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Note

Study of properties of modified silicones at solid–liquid interface: Fabric–silicone interactions

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Abstract

Silicones are special reagents that impart desired surface properties such as softness, bounciness and antiwrinkle properties to fabrics and related materials. Although these finishing processes have been practiced routinely, very little is known about the mechanisms involved in modification so that they could be improved. The current study was undertaken to develop basic understanding of the mechanisms responsible for surface modification of fibers using silicones. PDMS based amino silicone emulsions, quaternized to various degrees using dimethyl sulphate, were used in the present study. The electrokinetic properties of the modified silicones were studied as a function of pH. It was expected that the silicone emulsions would show a steady positive zeta potential throughout the pH range due to the quaternization by dimethyl sulphate. Surprisingly, a sudden drop in the zeta potential was observed around pH 8 with the samples turning hazy in the pH range of 8–10. Turbidimetric studies also showed a sudden increase in the turbidity in the pH range 8–10 where commercial processes also encounter problems. It was concluded that the emulsions were destabilized at pH 8–10 thus rendering them ineffective for surface treatment. In order to identify reason for the improvement in fabric properties, fiber structure was monitored using atomic force microscopy. It was observed that the treated fibers were far smoother, relaxed and uniform as compared to the untreated fibers. Thus the morphology of the fabric is modified in a specific way by treatment with specialty silicones.

Keywords: Silicone emulsions; Fabric finishing; Zeta potential; AFM

1. Introduction

Fabrics and other such materials undergo finishing operations with surface active materials to impart desired surface properties [1]. In the case of textiles, such modification is accomplished through either the padding or the exhaust process. In both of these processes finishing compounds are transferred from aqueous solution phase to the fabric surface and then cured through the application of heat, leading to the desired surface finish. While the finishing compounds are transferred to the fabric through the physical entrapment in the padding process, the actual exhaustion of the compound from the solution phase on to the fabric is accomplished through specific adsorption in the exhaust process. The exhaust process is more difficult to control, as it requires much stringent control of the surface/solution interfacial conditions as well as structure and purity of surface active agents. Silicones have been used as premium finishing agents as they offer durable, longer lasting, surface modifications to the fabric [2,3]. Surface and bulk characteristics of fabrics such as softness (surface or inner), bounciness, tear strength, dry feel, wet feel, hydrophobicity, hydrophilicity and several other fabric properties can be enhanced significantly by modifying silicones for desired transport and interfacial properties.

Although the process of fabric treatments have been practiced worldwide for decades, the actual mechanisms are complex and are not well understood. Most of the studies have looked from the system viewpoint, emphasizing dyeing, enzyme treatment, and process equipment. However, surface

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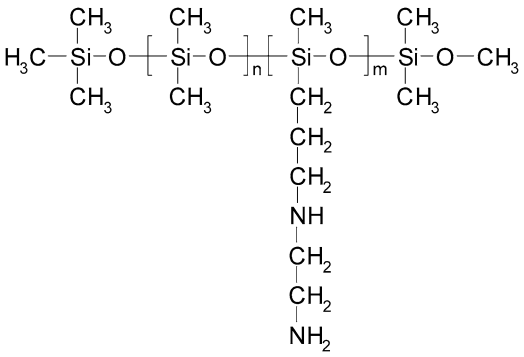


Fig. 1. Basic structure of diamino silicone used for emulsion formulation.

chemical viewpoint, which could give valuable insight into how the surface properties of fabric are altered to give softness, wrinkle-freeness and bounciness, has usually been ignored. Also most of the reported work is in patent form and very few studies have been published in research journals [4–7].

PDMS (polydimethyl siloxane) is the most widely used silicone based surface active agent [8] that represents the most basic structure consisting of siloxane segment repeat units varying in numbers from 100 (<50 cps viscosity) to few thousands (>100,000 cps). Amino silicones are among the largest used silicones for the textile industry. The basic structure of the silicones used ((aminoethylaminopropylmethylsiloxane)–(dimethylsiloxane) copolymer) in this study is shown in Fig. 1. The amino group is modified to obtain various physical properties

These silicones are applied to the fabric surface through micro or macro emulsions. In the actual process, micro or macro droplets of silicone are sorbed on to the fabric surface leading to its surface modification. These processes appear to be enhanced by the electrokinetic characteristics of silicone droplets and the fabric surface. Amino silicone being positively charged is expected to be strongly sorbed on the negatively charged cellulose or polyester and blended fabrics.

