



## Sol–gel coating processing optimization for natural fibres

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**Abstract.** Functionality of natural fibres can be enhanced by sol–gel technology. The sol–gel process has to be adapted with regard to the type of coated fibres and to the applied sol. In this research, pure cotton and hemp fibres were modified by the sol–gel technology with different processing parameters. The morphology of coating depending on the dipping time and sol composition, were studied by scanning electron microscopy (SEM). The aim of this research was to study the influence of different processing parameters of sol–gel methods like dipping time, the influence of sol compositions on the coating morphology and quality, and to obtain durable and smooth coatings for surface modification of natural fibres.

**Key words:** natural fibres, sol–gel method, silica precursor, coatings.

### 1. INTRODUCTION

The knowledge of fine structure and chemical composition of natural fibres has stimulated research and development to find methods of improving the chemical and physical properties of natural fibres [1]. The sol–gel method has been studied for several decades to prepare ceramic precursors and inorganic glasses at relatively low temperatures. The tetraethyl orthosilicate (TEOS) is a common silica precursor, because it has a relatively slow and controllable rate of reaction [2]. Certainly, one of the most technologically important aspects of sol–gel processing is that prior to gelation, the sol is ideal for preparing thin films by such common processes as dipping, spinning, or spraying [3]. The sol–gel technology led to conceptually novel materials composed of organic and inorganic groupings [4].

Research experiments indicate that the main limitation for the sol–gel technology application with respect to textiles is determined by low thermal stability of most

textile materials, which is usually below 200 °C and for many materials significantly lower. Hence, the sol–gel process has to be adapted with regard to the type of textile coated and the applied sol [5]. To give the desired complementary character, SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO and CaCO<sub>3</sub> can be applied to the surface of cellulosic substrates [6–8].

The fibre treatment process of dipping was chosen because the total immersion guarantees complete wetting of the product which, in almost all cases, led to uniform distribution of the coating materials covering the whole substrate and simultaneously because incomplete coverage of the fibres might decrease the durability of the sol coatings applied. The combination of the coating and the textile carrier is responsible for the tear resistance, adhesive strength, combustion behaviour and long-term durability of the end product [9]. The applications for everyday life, such as umbrellas, shelters, camps, garments, and advertisement materials are made of fibres covered by the sol–gel coatings [10]. Recently, a lot of fabric is used with sol–gel finishings, such as polyamide, polyester, cotton, aramid, polyacrylonitrile, viscose and others [11].

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Used in the research, the sol-composition allows assigning to the textiles the property of hydrophobicity, providing that qualitative, evenly distributed coating is obtained. To give additional antimicrobial properties to the surface of the fibres the zinc acetate dihydrate (ZAD) was used.

## 2. MATERIALS AND METHODS

Two types of the commercial plain weave 100% cotton fabrics (linear density 187 g/m<sup>2</sup> and 151.5 g/m<sup>2</sup>) were used in the research. The hemp fibres were obtained from a trial plot at the Agriculture Science Centre of Latgale in Vilani district, Latvia. Hemp stems were cultivated in 2014 and left dew retting on the field for 4 weeks. Hemp fibres were ground to 1 mm.

The sols were prepared from TEOS in ethanolic solution by acid-catalyzed hydrolysis and condensation, see reagents in Table 1. The sol for the cotton and hemp were synthesized according to wt% shown in Table 2.

Nanosols were prepared by a controlled hydrolysis, adding ethyl alcohol slowly into TEOS with continuous stirring, after adding deionized water and hydrofluoric acid. Solutions were stirred for 30 min and afterwards mixed with ZAD, with continuous stirring for 10 min. The stirring process was performed at room temperature or at 50 °C. The obtained nanosols were clear and homogeneous. To evaluate the coating quality, different fabric samples were prepared with TEOS concentrations of 2, 3 and 4 wt% and various ZAD concentrations of 2.5, 5, 7.5, 8 and 10 wt%.

Cotton fabric and ground hemp fibres were dipped into the prepared nanosols bath, the fabrics and chaotic oriented fibres were taken off horizontally and soaked for 10 min at room temperature or at 50 °C. The humidity of the air was 65 ± 2% and room temperature was 20 ± 2 °C; the samples were then dried horizontally at 90 °C and heated at 120 °C.

To explore the coating of thin films, a morphological analysis of the fibres' surfaces was carried out by SEM (Tescan, Mira//LMU Schottky, Czech Republic and Hitachi S-3400N, Japan).

