Functionalisation of cotton fabric by antimicrobial and repellent finishing

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Abstract

The aim of the research was to prepare a multifunctional antimicrobial, water and oil repellent finish on cotton fabric by sol-gel process. A nanoparticle silica sol containing silver nanoparticles as an inorganic biocide and fluoroalkylfunctional oligosiloxane as a water and oil repellent agent was applied to the plane-wave 100 % cotton fabric with a pad-dry-cure method, including full immersion at 20 °C, wet pick-up of 80 % at 20 °C, drying at 100 °C and curing at 150 °C for 5 minutes. The antimicrobial activity of the coating was estimated for the *Escherichia coli* (ATCC 25922) bacteria according to the AATCC 100-1999 Standard Method. Oil repellency was determined according to AATCC Test Method 118-1998. Static contact angles of n-hexadecane and water on the finished fabric surface were measured with a goniometer (DSA100, Krüss). The results of the antimicrobial test showed that the release of silver ions from the silica coating causes a 100 % bacteria reduction. The presence of fluoroalkylfunctional groups in the coating affects a very high increase of oil and water repellency with the oleophobicity grade of 6 and a static contact angel of n-hexadecane equal to 126^{o} and of water equal to 140^{o}. These results confirm that the applied nanostructured silica coating enables the simultaneous antimicrobial and repellent properties. It was also found that the coating does not significantly impair the physical-mechanical properties of the fabric.

1 Introduction

The modern stile of life dictated the development of textile having multifunctional properties such as appropriateness for colouring with different dyes, washing fastness, easy care, water and oil repellency as well as antimicrobial activity (1, 2). For polymeric fibres multifunctional properties are relatively easy to achieve by applying suitable polymerization process and techniques, combined with use of appropriate raw materials for their preparation. On the other hand functionalization of natural fibres is more difficult to achieve, particularly when the desired finishes have to impart hydrophobicity, oleophobicity and antibacterial properties at once.

In the last decade, the functionalisation of textiles can be achieved by the sol-gel technology which enables the formation of the nanocomposite coating with the organic-anorganic hybrid structure (3). From the literature, chemically or physically modified sols are used for textile coating. In chemical modification trialkoxysilanes containing an organic substituent, such as alkyl, fluoroalkyl, epoxyalkil or biological components are mainly used (4-6). In physical modification different additives, such as inorganic colloidal metals, oxides and pigments, dyes, organic polymers or biopolymers are immobilised into the hybrid polymer structure (7-10). With the use of an appropriate precursor combination, a multifunctional coating on fibres could be formed from only one solution (sol). The fibre surface would be characterised by different simultaneous properties – it could be hydrophobic, oleophobic, antimicrobial, inflammable, antistatic, UV protective, biocatalytic.

In the framework of this study we aimed to prepare a multifunctional sol-gel coating on the cellulose fibres which would gain superhydrophobic, oleophobic and antimicrobial properties. For these reason mixture of different precursors, recently available on the market, i.e. an organic-inorganic hybrid with sufficient reactivity to allow incorporation of well dispersed metallic nanoparticles and oleophobic fluoroalkoxysilane, were used. According to our knowledge such a combination of commercial silanes and nanometallic Ag particles has not been reported so far. With regard to this, simultaneous antimicrobial and oil repellent properties were studied.

2 Experimental

2.1 Materials

Plane-wave 100 % cotton woven fabric with a mass of 164 g/m^2 was used in the experiments. In pre-treatment processes the fabric was bleached in an H_2O_2 bath, mercerised in NaOH solution and neutralised with diluted CH_3COOH solution.

As an antimicrobial agent, iSys AG - a dispersion containing nanosized silver (Ag), was used in combination with iSys MTX (CHT, Germany) - a reactive organic-inorganic binder (RB). As a water and oil repellent agent, Dynasylan F 8815 (Degussa, Germany) - a fluoroalkylfunctional water-born siloxane (FAS), was used. All products can be mixed with water to any desired concentration.

2.2 Finishing of cotton fabric

For finishing of cotton fabric a sol mixture of 10 % FAS, 3 g/l Ag and 15 g/l RB (Ag-RB-FAS) was prepared and applied by the pad-dry-cure method, including full immersion at 20 °C, wet pick-up of 80 ± 1 % at 20 °C, drying at 120 °C and curing at 150 °C for 1 minute.

