Silicone emulsions

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Abstract

Silicone polymers are a class of hybrid organic/inorganic polymers, that show desirable surface properties such as low surface energy and high flexibility, which enables even a very high molecular weight chain to achieve optimal orientation at the interface. They have excellent physical properties such as water repellency, heat stability, and high resistance to chemical and UV attack.

Silicone polymers have dual characteristics, because of which they can either be used as emulsifiers or act as the continuous/dispersed phase of the emulsion. The results of an anionically modified silicone polymer indicate that it can stabilize an emulsion of water in cyclic silicone oil (D5) only in a narrow range of compositions around 80% water and 20% oil, formulated at low shear rates. A silicone emulsion stabilized by hydrocarbon emulsifiers shows drastic changes in their electrokinetic and optical properties under external perturbations, for example pH change. Advanced analytical tools such as atomic force microscopy (AFM) illustrated that a coating of silicone emulsion causes a solid substrate like fabric to smoothen out. This article further discusses the various types of silicone emulsions and their applications.
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Keywords: Silicone; Emulsion; Poly(dimethyl siloxane); PDMS; Zeta potential; Turbidimetric analysis; Phase diagram; HLB

Contents

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1. Introduction

Emulsions are heterogeneous systems consisting of one immiscible liquid dispersed in another, in the form of droplets which may have thermodynamic instability [1]. They are used in a wide spectrum of industrial applications including pharmaceutical, food, cosmetics and textiles. Due to a small droplet size of the dispersed phase, the total interfacial area in the emulsion is very large. Since the creation of interfacial area incurs a positive free energy, the emulsions are typically unstable thermodynamically. Nevertheless, it is possible to make emulsions with very long stabilities by use of emulsifiers. Emulsifiers accumulate at the oil/water interface and create an energy barrier against flocculation and coalescence of the droplets. The emulsifiers can be ionic, non-ionic or zwitterionic surfactants, proteins or amphiphilic polymers [11].

Silicone (e.g. poly(dimethyl siloxane) and derivatives) polymers are the only class of hybrid organic/inorganic polymers that have been commercialized extensively (Fig. 1). Historically, they have been used in non-aqueous systems, such as mold release agents and polyurethane foams. More recently there has been considerable interest in utilizing them in aqueous media, such as for example, for super spreading of aqueous systems on hydrophobic surfaces. In both media, silicones show excellent performance as surface active agents reducing the surface tension to as low as 21 mN/m [2].

Silicones differ considerably from their organic counterparts due to their weak intermolecular attractive forces. Structurally they are characterized by (1) Si–O–Si bond angles that are larger than C–O–C bond angles, (2) Si–O bond lengths that are longer than C–O–C or C–C bonds, (3) a greater freedom of rotation around the Si–O bond compared to the C–C bond and (4) freely rotating methyl groups which can orient towards interfaces and also result in large excluded or "free" volume for the polymer chains [3]. Silicones are water repellent, heat stable, and highly resistant to chemical attack. It is to be noted that from a nano-scale point of view that silicones are not soluble in either hydrophilic or a variety of hydrophobic solvents; instead they often form a third phase [4]. Due to these special properties, silicones are finding applications in such diverse industries as cosmetics [5], drug delivery [6], fabric care [7,8] and paints and inks [9]. They are also commonly used as oils, rubbers, hydraulic fluids, electrical insulation and moisture proofing agents. Silicones with amino modifications have been well recognized by the industry as most suitable for surface modification of fabrics and garments [7]. In certain applications where two non-aqueous phases are in contact, such as in the manufacture of polyurethane foam from polyols and poly-isocyanates, silicones are the only compounds that are active at
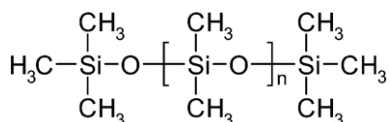
interfaces [10]. Because of such properties as mentioned above there is a considerable interest in silicones among researchers.