**Table 1.** Reagents for nanosols

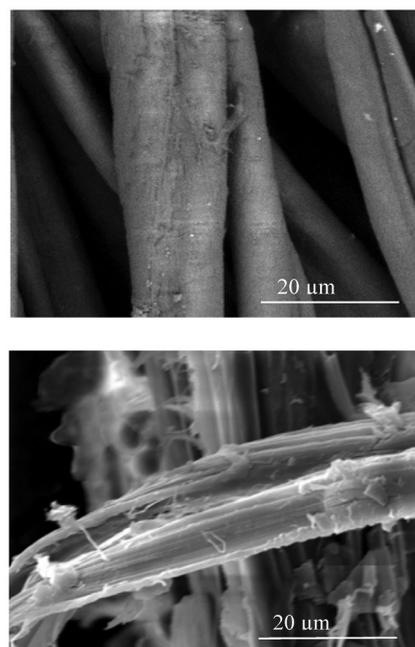
Reagents	Manufacturer	Purity
TEOS	Alfa Aesar, Germany	99%
Ethanol	Enola Chemical Co., Ltd	99%
Hydrofluoric acid	Enola Chemical Co., Ltd	40%
Zinc acetate dihydrate	Enola Chemical Co., Ltd	98%

**Table 2.** Prepared samples

TEOS, wt%	ZAD, wt%	Fibres	Mixing/Dipping, °C	Dipping time, min
2	5	Cotton	Room temperature; 50	10
2	7.5	Cotton	Room temperature; 50	10
2	7.5	Hemp	50	10
2	8	Hemp	50	10
3	2.5	Cotton	Room temperature	10
3	5	Cotton	Room temperature	10
3	7.5	Cotton	Room temperature	10
3	10	Cotton	Room temperature	10
4	2.5	Cotton	Room temperature	10
4	5	Cotton	Room temperature	10
4	7.5	Cotton	Room temperature	10; 30
4	10	Cotton	Room temperature	10

## 3. RESULTS AND DISCUSSION

In order to assess the morphology and structures of the coatings deposited on the textile surfaces by the sol–gel processes, SEM observations had been performed. Fig. 1 presents the images of SEM of the control sample



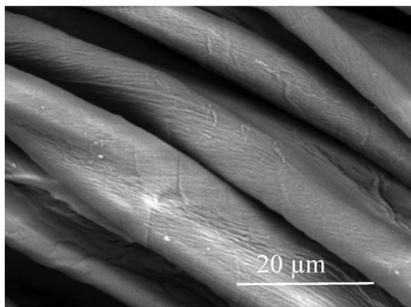
**Fig. 1.** Uncoated cotton (up) and hemp (bottom).

(uncoated). The result of SEM showed that the control cotton fibres were flat with a twisted ribbon-like structure caused by spiralling of cellulose fibrils. The normal spiral structure of cotton sample with a clearly defined feature was observed. The presence of natural folds running parallel along the cotton fibre's axis was observed. The untreated cotton fibre surface was described as a smooth fibre's surface and consists mainly of cellulose.

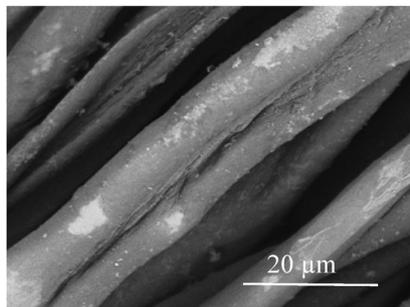
On the hemp fibre's complex surface, Fig. 1. shows that growth directions and the shape of the cells are not as smooth as cotton. The hemp fibre diameter is about 20 µm. It consists of cellulose, hemicellulose, lignin,

pectins, etc. The different chemical composition of the hemp fibres makes them more sensitive to hydrolysis of the acid, the rough surface makes it difficult to apply a coat even when drying the fibres. A thicker coating layer is formed in cavities and slits. After processing hemp fibres at pH 2 by sol-gel method, fibres become thinner. After the heat treatment, hemp changes colour quicker than cotton; heating lasts for 10 min at 120 °C.

The series of SEM images in Figs 2–18 reveal the evolution of the surface structures during the treatment process depending on different sol concentrations and processing parameters. The SEM images in Figs 2–16



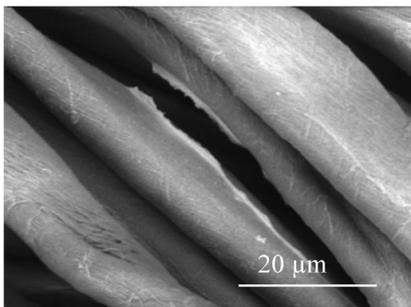
**Fig. 2.** TEOS 2 wt% and ZAD 2.5 wt% coated cotton, mixing/dipping at room temperature.