2.3 Analyses and measurements

2.3.1 Antimicrobial activity. The antimicrobial activity of the coatings was estimated by the AATCC 100-1999 Standard Method for the Gram-negative bacteria *Escherichia coli* (ATCC 25922). Antibacterial activity was expressed by the reduction of bacteria, *R*, which was calculated as follows:

$$R = \frac{(B - A)}{B} 100 \quad (\%) \qquad (1)$$

where A is the number of bacteria recovered from the inoculated swatch of cotton sample in the jar incubated over the desired contact period (24 hours) and B is the number of bacteria recovered from the inoculated swatch of cotton sample in the jar immediately after inoculation (at “0” contact time).

2.3.2 Oil repellency. The oil repellency of the finished cotton samples was determined under static conditions using the AATCC test method 118-1978, where eight hydrocarbon liquids in a series of decreasing surface tension were used: 1 – paraffin oil (γ_L = 31,2 mJ/m^2), 2 – 65:35 mixture of paraffin oil and n-hexadecane (γ_L = 28,7 mJ/m^2), 3 – n-hexadecane (γ_L = 27,1 mJ/m^2), 4 – n-tetradecane (γ_L = 26,1 mJ/m^2), 5 – n-dodecane (γ_L = 25,1 mJ/m^2), 6 – n-decane (γ_L = 23,5 mJ/m^2), 7 – n-octane (γ_L = 21,3 mJ/m^2) and 8 – n-heptane (γ_L = 19,8 mJ/m^2). Drops of standard test liquids were placed at different spots on the fabric surface and observed for wetting. The repellency rating was expressed by the highest numbered test liquid which did not wet and penetrat the fabric in 30 seconds.

2.3.3 Contact angle measurements. Contact angle measurements of water, diiodomethane and n-hexadecane on the finished cotton samples were made on a DSA 100 contact angle goniometer (Krüss, Germany), which works on the principle of the goniometer-sessile drop technique. Ten measurements, in which liquid drops were placed on different spots all over the fabric samples, were used for the determination of the average contact angle values with a precision of $\pm$ 3^o. All the values reported here correspond to contact angles obtained under stationary conditions, i.e. 60 s after the liquid drops were applied to the fabric.

2.3.4 Recovery from creasing. Recovery from creasing was determined according to the ISO 2313 Standard. The crease recovery angle, α, was calculated from the mean values of ten measurements in warp and weft directions as follows:

$$\alpha = \frac{\alpha_1 + \alpha_2}{2} \qquad (2)$$

where α_1 in α_2 are the mean values of the angles obtained in warp and weft directions, respectively.

2.3.5 Bending rigidity. The handle of the finished cotton samples was determined by the 'Shirley' stiffness test according to ASTM Standard D-1388-64. The bending rigidity, *G*, was determined from the bending length, *l*, which was obtained when a fabric sample was bent under its own weight to a definite extent. *G* is defined as:

$$G = \sqrt{G_1 + G_2} \qquad (3)$$

where G_1 and G_2 are the bending rigidities in warp and weft directions equal to:

$$G_{1(2)} = T\left(\frac{l_{1(2)}}{2}\right)^3 \qquad (4)$$

where *T* is the fabric weight per unit area. The results represent the mean values of ten measurements.

2.3.6 Breaking strength. Breaking strength was measured with an Instron 5567 dynamometer in accordance with SIST ISO 5081:1996. The relative reduction in breaking strength, q_{red}, of the finished cotton samples compared with the unfinished one was calculated from the mean value of the breaking strength of ten specimens, using the following relationship:

$$q_{red} = \frac{F_f}{F_{un}} \qquad (5)$$

where F_f and F_{un} are the breaking strength of the finished and unfinished cotton samples, respectively. Measurements were made in warp and weft directions. Before testing, the samples were conditioned at 65 ± 2 % relative humidity and 20 ± 1 ^{o}C for 24 hours.

2.3.7 Air permeability. Air permeability measurements were carried out according to the SIST EN ISO 9237:1999 Standard. From the amount of air passed through the sample under a pressure of 20 mm H_2O, the air permeability was determined as Q given by:

$$Q = q / 6a \qquad (6)$$

where *q* is the volume of air flowing through the sample of area, *a*, expressed in l/h and *Q* is the volume of air in m^3 passing through 1 m^2 of the fabric per minute at the required pressure. The results represent the mean values of twenty measurements.

