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Silicon-compound coating for preparation of water repellent cotton fabric by admicellar polymerization

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ABSTRACT

Admicellar polymerization of two silicon compounds, methacryloxymethyltrimethylsilane (MSi) and methacryloxypropylpentamethyldisiloxane (MDSi) was investigated using two silicone surfactants, a nonionic and a cationic. Adsorption of the cationic surfactant on cotton was found to be higher than that of the nonionic surfactant. The polymer film on the surface was characterized by SEM, FTIR and XPS and the results showed that a thin polymer coating was successfully formed. The treated fabrics showed good water repellency as determined by contact angle measurement and the MSi-treated cotton showed better water repellency than the MDSi-treated cotton in terms of wetting time.

1. Introduction

Fabric finishes impart many desirable features to clothing including softness, wrinkle-free laundering, anti-static cling and color fastness. The interest in water-repellent finishes has increased significantly in recent years. The wettability of a material depends mainly on surface energy which is affected by chemical composition and on surface morphology. Fluorinated compounds have been widely used as they have very low surface energy. For this reason, many studies are based on treating textiles with fluorinated compounds [1–3]. However, certain fluorochemicals were found to have potential risk to humans and the environment, and they have high cost. Nowadays, researchers have renewed interest in the use of silicon compounds to create a hydrophobic surface [4–6], an option that has been known for more than 50 years [7]. The choice of silicone is based on its unique properties such as water repellency, flexibility at low temperature, good heat and cold resistance, and good electrical properties. In terms of hydrophobicity, fabrics and other substrates coated by silicon compounds show very good water repellency [8–10]. Indeed, Gao and McCarthy recently reported a "perfectly" hydrophobic surface prepared by phase separation of a methylsiloxane network over a silicon wafer [11].

Admicellar polymerization is a versatile method for forming an ultrathin polymeric film on a substrate surface [12–19]. For textile materials, this method has been found to have many advantages over conventional coating methods. It is water-based and can be carried out using the conventional exhaust dyeing machines. Moreover, films formed by admicellar polymerization can be nanoscale in dimension [15], so that fabrics retain good pliability and soft touch. For these reasons, the method has been used on textile materials to produce functional fabrics with anti-microbial, UV blocking, conductivity, and flame retardant properties [20–26]. However, there has been no report on preparing a water-repellent cotton using silicon compounds via admicellar polymerization.

In this study the commercially available silicon compounds, methacryloxymethyltrimethylsilane (MSi) and methacryloxypropylpentamethyldisiloxane (MDSi), were chosen as the monomer to form a hydrophobic surface based on their anticipated suitability for admicellar polymerization. Their structures are shown in Fig. 1. Two commercial silicone surfactants, a low molecular weight nonionic Sylgard® 309 and a cationic Dow Corning® 949, were chosen for monomer adsolubilization. The latter of these represents a variation on admicellar polymerization since it contains a polyelectrolyte. Polyelectrolytes can induce aggregation at lower concentrations through hydrophobic and electrostatic interactions and may provide enhanced film stability with multiple binding sites or trains typical of these macromolecules on adsorption [27]. Coated fabrics were characterized using SEM, FTIR, XPS, and their water-repellency was determined by a drop test and contact angle measurements.

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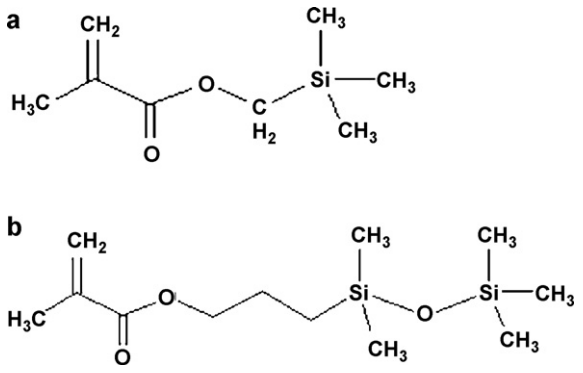

Fig. 1. Structures of (a) methacryloxymethyltrimethylsilane (MSi) and (b) methacryloxypropylpentamethyldisiloxane (MDSi).

2. Experimental

2.1. Materials

Twill white cotton 60" 07/07 cm:2 SKU:1690916 was purchased from Oak Hill Quality Cotton Fabrics RN 4/324. Prior to use, the fabric was washed with water at 70 °C several times to remove any remaining surfactant. The BET area of the fabric was found to be 0.96 m^2/g using a Quantachrome Autosorb 1.

Surfactants Sylgard® 309 (a mixture of 2-(3-hydroxypropyl) heptamethyl-trisiloxane, ethoxylated acetate, CAS #125997-17-3, allyloxy polyethylene glycol monallyl acetate, CAS #27252-87-5, and polyethylene glycol diacetate, CAS #27252-83-1) and Dow Corning® 949 cationic emulsion (a mixture of amodimethicone [28] CAS #308070-89-5, cetyl trimethylammonium chloride (CTAC), and trideceth-12, CAS #24938-91-8) were obtained from Dow Corning Corporation. We selected methacryloxymethyltrimethylsilane (MSi, >95%) and methacryloxypropylpentamethyldisiloxane (MDSi) for silicone monomers (Gelest). Azobisisobutyronitrile (AIBN) (99%) and ethanol (99%) were purchased from Aldrich Company while ethanol came from Pharmco Aaper. All chemicals were used without further purification.

