



Application of superhydrophobic sol gel on canvas



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ABSTRACT

In this study, a superhydrophobic sol gel (SHSG) was used to promote self-cleaning ability of canvas. Four kinds of coating methods were studied and water impact test was used to assess the quality of the coating. The scraper method rendered a relatively flat surface; and water contact angles (WCAs) of two bilayers polytetrafluoroethylene (PTFE)/SHSG-coated canvas were $153.3^\circ \pm 3.1^\circ$ and $141.7^\circ \pm 3.3^\circ$ before and after water impact of 2 h, respectively. SEM, energy dispersive x-ray spectrometry (EDX), and FTIR were applied to characterize the PTFE/SHSG coating. Although SHSG was dropped on top of the PTFE film during sample preparation, the analysis of EDX and FTIR indicated that the chains of PTFE extended upward and SHSG moved downward during the heat treatment with preheat. The combination of SHSG with PTFE promoted not only hydrophobicity but also the strength and weatherability of the canvas. The tensile strength of a PTFE/SHSG-coated canvas was always superior to a PTFE-coated canvas during accelerated weathering test. After accelerated weathering test of 300 h, the two bilayers PTFE/SHSG-coated canvas had a tensile strength of 237 kg, static WCA of $143.7^\circ \pm 2.1^\circ$, a contact angle hysteresis of 8° , and a sliding angle of 4° , which represented an outstanding self-cleaning ability.

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1. Introduction

The application of nanotechnology to the traditional textile industry, including natural, artificial or synthetic fibers, has attracted considerable interest in recent years [1–20]. Due to the extraordinary photocatalytic activity, non-toxicity, high availability, biocompatibility, and low price, TiO₂ nanoparticles have been applied extensively onto textile materials to obtain UV-protecting, self-cleaning, superhydrophobic or superhydrophilic as well as anti-bacterial properties [1–4]. Nitrogen doped TiO₂-cotton fabrics or TiO₂ combined with different metals ions (Fe, Co, Zn, and Ag) cotton fabrics showed significant photocatalytic activity in the degradation of methylene blue or methyl orange under visible-light irradiation [2–4]. Since silver or silver ions are effective against many disease-causing organisms in the body, and relatively non-toxic for human cells, silver nanoparticles are widely applied onto textile materials to impart antibacterial ability [5–8].

Silica sol has been used by many researchers to produce superhydrophobic textiles [6–14]. The abundant hydroxyl groups on the cotton fiber surface favor upload and attachment of hydrolyzed SiO₂ nanoparticles on the surface. The roughness, at two levels (micro- and nanoscales), enabling trapping of air under

water droplets can be obtained through adequate condensation of hydrolyzed SiO₂ sol. The low surface energy characteristic can be achieved by the modification of sol gel with a long chain alkyl silane or fluorochemicals. ZnO nanorod arrays or nanoparticles, due to their antibacterial properties and cost-effectiveness compared to silver nanoparticles, have also been created on cotton substrates and subsequent hydrophobic modification with a long chain alkyl silane, fluoride or stearic acid [15–19]. Since the surface tension of oil, such as hexadecane 27.5 mN/m, is lower than that of water (72.1 mN/m), the superhydrophobic surface is also superoleophilic. This characteristic can be used in fabrication of superhydrophobic and superoleophilic textiles for the treatment of increasing industrial oily wastewater and polluted oceanic water, as well as the frequently occurring accidental oil spills [11–13,15,18,20]. Xue et al. [11] used tetraethoxysilicate (TEOS), 1,1,1,3,3,3-hexamethyl disilazane (HMDS), n-hexane, ammonia solution, hydrochloric acid (HCl) to fabricate superhydrophobic and superoleophilic textiles for oil–water separation. However, n-hexane can cause neuropathy. A superhydrophobic and oleophilic sol–gel nanocomposite coating with oil contact angle of $<10^\circ$ will improve oleophobic property through the further lowering of surface energy by the presence of a fluorochemical [21,22].

Fluorochemicals have been employed for hydrophobic and oleophobic surface modifications in many of the reported works [10,14,15,21–23]. However, most fluorinated materials may cause serious risks to human health upon coming in contact with skin.

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In addition to fluoride, several other chemicals are also used in the fabrication of the above mentioned functional textiles. It has not been investigated extensively if these textiles trigger any allergy upon skin contact. However, this may not be a case for a superhydrophobic canvas since it does not come in contact with human body upon use.

Canvas is used as the substrate of an oil painting. The application of polar organic solvents as cleaning tools for painting surfaces is still a widely adopted technique. Unfortunately, the capillary penetration of a liquid into the paint layers can lead to swelling and leaching of the original organic components (mainly varnishes and binding media) constituting the layered paint structure [24]. Dei et al. [25] developed a new approach with gels which was intended to minimize the time necessary to achieve the desired cleaning action, and then removed the gel by converting it to a low-viscosity fluid in situ by a rapid, mild chemical perturbation. Instead of using gel with liquid cleaning agents, a superhydrophobic and superoleophilic coating can impart the canvas a self-cleaning property.

Canvas is widely used in outdoor pavilions, awnings, multi-purpose sports complexes, huge span tension membrane roofs, tents, etc. To provide a comfortable environment for users, it must possess properties of durability, inertness, cleanability, and easy-care attributes. It should function as a self-cleaning system; and airborne dirt should be automatically washed off by rain. After extended periods of outdoor exposure, it should retain a high degree of flexibility and strength. Nevertheless, the research about self-cleaning of canvas is very rare.

