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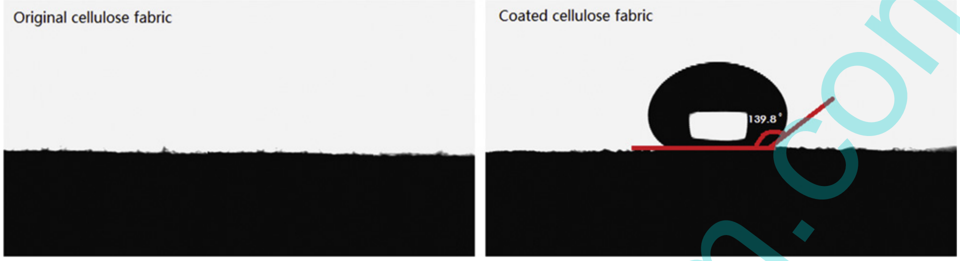
Water-repellent functional coatings through hybrid SiO_2/HTEOS/CPTS sol on the surfaces of cellulose fibers

Yunjie Yin, Chaoxia Wang*

Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University, 1800 Lihu Road Wuxi, 214122, China

GRAPHICAL ABSTRACT



HIGHLIGHTS

- ► A water-repellent coating is deposited from a hybrid SiO_2/HTEOS/CPTS sol.
- ► The contact angles of water on the coated fabric are improved.
- ► The breaking strengths of the coated fabric are increased.
- ► The droplet shapes analysis indicates the water repellent is universal.

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ABSTRACT

A water-repellent functional hybrid coating is deposited on the surfaces of cellulose substrates from a hybrid SiO_2/HTEOS/CPTS sol prepared by acid-catalyzed hydrolytic co-polycondensation of tetraethoxysilane (TEOS), γ-chloropropyltriethoxysilane (CPTS) and hexadecyltrimethoxysilane (HTEOS). The contract angles of water on the fabric coated with hybrid SiO_2/HTEOS/CPTS sol are improved to 139.8°, and the enhancement are mainly achieved by the combination of low surface energy chemical compositions (HTEOP and CPTS) and rough surface geometrical structure which is demonstrated by Atomic force microscopy (AFM) and Scanning electron microscope (SEM). The hydrostatic pressure analysis confirms that the hydrostatic pressure of fabric coated with hybrid SiO_2/HTEOS/CPTS sol is 4.1 kPa, which is significantly higher than that of the control sample (1.7 kPa). The droplet shapes analysis indicates that the water repellent of the fabric sample is universal. The breaking strengths of the fabric coated with hybrid SiO_2/HTEOS/CPTS sol are increased 3.4% in the warp direction and 15.4% in the weft direction comparing to that of the untreated sample, respectively. Whereas, the elongation rates of in the warp direction and weft direction are decreased by 5.6% and 7.7%, respectively.

1. Introduction

Hydrophobic and water-repellent coatings derived have been investigated in recent years because of their high commercial and

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* Corresponding author. Tel.: +86 0510 85912105; fax: +86 0510 85912105.
E-mail address: wangchaoxia@sohu.com (C. Wang).

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industrial importance [1–3]. As a significant property, wetting plays an important role in many natural and technological processes. Cellulose fiber, for example cotton, is intensely hydrophilic for massive hydroxyl groups, and the water-repellent behavior of the fiber surfaces is one of the most important characteristics in both theoretical research and industrial applications [4–6]. The wettability of liquid to fiber surface is governed by the chemical properties of fiber surface and its surface morphology.