2. Materials and methods

The silicone emulsions were donated by Elkay Chemicals, India and used as received. The nature and composition (i.e. surfactant content and degree of quaternization of amino silicone) of these emulsions is given in Table 1. The nomenclature of these emulsions also reflects the composition, as, for example, LK-L0-2575 refers to the name of the company (LK) followed by surfactant type (L for lauryl), degree of quaternization (0 for 0%) and surfactant content (25%) and total content of silicone oil and water (75%). The total silicone oil content (also referred as solid content) in the emulsion is 20%.

Table 1
Composition of silicone based emulsions

Surfactant	Degree of quaternization			
20%	0%	15%	35%	70%
25%	0%	15%	35%	70%

The pH of the solutions was adjusted using Fisher standard hydrochloric acid and sodium hydroxide solutions. Reagent grade potassium chloride from APACHE Chemicals, Inc., was used to adjust the ionic strength of solutions. Triple distilled water was used for the dilution purposes.

The silicone emulsion was diluted to desired amount using 10^{-3} M KNO_3 solution and the pH was adjusted using HCl or NaOH. The solutions were magnetically stirred for overnight and ultrasonicated for 15 min before the actual experiment. The zeta potential was then measured using a Zeta meter by applying 40 V. The atomic force microscopy (AFM) system used was Nanoscope III from Digital Instruments. The measurements were performed in air in tapping mode using a V-shaped Si_3N_4 cantilever (BS-SiNi-30, Nanoscience Instruments) covered with gold on the back for laser beam reflection. All images were collected in the height mode which keeps the force constant. The turbidity measurements were made at 25 °C with a Shimadzu UV-240 spectrophotometer ($\lambda = 350$ nm, cell length = 5 cm). The change in turbidity of each silicone emulsion was recorded at definite time intervals (18 h after sample preparation).

3. Results and discussion

3.1. Zeta potential studies

As shown in Table 1, two different surfactant ratios with different degree of quaternization varying from 0 to 70% were used in these tests. In the case of nonylphenol ethoxylate the amino silicone was not quaternized (i.e. 0%). These emulsions were diluted from 20% solid (silicone) content to 0.1% to make

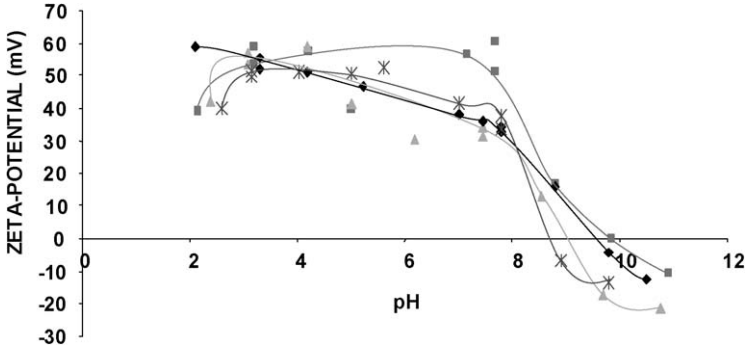


Fig. 2. Zeta potential of silicone emulsion as a function of pH: (a) ■ LK-L0-2080; (b) ▲ LK-L15-2080; (c) ◆ LK-L35-2080; (d) ⚹ LK-L70-2080.

