At the nano-level modified cotton knitwear prototype development

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Abstract. This article reviews efficiency of the fluorine, silica and zinc compounds containing textile coating conformity with the day-to-day wearing conditions of cotton knitwear used as the first level clothing to the wearer skin. Silica sol modified with the zinc acetate dehydrate was used for the weft knitted cotton single-jersey and double-jersey fabrics chemical modification. The experimental part of the presented research includes the evaluation of the fabrics structure characteristics, air and vapour permeability and water-repellent abilities. The wettability of cotton textiles were evaluated by the water contact angle before and after modification as well after hydrothermal treatment. Images of the obtained modified fibres surfaces analysed by scanning electron microscopy, and fibres surface chemical composition has been determined with dispersive X-ray analysis. Conformity of the inserted additional functions to the modified textiles were determined by testing textiles “in vivo” in experimental wearing process where 100 volunteers of different professions had participated.

1. Introduction
Future trends of textile industry include production of multifunctional materials from natural fibres with integrated additional functional properties such as UV protection, antimicrobial activity, water-repellence, photocatalytic qualities etc. and the combination of these functions into a single textile [1-2].

The sol-gel method adapted for the treatment of cotton woven fabrics, the optimized methods of sol synthesis and appropriate content of sol, as well as combination of processing and post-processing modes were developed [3-5]. The wide range of tests show that woven cotton fabrics modified with the developed technology in a single process could provide antimicrobial, water-repellent properties and protection against both UVB and UVA spectrums preserving the air permeability and hygroscopicity required to ensure the necessary level of wear comfort [3-7].

The goal of this research is adapted sol-gel process to the knitted goods assortment wear as base layer or first to the body layer. Conformity of the inserted additional functions to the modified textiles determined by testing textiles “in vivo” in experimental wearing process

2. Materials and methods

2.1. Experimental procedures and materials
Samples of untreated and modified jersey knitwear with attributed legends were prepared according to the description of variants in Table 1.
Table 1. Description of fabric variants under investigation

| Legend of sample | Description                                      |
|------------------|--------------------------------------------------|
| 1NN              | Single-Yersey, initial                           |
| 1AN              | Single-Yersey, sol-gel coating                   |
| 1AM              | Single-Yersey, sol-gel coating, washed           |
| 2NN              | Double-Yersey, initial                           |
| 2AN              | Double-Yersey, sol-gel coating                   |
| 2AM              | Double-Yersey, sol-gel coating, washed           |

Chemicals used for sol synthesis seen in Table 2, structural parameters of knitted fabrics variants shown in Table 3.

Table 2. Chemicals used in sol synthesis

| Substance                        | Chemical formula | Producer/Distributor            | Purity, % |
|----------------------------------|------------------|--------------------------------|-----------|
| Tetra-ethil-orto-silicate (TEOS)  | C₈H₂₀O₄Si        | Alfa Aesar, Germany            | ≥98 %     |
| Ethanol                          | C₂H₅OH           | ES (Ltd."Enola")              | ≥99,98    |
| Hydrofluoric acid                | HF               | ES (Ltd."Baltalab")           | 38-40%    |
| Zinc acetate dihydrate           | Zn(CH₃COO)₂·2H₂O | ES (Ltd.,"Baltalab")          | Analytical pure |

The sols used in this work were prepared following the method developed in [3-5]. To meet requirements of EN ISO 105C10-A01:2006 the standard Soap without brightening agents (SDC reference detergent type 1) suitable for use in procedures specified in ISO 105:1989:C01 to C05 used for washing. Soap concentration 5 mg/l in water, professional equipment Electrolux-W 465H (30°C, 20 min, 700 min⁻¹) with the following drying at 22 ± 2°C used for hydrothermal treatment.

