental temperature ranged from 18 to 25°C, and the humidity ranged from 40 to 60% RH.

2.2.3 Wiping-off efficacy

We prepared standard towels using different concentrations of an EA-based softener (product name is Humming, Kao Corporation, Japan). An untreated towel and a 0.1% o.w.f. softener-treated towel were used as standard towels, with sensory scores of 5 and 1, respectively. Scores ranging from 1 to 5 were allotted by the panelists. The sensory evaluation of the wiping-off efficacy was conducted using this 5-level scoring system by comparing the test sample towel with the standard towels (n = 5).

2.2.4 Softness level

Standard towels were prepared using different concen-

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trations of an EA-based softener (product name is Humming, Kao Corporation, Japan). An untreated towel and the towels treated with 0.025, 0.05, 0.075, 0.1, and 0.125% o.w.f. softener concentrations were used as standard towels, with sensory scores ranging from 1 to 6, respectively. The evaluation of the softness was conducted by comparing the six different levels of standard towels (five panelists; n = 5).

2.3 Determination of the adsorption amount of softener and particles

2.3.1 Adsorption of softener on towels

Softening experiments were performed using cotton towels (TW220, Takei Corp., Japan). Before the experiment, the towels were pre-washed using a fully automatic washing machine. Here, 24 cotton towels and 52.22 g of a nonionic detergent (Emulgen, Kao Corporation, Japan) in a 10% aqueous solution were loaded into the washing machine (NA-F702P, Panasonic Corp., Japan) with 42 L of water and pre-washed as follows. The samples were washed for 9 min (with water containing the aforementioned nonionic detergent), rinsed twice with water, and spin-dried for 3 min. This step was repeated three times. Thereafter, the samples were washed for 9 min (with water only), rinsed twice with water, and spin-dried for 3 min. These “pre-washing” steps were repeated twice.

Subsequently, the samples were treated with the softener. Two pre-washed cotton towels were treated with an aqueous solution containing the softening agent in a small washing machine (MiniMini Washer NA-35, Panasonic Corporation, Japan). The bath ratio (ratio of the water weight to the cloth weight) was set to 30, and tap water from Wakayama city, Japan, at 25°C, was used for the process. The softening agent was first dispersed in water, following which the two towels were added while stirring for 5 min. After the softener treatment, 10 mL of water containing the residue of softener from the bath was taken and diluted with a little amount of ethanol (EtOH). This was used as the sample for liquid chromatography-mass spectrometry measurement to determine how much of the softener is left in the residual water, i.e., the amount of softener adsorbed by the towel. The standard solution used for the standard calibration curve was an EA-based softener (Humming, Kao Corporation, Japan; 16.8 wt.% of EA). It was diluted with EtOH, and the resulting solutions, with concentrations of 0.01, 0.05, 0.1, 0.5, and 1.0 μg/mL of EA, were used to plot the standard calibration curve.

High-performance liquid chromatography-mass spectrometry (HPLC-MS) was used to measure the amount of the softening agent adsorbed onto the towels. The equipment used for this study were a HPLC-MS instrument (UPLC Aquity, Waters, USA) and an MS instrument (Quattro Micro API, Waters, USA) with electrospray ionization (ESI) in the positive mode. The ionization conditions for the electro-spraying process were optimized by an automatic calibration system. The analytical column, Imtakt Unison C18-HT (diameter 2 mm × 50 mm, 3 μm, Imtakt, Japan), was operated at 40°C.

A 10 mM aqueous acetic ammonium solution was used as mobile phase A, and a 10 mM acetic ammonium MeOH solution was used as mobile phase B. The gradient condition was set from 50 to 100% of B over 2 min and maintained for 6 min at a flow rate of 0.5 mL/min. For selected ion-monitoring measurements, the protonated molecular ions [M + H+] were used with m/z values of 371.3, 399.3, and 609.5 for ester amide.