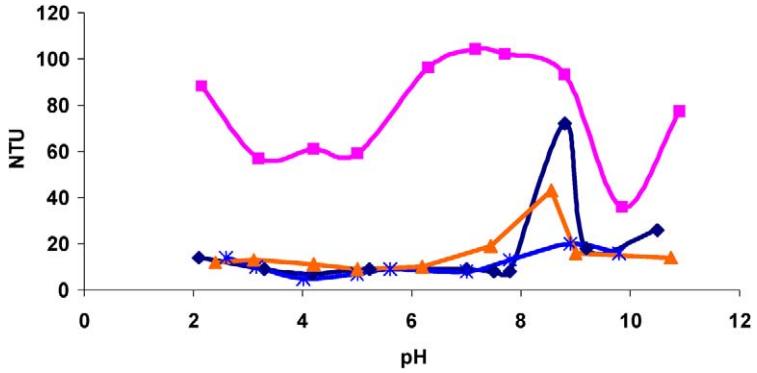
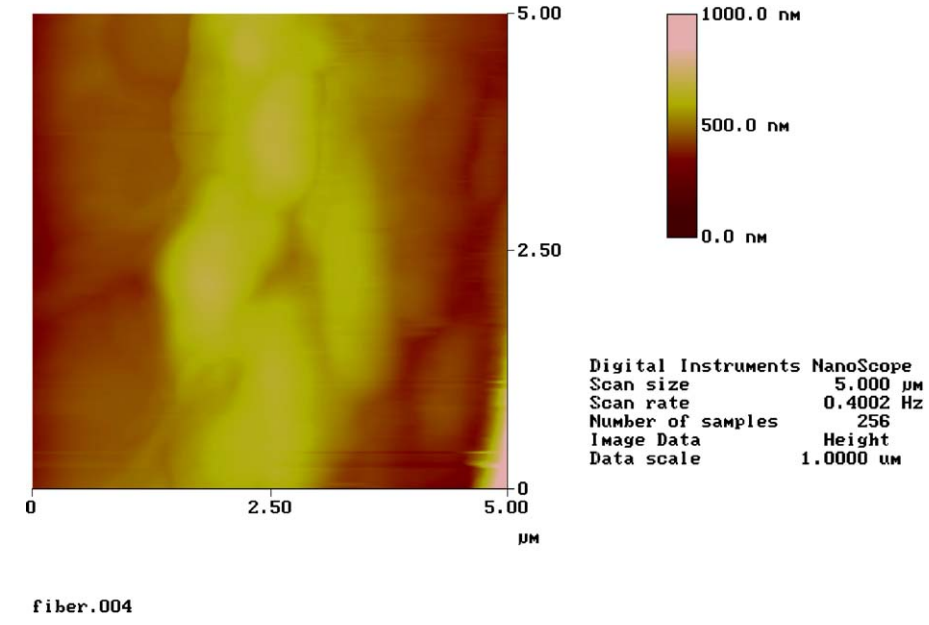
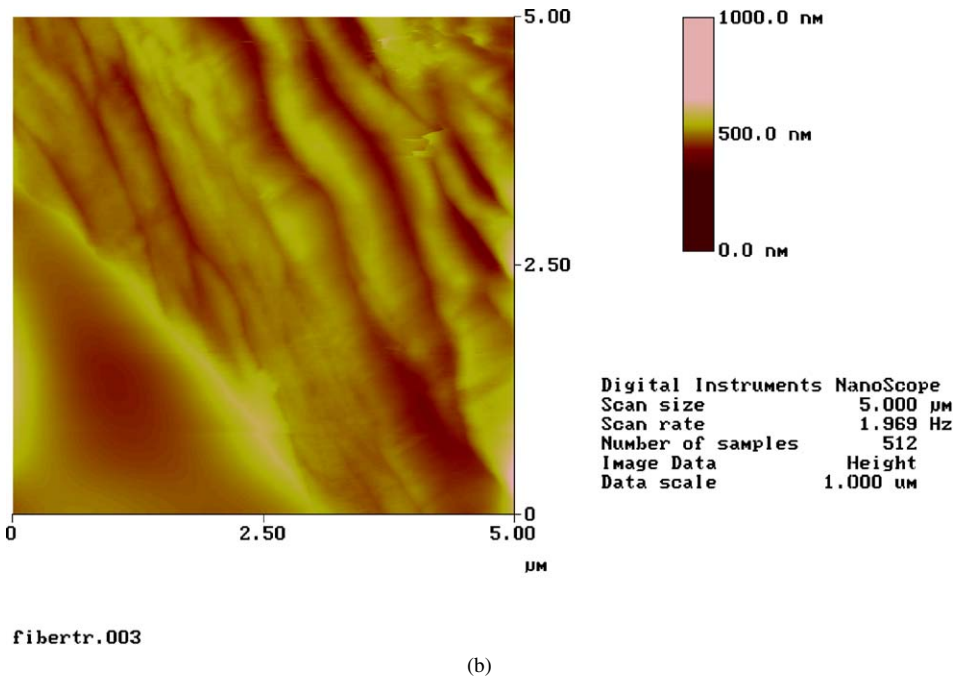