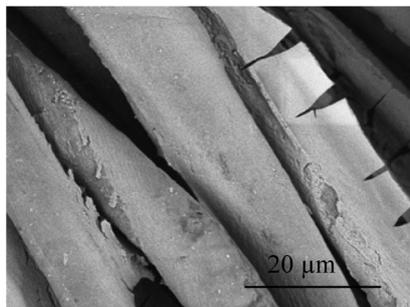
**Fig. 3.** TEOS 3 wt% and ZAD 2.5 wt% coated cotton, mixing/dipping at room temperature.



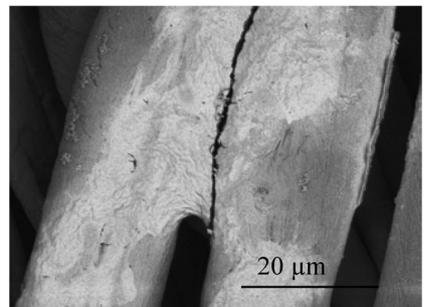
**Fig. 4.** TEOS 4 wt% and ZAD 2.5 wt% coated cotton, mixing/dipping at room temperature.



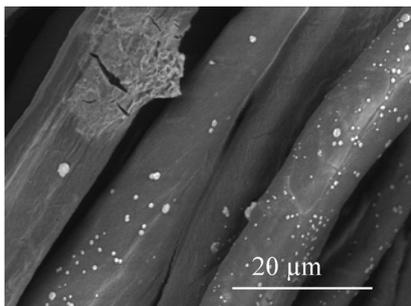
**Fig. 5.** TEOS 2 wt% and ZAD 5 wt% coated cotton, mixing/dipping at room temperature.



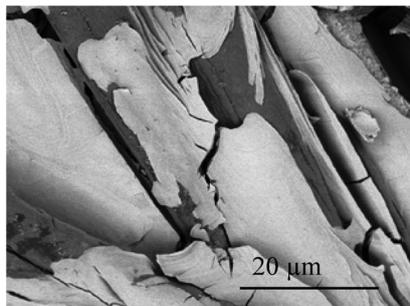
**Fig. 6.** TEOS 3 wt% and ZAD 5 wt% coated cotton, mixing/dipping at room temperature.



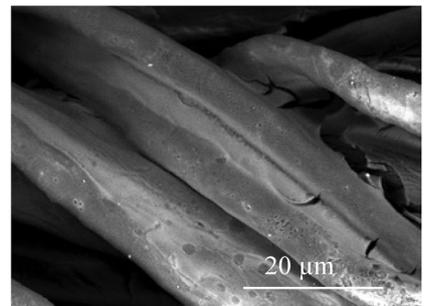
**Fig. 7.** TEOS 4 wt% and ZAD 5 wt% coated cotton, mixing/dipping at room temperature.



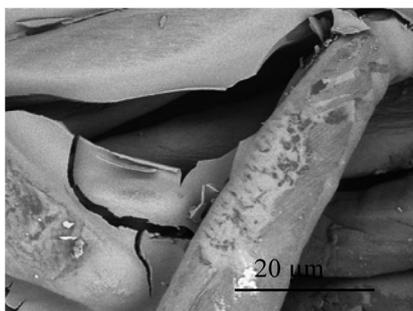
**Fig. 8.** TEOS 2 wt% and ZAD 10 wt% coated cotton, mixing/dipping at room temperature.



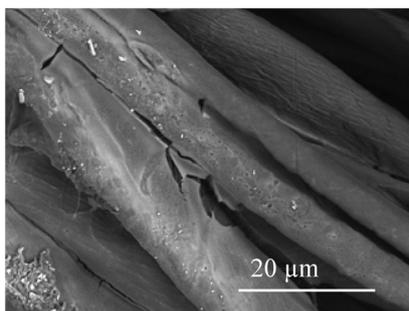
**Fig. 9.** TEOS 3 wt% and ZAD 10 wt% coated cotton, mixing/dipping at room temperature.



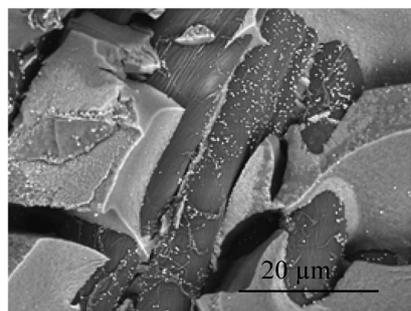
**Fig. 10.** TEOS 4 wt% and ZAD 10 wt% coated cotton, mixing/dipping at room temperature.