Due to this broad range of benefits, many attempts to understand and manufacture water-repellent surfaces have been spent. Hence, many approaches, such as sol–gel method, lithographic patterning, phase separation, layer-by-layer assembly technique, and glancing angle deposition have been developed for the design and fabrication of hydrophobic surfaces [7–9]. Gashti [10] embedded hydrophobic silica nano-particles on the cotton surface using 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinking agent and sodium hypophosphite as a catalyst to increase the contact angle to 132.4°, and also showed a good thermal stability. Andou [11] reported a simple method to produce a hydrophobic surface created by continual vapor-phase-assisted surface photopolymerization (photo-VASP) of 2,2,3,3,3-pentafluoropropylmethacrylate (FMA), The cellulose fibers coated by the thin polymer layer retained their original tactile nature and demonstrated superior water repellency, with a controlled static contact angle >130°. Shen et al. reported that cotton fabrics were treated by plasma in hexafluoropropene (C_3F_6) atmosphere under different experimental conditions. Cotton fabrics after plasma treatments for 1 min, contact angles could reach 120° or higher while wet-out time could be as high as 60 min. Among these approaches, the sol–gel method has been found to be a simple and effective technique for depositing water-repellent coatings onto substrates. Moreover, it gives rise to advantages such as large deposition areas, uniform deposits on the objects with desired shapes, and short processing times.

To make the silica coating hydrophobic, some organic materials are applied to the inorganic sol matrix in such a manner that the surface behaves as a repellent toward water, i.e. the water droplets tend to contract and forms nearly spherical pearl on the modified silica surface [12–16]. The treatment of textiles with inorganic/organic sols opens numerous new possibilities for the improvement of their applicative properties and the functional properties of the fiber surface. Combining chemical and physical modification offers unlimited potential for the development and application of inorganic sol coatings that can be used for the functional textiles, including improved stability against mechanical or thermal destruction, improved water, oil and soil repellence, and so on [17–20]. Silica coupling agents have been widely used as structural units to construct a variety of silica based hybrid materials. After doped into the matrix sol, the functional properties of silica coupling agent are presented on the surface of sol–gel hybrids coating [21–25].

In a previous work [26], the authors prepared a functional sol, which could enhance the anti-ultraviolet, anti-bacterial properties on cellulose fibers. In this study, the authors concern to prepare a water-repellent fabric via coating hybrid SiO_2/HTEOS/CPTS sol. The contract angle and hydrostatic pressure properties are examined. The mechanical properties and the surface morphology of the fibers are analyzed in detail.

2. Experimental

2.1. Materials

The cellulose fabric-poplin 100% cotton woven fabric weighting 141.0 g m^{-2} was used, which was produced by Jiangsu Hongdou Industrial Co., Ltd. (China). The hexadecyltrimethoxysilane (HTEOS, Mw 346.62) was gained from Jiangsu Zhangjiagang Guotai-Huarong New Chemical Materials Co. Ltd. (China). The γ-chloropropyltriethoxysilane (CPTS, Mw 240.79) was offered by Hubei Jianghan Chemical Co., Ltd. (China). The tetraethoxysilane (TEOS, M.W. 208.33), tetrabutyl titanate (TBT, M.W. 340.36), ethyl alcohol (EtOH) (95%), sodium chloride, sodium carbonate and HCl (37%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). All the chemicals are analytically pure.

2.2. Preparation of the hybrid SiO_2/HTEOS/CPTS Sol

The hybrid SiO_2/HTEOS/CPTS sols were prepared via acidic hydrolysis of TEOS solved in a mixture of ethanol (95%) and deionized water. The hydrolysis was performed by stirring a mixture of 1 mol TEOS, and 8 mol ethanol; the molar ratio of the TEOS and H_2O was 1: 5 at 25 °C temperature. 0.027 mol L^{-1} γ-chloropropyltriethoxysilane (CPTS) was added into the solution. Then 4 wt% hydrophobic additives HTEOS was added to the above sol. The pH value was adjusted to 2.69 with HCl (1 mol L^{-1}, approximately 0.80 mL). The sol was obtained after stirred at 65 °C for 6 h and aged for 24 h [27,28].

2.3. Treatment of the cellulose fibers

The fabrics were submersed into the hybrid SiO_2/HTEOS/CPTS sol for 5 min and padded two times with a P-130 padder produced by Taiwan Rapid Co., Ltd. at the room temperature. The wet pick-up, which is the ratio of the weighting increment of solution after padding and the original weight of the fabric, was 75%. Then the fabrics were dried at 90 °C for 20 min and baked at 160 °C for 2 min with an appropriate tension in a curing oven (Mini Thermo 350, Thermo Co. Ltd. USA) [26,29].