This work investigated the application of superhydrophobic sol gel (SHSG) on canvas. The SHSG was synthesized from TEOS, HMDS, HCl, and ethanol. Therefore, it is fluorine free. The optimal method of applying SHSG and polytetrafluoroethylene (PTFE) simultaneously on the canvas was studied systematically. Water impact test for 2 h was used to assess the endurance of the coating. Contact angle tester was used to determine the water contact angle (WCA) before and after water impact test. Scanning electron microscopy (SEM) and energy dispersive x-ray spectrometry (EDX) were used to analyze the variation of surface morphology and distribution of SHSG and PTFE in the coating. The 3D surface morphologies of the films were investigated using an atomic force microscope (AFM). Fourier transform infrared spectroscopy (FTIR) was used to identify chemical bonding between molecules in the coating. Tensile test was conducted to determine the effect of sol gel addition on the strength of the canvas. Accelerated weathering test was performed to estimate the weatherability of the PTFE/SHSG-coated canvas.

2. Experimental

2.1. Materials

PTFE powder of 300 nm was purchased from DU PONT. Fluorine surfactant S420 was purchased from AGC SEIMI CHEMICAL CO. The PTFE emulsion with model number Zewffl Gk570 was purchased from TAIWAN DAIKIN ADVANCED CHEMICALS. The main component of this PTFE emulsion is PTFE. The diameter of fiber glass yarn is 4 μm . Fiber glass yarns are weaved into a fiberglass cloth with a density of 24 strips of fiberglass yarns in both vertical and horizontal directions. The mass density of the fiberglass cloth is 450 g/m^2 . The commercial canvas with PTFE membrane was purchased from Chukoh Chemical Industries (Japan) with model number of FGT-600.

2.2. Sample preparation

SHSG with tri-methyl-modified silica sol was synthesized through the reaction of hexamethyldisilazane (HMDS) and

hydrolyzed tetraethoxysilane (TEOS) as described in detail elsewhere [26,27]. Four kinds of samples were prepared in this study.

Sample A:

SHSG, aged for 7 days, was deposited on the commercial canvas through a dropper and then heat treated at 200 °C for 2 h.

Sample B:

PTFE powder, fluorine surfactant S420, and SHSG in mass ratios of 1:1:1, 1:2:2, and 1:2:4 were stirred uniformly using a homogenizer, deposited on the fiberglass cloth through a dropper and then heat treated at 200 °C for 2 h.

Sample C:

Fiberglass cloth was dipped into PTFE emulsion (Zewffl Gk570 Taiwan Daikin) and then lifted to coat with SHSG by a dropper. After heat treatment at 200 °C or 300 °C for 2 h, one bilayer of PTFE/SHSG was obtained. One, two, three or five bilayers of PTFE/SHSG were coated on the fiberglass cloth.

Sample D:

The scraper with four blades was used and film thicknesses of 30, 60, 90 or 120 μm were scraped out by the four blades, respectively. The fiberglass cloth was dipped into PTFE emulsion (Zewffl Gk570 Taiwan Daikin). A film thickness of 30 μm was scraped out by the scraper. The SHSG was dropped onto the PTFE film. A film thickness of 60 μm , containing PTFE and SHSG, was scraped out by the scraper. After heat treatment at 200 °C or 300 °C for 2 h, one bilayer of PTFE/SHSG was completed. The total thicknesses of two and three bilayers of PTFE/SHSG were 120 and 180 μm , respectively.

The fiberglass cloth coated with PTFE and SHSG of samples B, C and D are designated as PTFE/SHSG-coated canvas.

2.3. Sample tests

2.3.1. Water impact test

In order to estimate the rain shock endurance of all the samples, a water column with cross sectional area of 1.7 cm^2 was impacted on the samples from a height of 45.5 cm for 2 h. Water impact velocity was estimated to be about 2.99 m/s, and WCA was measured.

2.3.2. Tensile test

Samples of 40 \times 150 mm were subjected to tensile strength measurements by the 8801 servohydraulic testing system of Instron Engineering Corporation. The tensile test machine worked at a rate of 100 mm/min with the initial distance between the clamps equal to 110 mm. Maximum load at break was determined for samples with different processing conditions.

2.3.3. Accelerated weathering test

The samples were mounted in a Global UV testing chamber (Ci4000 Xenon Arc Weather-Ometer, ATLAS, USA) by means of a custom-made sample holder. According to test program of ISO 4892-2, the test conditions included ultraviolet irradiation of wavelength of 300–400 nm with intensity of 60 W/m^2 , black panel temperature of 65 °C, chamber temperature of 38 °C, and relative humidity of 50%. WCA of the samples was measured for every 50 h, and tensile test was conducted for every 100 h of accelerated weathering test.

2.4. Characterization of PTFE/SHSG coating

The WCA of all the samples, determined using a contact angle tester, was an average of three independent measurements for each sample. Advancing contact angle measurements were performed by adding liquid to the water droplets, and receding contact angle measurements were made by removing liquid from the drops. The sliding angle was defined as the smallest tilted angle θ of the PTFE/SHSG-coated canvas at which the deposited water droplets slid off immediately after dispensing from a needle.

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