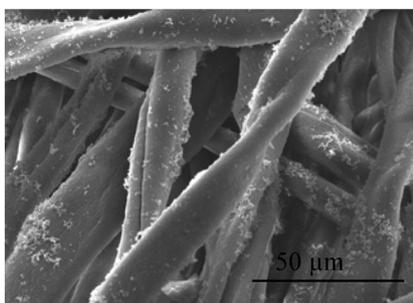
**Fig. 11.** TEOS 3 wt% and ZAD 7.5 wt% coated cotton, mixing/dipping at room temperature.



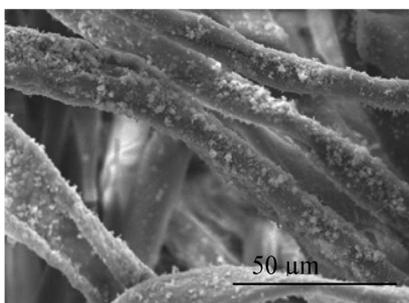
**Fig. 12.** TEOS 4 wt% and ZAD 7.5 wt% coated cotton, dipping time 10 min, mixing/dipping at room temperature.



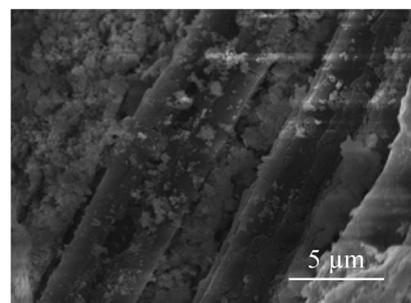
**Fig. 13.** TEOS 4 wt% and ZAD 7.5 wt% increased mixing/dipping time 30 min, mixing/dipping at room temperature.



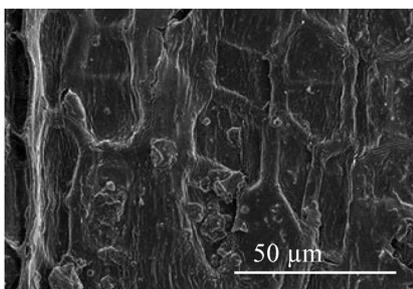
**Fig. 14.** TEOS 2 wt% and ZAD 5 wt% coated cotton, dipping temperature 50 °C.



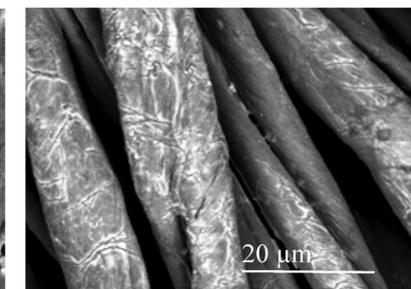
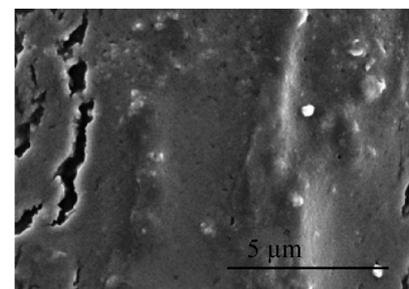
**Fig. 15.** TEOS 2 wt% and ZAD 7.5 wt% coated cotton, dipping temperature 50 °C.



**Fig. 16.** TEOS 2 wt% and ZAD 8 wt% coated hemp fibres, dipping temperature 50 °C.



**Fig. 17.** TEOS 2 wt% and ZAD 7.5 wt% coated hemp, dipping temperature 50 °C.



**Fig. 18.** TEOS 2 wt% and ZAD 7.5 wt% coated cotton, mixing/dipping at room temperature.

show obvious changes in surface morphology of the cotton and hemp fibres after sol coating, compared with uncoated fibres in Fig. 1.

With the ZAD concentration 2.5 wt%, the obtained coatings are not complete and are mainly in the form of precipitations on fibre surface that can be explained with too low concentrations of ZAD (Figs 2–4). With increasing ZAD concentrations formation of more complete and thicker coatings on the surface of the fibres was observed (Figs 5–10).

With TEOS concentration 4 wt%, thick coatings with cracks and bridges between the fibres were observed (Figs 7, 10). Examples of bridging are shown in the SEM

micrographs in (Figs 6, 8). Under mechanical stress, thick sol coatings and bridges between fibres crack, reducing coating durability.

By reducing the TEOS concentration to 3 wt%, we observed precipitation and exfoliated layers with cracks on the fibre surface and with parallel increasing of ZAD concentration, we observed an increased amount of cracked layers (Figs 6, 9). With TEOS concentration 2 wt% and with the same concentrations of the ZAD we obtained coatings without cracks and bridges (Figs 5, 8).