2.2. Adsorption isotherm

Adsorption isotherms of Sylgard® 309 and Cationic 949 on cotton were obtained by exposing a 5.5 cm × 5.5 cm cotton fabric to 20 mL of surfactant solution of known initial concentration. The vial was sealed and placed in a water bath at 30 °C and shaken at 120 rpm for 15 h. After that, the fabric was taken out and concentrations of the supernatant were determined by Total Organic Carbon analyzer (TOC), Shimadzu TOC 5050, Auto Sampler Shimadzu ASI 5000A, Solid Sample Module SSM 5000A. The amount of surfactant adsorption on cotton was calculated by taking the difference between the initial and final concentrations of the surfactant in the vial.

2.3. Adsolubilization

Monomer adsolubilization was measured for MSi and MDSi using Shimadzu UV 2450 UV-Visible Spectrophotometer at λ_{max} = 203 nm. A 5.5 cm × 5.5 cm sized cotton fabric sample was placed in a vial containing 20 mL reaction solution. The solution consisted of the monomer and surfactant, and the process of adsorption and adsolubilization was carried out for 1 h at 60 °C and shaken at 120 rpm. Each of the monomers, MSi and MDSi, was paired with Sylgard® 309 and Cationic 949. The initial monomer concentrations used were 7 mM for MSi and 10 mM for MDSi. The initial surfactant concentrations were 500 ppm for Sylgard® 309 and 1000 ppm Cationic 949.

2.4. Admicellar polymerization

A 5.5 cm × 5.5 cm cotton fabric was placed in a 20-mL vial containing 500 ppm Sylgard® 309 solution or 1000 ppm Cationic 949 solution. Initial concentrations of Sylgard® 309 and Cationic 949 were below the CMC. MSi and AIBN solutions were prepared in ethanol at a level determined to give the final desired concentration and then added to the surfactant solution. The initiator:monomer molar ratio was kept at 1:2 and the volume of ethanol was kept at 10%. The sealed vial was then placed in a water bath at 30 °C and shaken at 120 rpm for 24 h to allow surfactant adsorption and monomer adsolubilization to occur concurrently. The temperature was then raised to 70 °C to initiate the polymerization reaction. After 15 h of polymerization, the fabric was taken out from the vial and inserted in a vial filled with DI water at 70 °C and shaken at 120 rpm for 15 min. This was repeated twice, for a total of three times, in order to remove the excess surfactant. The fabric was finally placed in an oven at 60 °C until dry. Polymerization of MDSi on the cotton fabric was carried out in the same way as polymerization of MSi described above. Additional runs with shorter reaction times were carried out at The University of Oklahoma using 1 h at 60 °C for adsorption and adsolubilization with 7 mM MSi or 10 mM MDSi followed by reaction for 2 h at 80 °C before being placed in an oven at 80 °C until dry. All results refer to the longer reaction time unless otherwise noted.

2.5. Characterization of the polymer coating on cotton surface

Surface morphology of the coated fabric was determined by scanning electron microscopy (SEM) (JEOL, JSM 5200, 15 kV). The chemical groups present on cotton surfaces were analyzed by Fourier transform infrared attenuated total reflectance spectroscopy (FTIR–ATR) with a ZnSe plate in the wavenumber range of 4000–650 cm^{-1}. The spectrometer used was Nexus 670 spectrometer (Nicolet) with 50 scans at a 4 cm^{-1} resolution. For the coating prepared at shorter reaction times, imaging and elemental analysis was carried out using X-ray analysis on a Zeiss 960A SEM equipped with Oxford Link Energy Dispersive Spectroscopy (EDS) with a thin window and using IXRF EDS 2008 software at a beam energy of 5 keV. Surface analysis of samples was also performed on a Physical Electronics PHI 5800 ESCA system equipped with an AlKα X-ray mode operated at 350 W and 15 kV. The base pressure of the UHV XPS chamber was ~1.0×10^{-8} torr. Each spot size was 400 μm and 187.85 eV pass energy was used during the data acquisition.

2.6. Water repellence and contact angle

Water repellency of the fabric was determined initially by the drop test prior to measuring contact angle or running other tests. A 10-μL drop of distilled water was carefully placed on fabric with no impact force using a syringe. The time taken for the droplet to disappear was measured up to a maximum of 30 min.

The water contact angle of the treated surface with water was measured using a KRÜSS contact angle measurement instrument, DSA 10-Mk2. Contact angles for samples coated at shorter reaction times were determined using an I.T. Concept drop shape analyzer. Two droplets each of 20 μL volume was measured for a total of 10 min and the average of the final values reported.

3. Results and discussion

Recent efforts to form silicon-based hydrophobic coatings on fabrics [9,29] and other substrates [30] have included sol–gel