Since silicones are insoluble in both water and most hydrocarbons, a very common mode of delivering them is in the form of emulsions. The delivery of silicones in hydrocarbons has gained little interest, therefore we will only consider water-continuous emulsions in this paper. Silicone emulsions typically contain water, silicone oil and a surfactant. Given that a siloxane chain (i.e. containing –Si–O– in the chain) is incompatible with water, the choice of the surfactant and processing equipment is very important. The most common processing equipment used for making emulsions is a homogenizer, which uses mechanical energy to break one of the phases into small droplets [4]. Choice of an emulsifier required to reduce the interfacial tension and stabilize an emulsion can be decided based on a modified HLB (hydrophilic–lipophilic balance) concept. This paper considers binary and ternary silicone emulsions along with applications associated with them.

2. Discussion on HLB

Surfactants are chosen for various purposes based on the hydrophilic and lipophilic groups that constitute the molecule. This is conveniently represented in the form of a scale called hydrophilic–lipophilic balance (HLB). Direct application of conventional HLB concept for choosing an emulsifier in conjunction with silicone surfactants often results in misleading HLB values due to the fact that silicones are organic/inorganic hybrids and hence fall neither into the conventional categories of hydrophilic or hydrophobic. Moreover, prediction of the HLB and emulsification properties of blends of silicone and hydrocarbon surfactants is an additional challenge. To further complicate, there are many new silicone compounds which combine hydrophilic (water-soluble), siloxane (silicone-soluble) and hydrocarbon (oil-soluble) moieties into the same molecule. The introduction of these types of molecules and our inability to fit them into the conventional 2D HLB (i.e. only hydrophile and organophile indices) concept has resulted in difficulties for predicting the behavior of these compounds.

The difficulties mentioned above have led to the development of a concept called "3 dimensional HLB". This approach was first developed by Anthony and O'Lenick [12]. This empirical system is an extension of the HLB concept, and it is so named because it includes contributions from the three components related to portions of the molecule that are soluble in either silicone, oil or water. This 3D HLB system is similar to the conventional HLB scale except that it is represented on triangular coordinates instead of a linear (2-component) HLB scale. One of the boundary lines of this triangle system represents the conventional HLB system. The three parameters of 3D HLB system can be calculated as follows:

$$X = 20 \times M_H/M \quad Y = 20 \times M_L/M \quad Z = 20 - X - Y$$

where,

X represents coordinate of water-loving portion
Y represents coordinate of oil-loving portion

Fig. 1. Structure of poly(dimethyl siloxane) (PDMS).

Z represents coordinate of silicone-loving portion and M_H, M_L and *M* represent molecular weights of the respective hydrophilic, lipophilic and total molecular segments.

3D HLB concept depends on the relative weight of the hydrophilic, oleophilic and silophilic groups. As shown previously by Davies [39], there is a relation between the molecular structure of a surfactant molecule and the HLB value based on linear free energy concepts. Similar work should also be extended for 3D HLB concept in future.

3. Binary emulsions

Emulsions can be stabilized by silicone surfactants or hydrocarbon surfactants. There exists a clear distinction among the two systems, as briefed below.

3.1. Emulsions stabilized by silicone surfactants

The success of silicone emulsifiers is related to their special character, which differs in many respects from that of low molecular weight organics and polymeric emulsifiers:

- High flexibility of the silicone backbone with even very long chains being able to achieve optimal orientation at interfaces in a relatively short time.
- Behavior of silicones has hydrophobic as well as oleophobic character.
- Ease of synthesis and great versatility for tailoring their properties.

Silicone emulsifiers can be polymeric or oligomeric and can possess one or more hydrophilic functional groups. Moreover the nature of functional groups can be ionic or non-ionic. The general structure of silicone surfactants is represented in Fig. 2.

