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SHORT COMMUNICATION

Fabricating superhydrophobic surfaces by molecular accumulation of polysiloxane on the wool textile finishing

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Abstract In the present study, a novel and simple method of obtaining superhydrophobic surface through the migration of organic siloxane segments in the acrylate side chains to the outmost layer and forming the nano-protuberance on the micro-roughness wool fabrics was described. The chemical compositions and morphologies of the untreated/treated fabrics were characterized by the scanning electron microscopy and X-ray photoelectric energy spectroscopy. Meanwhile, the surface hydrophobicity was evaluated by the static contact angle measurement. The scanning electron microscopy photographs showed that the fiber surfaces of the treated fabrics were obviously granulated, and a wax film covered on the fibers could be observed. X-ray photoelectron spectroscopy analyses and static contact angle measurement further testified that the component of the wax was almost siloxane and that the surfaces of the treated fabrics had superhydrophobic property. The above results indicated that this method could be extended to prepare superhydrophobic surfaces by migrating the low-surface-energy matter and fabricating the nanoscale roughness on the micro-roughness material surfaces.

Keywords Polysiloxane · Wool · Fiber · Migration · Superhydrophobic surface

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Introduction

In the past few years, superhydrophobic surfaces, i.e., surfaces with a water contact angle (WCA) more than 150°, have aroused considerable attention among researchers because of its great potential in a wide range of practical applications [1]. An excellent water repellency property usually derives from the specific chemical composition, the suitable microstructure, and the morphology of the solid-phase surfaces [2, 3]. So far, considerable attempts in trying to synthesize novel materials with lower surface energy and higher contact angle have been made. Among them, an effective way is to incorporate hydrophobic compositions such as organic silicon and organic fluorine into the synthesized materials [4–6]. By adopting such methods, the contact angle of the resultant surface could usually reach as high as 120°. However, for conventional technologies, there still exist great difficulties in reaching a higher value of WCA. With the fast development of nanotechnology, it has been possible to fabricate the superhydrophobic surfaces from the microcosmic scale by the diverse techniques including the sol–gel method [7], self-assembly [8, 9], plasma treatments [10, 11], template-based extrusion method [12], laser etching [13], etc. Nevertheless, these methods usually require special equipments or stringent conditions.

In this study, a novel, simple, and economical method of obtaining a superhydrophobic surface (CA=168.5°) on the wool textile finishing was, for the first time, put forward. This could be achieved by devising a comb-like polymer comprising acrylate and organic siloxane because the combination of acrylate and organic siloxane could exhibit some unique characteristics: First, the acrylate polymer chains could contribute to the increase of the cohesiveness and film-forming properties; Second, the long Si–O–Si chains, characterized by their low surface energy [14, 15], could be utilized to enhance the water repellency; What is more, the Si–O–Si chains could immigrate towards the surface of the outer layers [16, 17], resulting in forming a surface with roughness in nanosize scale.

To achieve this goal, the poly(acrylate-*g*-siloxane) was prepared by emulsion copolymerization of acrylate with silicone oligomers containing a double bond. After being treated with the resulting emulsion, the wool textile finishing could exhibit excellent superhydrophobicity. Scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), as well as static contact angle measurement, were adopted in characterizing the untreated/treated fabrics.

Experimental sections

Materials

Butyl acrylate (BA) and methyl methacrylate (MMA) obtained from Xilong Chemical (China) were distilled under reduced pressure for further use. Silicone oligomers containing a double bond were prepared in our lab. Dodecylbenzene sulfonic acid (DBSA) was used as catalyst and surfactant for D_4 polymerization. Sorbiten monolaurate (Span20) and ammonium persulfate (APS) were both of analytical grade and were used directly.

Preparation of poly(acrylate-*g*-siloxane)

The poly(acrylate-*g*-siloxane) was prepared by emulsion copolymerization of acrylate with the silicone oligomers containing a double bond (SiDA). The polymerization was conducted in a 150-ml four-necked flask equipped with mechanical stirrer, thermometer, reflux condenser, and inlet of nitrogen. Typically, the preparation operation consisted of two steps. First, 55 g deionized water, 0.5 g DBSA, 0.5 g Span20, 6 g MMA, 6 g BA, and 0.5 g siloxane oligomers were simultaneously added into the flask. After deairing with nitrogen for 30 min, the 10 g deionized water dissolving 0.05 g initiator APS was added into the reactants at 50 °C. Then, the polymerization was conducted at 80 °C for 20 min until the autoacceleration process finished. Second, the residual monomers comprising 18 g MMA, 18 g BA and 1.5 g siloxane oligomers, and 10 ml initiator solution containing 0.05 g APS were slowly dropped into