It can be concluded that the sols with the high concentrations led to the increase of the coating thickness, occurrence of bridging between nearby fibres and

cracking of coating, which results in a lower flexibility of the treated fabric. Additionally, a higher sol concentration might cause less uniform coatings on the textile, since highly concentrated sols might contain more agglomerates and precipitates compared with more diluted sols. Using diluted sols led to more homogeneous coatings and fewer uncoated fibre areas compared with using higher concentration sols [12].

The SEM images in Figs 12 and 13 reveal the evolution of the surface structures during the treatment process depending on different dipping time and the same sol concentration. With dipping times from 30 min, thick coatings cracked during drying (Fig. 13). It can be explained by the fact that if the sol coating exceeds a certain thickness, cracks and surface damages occur because of the shrinkage of the coating networks during the evaporation of the solvent, leading to tensions in the resulting films.

For the textiles with a low thermal stability, the drying temperatures of the coatings are very limited and it is very difficult to dry textiles after the sol–gel coating at temperatures higher than 120–160 °C. For some natural textiles and fibres, for example, the hemp fibres used in the research, appropriate temperature regimes are not higher than 90 °C. It is possible to obtain increased organic solvent evaporation during the sol preparation by mixing sol at higher temperatures. During the present research, the sols mixing temperature was increased from room temperature to 50 °C. It should be noted that the obtained coatings differ from those previously discussed (Figs 2–10, 17, 18).

Using a mixing/dipping temperature of 50 °C (Figs 14–17) with TEOS concentration 2 wt% and with the same concentrations of the ZAD, complete coatings without cracks and bridges between fibres were obtained. The SEM image in Figs 14–16 also indicates that the surface of the fibres became much rougher than uncoated fibres and coatings obtained with sols mixed at room temperature. In comparison with the aforementioned coatings (Figs 14–17), the obtained coatings in Figs 11–13 are uniform and the coverage of the textile fibres is complete. Large aggregate formations were observed on coatings with higher ZAD concentration, see Fig. 16.

With TEOS concentration 2 wt%, we obtained smooth coatings without cracks and bridges, but the ZAD increase in sol creates surface roughness on a nanolevel, Figs 2–5. Comparing coatings prepared at room temperature with those at 50 °C, samples at 50 °C revealed that mixing is homogeneous (Figs 5, 6) but they have visible micro cracks resulting from the drying process (Fig. 5, right). The occurrence of the stress or crack formation during the gelation can be explained by the formation of pores within the gel that are filled with

the solvent. During the continuing evaporation of the solvent and the further condensations of the gel, these pores collapse, resulting in the aforementioned increase of tension. For water repellent finishing, a cracked coating might impair the repellency if the water is sucked into the crack or even into the fibre due to capillary forces.

#### 4. CONCLUSIONS

The use of sols with increasing concentration will lead to an increased thickness of the coatings and simultaneously an increased occurrence of bridging of nearby fibres resulting in a lower flexibility of the treated fabric. All sol processing parameters have high impact on the obtained coating morphology and quality, they must be studied in more detail in the future because the quality of the coating has a high impact on the durability, adhesion and end product properties.

From the SEM observations, it follows that after sols composition and processing parameters optimization, sols can be deposited on cotton fibres in the form of thin xerogel coats, which completely and uniformly cover the fibre surface, with no cracks or fractures and therefore should positively influence their resistance, as is clearly seen in the SEM images. However, hemp fibres with the same coating, during the drying process, form cracks and are more sensitive to drying temperatures.

ZAD use increases the surface roughness and samples with 7.5–8 wt% of sol content form visually high-quality coatings are worth further testing, for both hemp and cotton.

#### ACKNOWLEDGEMENTS

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## Sool-geelprotsessi optimeerimine looduslike kiudude katmiseks

Zane Zelca, Svetlana Vihodceva ja Silvija Kukle

Looduslike kiudude funktsionaalsust saab suurendada sool-geeltehnoloogiaga katmise abil, kusjuures protsessi tuleb kohandada vastavalt kaetavate kiudude tüübile ja rakendatud soolile. Selles uuringus modifitseeriti puhtast puuvillast ja kanepist kiude erinevate parameetritega sool-geeltehnoloogia abil. Skaneeriva elektronmikroskoopia abil uuriti katte morfoloogia sõltuvust erinevatest protsessi parameetritest (katmise ajast ja kasutatud soolidest). Töö eesmärgiks oli uurida erinevate sool-geelmeetodi töötlemisparameetrite mõju pinnakatte morfoloogiale ja kvaliteedile, et saada looduslike kiudude pinnale vastupidavaid ning siledaid katteid.