In contrast to low-molecular-weight surfactants, multifunctional polymeric emulsifiers can attach to an interface via several segments. The energy of adsorption is equal to the sum of the interactions of all segments, and can be considerably greater than the energy of individual monomeric surfactants. Hence these multifunctional polymeric emulsifiers can adsorb very strongly at an interface. They can be used in low dosages and are very efficient in generating highly stable emulsions. Polymers neither readily desorb from an interface, nor migrate through the bulk phase because of their strong adsorption to the interface.
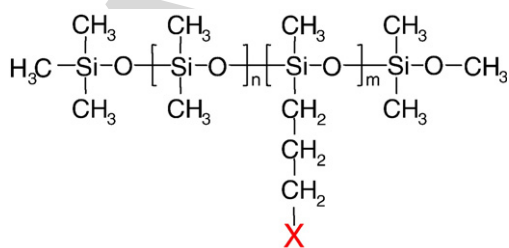

Fig. 2. General structure of silicone surfactant. *X* represents hydrophilic modification. For monomeric surfactant, $n=0$ and $m=1$.

The modifying functional groups attached to silicones can be charged or uncharged and are defined as non-ionic silicone surfactants and ionic silicone surfactants.

3.1.1. Emulsions stabilized by non-ionic silicone surfactants

Silicone polymers comprising a non-ionic hydrophilic group and a hydrophobic poly(dimethyl siloxane) chain (also known as silicone copolyols) have been studied for their emulsifying properties in some detail [3,10,13]. The molecular architecture of these polymers can be tailored to suit specific applications. In most cases, the hydrophilic moiety of choice has been poly(oxyethylene) (EO groups) because of its good water solubility and ease of synthesis with a wide range of molecular weights. The hydrophilicity/hydrophobicity of these polymers can be controlled by varying the chain length of EO groups, partial or complete substitution of EO with poly(oxypropylene) (PO groups), or by varying the degree of modification in the case of grafted polymers [13]. Silicone copolyols can also be modified with various alkyl chains in order to make them compatible with hydrocarbon oils, thereby making them good stabilizers for emulsions of hydrocarbon oil and water. An additional advantage of silicone copolyols is that their surface active properties (surface activity, self-association, and phase behavior) have been extensively measured. They remain liquid even for very high molecular weights, and can be used to form reverse micelles [14] and water-in-oil emulsions. Such emulsions are widely used in the cosmetics industry as either antiperspirants or creams for skin care and sun protection. They are also used for polishing applications and emulsion polymerization. A recent paper describes the use of such formulations in inks, agricultural, textile, paints and coatings applications [15].

In addition to linear silicones, cyclic silicones are also employed in industry due to their special volatile character. There has been some work done on the phase diagrams of cyclic silicone oils (D4, D5) and linear silicone chains, mixed with water and non-ionic silicone surfactants [16,17]. These phase diagrams show a variety of regions including simple micellar solutions (L_1 and L_2), microemulsions, and liquid crystalline phases. A detailed discussion on various systems and the temperature dependence of such systems is given elsewhere [10].

3.1.2. Emulsions stabilized by ionic silicone surfactants

Although non-ionic surfactants are very effective in lowering interfacial tensions of aqueous systems, they are not very tolerant of pH variations and tend to hydrolyze to long chain alcohols. Since long chain alcohols are irritants, non-ionic silicone surfactants are not suitable for use under all pH conditions. Moreover, a very long chain of polyethylene oxide and/or polypropylene oxide is often needed to make a non-ionic silicone water-soluble. Therefore in a given weight of non-ionic silicone surfactant, the silicone fraction is usually much reduced. All of these disadvantages of silicone copolyols can be avoided by using ionic silicone surfactants; however very little information exists for these materials. The added advantage of the ionic surfactants is that they behave as polyelectrolytes and hence can modify the rheological properties of their formulations, as desired particularly in cosmetic products.

In the past some work has been done on solution properties of cationic [18], anionic and zwitterionic [19] silicone surfactants; but very little work has been done on the emulsifying properties of these ionic varieties. Somasundaran's group is evaluating the emulsifying ability of several anionic, cationic and amphoterically modified silicone polymers. Results obtained so far indicate that the tested anionically modified silicone polymer stabilizes an emulsion of water in cyclic silicone oil (D5) but interestingly in a narrow window around composition of 80% water and 20% oil. The phase diagram is shown in Fig. 3. These emulsions were observed to be stable even after 1 month at the room temperature. Although, the emulsions were made by employing a magnetic stirrer, i.e. at low shear rate, high shear rates are often advisable for polymeric emulsifiers in order to uncoil the polymer chains and disperse them well at the oil–water interface.