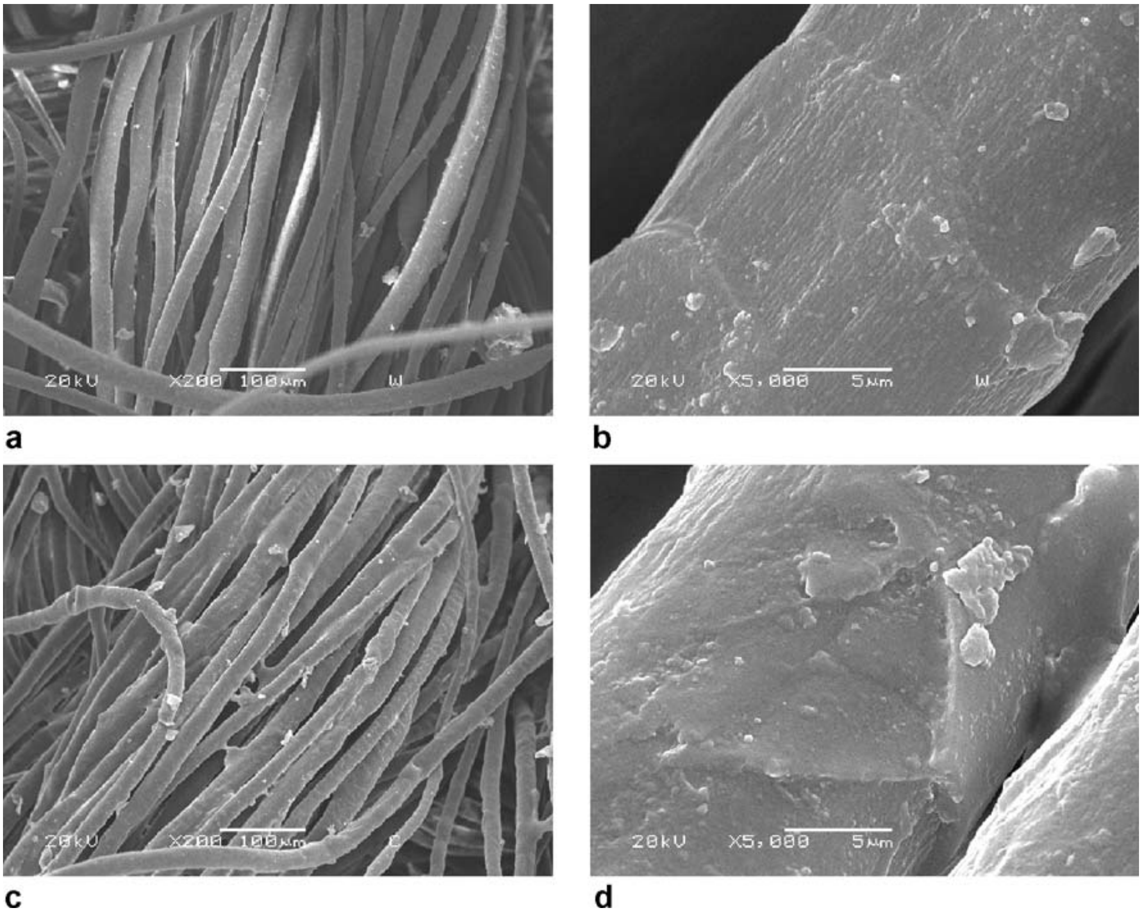


Fig. 1 SEM images of woolen fibers before (**a**, **b**) and after (**c**, **d**) treated by polydimethylsiloxane (*PDMS*)–acrylate emulsion