2.4. Surface tension and contact angle measurement

The surface tension was measured by Wilhelmy Plate method and Du Noüy Ring method using the KRÜSS DSA100 Drop Shape Analysis System (KRÜSS GmbH, Germany) at 18 °C. The surface tension was recorded when the water drop is the largest below the sample pinhole.

The contact angle of water and the wetting time were measured also using the KRÜSS DSA100 Drop Shape Analysis System. The contact angle values were recorded after 3 s when the water drop began to still on the cellulose matrixes. A water drop was recorded every 10 min, and when the contact angle was 0°, the recorded time just was the wetting time. The experiments were carried out under ambient conditions. The temperature (18 °C) and the relative humidity (40%) of the environment were kept constant [28].

2.5. Hydrostatic pressure measurement

The hydrostatic pressure reflects the water repellent and hydrophobicity of matrix. With lower surface free energy and thicker deposition, matrix has a larger hydrostatic pressure. According to AATCC-127-2008, treated fabric matrix (17 cm × 17 cm) is conditioned at 25 °C and 65% relative humidity for 4 h. The relative height of the water column is recorded when the water exudes in three different places from the matrix. The pressure is equal to the relative height of the water column. The hydrostatic pressure values is obtained by the formula,

$$P(\mathrm{Pa}) = \rho g h \qquad (1)$$

where h is the height of hydrostatic pressure (m); ρ is the density of H_2O, and usually it is 1.0×10^3 kg m^{-3}; g is the acceleration of gravity (m s^{-2}), and the value of the acceleration of gravity is most accurately known as 9.8 m s^{-2}. Five pressure readings are taken from each fabric matrix and the mean value is recorded.

2.6. Tensile strength and elongation measurements

According to ISO 13934-1:1999, the fabrics were conditioned at 20 °C and 65% R.H. for 24 h prior to testing on the machine YG (B) supplied by Wenzhou Darong Textile Instrument Co., Ltd. The tensile strengths and elongations were averaged of three measurements in the weft and warp direction, respectively.

2.7. Droplet shape analysis

Some liquid droplets were dropped onto the fabric sample coated with hybrid SiO_2/HTEOS/CPTS sol, the droplet shapes from front and top directions were recorded by a digital camera. The relation of surface tension and the droplet shape was discussed.

2.8. Atomic force microscopy measurement

The topography of the hybrid coating on mica sheet was investigated by atomic force microscopy (AFM) at 25 °C and 40% relative humidity using a CSPM4000 AFM made by Benyuan Co., Ltd. (China) operating in contact mode. The tip is slowly scanned across the surface of the hybrid coatings. The force between the atoms on the surface of the scanned material and those on the scanning tip lead to the tip to deflect. This deflection is recorded by using a laser focused on the top of the cantilever and reflected onto photodetector. The photodetector signals are used to map the surface characteristics of specimens with resolutions down to the nanoscale.

2.9. Scanning electron microscope measurement

The scanning electron microscope (SEM) photographs of coated matrix were tested by a JSM-5610 scanning electron micro-scope (JEOL Ltd., Tokyo, Japan) under 5000× magnifications. The cellulose matrixes were dehydrated and dried, and then deposited with gold coating in a sputtering unit at a current of 10 mA.

3. Results and discussion

3.1. Contract angle of water properties

Original cellulose fiber is hydrophilic for massive hydroxyl groups on the surface of fibers, and water droplet placed on the surface of cellulose fabric sinks completely into the fabric in 3 seconds as shown in Fig. 1a. However, the surface of a treated cellulose fabric nearly supports the formation of spherical water droplets (Fig. 1b). The contact angle increases to 139.8° and is larger than the threshold 90°, which indicates the cellulose fabric is hydrophobic. The contact angle is higher than that coated by hybrid SiO_2/HTEOS sol (131.4°) or SiO_2/CPTS sol (128.5°). The changes of the wetting property are related to the chemical component of the fiber surface. Via dehydrating and condensation reactions, the Si—O—Si chains are deposited on the surface of cellulose fabric and much hydroxyl groups on the surfaces of cellulose fabric are enclosed by the hybrid coating. The residual components $CH_3(CH_2)_{15}$— and γ-$(CH_2)_3$— are hydrophobic, and will continue to improve the hydrophobic property of the fabric samples. As the coating components: Si—O—Si, and γ-$(CH_2)_3$— in hybrid coating can improve the hydrophobicity, the contact angle of fiber coated with hybrid SiO2/HTEOS sol is remarkable.