It was observed that 80% water was stabilized as an inverse emulsion in 20% of the oil phase. The droplets were relatively large ranging to tens of microns. It is noted that, these concentrated macroemulsions were stable for weeks even with just 0.2% surfactant.

3.2. Emulsions stabilized by hydrocarbon surfactants

Silicone oils can often be emulsified by hydrocarbon surfactants also, where the silicone polymer acts as the oil phase instead of being the surfactant. Poly(dimethyl siloxane) (PDMS) oils are widely used in industry for controlled release [20], foam control agents, lubricants, fabric treatment [8] and base fluids in a number of products like cosmetic preparations and polishes. In spite of this little has been published in the open literature.

Binks and Dong [21] have investigated several aspects of the emulsion and equilibrium phase behavior of mixtures of water, non-ionic surfactant (C_nE_m) and silicone oil (PDMS). Emulsions may be inverted from oil-in-water to water-in-oil by increasing the temperature or the concentration of NaCl electrolyte. The apparent phase inversion temperature (PIT)

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

increased with increase in the number of oxyethylene groups in the surfactant (E_m), and decreased with increase in the surfactant alkyl chain length (C_n). The PIT also decreased when NaCl was added but increased in the presence of tetrabutylammonium bromide as electrolyte [21].

3.3. Electrokinetic and turbidity properties

Purohit et al. [8] are studying the interactions of functionalized silicones with various fabric substrates in order to understand the underlying mechanisms of interaction. In this study modified amino silicones are emulsified using non-ionic surfactants (lauryl and nonylphenol ethoxylates) to form oil-in-water emulsions. There the emulsion acts as a delivery agent for the silicone droplets, which impart the desired physical properties to the fabric substrates. These emulsions are stabilized by excess surfactant (usually 20–25%) since during the actual application they are diluted to a great extent. The electrokinetic properties of the emulsions were monitored in this study since charge plays an important role in the interaction with the fabric substrates. As shown in Fig. 4, the zeta potential remains 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 being 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 demonstrate a steady positive behavior
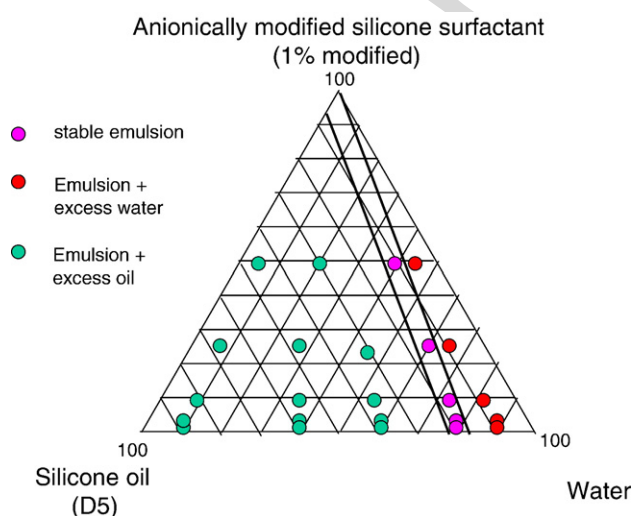