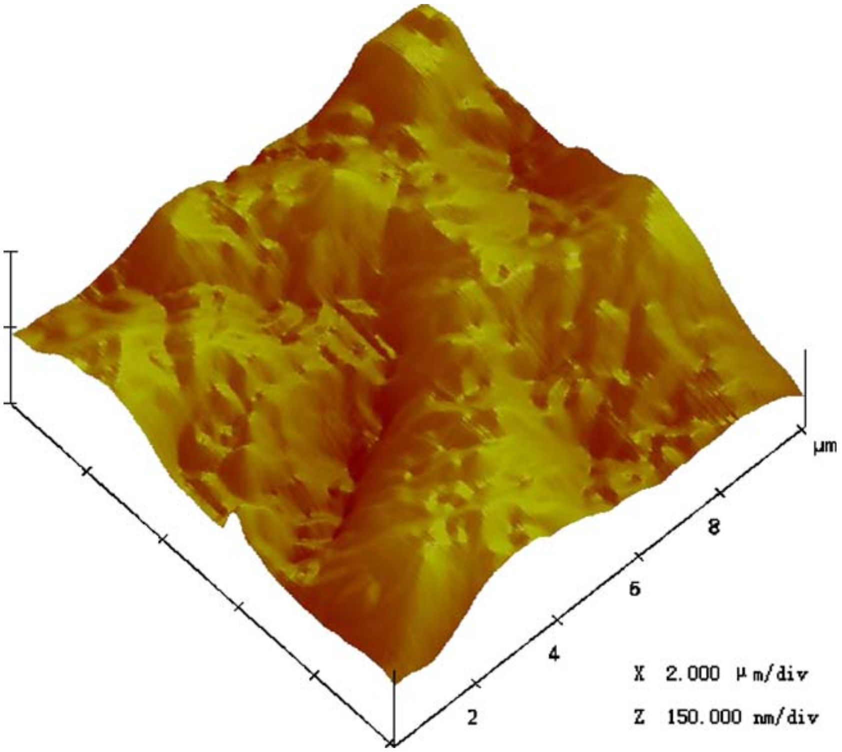


Fig. 2 AFM topography mapping images of PDMS–acrylate film

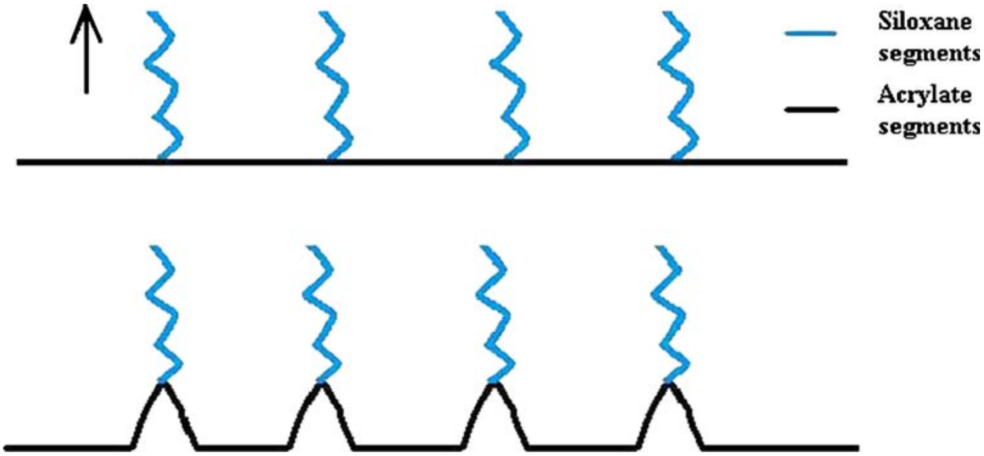
the reaction system within 2 h, respectively. Afterwards, the reaction was conducted at the same temperature for another 6 h. After the reaction finished, the resulting emulsion was treated with aqueous ammonia to adjust the pH value 6–7.

Fabrication of superhydrophobic surface

A pierce of square wool textile finishing (25 cm^2) was purified by washing with water and drying before it was immersed in the resultant emulsion for 10 min. Then, this textile was taken out and placed into a vacuum drier at 60 °C under reduced pressure for 24 h so that a clean and dried textile could be obtained.

Characterization of the treated textile

SEM (JEOL JSM-5900LV, Japan) was used to observe the morphology of the surface of the textile before and after treatment. Besides, AFM (NanoScope III, Multimodemicroscope, Digital Instruments, Santa Barbara, CA, USA) was used under non-contact tapping mode to observe the surface's topography and roughness. In the measurement, the ultra-sharp silicon cantilever with the length of 125 μm was used, and the resonance frequency was set at 3/4 325 kHz. All measurements were performed in ambient air conditions. The tip height was 15–20 μm with a nominal radius of curvature of <10 nm. Quantitative measurements



Scheme 1 Schematic representation of the formation of surface enrichment

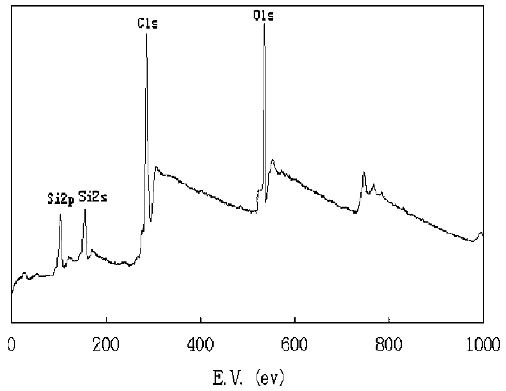


Fig. 3 X-ray photoelectron spectra of the treated fabrics

of the local root mean square of the surface roughness, which defines the height fluctuations in a given area, were determined from the 5×5-μm^2 and 10×10-μm^2 scans using the software provided by the manufacturer. Chemical composition of the surface layer was determined by X-Ray photoelectron spectrometer using Al Kα radiation (AXIS Ultra DLD XPS, Kratos Analytical, England). To measure the hydrophobicity of polymer surfaces, the measurement of static contact angle was performed by the sessile drop technique on an optical contact angle goniometer (ERMAG-1, Japan). For each measurement of contact angle, parallel testing was repeated for at least three times.