The adsorption ratio of EA to cotton cloth was calculated using the following equation: adsorption ratio of softener (%) = 100 × (EA concentration before treatment − EA concentration after treatment)/(EA concentration before treatment).

2.3.2 Adsorption of hydrophilic particles on the towel

Two towels (140 g) and 4200 mL of tap water were put into a washing machine (NA-F702P, Panasonic Corp., Japan) and stirred for 5 min while adding 0.98 mL of an EA-based softener (Humming, Kao Corporation, Japan; EA active component rate is 16.8 wt.%). Predetermined amounts of the hydrophilic particle dispersion were added. After the treatment and removal of towels, 1 L of the residual water was evaporated completely. The dried residue was dissolved in 1 mL of deuterated trichloromethane (CDCl3) and used as the sample to measure the residual hydrophilic particles, which were not adsorbed by the cotton fabric. This method was also applied to the untreated towels.

Proton nuclear magnetic resonance (1H-NMR) was used to measure the amount of particles adsorbed by the cotton fabric. A 1H-NMR instrument (Agilent Technologies) operating at 400 MHz was used. The number of integrations was set to 32. The amount of particles adsorbed was calculated using the integrated intensity around 2 ppm, which is attributed to methylene (-CH2-) derived from the polymer. The following relation is used: adsorption rate of particles (%) = 100 − [100 × (integrated intensity after treatment)/ integrated intensity before treatment].

2.4 Measurement of contact angles

Hereinafter, all the contact angles were measured using ion-exchange water as the liquid.

2.4.1 Measurement methods

We used the sessile drop standard arrangement for contact measurement. A drop lying on the solid surface forms a characteristic contact angle with the surface at the three-phase contact point. We calculated the contact angle using a half-angle method. In this measurement, we used ion-exchange water as the experimental liquid, and the purity was not determined.
2.4.2 Contact angle of the softener layer
Two mica plates with a size of 5 cm × 1 cm were treated with 2.5 mL of a 33-ppm dispersion of EA and water, and 2.5 mL of a mixture of a 33-ppm EA solution and small hydrophilic particles; thereafter, they were dried naturally overnight. The contact angles were measured using a DropMaster-500 instrument (Kyowa Kaimen Kagaku, Japan).

2.4.3 Contact angle of a hydrophilic polymer (cationic starch)
First, the surface tension of the cationic starch powder was determined using a wetting indicator (Wetting tension testing mixtures: JIS_K6768. ISO8296 Wako Pure Chemical Ltd, Japan). The contact angle of the cationic starch powder was calculated using the Fowkes and Young equations.

2.4.4 Contact angle of a single cotton fiber
To directly measure the contact angle of a single cotton fiber, a water droplet was dropped onto the fiber. The measurement instrument: DM-700, made by Kyowa Kaimen Kagaku, Japan, was used. The contact angle was immediately measured before the droplet lost its volume by evaporation and adsorption onto the fiber.

3 Results and Discussion
3.1 Water-wiping efficacy
Here, we compare the water absorbency of cotton cloths with and without the softener. For the untreated towel, the water spread immediately on the surface and inside the cloth. For the softener-treated cotton, the diffusion rate of water was low, and the water droplets remained as a bulge for some time. Thus, the amount of residual water in the untreated towel was calculated to be 7.5% (average value). When the softener concentrations were set to 0.1% o.w.f. and 0.3% o.w.f., the amounts of residual water were 21.2% and 36.4%, respectively. These results show that it was difficult to wipe water off the skin using softener-treated towels (Fig. 1).

In addition, the panelists performed a relatively high number of complex and labor-intensive bodily movements during the wiping-off process when using the softener-treated towels (Fig. 2). This indicates that there were more hand movements during the wiping activity. Since there was some residual water on the skin, the panelists considered the wiping process less effective, which increased the psychological and physical burden on them. Thus, the complex and dynamic wiping efficacy could not have been measured by any simple methods, such as the Byreck method, water-droplet method (JIS L 1907), or sedimentation method. In this study, we defined the efficacy of removing water from the surface of the skin as the "wiping efficacy," which is a very primitive concept that we evalu-
lated with a 5-level sensory method (Figs. 3 and 4). The relationship between the "wiping efficacy" and the softener concentrations was evaluated using this new functional axis. We can, thus, conclude with certainty that the wiping efficacy decreased when the EA softener concentration increased. A score of 1 was allotted for a softener concentration of 0.075% o.w.f.