Fig. 3. Phase diagram of silicone oil–water–acid modified silicone surfactant. The phase diagram is measured at 25 °C, no added electrolyte and pH ~ 6.
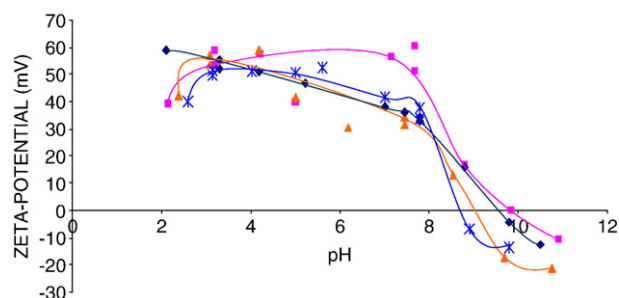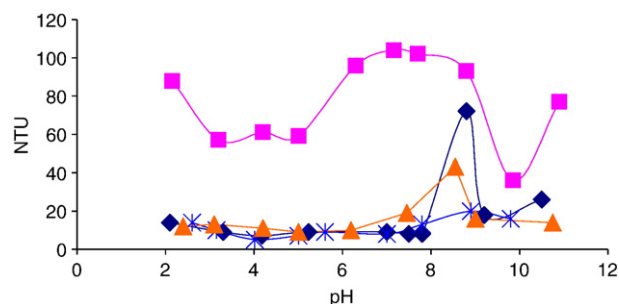

Fig. 5. Zeta potential of silicone emulsion as a function of pH: (a) ■ LK-L0-2080, (b) ▲ LK-L15-2080, (c) ◆ LK-L35-2080, (d) ✳ LK-L70-2080.

and the quaternized groups were expected to be stable in all pH range.

It was also observed [8] that the emulsions turned hazy at higher pH (about 8–10) for all the samples tested. This behavior is noteworthy since this was the range in which commercial operations ran into difficulties. To further investigate the haziness observed, turbidometric analysis was performed for all the samples used for zeta potential studies. As shown in Fig. 5, a sharp increase in turbidity was observed in the range of pH 9–10 where electrokinetic behavior also changed sharply and this was attributed to breaking of the emulsions.

4. Ternary emulsions

One of the main problems of the emulsions is phase separation due to differences in specific gravity of the two phases. This can be prevented by using dispersion of one phase in the form of small droplets in the large droplets of the second phase, which is further dispersed in the continuum of the first phase.

Ternary emulsions, also termed double emulsions, are complex liquid dispersion systems known also as 'emulsion of emulsion', where the droplets of one liquid dispersion are further dispersed in another liquid [22,23]. The inner dispersed droplets in the double emulsions are separated (compartmentalized) from the outer liquid phase by a layer of another phase [11,23]. Usually the size of the droplets of the inner emulsion is small (1 µm or less) while the size of the outer emulsion globules is significantly larger (20–100 µm) [24]. These types of emulsions are particularly important when protection of a sensitive attribute of the internal phase is required [10].

Polymeric surfactants are typically chosen to stabilize such emulsion systems because they adsorb at the interface more strongly than monomeric surfactants. The use of low molecular weight surfactants as emulsifier entails adsorption at a single anchoring point on the interface, which then tends to allow the surfactant to desorb or migrate easily and thereby allowing film thinning and phase separation. On the other hand, macromolecular surfactants have the advantage of attaching to a surface via several segments. Even if the free energy of adsorption per segment is low, the attachment of several segments leads to a large total free energy of adsorption. As a result, their adsorption onto surfaces is less reversible and they can be used efficiently even at lower concentrations. Polymers can stabilize the droplets via both steric and depletion stabilization mechanisms [25]. Polysiloxanes grafted with non-ionic poly(ethylene oxide) moieties have proven to be excellent steric stabilizers for this kind of emulsion [26]. The high emulsifying power of silicone-derived emulsifiers, their strong adsorption to the W/O interface and the pronounced elasticity of the interfacial film formed by these emulsifiers are the basis for the stability of double emulsions with silicones [10]. Such hydrophilic emulsifiers, along with alkyl-modified polyacrylates and monomeric surfactants, can be used to make both O/W/O and W/O/W double emulsions. The inner phase can be well homogenized at high shear rates and the droplets can be reduced to submicron sizes. This emulsion then forms the discrete phase in a double emulsion, which is usually prepared by gently stirring the first emulsion with the outer phase. These emulsions have been evaluated on the basis of their stability and resistance to osmotic gradients of solutes stored in the inner phase [27].