Results and discussion

SEM was used to observe the surface characteristics of untreated/treated textiles, and the images were shown in Fig. 1. As could be seen, the average diameter of woolen fibers was in the range of 10 to 40 μm, so it should possess comparatively high water repellency because of the microstructure[1, 18], but the composition of woolen fibers was made up of protein which could absorb water easily. Although the outer surface was covered by epicuticle, which could produce some effect on water repellency, the disposal to the woolen fibers like alkali, chlorination, and amine treatments usually destroyed the outer layer and altered the capability of water repellency [19].

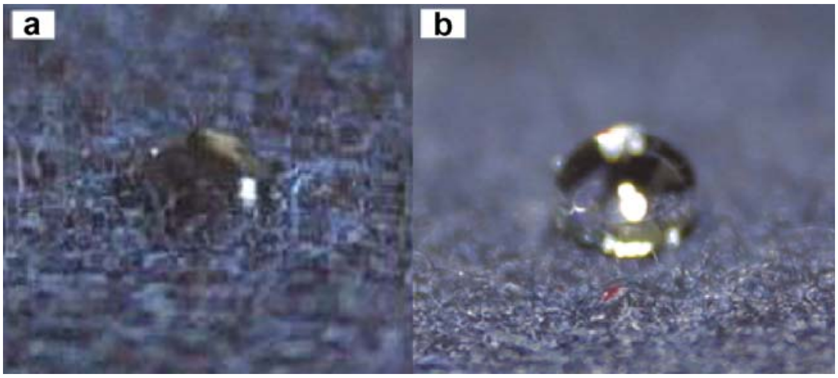
The images of woolen fabrics before and after treatment by the poly(acrylate-*g*-siloxane) emulsion were shown in Fig. 1. It could be seen that the surfaces of fibres in (a) is slippier than that of in (c). Besides, after the treatment, some of the fibers were felted each other, which could make the surface connected more enclosed and prevent the penetration of water. For further observation, the image was zoomed 5000 times. There were some of regular thin stripes on the surface of untreated fibers (b). Just because of the regular thin stripes, the water drop would spread on the surface. It is well known that surface with a certain extent of roughness usually could gain strong water repellency [18, 20], so, we wish that the treatment would alter the surface roughness so as to create hydrophobic surface.

From Fig. 1d, the regular thin stripes disappeared; some ceraceous matter appeared and tightly enwrapped the fibers, which was likely caused by acrylate-*g*-siloxane polymer. The backbone of fibers was connected with polyacrylate and polysiloxane segments due to the low surface energy and high flexibility and could migrate to the outmost surface [16, 17], resulting in the formation of irregular ceraceous matter with nanostructure. The refined surface morphology was further observed by AFM. As shown in Fig. 2, the surface was comparatively rough, and the average roughness approached 49.62 nm. Thus, the surface with low energy and nano-microstructure [1] could be obtained. Moreover, along with the siloxane segments migration, simultaneously, it would drive the peripheral part of acrylate chain units to move to the outer layer. The schematic formation was shown in Scheme 1.

To further confirm this suppose, the surface composition and wetting behavior of treated woolen fabrics were measured by X-ray photoelectron spectra and static contact angle method, respectively. The results were shown in Figs. 3 and 4.

The XPS result of poly(acrylate-*g*-siloxane) was displayed on Fig. 3. The characteristic peak of Si 2s and Si 2p in Fig. 2 manifested that the presence of Si element on the surface of the fibers was evident, that is to say, the siloxane segments

Fig. 4 Water contact angle of woolen fibers before (**a**) and after (**b**) immersed treatment by poly(acrylate-*g*-siloxane) emulsion



had migrated on the outermost surface [16, 21, 22]. It could be seen that only carbon, oxygen, and silane elements were observed, and the experimental composition (C/Si=3.58) was very close to the theoretical value of the siloxaned macromonomer (2.73), but was less than the theoretical value (34.04) of all monomer (macromonomer 5 wt% and acrylate 95 wt%). This also indicated that the siloxane segments had fully covered the external surface of the fabrics.

Figure 4 showed the water contact angle pictures of woolen fabrics before and after treatment. When the water drop was dripped on the untreated fabrics surface, it would vanish rapidly because of the strong water absorption of fabrics. Whereas, the water drop displayed a large contact angle (168.5°) on the treated sample, which testified that the superhydrophobic surface has been created.

Conclusions

The low-surface-energy surface with micron and nanosize binary structures have been successfully fabricated based on the molecular design and the migration of the siloxane segments. With acrylate-*g*-siloxane polymer covered on the surface of woolen fibers, the surface manifested strong water repellency, and the contact angle could reach as high as 168.5°. It was the first attempt in utilizing the movable polymeric segments to create a superhydrophobic surface.

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