Fig. 3. Turbidity of silicone emulsions as a function of pH: (a) ■ LK-L0-2080; (b) ▲ LK-L15-2080; (c) ◆ LK-L35-2080; (d) ⚹ LK-L70-2080.



(a)



(b)

Fig. 4. AFM images of (a) untreated fabric, (b) treated fabric.

it possible to measure the zeta potential. The zeta potential was expected to remain fairly constant (in the positive range) over the pH range of 2–11, due to the presence of amino groups. The results obtained for silicones with 20% lauryl surfactant and various quaternization are shown in Fig. 2. As seen in Fig. 2 the zeta potential remained fairly constant for 0 and 70% quaternized silicones up to pH 8. Around pH 8 there is a sharp fall in the zeta potential with the isoelectric point in the range of pH 9–10 for the four different samples. Due to the quaternization of amino groups by dimethyl sulphate the zeta potential was expected to show a steady positive behavior. The quaternized groups were expected to be stable in all pH range thus giving a steady positive zeta potential.

3.2. Turbidimetric studies

It was also observed that the solutions turned hazy at higher pH (about 8–10) for all the samples tested. Since this was the range in which commercial operations ran into difficulties, this behavior is considered important. To further investigate the haziness observed, turbidimetry analysis was performed for all the samples used for zeta potential measurement. As shown in Fig. 3, there was a sharp increase in turbidity in the range of pH 9–10 and this is attributed to the breaking of emulsions. This result was important since it showed that these silicone emulsions are highly pH intolerant. The above results showed that the emulsions were destabilized in the pH range of 8–10. The turbidity increase indicated a change in the emulsion particle size, which needs to be further investigated.

3.3. AFM studies

The above studies give an insight into the behavior of the finishing reagents. In order to determine how the surface treatment alters the surface properties of fiber, we studied the morphology of fibers with AFM. A series of tests were performed on the treated as well as the untreated fibers. The results are shown in Fig. 4.

The fibers produced in a textile mill and those which have not undergone any special surface treatment are termed untreated. The treated fibers had undergone a silicone finishing by exhaust process. Fig. 4a shows the AFM picture of untreated fiber while Fig. 4b shows that of a treated fiber. It can be seen from these figures that the treated fiber is more uniform, well stacked and relaxed as compared to the untreated fiber. The image of untreated fiber is slightly blurry due to the difficulty in probe motion but the image of treated fiber is more clear and thus just smoother surface. Also it appears as if a single fiber structure is divided into many fibers after the silicone treatment. This indicates that the silicone treatment is responsible for changes in the micro properties of the fibers, and can be used to modify microstructural properties of fibers to induce smoothness, bounciness and other desirable properties in the fabric.

4. Summary

In summary, this work describes the study of electrokinetic properties of silicone emulsions used for surface treatment. The zeta potential of organomodified silicone emulsions shows isoelectric point in the range of pH 9–10. The turbidimetric studies show the likelihood of emulsion destabilization in alkaline pH. This is significant finding, having practical implications in the industrial applications. As far as the authors know, it is the first time that AFM studies have been reported to understand the microstructural properties of fabrics. The results show treated fabric to be far more smoothened and relaxed as compared to untreated fabric.

Acknowledgments

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