When we used a DOE softener (product name is Touch, Kao Corporation, Japan) and an ion-complex softener (product name is Humming, Kao Corporation, Japan), a higher wiping efficacy than that of the EA softener was found. However, this efficacy decreased with increasing softener concentration. Consequently, it was confirmed difficult to have both a completely dry feel, close to that felt using non-treated cotton towels, and excellent softness.

3.2 Softener system for high wiping efficacy and high softening effect

3.2.1 Control factors of water absorbency

A cloth has hierarchical high-order structures, e.g., single fibers form yarns, which form a cloth (Fig. 5). When water comes in contact with the surface of a cloth, a capillary force maintains it not only in the cotton lumen or its amorphous moiety but also in the gaps of the various hierarchical structures. To increase the wiping efficacy, we attempt to facilitate the rapid movement of the water from the surface to the inside of the cotton cloth (similar to the case with a non-treated cotton cloth). Based on microscopic observations of the various types of gap sizes in the towels, the average gap results were determined: ca. 60 μm between yarns, ca. 10 μm between yarns, and ca. 20 nm between single fibers. Based on the Lucas–Washburn equation (Equation (1)), the amount of water flow when the physical properties of water are unchanged (γ, η) can be calculated as follows:

\[ l = \frac{\sqrt{\frac{R \cos \theta}{2 \eta}} \cdot t \cos \theta - \frac{1}{2}} {t \cos \theta - 1}, \]

Here, \( l \) is the amount of water flow, \( \gamma \) is the surface tension of water, \( R \) is the radius of the flow path based on the structure of the cloth, \( \theta \) is the contact angle of the cotton surface, \( \eta \) is the viscosity of water, and \( t \) is the time; the only controllable parameters are \( R \) and \( \theta \). However, \( R \) can only be regulated by textile manufacturing companies. Using this equation, since the gap between yarns is ca. 60 μm and that between single fibers is ca. 10 μm on average, the contribution of the lumen (200 nm) to \( l \), at the center of a single fiber, is very small so that it is negligible. Therefore, the only adjustable factor for improving the water absorbency is the contact angle (\( \theta \)) on the surface of a single cotton fiber. Actually, the water flow influenced by softening agents, which change the surface properties of the yarn and single fiber, particularly around the surface. Unfortunately, this is unfavorable as it reduces the water absorbency.

3.2.2 Softener chemical structure

Fig. 3  Softener chemical structure.

Fig. 4  Relationship between softener concentration and efficacy.

Fig. 5  Gap size of different hierarchical structures of cotton cloth: single fibers, yarns, and cloth.
3.2.2 Introduction of hydrophilic domains on a softener-treated surface

To improve the hydrophilicity of a softener-treated cotton surface, we applied a hydrophilic low-molecular-weight compound at first. However, this kind of material is easily dissolved in water and does not remain on the surface of the cotton during the laundry process. Subsequently, we tested the hydrophilic cationic linear polymer that exhibits polydentate-type multipoint adsorption on the negatively charged cotton fiber surface. In this case, we intended to construct “hydrophilic domains” on the hydrophobic softener-treated cotton fiber/yarn surfaces, which would mean that these materials are co-adsorbed with the softener on the surface of the cotton. Thereafter, we tested 0.1% o.w.f. of cationic starch and poly-dimethyl aminoethyl methacrylate (PQDM) with the EA-based fabric softener. In all cases, we could not achieve any meaningful improvement of the water-wiping efficacy. This result indicated that the simple control of the contact angle by introducing hydrophilic regions among the hydrophobic softener regions on the cotton yarn/fabric surface is not effective, and it also indicated that we have to create another new model to overcome this challenge.

