Durable hydrophobic sol-gel finishing for textiles

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Abstract. The surface of cotton textile was modified to create a water-repellent finishing by depositing a modifying coatings using the sol-gel technique. Treated textiles evaluated using scanning electron microscopy, X-Ray powder diffraction (XRD). The wettability of treated fabrics was characterized by water contact angle and drop test. The results showed that the cotton textile treated with 7.5 wt.% zinc acetate dihydrate sol showed excellent hydrophobic properties, water contact angle could reach 145°C without decreasing after 50 hydrothermal treatment cycles.

1. Introduction
Hydrophobic fabrics recently have attracted great attention because of their importance in industrial applications due to their unique characteristics like self-cleaning, anti-contamination, antisticking [1, 2]. Cotton has always been the principal clothing fiber due to its outstanding properties such as softness, comfort, biodegradation, high mechanical stability etc. But the abundant water-absorbing hydroxyl groups on cotton surface make the fiber absorbent and easily stained by the liquids [1, 3, 4]. The hydrophobic properties to cotton textile can be brought by sol-gel technology. Chengyu Pan et. al. [5] were successfully modified cotton textile with Al(NO₃)₃ and sodium stearate by a sol-gel process for the hydrophobic properties imparting. Lihui Xu et. al. [1] studied the superhydrophobic properties imparting to the cotton with treatment by the SiO₂ hydrosol and alkylsilanol - hexadecyltrimethoxysilane solution. Montarsolo Alessio et. al. [6] used silica-based sol with hydrophobic additives (N-propyltrimethoxysilane, hexadecyltrimethoxysilane and fluorooctyltriethoxysilane) to prepare hydrophobic coating.

Hence, the first goal of this article is to investigate the action of zinc acetate dihydrate as a hydrophobic finishing agent in the presence of tetraethoxysilane and hydrofluoric acid to cotton textile at a low temperature. The second goal, in the present study are observed one step process to create durable hydrophobic cotton textiles.

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2. Experimental

2.1. Materials, chemicals, sol preparation and textile treatment
The commercial plain weave 100% cotton fabric with the thickness 0.40 mm, surface density 187 g/m² and porosity 69.80 %. The analytically pure chemicals tetraethoxysilane (TEOS, C₈H₂O₄Si, Alfa Aesar, Germany), ethanol (C₂H₅OH), hydrofluoric acid (HF, Alfa Aesar, Germany), deionized water and zinc acetate dihydrate Zn(CH₃COO)₂·2H₂O (Scharlau, Spain) were used. Sols were prepared by a controlled hydrolysis, by previously described method [7]. Samples were prepared with zinc acetate dihydrate 2.5, 5 and 7.5 wt.% concentration. The fabric samples were dipped into the prepared sol for 10 minutes at room temperature. Subsequently, the samples were dried at 90 °C for 10 minutes with thermal post-treatment at 120 °C for 2 minutes or with combined curing and drying in one step at 90 °C for 30 minutes.

2.2. Modified textiles testing
The resistance of hydrophobic finish to hydrothermal treatment, samples were washed at 40 °C for 30 minutes without steel balls with 5mg/l standard non-phosphate detergent without optical brighteners [8]. After each washing cycle samples were rinsed with distilled water and dried under nominally ambient conditions (i.e. 20 ± 2 °C and a relative humidity of 65 ± 2 %) [9].

The determination of liquid absorbency was made by the drop test in accordance with AATCC Test Method 79 [10]. The water contact angle measurements were made by the drop method by an optical tensiometer Theta Attension (Finland).

Scanning electronic microscope (SEM) measurements were carried out using Tescan Mira (Czech Republic) and Hitachi S-3400N (Japan).

Powders acquired after drying at temperature from 100 to 500 °C were characterized by X-Ray powder diffraction (XRD) recorded for 2θ at a scan rate of 1º min⁻¹ using an Ultima+ X-ray diffractometer (Rigaku, Japan) with CuKα radiation.

3. Results and Discussion

3.1. Water absorbency and water contact angle
After the cotton textile treatment by 5 wt. % or 7.5 wt. % zinc acetate dihydrate sol, the water absorbency velocity was decreased from 11 seconds (Fig. 1) to > 30 minutes (Fig. 2). The textile treatment with 2.5 wt.% zinc acetate dihydrate sol doesn’t change the water absorbency velocity significantly which increased to approximately 2 minutes. The number of cycles of the hydrothermal treatment (50 cycles) has not affected the water absorbency velocity of the textiles modified by 7.5 wt.% zinc acetate dihydrate sol, the water absorbency velocity remains > 30 minutes; water absorbency velocity of the textile modified by 5 wt. % zinc acetate dihydrate sol was decreased only after 50 cycles of the hydrothermal treatment up to 2 minutes.

