Surface modification of cotton by tetraethylorthosilicate and tetrabutyltitanate

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Abstract

To obtain the hydrophobic water repellant characteristics, cotton fabrics were treated by the following seven combinations: TEOS_SA, TEOS_Cl-TMOS, TEOS+Cl-TMOS, TBOT_SA, TBOT_Cl-TMOS, TBOT_SA (50 °C) and TBOT_Cl-TMOS (50 °C). The hydrophobicity of the treated cotton fabrics was tested by dropping a small droplet (0.05 mL) of water on the surfaces. It was found that the water droplet was stable longer than 2 hours in the case of cottons coated by TEOS+Cl-TMOS, TBOT_SA, TBOT_Cl-TMOS, TBOT_SA (50 °C) and TBOT_Cl-TMOS (50 °C). However only cottons treated by TBOT_SA, TBOT_Cl-TMOS and TBOT_Cl-TMOS (50 °C) retained their hydrophobicity after being washed by detergent. The contact angles of these cotton samples were measured. It was found that the best coating solution to give highly hydrophobic cotton was TBOT_Cl-TMOS (50 °C). Raising the temperature of the TBOT solution may increase the rate of the hydrolysis and condensation processes on the cotton surface. Moreover the hydrophobization process using Cl-TMOS solution at 50°C may increase the bond formation between hydroxyl groups of TiO_2 surface and methoxide groups of Cl-TMOS.

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Introduction

Since the discovery of the lotus effect (Barthlott *et al*., 1997; Neinhuis *et al*. 1997; Otten *et al.* 2004), hydrophobic surfaces have received great attention because of their wide range of applications such as frictionless flow water pipes (Watanabe *et al*., 2001), hydrophobic treatment on vehicle windshields (Shang *et al*., 2005) and hydrophobic fabrics (Hsieh *et al*., 2008).

Recently, as markets in leisure and outdoor sport textiles have been expanded, the needs for hydrophobic fabrics have increased. There have been some reports on the improvement of hydrophobic properties of several kinds of fabrics using nanostructures achieved by nanotechnology (Hsieh *et al*., 2008; Xu *et al*., 2008; Hoefnagels *et al*., 2007; Yu *et al*., 2007). Cotton has always been the principal clothing fabric due to its attractive characteristics such as softness, comfort, warmness, biodegradation and low cost. However the abundant water-absorbing hydroxyl groups on cotton surfaces make the fabrics absorbent and easily stained by liquid water.

Gold particles have been incorporated into cotton fabrics to induce a dual-size surface topology (Wang *et al*, 2007). Anyway, there is no chemical bond between the gold particles and cotton fiber. However, this method is quite expensive. The alternatives have been attempted by using silica and titania. A layer of silica on the surface of a regenerated cellulose fiber was grown *via* a sol-gel process (Hribernik, *et al*., 2007). Light weight cotton fabrics were modified with titania and titania-silica nanosol in order to improve UV radiation protection (Abidi *et al*., 2007).

In this work, hydrophobic cotton fabrics were prepared *via* sol gel coating of SiO_2 or TiO_2 by using tetraethylorthosilicate (TEOS) or tetrabutylorthotitanate (TBOT) as a precursor. The surface was subsequently hydrophobized by stearic acid (SA) or chloropropyltrimethoxysilane (Cl-TMOS). The hydrophobicity of the modified cotton fabrics before and after washing was examined by contact angle measurements and the time for a small water droplet being stable on the cotton surface.

Experimental

1. Preparation of TEOS solution

Solution A was prepared by adding 2.03 g (9.76 mmol) of TEOS into 3.42 mL of anhydrous ethanol with continuous stirring. Solution B was prepared by mixing 1.32 mL of distilled water, 3.42 mL of anhydrous ethanol and 0.16 mL of conc.NH_3. Solution A was slowly added into solution B. The reaction mixture was stirred for 24 h at room temperature to obtain a colorless TEOS solution.

2. Preparation of TEOS + Cl-TMOS solution

Solution A was prepared by consecutively mixing 8.11 g (39 mmol) of TEOS, 0.78 g (3.9 mmol) of Cl-TMOS and 3.42 mL of anhydrous ethanol. Solution B was prepared by mixing 1.32 mL of distilled water, 3.42 mL of anhydrous ethanol and 0.16 mL of conc.NH_3. Solution A was added slowly into solution B. The mixture was stirred for 24 h at room temperature to obtain a colorless TEOS + Cl-TMOS solution with 10:1 molar ratio of TEOS:Cl-TMOS. The similar method was used to prepare 4:1 of TEOS:Cl-TMOS by changing the mass of Cl-TMOS to 1.95 g (9.75 mmol).

3. Preparation of TBOT solution

Solution A was prepared by mixing 4.25 g (12.49 mmol) of TBOT, 1.25 g (12.49 mmol) of acetylacetone and 10 mL of anhydrous ethanol. Solution B was prepared by mixing 0.75 mL of distilled water, 10 mL of anhydrous ethanol and 2.5 mL of conc. CH_3COOH. Solution A was slowly added into solution B. The reaction mixture was stirred for 24 h at room temperature to obtain a TBOT solution.