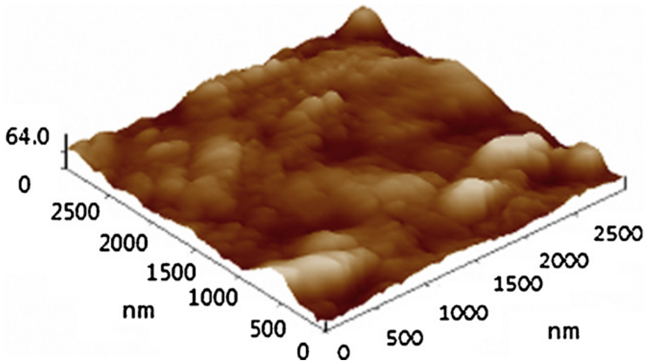

Fig. 2. The AFM image of cellulose fiber surface coated with the hybrid SiO_2/HTEOS/CPTS sol.

From Fig. 2, the micro-surface coated with hybrid SiO_2/HTEOS/CPTS sol on mica sheet is relatively scraggy and some weak peaks are displayed. By the Imager Statistical Analysis Software, the mean roughness is 16.4 nm and the root mean square is 21.1 nm. For fabric surface is a rough surface, according to Wenzel model,

$$\cos\theta^* = r\cos\theta_e \tag{2}$$

where θ^* is the apparent contact angle of the fabric sample which corresponds to the stable equilibrium state. The roughness ratio is defined as the ratio of true area of the fabric surface to the apparent area of the ideal smooth surface and $r \geq 1$. θ_e is the Young contact angle as defined for an ideal smooth surface. When a substance surface is hydrophobic, and $90° < \theta_e < 180°$, so $\cos\theta^* < \cos\theta_e$, then $\theta^* > \theta_e$, which indicates that a larger roughness of a fabric surface can improve the hydrophobicity on a hydrophobic fabric surface [28,30]. According to Eq. (2), the surface free energy, which is determined by the surface hydrophobic groups, such as $CH_3(CH_2)_{15}$—and γ-$(CH_2)_3$—, will affect the θ_e, and the r is roughness, so the effects of the two factors to wettability also can be analyzed by Eq. (2).

3.2. Contact angle property

During the measuring process, a water droplet was placed on the cellulose fabric coated with hybrid SiO_2/HTEOS/CPTS sol. As the evaporating action, the size and contact angle of the water

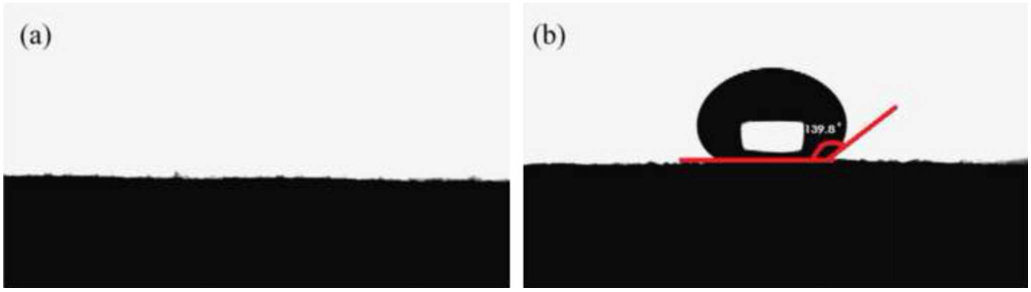

Fig. 1. The contract angles of water on the original cellulose fabric (a) and fabrics coated with hybrid SiO_2/HTEOS/CPTS sol (b).