![Figure 1. Water absorbency (drop 20 μL) untreated cotton](image1)

![Figure 2. Water absorbency (drop 20 μL) after treatment by 5 wt. % zinc acetate dihydrate sol](image2)

For untreated textiles and treated with 2.5 wt.% zinc acetate dihydrate sol the fast water absorbance was observed (Fig. 3). It was found that samples treated with sol within the range of zinc acetate
dihydrate concentration 5 wt.% - 7.5 wt.% showed hydrophobicity with contact angle not less than 144° before hydrothermal treatment (Fig. 4, Tab. 1). The different decrease of contact angle was observed after hydrothermal treatment. The cotton textile treatment by 5 wt. % zinc acetate dihydrate sol provides the water-repellent properties also after 20 cycles of the hydrothermal treatment. The cotton textile treatment by 7.5 wt. % zinc acetate dihydrate sol provides the water-repellent properties to cotton textiles even after 50 cycles of intensive hydrothermal treatment (Fig. 5).

![Figure 3. Water contact angle measurements (drop 5 µL) untreated textile](image1)

![Figure 4. Water contact angle measurements (drop 5 µL) treated by 7.5 wt.% zinc acetate dihydrate sol](image2)

![Figure 5. Water contact angle measurements (drop 5 µL) treated by 7.5 wt.% zinc acetate dihydrate sol after 50 hydrothermal treatment cycles](image3)

### Table 1. Water contact angle of modified textiles and after hydrothermal treatment

| Zinc acetate concentration | Thermal post-treatment temperature | Treated 1 hydrothermal treatment cycle | 20 hydrothermal treatment cycles | 50 hydrothermal treatment cycles |
|---------------------------|-----------------------------------|---------------------------------------|----------------------------------|----------------------------------|
| 5 wt.%                    | 90 °C 30 min                       | 148.93                                | 146.77                           | 104.84                           |
|                           | 120 °C 2 min                       | 149.24                                | 147.69                           | 117.54                           |
| 7.5 wt.%                  | 90 °C 30 min                       | 144.48                                | 147.23                           | 151.29                           |
|                           | 120 °C 2 min                       | 145.06                                | 145.43                           | 140.77                           |

3.2. SEM micrographs analysis

The surface of the treated and untreated cotton textile samples was observed and compared using SEM. Untreated cotton textile has grooves and cracks (Fig. 6), in contrast such characteristics completely disappeared on the surface of the treated cotton textile with sol within the range of zinc acetate dihydrate concentration 5 wt. % - 7.5 wt. % (Fig. 8-9); in case of textile treated with 2.5 wt. % zinc acetate dihydrate sol the cracks and grooves are still observed. SEM micrographs (Fig. 7-9) prove that the textiles by zinc acetate dihydrate sol are coated homogenously. Regardless of the zinc acetate concentration (5 wt. % or 7.5 wt. %), there is a thin coating obtained with single particles and particles agglomerates dispersed in the film, some particle agglomerates consolidates and form irregular several micrometer wide and/or long clusters on the textile surface (Fig. 8 and 9).

![Figure 6. Untreated](image4)

![Figure 7. Treated by 2.5 wt.% zinc acetate dihydrate sol](image5)
3.3. XRD
It was concluded that the difference between untreated and treated cotton textile cannot be identified by XRD, that can be explained by the fact that the archived coatings are very thin and treated textile contain a small amount of the modifying chemical elements. XRD analyses of sol powder evince that crystalline phase of the ZnO appears starting from the temperature 300 °C, in the range of the temperature from 300, 400 and 500 °C SiO$_2$ is also obtained; from the 400 °C the formation of the willemit - Zn$_2$(SiO$_4$)$_2$ begins. At lower temperatures that are appropriate for the cotton textile thermal treatment – from 100 to 200 °C - occurs a partial decomposition of the zinc acetate dihydrate and basic zinc compound formation. The functional coating primarily consist from zinc acetate (C$_4$H$_6$O$_4$Zn), silica compounds: H$_2$Si$_3$O$_7$(H$_2$O) and H$_2$Si$_14$O$_29$•5.4H$_2$O, and probably from insoluble basic zinc compounds or zinc oxide in amorphous phase.

4. Conclusion
The coated cotton textile exhibited excellent hydrophobicity with the water contact angle reached 145 °C after treatment and 150 °C after the 50 hydrothermal treatment cycles, as well high durability of the coating that withstand 50 cycles of the hydrothermal treatment (washing-drying). Zinc acetate dihydrate sol allow to deposit thin, homogenous functional coatings with dispersed single particles and particles agglomerates.

The method is simple and may have some promising applications for cotton materials to generate hydrophobic surfaces.

5. References
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