3.2.3 Co-introduction of rough hydrophilic domains on a softener layer

Therefore, our focus was on how to introduce a new “additional” and effective hydrophilic surface on a hydrophobic softener-treated cotton surface. The Wenzel equation (Equation (2)) is used to calculate the contact angle between a rough surface and a liquid:

\[ \cos \theta_B = a \cdot \frac{(\gamma_s - \gamma_d)}{\gamma} = a \cdot \cos \theta_w, \]  

Equation (2)

Here, \( \theta_w \) is the contact angle on a rough surface; \( \theta_B \) is the contact angle on a flat surface; \( a \) is the ratio of the actual surface area to the calculated surface area (that is, the “roughness factor of Wenzel”); and \( \gamma_s, \gamma_d, \) and \( \gamma \) are the solid-solid, solid-liquid, and liquid-liquid surface tension values, respectively.

According to the theory of Wenzel, fine concave and convex structures on the surface can enhance the original contact angle. This means that the introduction of convex structures on a hydrophobic surface (those having a contact angle over 90°) would lower the surface energy, thereby increasing the contact angle. In this regard, the lotus leaf is a good example. The numerous fine convex structures on the lotus leaf surface bring about a drastic change in the contact angle, which results in a super-hydrophobic surface. The artificial surface constructed by alkyl ketene-dimer wax is also a good example.

This idea of fine roughness on the surface can be useful to effectively introduce hydrophilic domains on a softener-treated surface. A new model is introduced: the Cassie–Baxter–Onda equation (Equation (3)) that was derived by Onda as a modification of the “Cassie–Baxter equation” to facilitate the creation of a new approach (Fig. 6). The contact angle on a flat surface; \( a \) is the ratio of the actual surface area to the calculated surface area (that is, the “roughness factor of Wenzel”); and \( \gamma_s, \gamma_d, \gamma_l \) are the solid-solid, solid-liquid, and liquid-liquid surface tension values, respectively.

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The last term in the equation, \( n \cdot 4 \pi r^2 \cos \theta_2 \), corresponds to the newly added surface due to the introduction of convex hydrophilic particles (ref. Equations from 4 to 8). In this equation, since \( n \) is the number of small hydrophilic particles per unit area, the coefficient of the last term, \( n \cdot 4 \pi r^2 \), is also dimensionless similar to the other terms.

\[
\cos \theta = (1 - x) \cos \theta_1 + x \cos \theta_2 + n \cdot 4 \pi r^2 \cos \theta_2 \tag{3}
\]

where \( \cos \theta_1 \) is the contact angle of water on the fiber surface; \( \cos \theta_2 \), the contact angle of water in the hydrophilic softener layer; \( \cos \theta_3 \), the contact angle of water on the hydrophilic particle; \( x \), the cover ratio of the hydrophobic softener layer over the fiber surface \((0 \leq x \leq 1)\); and \( n \cdot 4 \pi r^2 \), the unitless surface area introduced by the small particles.

We applied both the EA softener and small hydrophilic particles (with a diameter of 140 nm) to the cotton fabric. The treatment concentrations of both products were set to 0.1% o.w.f. The adsorptions of these two materials were 94% and 91%, respectively (Fig. 7). This nano emulsion is insoluble material, so filtration system in washing machine could be highly expected. This implies that the materials were almost completely adsorbed on the surface of the cotton fabric.

When the water droplet was put on the surface of the cotton cloth treated by the two components above, the diffusion rate and absorbency of water were apparently improved compared to the case with only softener. To confirm the reason for the change in wettability, the contact angles were measured on a mica surface. The contact angle was 85° for the softener-treated surface and 58° with the additional use of small hydrophilic particles (Fig. 8). The contact angle was not measured directly on the cotton fabric for two reasons: first, the roughness of cotton cloth was higher than the diameter of the water droplet used in the measurement tool; second, it was difficult to obtain an evenly adsorbed condition using small hydrophilic particles.

