DOI: 10.1002/ange.201105069

Fabric Coatings

Durable, Self-Healing Superhydrophobic and Superoleophobic Surfaces from Fluorinated-Decyl Polyhedral Oligomeric Silsesquioxane and Hydrolyzed Fluorinated Alkyl Silane**

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Super-liquid-repellent surfaces have attracted much attention in both scientific and industrial areas.[1] They are often deemed superhydrophobic or superoleophobic depending on the liquid to be repelled. Superhydrophobic surfaces have a water contact angle greater than 150°. They have interesting nonsticking, self-cleaning, and anti-contamination functions. The emerging applications include separation of oil from water,[2] energy conversion,[3] protection of electronic devices,[4] adjusting cell/substrate adhesion in the biomedical area,[5] and reducing fluid resistance for aquaculture and microfluidic devices.[6] In contrast, superoleophobic surfaces can be rather complicated, but they have great potential applications in antifouling from hazard chemicals and biological contaminants.[7] Although any solid surface can be characterized as superoleophobic as long as its contact angle with an oily fluid is greater than 150°, the surface properties revealed from the contact angle measurement using different contacting oils could be considerably different. For example, a surface that is superoleophobic to certain oily fluids may have lower repellency or even be wettable by other oily fluids of a lower surface tension. It is normally easy to make a surface super-repellent to oils of a high surface tension, but difficult to prepare superoleophobic surfaces against oily fluids that have a surface tension below 35 $mN\,m^{-1}$.

Most super-liquid-repellent surfaces have poor durability.[8] Chemical oxidation from exposure to air, a special chemical environment, strong light, or physical rubbing could cause the surfaces to lose their super-repellency permanently. It is imperative to improve the durability for practical applications.[9] Recently, great progress has been made to develop mechanically robust superhydrophobic surfaces and laundering-durable superhydrophobic fabrics.[10] On the other hand, the bioinspired self-healing ability has been proposed to be a promising solution to improve the durability of synthetic superhydrophobic surfaces.[11] Recently, Li et al.[12] reported a self-healing superhydrophobic coating that was prepared by chemical vapor deposition (CVD) of a fluoroalkyl silane on a layer-by-layer assembled porous surface, and self-healing was derived from the reacted fluoroalkyl silane embedded in the rigidly flexible coating layer. Wang et al.[13] also reported the formation of a self-healing superamphiphobic surface on anodized alumina by filling the intrinsic pores with a low-surface energy liquid.

In the recent study, we have also found that fabrics coated with a hydrolysis product from fluorinated-decyl polyhedral oligomeric silsesquioxane (FD–POSS) and a fluorinated alkyl silane (FAS) have a self-healing superhydrophobic and superoleophobic surface and the coating shows excellent durability to acid, UV light, machine wash, and abrasion. Herein, we first report on its novel multiple self-healing ability and durable performance.

The chemical structures of FD-POSS and FAS are shown in Figure 1 a. The coating solution was prepared by dissolving FD-POSS in five times its weight of FAS, and the resulting viscous solution was then dispersed in ethanol. After ultrasonication for 30 min, a homogeneous dispersion was obtained. Figure 1 b shows the appearance of an FD–POSS/FAS dispersion in ethanol. Such a suspension was stable at

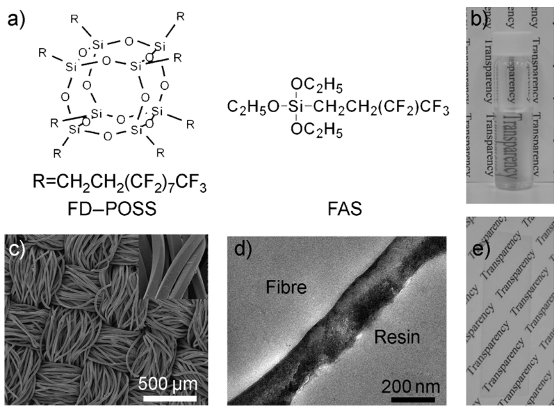

Figure 1. a) Chemical structures of FD–POSS and FAS; b) picture showing show the FD–POSS/FAS dispersion in ethanol; c) SEM images of the FD–POSS/FAS coated polyester fabric (inset SEM image of larger magnification); d) TEM image of the cross-sectional view of the coating layer; e) a photo of a glass slide coated with FD–POSS/FAS.