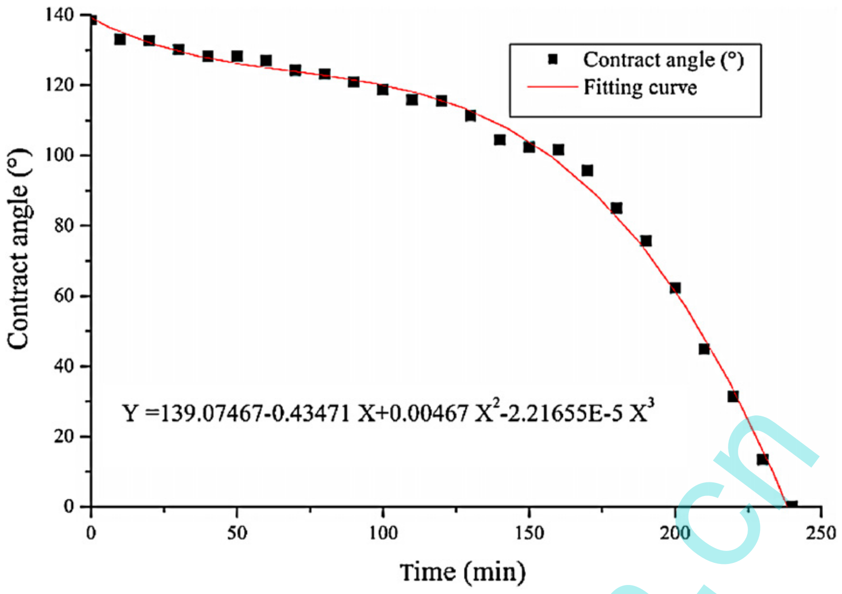

Fig. 3. Contract angles of water on the fabric coated with hybrid SiO_2/HTEOS/CPTS sol and its simulated functional equation.

droplet was changed. After approximately 240 min the contact angle decreased to 0° (Fig. 3). In this process, the decrease of contact angle is recorded every 10 min. According to the changes of the contract angle, a functional equation is simulated.

$$y = A + B1x + B2x^2 + B3x^3 \tag{3}$$

where y is contact angle (°), x is time (min); the parameter $A = 139.07467$, $B_1 = -0.43471$, $B_2 = 0.00467$ and $B_3 = -2.21655 \times 10^{-5}$. Other parameters are showed in Table 1.

From Table 1, the R-square of the fitted equation is 0.99664 and the reliability is high. The probability value is <0.0001, and smaller than the threshold 0.01, which indicates that the fitted equation is highly significant and the fitted result is credible.

3.3. Hydraulic pressure properties

Fig. 4 shows the hydrostatic pressures of the cellulose fabric coated with hybrid SiO_2/HTEOS/CPTS sol and the original fabric. It clearly indicates that the hydrostatic pressure of fabric coated with hybrid SiO_2/HTEOS/CPTS sol (4.1 kPa) is significantly higher than that of the control sample (1.7 kPa). The hybrid SiO_2/HTEOS/CPTS sol deposits coatings on the cellulose fiber, and the poriness among the fibers and yarns is decreased. The increased compactability and thickness of the cellulose fabric contribute to prevention the H_2O passing through the fabric. And the low surface free energy, aroused by silica and silica coupling agent, decreases the diffusivity of the H_2O on the fabric.

Table 1
Regression analysis.

Parameter	Value	Error
A	139.07467	1.68707
B_1	−0.43471	0.06214
B_2	0.00467	6.0893×10^{-4}
B_3	-2.21655×10^{-5}	1.66621×10^{-6}

R-square (COD)	Standard deviation	Number	Probability value
0.99664	2.43248	25	<0.0001

3.4. Droplet shape analysis

Some kinds of liquid droplets are dropped onto the fabric coated with hybrid SiO_2/HTEOS/CPTS sol. The sequence of the surface tensions about the liquids is H_2O (72.01 N m^{-1}) > rainwater (71.36 N m^{-1}) > tea water (70.43 N m^{-1}) > coke (66.16 N m^{-1}) > liquid soap (29.35 N m^{-1}). At the same conditions, the droplet sizes of the liquid droplets are in the order: deionized water > rainwater > tea water > coke > liquid soap. The spreadability is related to the surface tension, and a larger surface tension can result in a larger contract angle on the same substance. From Fig. 5a–e, all the contract angles of liquid droplets are larger than 90°, which indicates the water repellent of the fabric sample is universal. From Fig. 5a–e, the projected area of the liquids droplets is deionized water > rainwater > tea water > coke > liquid soap, which is consistent with the sequence of surface tension.

