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Modification of surface properties of cellulosic substrates by quaternized silicone emulsions

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ABSTRACT

The present work describes the effect of quaternization of silicones as well as the relevant treatment parameter pH on the frictional, morphological and relaxation properties of fabric substrates. Due to their unique surface properties, silicone polymers are extensively used to modify surface properties of various materials, although the effects of functionalization of silicones and relevant process conditions on modification of substrates are not well understood. Specifically we show a considerable reduction in fabric friction, roughness and waviness upon treatment with quaternized silicones. The treatment at acidic pH results in better deposition of silicone polymers onto the fabric as confirmed through streaming potential measurements which show charge reversal of the fabric. Interestingly, Raman spectroscopy studies show the band of C–O ring stretching mode at $\sim$1095 cm^{-1} shift towards higher wavenumber indicating lowering of stress in fibers upon appropriate silicone treatment. Thus along with the morphological and frictional properties being altered, silicone treatment can lead to a reduction in fabric strain. It is concluded that the electrostatic interactions play an initial role in modification of the fiber substrate followed by multilayer deposition of polymer. This multi-technique approach to study fiber properties upon treatment by combining macro to molecular level methods has helped in understanding of new functional coating materials.

1. Introduction

Silicone polymers are an important class of high performance materials which are used to impart properties such as softness, bounciness and feel to substrates (fabric, hair, skin etc.), although the exact mechanisms causing these changes are unknown. Silicone polymers differ markedly from their organic counterparts such as paraffin waxes and fatty acid derivatives due to their weak intermolecular attractive forces and the resulting low surface energies. Studies [1] have shown that silicones have unique physical and chemical properties such as good thermal and oxidative stability, relatively low dependence of physical properties on temperature and chemical inertness. Straight chain and cross linked silicone polymers have been modified for specific applications which include pharmaceuticals [2], cosmetics and personal care [3], antifoaming [4], coatings [5], delivery [6] and paints and inks [7]. One of the important applications of silicones is imparting better properties such as softness, bounciness and feel to substrates (fabric, hair, skin). Amino silicones are by far the most extensively used functional silicones [8–11] for imparting desired surface properties to various substrates. They are commonly used in micro-emulsion form, exhibit positive surface charge in a certain pH range, and are shown to impart smoothness and uniformity to cotton fibers [12].

The silicone polymer literature, which is available extensively in the form of patents [13–16], generally focuses on optimization of primary and secondary emulsion technologies, defining appropriate molecular weight of polymers, modifying the functionalities and mixing ratios. Some efforts have been made to understand the fundamental aspects of interactions of silicone polymers with various substrates [17–19]. Jackowich et al. [17] showed that electrostatic forces play a role in heterocoagulation of oil droplets on hair keratin substrates. Skinner et al. [18] studied the effects of silicone softeners on textile surfaces by employing industrially relevant hand evaluation methods and molecular modeling. Recently Liu et al. [19] studied the dynamics of adsorption of amphiphilic block polymers on model textile substrates using QCM technique. Although most of these studies involved the use of emulsions for treatment of substrates the effect of emulsion stability on the deposition phenomena is not adequately understood. Also the effects of relevant conditions such as pH have been evaluated by subjective panel studies [18] and not through

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measurement of physical properties of fabric such as friction, roughness and strain relaxation.

This work focuses on the effect of pH on the deposition of functional silicones from emulsion phase along with the changes in physical and morphological properties of fiber substrates upon treatment. Our recent study [20] of silicone emulsions using the pyrene fluorescence technique showed that both the dilution and pH have an effect on emulsion stability with a critical surfactant concentration above which the emulsion destabilized. It was proposed that the emulsion stability (as function of pH and dilution) and the particle size distribution both play a significant role in their ability to impart desired macro and nano-surface properties to treated substrates through electrostatic interactions and selective binding. In this paper the effects of silicone modification on the fiber substrates are studied by multiple techniques, including frictional analysis, Scanning Electron Microscopy (SEM) and Raman spectroscopy at macro to nano-scales. We observe that frictional properties of fibers are markedly improved upon silicone treatment. Additionally the fibers are smoothened and uniform as observed from SEM studies with a reduction in roughness of the substrate. Spectroscopic investigation of fibers using Raman spectroscopy shows reduction in fiber strain (i.e. relaxation of fibers) upon appropriate silicone treatment. The present work shows that electrostatic interactions play an initial role in modification of surfaces followed by multilayer of polymer deposition as observed through imaging studies.