3 Results and Discussion

Results of the antibacterial activity (Table 1) showed that no reduction of bacteria *Escherichia coli* was found on the unfinished cotton sample. Moreover, there was even an increase in the number of bacteria recovered from the inoculated sample after 24 h of incubation in comparison to “0” contact time, indicating that pure cotton was a good media for bacteria growth. High reduction of bacteria occurred in the case of Ag-RB-FAS coated cotton, due to the presence of Ag nanoparticles. It is well known (11) that silver nanoparticles can react with sulphur-containing proteins inside or outside the cell membrane as well as with phosphorus moieties in DNK, which in turn affects bacterial cell viability. From the results obtained it can be concluded that the addition of FAS component did not block the leaching of metallic silver nanoparticles from the finished cotton fabric and therefore had no effect on the antibacterial activity of the Ag component.

Table 1 Reduction, *R*, of bacteria *Escherichia coli* (ATCC 25922) according to the AATCC 100-1999 Standard Method and oil repelency rating of untreated and treated cotton fabric.

Coating	*R* (%)	Oil repellency rating
Unfinished	/[a]	0
Ag-RB-FAS	100	6

[a] /: no reduction of bacteria.

The presence of fluoroalkyl functional groups in FAS-Ag-RB coating expectedly increased the oleophobicity of the unfinished cotton to the repellency rating of 6 (Table 1). According to the literature data (5, 6), a rating 6 is the highest rating, which has been obtained for textile fibres, and reveals a highly unwetted surface with superhydrophobic as well as oleophobic properties.

Hidrophobicity and oleophobicity of the Ag-RB-FAS coated sample were further confirmed by the results of the static contact angel measurements, where the sample was highly unwetted by water and diiodomethane, forming contact angle of 140^{o} and 126^{o}, respectively. Since surface oleophobicity could only be proved with the high contact angles of n-alkanes the contact angle of n-hexadecane was measured as well, reaching the value of 125^{o} (Fig. 2).

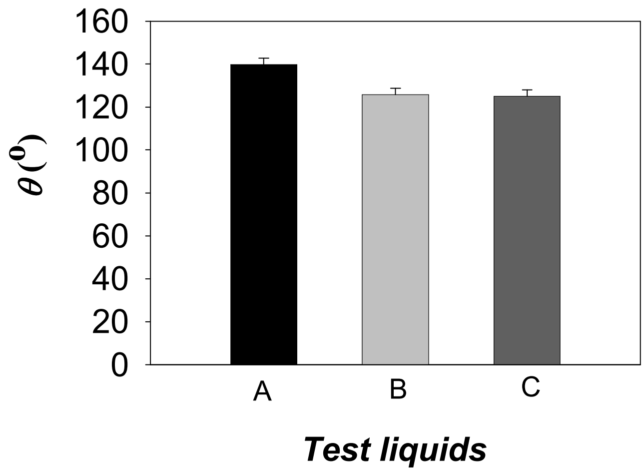

Fig. 2 Static contact angle, θ, of water (A), diiodomethane (B) and n-hexadecane (C) on finished cotton samples.

The influence of the Ag-RB-FAS coating on the physical properties of the cotton fabrics are presented in table 2. It can be seen that the application of Ag-RB-FAS coating decreased bending rigidity of the fabric, which was accompanied by an increase in the crease recovery angle. Treatment of cotton samples slightly decreased the fabric breaking strength in warp and weft directions as well as air permeability of the fabric. The former occurred as a consequence of polysiloxane network formation on the fibre surface, which partly covered the pores in the fabric structure, resulting in the impaired porosity.

Table 2: Crease recovery angle, α, bending rigidity, G, the relative reduction in breaking strength, q_{red}, and air permeability, Q of the studied samples samples.

Coating	α (°)	G (mg cm)	q_{red}		Q (m^3 min m^2)
			in warp direction	in weft direction	
Untreated	35,6±1,56	2525±159	/	/	27±1
Ag-RB-FAS	73,7±2,05	1650±100	0,99 ±0,02	0,97±0,02	23,5±1

4 Conclusions

Sol-gel technology is very appropriate technique for textile finishing which enables the formation of the repellent and antimicrobial nanocomposite coating with the organic-anorganic hybrid structure. Namely, from the results obtained it can be concluded that the addition of FAS component into Ag-RB coating has no influence on the antimicrobial activity of the silver nanoparticles, menwhile it still retains high hydrophobicity and oleophobicty.

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