3.5. The tensile properties of cellulose fibers

From Table 2, the hybrid coating with hybrid SiO_2/HTEOS/CPTS sol affects the breaking strength and elongation rate evidently. The breaking strengths of the fabric coated with hybrid SiO_2/HTEOS/CPTS sol are increased 3.4% in the warp direction and

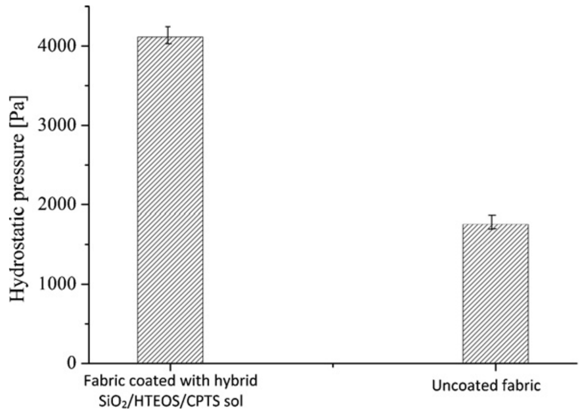

Fig. 4. The hydraulic pressure of the fabric coated with hybrid SiO_2/HTEOS/CPTS sol.

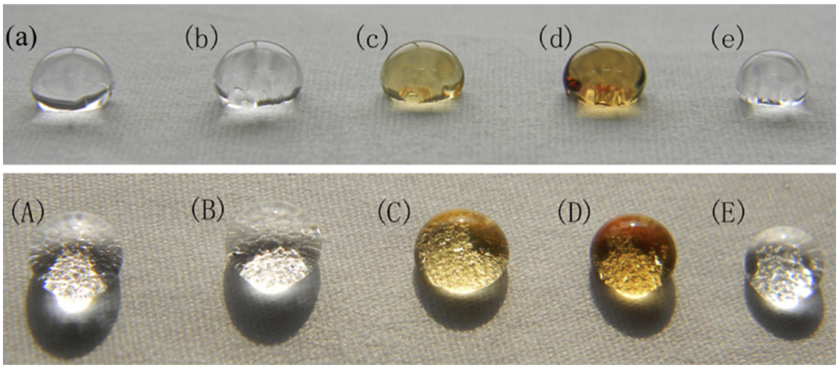

Fig. 5. The photos of the liquid droplets on fabric coated with hybrid SiO_2/HTEOS/CPTS sol: (a) deionized water, front view; (b) rainwater, front view; (c) tea, front view; (d) coke, front view; (e) liquid soap, front view; (A) deionized water, top view; (B) rainwater, top view; (C) tea, top view; (D) coke, top view; (E) liquid soap, top view.

Table 2
The tensile strength and elongation of cellulose fabrics.

Sample	Breaking strength (*N*)		Elongation rate (%)	
	Warp	Weft	Warp	Weft
Uncoated fabric	145	499	9	7.8
Fabric coated with hybrid SiO_2/HTEOS/CPTS sol	150	576	8.5	7.2

15.4% in the weft direction comparing to that of the untreated sample, respectively. During the process, the elongation rates are slightly decreased through the coating process, and the elongation rates of warp direction and weft direction are decreased by 5.6% and 7.7%, respectively. The reason for the breaking strength increase might be that although the weak acidic silica sol will affect slightly the structure of the cellulose (Fig. 6), the acidic SiO_2 is of chain structure and three-dimensional network is complete, so the acidic silica hybrid coating on the surface of the cellulose fiber increases the fiber strength. Moreover, the coated fibers can combine through the silica coating, and the fiber segments do not easily slide, which can increase the breaking strength of the cellulose yarns. The combination of the fiber segments via coatings will affect slightly the flexibility and slide. However, changes of the elongation rats are small and will not affect the natural use.