2.2. Test methods and equipment

Scanning electron microscope model MIRA/LM (Tescan HF, Czech Republic) was used to examine the surface microstructure of single jersey and double jersey untreated and treated with silica sol modified by zinc acetate dihydrate knits, as well after first hydrothermal treatment of fabrics subjected to the sol–gel treatment. EDX analysis applied to investigate chemical elements relative distribution on fabric surfaces (X-MaxN, Oxford instruments, Great Britain).

SDL Atlas Air Permeability tester (Canada) used for evaluation of air permeability properties and Permetest (Czech Republic) to evaluate vapour permeability.

Wettability of fabric surfaces investigated by wetting equilibrium angle tests with the optic tensometer Theta Attention (Finland)

The stretch and recovery properties of experimental knitted fabric samples determined by Fryma Fabric Extensometer.
Knitted fabrics structure parameters shown in Table 3 are evaluated in compliance with the corresponding EU standards adapted in Latvia, using test equipment of Textile Material Laboratory (RTU).

**Table 3. Knitted fabric structure parameters**

| Fabric Parameters                  | 1NN | 1AM | 2NN | 2AM |
|------------------------------------|-----|-----|-----|-----|
| Fabric average thickness, mm       | 0.90| 0.95| 0.63| 0.65|
| Surface filling, %                 | 94  | 94  | 169.8| 169.58|
| Horizontal density (loop count per 100 mm) | 120 | 120 | 200 | 200 |
| Vertical density (loop count per 100 mm) | 180 | 180 | 190 | 190 |
| Linear density of yarns, tex       | 94  | 97.9| 108.3| 110.9|
| Linear fill with yarns in horizontal direction, % | 93.6| 93.6| 168 | 168 |
| Linear fill with yarns in vertical direction, % | 70.2| 70.2| 79.8| 79.8|
| Volume weight of threads in fabric, mg/mm3 | 0.6 | 0.59| 1.81| 1.78|

3. Results and discussion

Micrographs of Figure 1 and Figure 2 show deposited amorphous coatings on fibres surfaces of fabric with separated clusters above (centre) and without coating bridges between fibres. SEM images testify that applied sol-gel process allow to cover every single fibre of knitted fabrics with the modifying coating and could be used to fabricate crack-free films on single and double jersey fabrics fibres.

![Figure 1](image1.png)

Although after treatment some agglomerates created by sol compounds stand out in contrast to the layer on fibre surface, in result of following hydrothermal treatment consolidation of agglomerates take place and flow into one layer as seen in Figures 1 and Figure 2, right.
Figure 2. Double jersey fabric fibres surfaces SEM images (from left to right): without treatment, after treatment with sol, after hydrothermal treatment

EDX analysis show presence of core chemical elements Si, Zn, and F of modifying chemical compounds (Table 4). Group “Other” includes such elements as Na, Cl and Ca as water from city Riga water supply system was used. In result of further consolidation of coating during applied hydrothermal treatment, relative proportions of chemical elements substantial changes depending on fabric surface specifics (Table 4).

Table 4. Relative distribution of chemical elements on the surfaces of fabrics

| Sample | C  | O  | F  | Si | Zn | Other |
|--------|----|----|----|----|----|-------|
| 1NN    | 63,15 | 36,17 |     |    |    | 0,69  |
| 1AN    | 63,86 | 25,36 | 4,95 | 0,38 | 3,16 | 2,3   |
| 1AM    | 61,84 | 31,19 | 1,25 | 0,87 | 5,01 | 0,54  |
| 2NN    | 60,87 | 39,13 |    |    |    | 0     |
| 2AN    | 45,34 | 28,93 | 5,34 | 3,68 | 10,14 | 0,52 |
| 2AM    | 56,91 | 29,82 | 3,44 | 1,73 | 4,81 | 3,21  |

One of the main traits ensuring physical comfort of wearer is air permeability of T-shirts fabric. It is seen from the Table 5 that air permeability decreases by 20 % for the single jersey samples and by 14% for double jersey ones after treatment with sol, but increase after following hydrothermal treatment correspondingly by 14 % and 18 % compare to air permeability of the initial condition. Regulations [8] standardize air permeability at least 150 mm/s for the children age group from 1 to 3 years and at least 100 mm/s for the age group from 3 to 18 years if textiles will be used as a first to the skin clothing layer. Therefore, T-shirt treatment with silica sol modified by Zn acetate dihydrate with the following hydrothermal treatment exceed this regulation even for youngest children age group.