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[**] Funding support from Australia Research Council through a discovery project and Australia defence is acknowledged. The authors thank Dr. Luhua Li for his kind support with the AFM imaging.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105069.

room temperature for at least 10 h. The FD–POSS/FAS suspension can be easily applied onto fabrics through a wet-chemical coating technique, such as spraying, padding, or dip-coating. In this study, a dip-coating method was used to apply the coating solution to fabrics; a plain weave polyester fabric was mainly used as a model substrate. After dip-coating, the coated fabric was dried at 135 °C for 30 min. Under the scanning electron microscope (SEM), the coated fabric looked uniform (Figure 1 c). The transmission electron microscope (TEM) image showed that a thin conformal film, with a thickness of around 100 nm, was formed on the fiber surface (Figure 1 d). Figure 1 e shows the coating prepared from the same FD–POSS/FAS suspension on a glass slide, which looks transparent. The UV/vis transmission spectrum of the coating on quartz plate revealed that the FD–POSS/FAS film was highly transparent in a wavelength range of 230-850 nm (see the Supporting Information).

Figure 2 a shows the colored liquid droplets (13 μL) on the coated polyester fabric (plain weave). The yellow-colored water, red-colored hexadecane, and blue-colored tetradecane all look like spheres. The contact angle (CA) measurement indicated that the coated fabric had contact angles of 171°, 155°, and 152° with water, hexadecane, and tetradecane, respectively. A series of organic solvents having different surface tensions have been used to explore the liquid repellency of the coated fabric. Figure 2 b shows the dependence of the CA on the surface tension. The CA was larger than 150° when the liquid surface tension was above 26.5 $mN\,m^{-1}$ (tetradecane); this result clearly indicates that the treated fabric is super-liquid-repellent and has both superhydrophobic and superoleophobic properties.

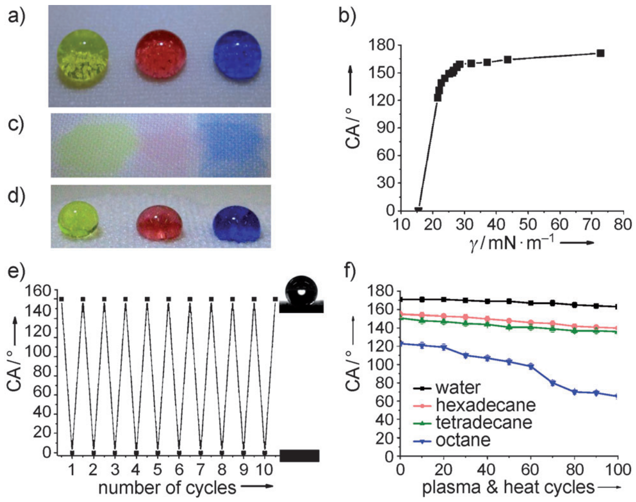

Figure 2. a) Photo of colored water (yellow), hexadecane (red), and tetradecane (blue) on the FD–POSS/FAS treated polyester fabric (for easy observation, a small amount of dyes, acid yellow 76, oil red, and oil blue, respectively, for water, hexadecane, and tetradecane, was added to the liquid droplets; the dyes had no influence on the contact angles); b) dependence of CA on the surface tension (γ) of liquids; c) photo of colored liquids on the coated fabric after plasma treatment; d) photo of colored liquids on the coated fabric after 100 cycles of plasma-and-heat treatments; e) CA changes in the first 10 cycles of plasma-and-heat treatments; f) CA changes with plasma-and-heat treatment cycles.