4. Preparation of Stearic acid (SA) and Cl-TMOS solutions

Stearic acid solution: 0.5 g of stearic acid was dissolved in acetone and the volume was adjusted to 100 mL.

Cl-TMOS solution: 0.5 mL of Cl-TMOS was dissolved in chloroform and the volume was adjusted to 50 mL.

5. Surface modification of cotton fabrics

Thin and thick cotton fabrics were cut into 4 cm x 4 cm pieces. Five pieces of each thin and thick cotton fabrics were separately immersed in each of the following combinations:

1. TEOS solution for 10 min and followed by SA solution for 10, 20 and 30 min at room temperature to yield TEOS_SA (10 min), TEOS_SA (20 min) and TEOS_SA (30 min).

2. TEOS solution for 10 min and followed by Cl-TMOS solution for 10, 20 and 30 min at room temperature to yield TEOS_Cl-TMOS (10 min), TEOS_Cl-TMOS (20 min) and TEOS_Cl-TMOS (30 min).

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3. TEOS + Cl-TMOS solution (10:1 and 4:1) for 10, 20 and 30 min at room temperature to yield 10TEOS + Cl-TMOS (10 min), 10TEOS + Cl-TMOS (20 min), 10TEOS + Cl-TMOS (30 min) and 4TEOS + Cl-TMOS (10 min), 4TEOS + Cl-TMOS (20 min) and 4TEOS + Cl-TMOS (30 min))

4. TBOT solution for 10 min and followed by SA solution for 10 min at room temperature to yield TBOT_SA (10 min).

5. TBOT solution for 10 min and followed by Cl-TMOS solution for 10 min at room temperature to yield TBOT_Cl-TMOS (10 min).

6. TBOT solution for 10 min at 50 $^{\circ}$C and followed by SA solution for 10 min at 50°C to yield TBOT_SA (10 min, 50°C).

7. TBOT solution for 10 min at 50 $^{\circ}$C and followed by Cl-TMOS solution for 10 min at 50 $^{\circ}$C to yield TBOT_Cl-TMOS (10 min, 50°C).

6. Washing process

The washing liquid was prepared by mixing 0.50 mL of the commercial washing liquid with 49.5 mL of distilled water. Each coated cotton was immersed in 10.00 mL of freshly-prepared washing liquid for 10 min. Then it was washed twice in 10.00 mL of distilled water. Then the cotton was dried at room temperature.

7. Characterizations

The hydrophobicity of the modified cotton fabrics before and after washing was examined by contact angle measurements using Dataphysics Model PSL250 instrument and the time for a small water droplet being stable on the cotton surface.

Results and Discussion

All coated cottons, both thin and thick were prepared and tested with a small droplet of water (0.05 mL). The time for a small water droplet being stable on the cotton surface for each combination before washing was measured and tabulated in Tables 1-5.

Table 1 Time for a stable water droplet on the cotton coated by combination 1 (before washing)

Solution	Time for a stable water droplet	
	Thin cotton	Thick cotton
TEOS	0 s	20 s
TEOS_SA (10 min)	0 s	1 h 39 min
TEOS_SA (20 min)	9 min 35 s	1 h 6 min
TEOS_SA (30 min)	7 min 25 s	15 min 20 s

Table 2 Time for a stable water droplet on the cotton coated by combination 2 (before washing)

Solution	Time (s) for a stable water droplet	
	Thin cotton	Thick cotton
TEOS_Cl-TMOS (10 min)	0	8
TEOS_Cl-TMOS (20 min)	0	9
TEOS_Cl-TMOS (30 min)	0	9

Table 3 Time for a stable water droplet on the cotton coated by combination 3 (before washing)

Solution	Time (h) for a stable water droplet on	
	Thin cotton	Thick cotton
10TEOS+Cl-TMOS (10 min)	> 2	> 2
10TEOS+Cl-TMOS (20 min)	> 2	> 2
10TEOS_Cl-TMOS (30 min)	> 2	> 2
4TEOS+Cl-TMOS (10 min)	> 2	> 2
4TEOS+Cl-TMOS (20 min)	> 2	> 2
4TEOS+Cl-TMOS (30 min)	> 2	> 2

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Table 4 Time for a stable water droplet on the cotton coated by combinations 4 and 5 (before washing)

Combination	Solution	Time (h) for a stable water droplet	
		Thin cotton	Thick cotton
	TBOT	> 2	> 2
4	TBOT_SA (10 min)	> 2	> 2
5	TBOT_Cl-TMOS (10 min)	> 2	> 2

Table 5 Time for a stable water droplet on the cotton coated by combinations 6 and 7 (before washing)

Combination	Solution	Time (h) for a stable water droplet	
		Thin cotton	Thick cotton
	TBOT (50 ^{o}C)	> 2	> 2
6	TBOT_SA (10 min, 50 ^{o}C)	> 2	> 2
7	TBOT_Cl-TMOS (10 min, 50 ^{o}C)	> 2	> 2

According to the data in Tables 1-5, the effective coating solutions were combinations 3-7. The cottons coated by these combinations were further washed by dilute detergent solutions. Time for a stable water droplet on the washed cottons was measured and tabulated in Tables 6-8. After being washed by detergent, the coated cottons by combinations 4, 5 and 7 (yellow highlight in Tables 7-8) retained their high hydrophobicity (t > 50 min). These samples were selected for the contact angle measurement and the data are presented in Table 9.