3.6. SEM analysis

The surface of the original cellulose fiber is smooth and reveals indistinctly natural grooves and characteristic parallel ridges (Fig. 7a), nevertheless after treated with hybrid SiO_2/HTEOS/CPTS sol, such characteristic surface features are nearly less visible and dense silica nanoparticles hybrid coating appears on the surface of

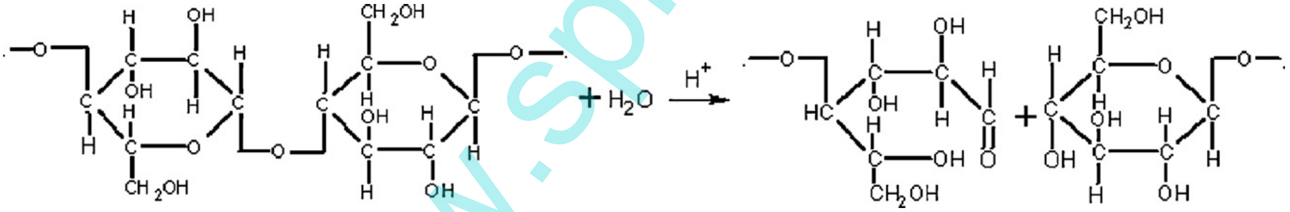

Fig. 6. Cellulose hydrolysis reaction.

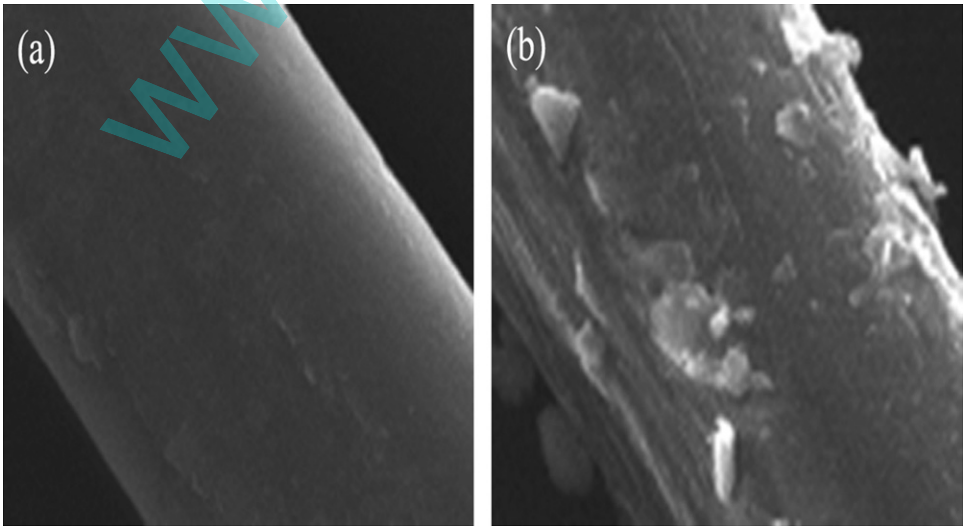

Fig. 7. SEM images of original cellulose fiber (a) and coated cellulose fiber with hybrid SiO_2/HTEOS/CPTS sol (b).

the cellulose fabric (Fig. 7b) [31]. The modified silica nanoparticles bring to a rough micro-surface (Fig. 2). Although the gap between fibers is slightly decreased according to Cassie model, which does not benefit wettability, the rough hybrid coating with a low surface free energy brings good hydrophobic property and benefits to the water repellency.

4. Conclusion

The interaction of sol–gel derived hybrid coatings and the cellulose fabrics are studied by analyzing the water-repellent and other properties. After hybrid SiO_2/HTEOS/CPTS sol coating, the contract angle of water can increase to 139.8°, and the water repellent properties are universal. The hydrostatic pressure of fabric coated with hybrid SiO_2/HTEOS/CPTS sol can increase significantly to 4.1 kPa from 1.7 kPa of the control sample without hybrid coating. Such properties are achieved by the combination of surface geometrical structure and low surface energy chemical compositions. The hybrid coating improves the breaking strengths of the fabric (about 3.4% and 15.4% in the warp direction and weft direction comparing to that of the untreated sample, respectively). The rough conditions of the hybrid coating on the cotton fiber are verified by AFM and SEM, which can further explain the improvement of the water repellence.

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