Table 5. Air permeability of T-shirts before and after applied treatments

| Sample | Single jersey | Double jersey |
|--------|----------------|---------------|
|        | Average, mm/s | Confidence int., mm/s | Average, mm/s | Confidence int., mm/s |
| NN     | 194,6         | + / - 4,0     | 163,0         | + / 6,40              |
| AN     | 155,9         | + / - 4,9     | 139,4         | + / - 8,5             |
| AM     | 229,4         | + / - 5,0     | 179,1         | + / - 6,3             |
Relative vapour permeability, the next important to wear comfort trait, decrease by 8.6 % for the single jersey samples and by 10.2 % for the double jersey ones after treatment with sol. After following hydrothermal treatment relative vapour permeability increase correspondingly by 0.8 % and 3.4 % compare to the vapour permeability of untreated samples (Figure 3) and could be considered as very high for both fabric types promising breathable first clothing layer to the skin.

![Figure 3](image3.jpg)

**Figure 3.** Influence of sol treatment and following hydrothermal treatment on the fabric vapour permeability.

The contact angle value on untreated double jersey cotton fabric due to the looser structure and the immediate absorption of the water drops is below 90 degrees (Figure 4, right). Untreated single jersey fabric is less absorptive due to the smooth surface of fabric and larger thickness (Table 3 and Figure 4, left). In result of treatment with the sol and especially after the hydrothermal treatment contact angle established above 130 degree (Figure 4) testifying the high surface water repellency conferred by the treatment.

![Figure 4](image4.jpg)

**Figure 4.** Surface wetting equilibrium angles: single jersey fabrics (left), double jersey (right)
Figure 5. Deformation properties of jersey fabrics after sol-gel treatment (left) and following hydrothermal treatment (right)

Cyclic loading test is a dynamic test that simulates deformations on fabric during its wear. The obtained results indicate that recovery ratio of weft knitted single jersey fabric drop from 45% before treatment to 20% and for double jersey from 45% to 30% in horizontal direction after sol-gel treatment (Figure 5, left) and do not change after hydrothermal treatment (Figure 5, right). In the same time recovery ratio after the surface modification in vertical direction increase from 10 to 15% for the single jersey and decrease from 15 to 5% for the double jersey in vertical direction remaining at 10% after hydrothermal treatment. Yarns forming loops in the jersey textiles may slide relative to each other and cause the knitted textiles permanently remain in a stretched state. The relatively large spaces between yarns in knitted textiles also tend to hold a relatively large quantity of water, thereby increasing the plastic deformation that occurs as a result of being saturated with water as seen from graphs of Figure 5, right, especially for double jersey fabric.

Elastomeric plated jersey fabric is one of the most common fabrics produced with a large-diameter circular knitting machines. The results obtained in [9] indicated that elastane and its amount has a significant effect on dimensional and elastic properties of cotton/Lycra® plated plain knitted fabric showing way to improve dimension stability and elastic properties of fabrics.

4. Conclusions
Sol-gel process with silica sol modified by Zn acetate dihydrate applied to the neat cotton jersey fabrics allow to cover every single fibre of fabric with the thin modifying coating and fabricate crack-free films on the single and double jersey fabric fibres.

First hydrothermal treatment after surface modifying is obligatory performed in order to favor further coating polycondensation and enhance of properties providing wearing comfort and surface water repellency.

Dimensional stability and deformation properties of modified weft knitted fabrics with sol-gel technology by silica sol with the Zn acetate dihydrate precursor drop down. As next step cotton/elastane plated knits could be investigated to improve deformation properties.

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