The preparation of double emulsions is both simple and inexpensive. In spite of these advantages, few commercial applications of double emulsions are known. This can be attributed to their thermodynamic instability and the uncontrolled, fast release of entrapped materials such as electrolytes or other dispersed materials. These emulsions are potential systems for sustained and slow release with possible applications in the areas of pharmaceuticals, enzyme fixation, cosmetics and agriculture [27,10]. Such emulsions can also develop high viscosity, which is desired in cosmetic applications for creams and lotions.

5. Applications

The most important applications of silicone-based emulsions, where the silicone component may be either the surfactant or the dispersed/continuous phase, are in the personal care industry. Organo-modified silicone types are of the most interest due to their unique properties, which are quite different from those of conventional hydrocarbon surfactants. Their structure gives the polymers flexibility and good flow properties even at low temperatures. They have good thermal and oxidative resistance, low surface tension, and can be either hydrophobic or lipophobic depending on their modification. These properties have led to their use in widespread applications in the cosmetic and pharmaceutical industries.

5.1. Personal care industry

Silicone emulsions for personal care appears either in the form of antiperspirant formulations or creams and lotions for skin care and sun protection. These are mostly water-in-silicone-oil emulsions that possess the special properties of silicones: excellent spreading and film-forming properties, gloss, dry non-sticky feel. Antiperspirants contain highly concentrated aqueous aluminium chlorohydrate emulsified in cyclic dimethylsiloxanes for easily applied formulations. The siloxanes facilitate application, reduce the stickiness of chlorohydrate and evaporate without giving a chilling effect. Non-volatile silicone oils are usually added to give a residual dry, non-sticky film. Hydrophobic water-soluble polydimethylsiloxane–polyoxyalkylene copolymers of relatively high viscosity are preferred as emulsifiers. These are made by increasing the molecular weight of the emulsifier [28]. Polish formulations in the form of water-in-silicone emulsions are obtained in a way similar to those described for antiperspirants. Silicones in these applications act to create easily spreading films and also facilitate the transport of other polishing oils and waxes. Typically these polishes contain abrasive material in the water phase and in addition to silicone fluid, other solvents like mineral oil and alcohols are included in the oil phase.

5.2. Textile industry

Fabrics and other such materials undergo finishing operations with surface active materials to impart desired surface properties [7]. Silicones have been used as premium finishing agents because they offer durable, longer lasting surface modifications to the fabric [29,30]. 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. These silicones are applied to the fabric surface through micro or macroemulsions. In the actual process, micro or macrodroplets of silicone are adsorbed onto the fabric surface leading to its surface modification.

We have studied the morphology of fibers using AFM in order to determine the manner in which the surface treatment alters their surface properties [8]. It can be seen from Fig. 6 that the treated fiber is more uniform, well stacked, and relaxed compared to the untreated fiber. Also it appears that 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 microproperties of the fibers, and can be used to modify microstructural properties of fibers to induce smoothness, bounciness and other such desirable properties in the fabric. The individual properties imparted to the fabric can be correlated to the molecular architecture of the silicone chains. For example, the proposed helical conformations of silicone chains may be responsible for the bounciness of the fabric substrates.

5.3. Other applications

Silicone oils and emulsions are used as lubricants in a variety of fields [31]. They are primarily used as lubricants and release agents for applications involving plastics, rubber and polyurethane/polystyrene foams. Various silicone emulsions are used as release agents for manufacturing rubberized belts, lubricants to prevent wear and increased abrasion resistance to latex rubber, as release agents in the printing industry, as lubricants for yarn and sewing threads to eliminate friction and tension,

and as finishes to improve water-repellency and scuff resistance for leather, vinyl and foam upholstery. In an interesting application silicone emulsions have been used as lubricants for pea-seed protectants [32].

Silicone emulsions have been employed to treat glass surfaces in order to add new advantageous properties such as the removal of a water film, lowering of the wettability towards water, and increase of the tensile strength. Advantages of lowered wettability of glass by silicone treatment in the pharmaceutical area include: (1) retardation of blood coagulation; (2) complete emptying of medicines from bottles.