Table 6 Time for a stable water droplet on the cotton coated by combination 3 (after washing)

Solution	Time (s)for a stable water droplet	
	Thin	Thick
10TEOS+Cl-TMOS (10 min)	0	0
10TEOS+Cl-TMOS (20 min)	0	0
10TEOS_Cl-TMOS (30 min)	0	0
4TEOS+Cl-TMOS (10 min)	31	12
4TEOS+Cl-TMOS (20 min)	61	16
4TEOS+Cl-TMOS (30 min)	28	23

Table 7 Time for a stable water droplet on the cotton coated by combinations 4 and 5 (after washing)

Combination	Solution	Time for a stable water droplet	
		Thin	Thick
	TBOT	0	0
4	TBOT_SA (10 min)	59 min 48 s	1 h 33 min
5	TBOT_Cl-TMOS (10 min)	50 min 18 s	25 s

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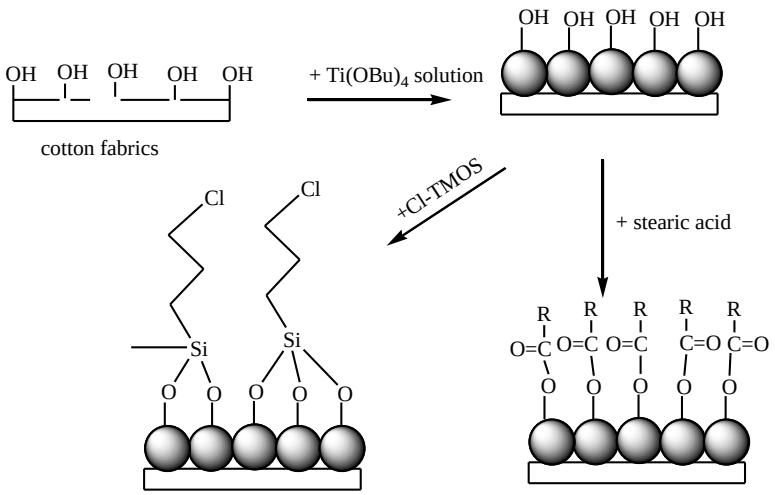
Table 8 Time for a stable water droplet on the cotton coated by combinations 6 and 7 (after washing)

Combination	Solution	Time for the droplet being stable on the surface	
		Thin	Thick
	TBOT (50 °C)	10 s	0 s
6	TBOT_SA (10 min, 50 °C)	14 s	0 s
7	TBOT_Cl-TMOS (10 min, 50 °C)	> 2 h	9 s

Table 9 Contact angles (CAs) of the coated cotton with high hydrophobicity before and after washing

Combination	Solution	Contact angle (°)	
		Before washing	After washing
4	TBOT_SA (10 min) (Thin)	123.89	133.51
4	TBOT_SA (10 min) (Thick)	141.14	106.03
5	TBOT_Cl-TMOS (10 min) (Thin)	138.40	117.47
7	TBOT_Cl-TMOS (10 min, 50 °C) (Thin)	136.80	137.77

The treatments of the cotton fabrics by combinations 4, 5, 7 help retain the hydrophobicity of the cotton surface as the proposed mechanism in scheme 1. The interaction between hydroxyl group of TiO_2 and carboxylic group of stearic acid may lead to the ester formation. Another possibility for this interaction is the weak interaction *via* hydrogen bond. However the explicit conclusion cannot be drawn due to the lack of proper spectroscopic evidence. While the Cl-TMOS can be graphed onto the TiO_2 surface resulting in the formation of Ti-O-Si. The cotton coated by combination 7, TBOT_Cl-TMOS (10 min, 50 °C), gave the highest hydrophobicity with the contact angle (before washing) of 136.80° and contact angle (after washing) of 137.77°. Raising the temperature of the TBOT solution may increase the rate of the hydrolysis and condensation processes on the cotton surface. Moreover the hydrophobization process using Cl-TMOS solution at 50°C may increase the bond formation between hydroxyl groups of TiO_2 surface and methoxide groups of Cl-TMOS.



Scheme 1 The medications of cotton surface according to the combinations 4, 5, 7

Conclusion

The hydrophobicity of the cotton surface can be enhanced using SiO_2 or TiO_2 as the coating material and using stearic acid or chloropropyltrimethoxysilane (Cl-TMOS) hydrophobized reagent. It was found that the thin cotton coated by combination 7, TBOT_Cl-TMOS (10 min, 50 $^{\circ}$C), gave the highest hydrophobicity. Graphing the TiO_2 surface by Cl-TMOS helps increase the cotton surface hydrophobicity. Raising the temperature of the coating solution increases the rate of the hydrolysis and condensation processes of TBOT and Cl-TMOS.

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