Furthermore, we measured the "efficacy." The weight of the residual water on the skin apparently decreased from 21 to 12.7 wt.% when small hydrophilic particles were used (Fig. 9). The efficacy was evaluated by changing the concentration of the particles. The efficacy improved with increasing concentration, reaching a value close to that of untreated cotton for a concentration of 0.15% o.w.f. (Fig. 10).

3.2.4 Change in wettability

In this experiment, we used small hydrophilic particles synthesized using the above-mentioned emulsification polymerization. The diameter of the particles was 140 nm. The particle surface was covered by cationic starch, resulting in a contact angle of 32°. We achieved both high efficacy and softening effect using the particles along with the softener. This level of compatibility is the highest we have achieved. Equation (3) describes this case. The derivation process for this equation is as follows. Young’s theory gives the contact angle on the surface of a softener-treated cotton as

\[
\cos \theta = \frac{\alpha_{\text{gw}} - \alpha_{\text{ls}}}{\alpha_{\text{sl}}} \tag{4}
\]

where \( \alpha_{\text{gw}} \) is the surface tension between water and air, \( \alpha_{\text{ls}} \) is the surface tension between air and the softener-treated cotton surface, and \( \alpha_{\text{sl}} \) is the surface tension between water and the softener-treated cotton surface. Equation (4) was derived by considering the balance of the three different forces (\( \alpha_{\text{gw}}, \alpha_{\text{ls}}, \) and \( \alpha_{\text{sl}} \)) at the contact point in Fig. 6.

In contrast, Cassie’s theory states that the interfacial tension on a complex surface composed of two different material surfaces is expressed as the average value of the different contact angles from the two components. This can be applied to the softener-treated surface in our study via Equations 5 and 6:
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\[ \alpha_{gs0} = (1 - x)\alpha_{gs0} + x\alpha_{gs1} \]  
\[ \alpha_{ls0} = (1 - x)\alpha_{ls0} + x\alpha_{ls1} \]

where \( \alpha_{gs0} \) is the surface tension between the cotton surface and air, \( \alpha_{ls0} \) is the surface tension between the cotton surface and water, \( \alpha_{gs1} \) is the surface tension between the surface of the softener-treated cotton and air, and \( \alpha_{ls1} \) is the surface tension between the surface of the softener-treated cotton and water. \( x \) is the ratio of the surface covered by the softener (0 \( \leq \) \( x \) \( \leq \) 1).

Here, we assume that the adsorption of the small hydrophilic particles is the point contact to the softener-treated surface. Therefore, along with the above equations, we can interpret the effective improvement of hydrophilicity with the addition of small hydrophilic particles to the softener as the combination of the Cassie model (for a complex surface) and the Wenzel model (introduction of additional surface area).

We can define the contact angle on the surface of a small hydrophilic particle as \( \theta_2 \), and \( n \), as the number of small hydrophilic particles per unit area having radius \( r \). The additional surface is expressed as \( n \cdot 4\pi r^2 \).

In this model, the surface tension between the small hydrophilic particle and air (\( \alpha_{gs2} \)) and the tensions between the small hydrophilic particle and water (\( \alpha_{ls2} \)) are expressed by Equations 7 and 8:

\[ \alpha_{gs} = (1 - x)\alpha_{gs0} + x\alpha_{gs1} + n \cdot 4\pi r^2 \alpha_{gs2} \]  
\[ \alpha_{ls} = (1 - x)\alpha_{ls0} + x\alpha_{ls1} + n \cdot 4\pi r^2 \alpha_{ls2} \]