In drilling of oil wells, the drilling fluids used can be brine-in-oil emulsions, which must be stable at high temperatures and pressures. Calcium chloride, calcium bromide or zinc bromide are used to obtain brines with high specific gravity to improve pressure control. These conditions require emulsifiers of high performance, which is the case for silicone-based emulsifiers [33]. In a similar application silicone emulsions of lower viscosity have been used for removal of chlorinated solvents from contaminated subsurface environments [34].

The market for drug delivery technologies has been expanding for some time. The fastest growing segments of this market are transmucosal and transdermal delivery technologies [35]. As pharmaceutical agents loose patent protection, pharmaceutical manufacturers look for methods to extend product lifecycles. Novel delivery methods can provide this extension. In this regard, silicones are combined with various pharmaceutical agents as antibiotics, antidepressants, anxiolitics, antifungals, antivirals, analgesics, and selected vitamins [36–38]. With zero order release rates, many of these pharmaceutical infused silicones can release 10 to 500 µg of agent per day.

6. Conclusion

Silicone emulsions possess intriguing properties such as stabilization of as much as 80% water in inverse emulsion form and are thus a subject of fundamental interest. Silicones depict some specialty applications, such as stabilization of polyurethane foams, which none other hydrocarbon surfactants can show.
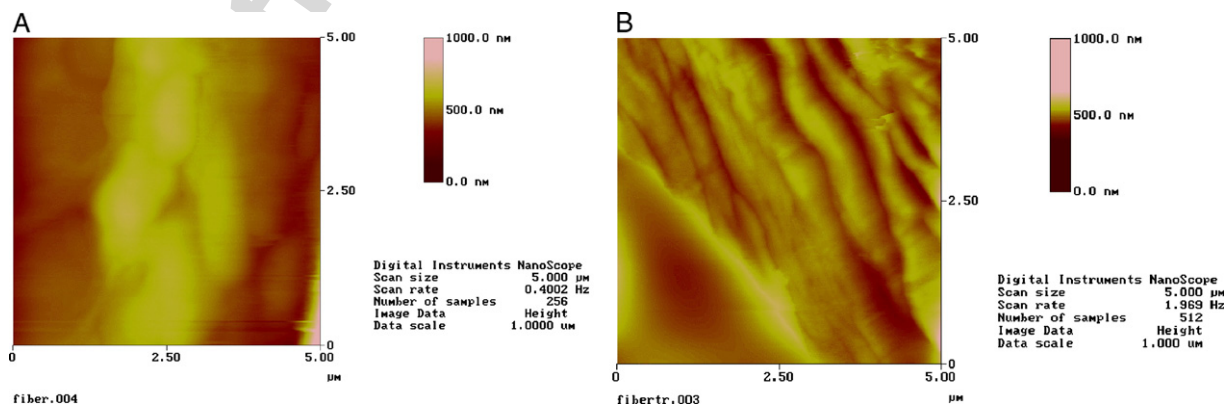

Fig. 6. AFM images of (A) untreated fabric, (B) treated fabric.

Because of such properties, even though relatively more expensive than the hydrocarbon surfactants, silicones are widely commercialized. Silicones are used in the form of binary as well as ternary emulsions and can be oil or an emulsifier. Polymeric silicones (polydimethyl siloxanes and amino-modified polydimethylsiloxanes) as well as cyclic silicones are mainly used as silicone oils in emulsions. Silicone surfactants, on the other hand, are essentially hydrophilically modified silicone polymers. In the past non-ionic ethylene oxide based silicone surfactants were given much attention, whereas very little work has been done on the ionically modified surfactants. While non-ionically modified surfactants give better water compatibility, the ionically modified surfactants are more effective when rheology of the formulation is important. Some of the important applications of silicone emulsions are reviewed in the paper. It is clear that silicones offer opportunities to produce new materials with unique properties at relatively low cost.

Acknowledgements

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