To demonstrate the self-healing ability, the coated fabric was damaged artificially by a plasma treatment using air as gas source. After the treatment, the surface became hydrophilic with a contact angle of 0° for water, hexadecane, and tetradecane (Figure 2 c). However, when the plasma-treated fabric was heated at 135 °C for 3 min, it restored its super-liquid-repellency (Figure 2 d), with contact angles of 171°, 155°, and 151° with water, hexadecane, and tetradecane, respectively. The treated fabric can maintain the superhydrophobicity even after 100 cycles of the plasma-and-heat treatment, suggesting excellent self-healing ability. However, the superoleophobicity changed with the plasma and heat cycles to a slightly larger extent compared with the superhydrophobicity. The contact angle with hexadecane was larger than 150° after 40 plasma and self-healing cycles (Figure 2 f). For tetradecane, the plasma-and-heat treatment only enabled the surface to maintain the oleophobicity with a contact angle below 150°, and 100 plasma-and-heat cycles led to a decrease of the contact angle from 152° to 136°. This finding indicates that the FD–POSS/FAS coated fabric has a reasonable self-healing ability to recover its oil-repellent state. Besides the heat treatment, the self-healing can also be performed repeatedly at room temperature simply by leaving the plasma-treated fabric for 24 h (see the Supporting Information).

Apart from plasma treatment, the coated fabric was also etched with strong acid and base solutions. Immersing the coated fabric in an aqueous KOH solution (pH 14) for 24 h resulted in reduction of the water and hexadecane contact angle, respectively, from 171° and 156° to 0° for both (Figure 3 a-1). When the KOH treated fabric was rinsed with water and heated at 135 °C for three minutes, the surface was restored to its original super-liquid repellent state (Figure 3 a-2), with water and hexadecane contact angles of 171° and 154°, respectively. Such self-healing action could be repeated several times (see the Supporting Information).

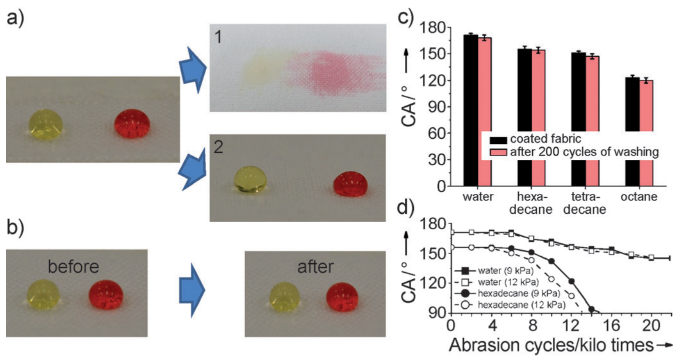

Figure 3. a) Photos of FD–POSS/FAS coated polyester fabric, 1) after 24 hr immersion in KOH solution (pH 14) and 2) the immersed fabric after rinsing with water and heating at 135 °C for 3 min; b) photos of FD–POSS/FAS coated polyester fabric before and after 24 hr immersion in H_2SO_4 solution (pH 1) and rinsing with water and drying in air at room temperature; c) CA of the FD–POSS/FAS coated polyester fabric before and after 200 cycles of machine wash, d) CA changes depending on the abrasion cycles.

When the coated fabric was immersed in an aqueous H_2SO_4 solution (pH 1) in the same period of time, however, the coated fabric showed no changes in water and hexadecane contact angles (Figure 3b). This result suggests that the coating is durable enough to resist acid attacks.

The UV stability was tested by short-distance irradiation of the coated fabric with a middle-pressure Hg lamp (450 W). After 24 h of irradiation, the fabric showed no changes in the super-liquid-repellency. For comparison, the uncoated fabric was also treated under the same condition. In just one hour of irradiation, the fabric turned hydrophilic with a water contact angle close to 0°.