2. Experimental

2.1. Materials

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 are given in Table 1. The nomenclature of these emulsions reflects the composition, for example, LK-L0-2080 refers to the name of the company (LK) followed by non-ionic surfactant type (L for lauryl ethoxylates), degree of quaternization (0 for 0%), surfactant content (20%) and total content of silicone oil and water (80%). The initial silicone oil content in the emulsion is 20%. For easier understanding, the emulsions are distinguished by the amount of quaternization in the subsequent discussion. The basic structure of amino silicone, quaternary amino silicone and Polydimethyl siloxane (PDMS) is given in Fig. 1. The cationic polymeric silicone was synthesized by simple methylation of the amino silicone. The quaternization reaction was carried out using methyl tosylate by stepwise addition method [27]. The stoichiometric ratio was selected so as to obtain 15%, 35% and 70% quaternization of amino groups (as shown in Table 1). It is to be noted that depending on the extent of quaternization there exist unquaternized amino groups in the cationic silicone.

The solution pH was adjusted using Fisher standard hydrochloric acid and sodium hydroxide solutions. Reagent grade potassium chloride from Sigma Aldrich was used to adjust the ionic strength of the solutions. Triple distilled water (TDW) was used for the dilution purposes. Pyrene, purchased from Sigma-Aldrich, was used as probe for fluorescence studies. Commercially scoured, bleached, and mercerized cotton woven fabrics were obtained and used as model substrates to study the interactions of polymers with solid substrate.

Table 1
Composition of silicone based emulsions.

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

2.2. Methods

The cotton fabrics were treated with silicone polymers using immersion coating technique. The substrate (cotton fabrics) was immersed into an emulsion bath (0.1% silicone content) for 30 min while stirring by magnetic bars. The fabric was then dried at 110 C for 45 min and washed 3 times with distilled water to remove any residual surfactant/polymer adsorbed onto the surface. The effect of transfer of polymer from emulsion bath onto the fabric substrates was studied by various techniques described below.

2.2.1. Steady state fluorescence

The silicone depletion from the treatment bath was studied using a steady state fluorescence technique by SPEX FluorMax 2 spectrofluorometer with pyrene as the probe at a concentration of 10^{-6} M. Fluorescence spectrum was obtained at the excitation wavelength of 335 nm within the scanning span of 350–600 nm [21,22].

2.2.2. Streaming potential

The zetapotential of irregular size and shape materials such as fiber, hair, polymer films, and paper pulp can be measured using the streaming potential technique [23], wherein an electrolyte solution is forced by external pressure through a porous plug of material or across a channel formed by two plates. The potential difference developed for a given applied pressure is measured by electrodes placed at either end of the plug. This technique was used to measure streaming potential of treated and untreated fabric substrates.

2.2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained on a Hitachi S4700 at an accelerating voltage of 0.8–1 kV for topographical information about the treated surfaces. The open source image manipulation software Gwyddion (gwyddion.net) was used for 3-D reconstruction of the original SEM data and analysis to obtain the roughness and waviness information of the fabric substrate.

2.2.4. Frictional analysis

Fabric-fabric frictional force measurements were performed using Instron Materials Testing System Series 4442 (Norwood, MA).

2.2.5. Raman spectroscopy

A Confocal Raman spectrometer acquired from Horiba Jobin Yvon was used for measuring the Raman spectra of fibers. The spectra were acquired by 532 nm laser using a 10× objective (Olympus), and aperture of 0.5. The spectrograph was equipped with an air-cooled CCD detector (Wright Instrument, UK) and a 600-g/mm grating, which allows the covering of a large spectral range from 500 to 3600 cm^{-1}. All spectra were acquired and preprocessed following this scheme: linear baseline subtraction and normalized using the bands at 1650 cm^{-1}.

3. Results and discussion

The goal of this work is to study the modification of fabric properties as achieved by amino silicone polymers applied from an emulsion phase. The depletion of silicone polymer from emulsion bath and transfer onto fabric was studied by pyrene fluorescence technique. The modification of fabric due to the treatment is studied using streaming potential (to measure the charge of fabric) and frictional force measurements. The overall morphological changes of fabric are monitored by SEM and modeled using open source software Gwyddion. These changes are further correlated to the