Here, \( n \cdot 4\pi r^2 \) is dimensionless, and \( n \) is the number of small hydrophilic particles per unit area. The following equations are, thus, obtained (Equations 9 and 3):

\[ \cos \theta = (1 - x)\frac{\alpha_{gs0} - \alpha_{gs1}}{\alpha_{gs0}} + x \left( \frac{\alpha_{gs1} - \alpha_{gs0}}{\alpha_{gs0}} \right) + n \cdot 4\pi r^2 \left( \frac{\alpha_{gs2} - \alpha_{gs0}}{\alpha_{gs0}} \right) \]  
\[ = (1 - x)\cos \theta_0 + x \cos \theta_1 + n \cdot 4\pi r^2 \cos \theta_2 \]

From Equation (3), two important points can be deduced. First, the hydrophilicity of the cotton cloth decreases when it is partially covered by the hydrophobic softener layer; the hydrophilicity can be improved using small hydrophilic particles. Second, the expected increase in hydrophilicity is high when the contact angle \( \theta_2 \) is little and the total surface area of the particles is large. Thus, we can understand why the efficacy is relatively high when small hydrophilic particles are used. It is simply because an "additional large hydrophilic surface (in total)" was introduced onto the cotton surface covered by the hydrophobic softener.

3.3 Softness level

In addition to the wiping efficacy, the softness level was also determined to be high enough as shown in Fig. 11. These results are favorable because we have long been attempting to develop a technology that enables us to make the high softening effect and the high water-wiping efficacy compatible. Currently, we do not fully understand why these two parameters are determined simultaneously. Through our investigation, however, we recognized that one of the characteristics related to the towel treatment condition was volume; towels treated with both softener and hydrophilic particles had a higher volume than other towels. Now we hypothesize that the simultaneous use of a softener and small hydrophilic particles changes the meniscus status during the drying process, which might inhibit the construction of a bound-water-mediated network between fibers via hydrogen bonding to a considerable extent. This may cause a decrease in the hardness/stiffness of the cotton towel without affecting the efficacy.
Conclusions and Perspectives

In summary, we found that using small hydrophilic particles with a softener to treat cotton fabrics results in improved efficacy and softness. The current softeners available in the market generally induce a trade-off between these two properties. Based on the evaluation results, it is evident that our proposed method is new and effective for overcoming this trade-off.

We developed a method to simultaneously achieve both a high softening effect and high efficacy for softener-treated cotton fabrics. The key concept of this technology is expressed in Equation (3): the addition of a new large hydrophilic surface via the introduction of small hydrophilic particles onto a cotton surface previously or simultaneously covered by a hydrophobic softening-agent layer. In this study, the hydrophilic particle used was obtained by the co-polymerization of vinyl acetate by cationic starch with an averaged diameter of 140 nm.

The core of our idea, however, is "the introduction of a hydrophilic convex surface" as shown in the Cassie–Baxter–Onda equation (Equation (3)). Therefore, the same effect is expected in principle even if the inner structure of the particle is composed of other materials, such as organic or inorganic materials. From our SEM observation of the adhesion conditions of small hydrophilic particles on the surface of a cotton fiber, we found that the hydrophilic particle used in this study did not maintain its original round shape (Fig. 7). This change was possibly caused by the low glass-transition temperature of the core polymer (polyvinyl acetate) or by its plasticization by water. A harder and hydrophobic core polymer, i.e., one with a relatively high glass-transition temperature, firmly encapsulated by a highly hydrophilic polymer, may result in high efficacy under a low treatment condition. Furthermore, if the radius ($r$) of the particle can be changed, Equation (3) can be transformed into Equation (10):

$$\cos \theta = (1 - x) \cos \theta_0 + x \cos \theta_1 + \frac{3V}{T} \cdot \cos \theta_2$$

where $r$ is the radius of the small particle, and $V$ is the total volume of the particles used: $V = n \cdot (4/3) \pi r^3$.

From this equation, we can deduce that the wettability of a softener-treated surface can be improved by changing only the diameter ($2r$) of the particle such as using small particles, even if the total volume of the particle is the same. It should be noted that in this case, the hydrophilic surface also increases. In a subsequent paper, we will report the results of the research on this phenomenon.

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Conflict of Interest

We don’t have any conflict.

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