The washing and abrasion durability was also studied. After 200 cycles of standard machine laundry, the coated fabric was found to still maintain the superhydrophobicity and superoleophobicity (Figure 3c). The abrasion durability was evaluated by the Martindale method using untreated fabric to simulate actual damage. During the test, 9 kPa and 12 kPa of pressure were employed, which are typically used for evaluating the coated fabrics for apparel and heavy duty upholstery usages, respectively. Figure 3d shows the change of the contact angle with the abrasion cycles. The coated fabric can withstand at least 6000 cycles of abrasion damages without changing its super-repellent feature. More abrasion cycles led to a decrease in both water and oil repellency. Such a durable coating with self-healing super-liquid-repellent surface can also be formed on other fibrous materials such as cotton and wool.

It should be noted that FD–POSS has been used with a thermoplastic elastomeric binder (Tecnoflon, BR9151) for developing oleophobic fabrics, and a hydrochlorofluorocarbon (Asahiklin AK-225) was used as solvent for preparation of the coating solution.[14] However, no self-healing liquid-repellent property was reported. In our work, FD–POSS and FAS were used as the coating material, and ethanol, a commonly used environmentally friendly solvent, was used as solvent. The finding that FD–POSS is soluble in FAS is also the first of its kind, which can be presumably attributed to the strong affinity of the fluorinated alkyl chains between the two chemicals. The formation of a stable FD–POSS/FAS suspension in ethanol could derive from the high polarity of the oxysilane group in FAS.

It was also observed that dissolving FD–POSS to FAS formed a clear viscous solution. However, after dispersion in ethanol for a certain period of time, the solution changed to a semisolid. Drying and heating it at 135 °C for 30 min resulted in a waxy resin. The FTIR analysis confirmed that the FAS in the FD–POSS/FAS blend after the coating treatments hydrolyzed into a silica structure (see the Supporting Information). The coating is a hydrolyzed FAS network with FD–POSS molecules embedded.

Heat treatment of the coating layer resulted in surface morphological changes. AFM images of the coating showed a rough surface and the surface became rougher after heat treatment (see the Supporting Information). The rough fiber surface formed by the FD–POSS/FAS coating, plus the inherent texture structure of fabric could be an important reason for the coated fabric to show super-liquid-repellent properties. The FD–POSS molecule comprises eight fluorinated decyl groups including 136 fluorine atoms surrounding the POSS cage, making the molecule extremely low in surface free energy. The FAS also has fluorinated alkyl chains, which are often used for hydrophobic surface treatments. FD–POSS with hydrolyzed FAS contributes to a low free-energy surface.

According to these results, the self-healing mechanism of the FD–POSS/FAS coating was proposed. Upon damaging the surface chemically, polar groups were normally introduced, resulting in reduced surface hydrophobicity/oleophobicity and increased surface free energy. Heating the coating layer increased the mobility of the FD–POSS molecules. As a result of molecular rotation and movement, the polar groups introduced tended to be hidden inside the coating layer, and more fluorinated alkyl chains were exposed to the surface, minimizing the surface free energy. The molecular rotation and movement could also take place at a lower temperature (e.g. room temperature) because of the low T_g (see the Supporting Information). Since the FD–POSS molecules are surrounded by hydrolyzed FAS resin, their movement is restricted considerably. As a result, the coating is stable even at the melting state. The eight flexible fluorinated alkyl chains of the FD–POSS molecule function to lubricate the molecule rotation, while the large POSS cage hinders the movement of FD–POSS molecules during melting.

In summary, we have demonstrated that fabrics coated with hydrolyzed FAS containing well-dispersed FD–POSS have a remarkable self-healing super-liquid-repellent surface with excellent durability against UV, acid exposure, repeated machine washes, and severe abrasion. Such a functional coating may be useful for the development of innovative protective clothing for various applications.

Received: July 20, 2011
Published online: October 11, 2011

Keywords: coatings · fabrics · hydrophobic effect · self-healing

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