

# Preparation of Highly Hydrophobic Cellulose Based Surfaces by Silica Particles and Fluorosiloxane Deposition

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**Abstract** – This work is focused on modification of cellulose filters surface in order to hydrophobise a material and decrease water drop adhesion to its surface. Proposed modification methods include deposition of silica particles to obtain desired material roughness and coating material with 1H,1H,2H,2H-perfluorooctyl triethoxysilane (FOTS) to decrease its surface energy.

**Keywords** – cellulose filter media, silica particles, 1H,1H,2H,2H-perfluorooctyl triethoxysilane (FOTS), roughness, hydrophobicity.

## I. Introduction

The purpose of this work is to improve the performance of modified cellulose filters dedicated to purifying diesel fuel from emulsified water and solid particles. The removal of these contaminants is essential due to the negative impact of the above mentioned impurities on engines and injection systems. Developing new methods of cellulose hydrophobisation is particularly relevant due to low-sulphur fuels containing biocomponents introduced into market in recent years. These types of fuel usually have a relatively low value of interfacial tension with water, which results in formation of stable emulsions and a more difficult separation of water.

The wettability of water droplets on solid surfaces is governed by two parameters: chemical composition of surface and its microstructure in a submicron scale. Due to this fact, techniques of preparation superhydrophobic surfaces comprise two steps: manufacturing a rough surface with a nanoparticles and its coating with a low surface energy component [1].

In presented research silica particles were deposited on cellulose fibers to increase their surface roughness and subsequent chemical modification with fluorosiloxane was carried out to decrease surface energy.

## II. Materials and characterization methods

The commercial filter material from Ahlstrom used in this research consists of the main cellulose filtration layer laid onto two polyester layers applied as a support. The material was modified to increase its hydrophobicity and to attenuate the adhesion of water to the surface. The original unmodified material was used as a reference to verify effects of modification.

To characterize the properties of separation materials, measurements of static contact angle (CA) and sliding angle for water droplets were carried out using the goniometer Dataphysics OCA 25 equipped with a tilting

base. The sliding angles were measured for water droplet volume equal to 50  $\mu\text{l}$ . These parameters define the ability of the filter material to repel water and thus prevent its accumulation on the surface. Moreover, the structure of modified material surface was verified using Scanning Electron Microscopy (SEM).

## III. Modification of the cellulose surface

In the first step of modification the monodisperse and spherical silica particles were deposited on cellulose fibers to increase fiber roughness. The silica particles were synthesized utilizing Stober reaction which involves the sol-gel process of aqueous alcohol solution of tetraethoxysilane (TEOS) with addition of ammonia as a catalyst [2]. The silica particles synthesis was carried out in 40°C for 90 minutes, where TEOS (14 ml) was added gradually to continuously mixed solution of ethanol (100 ml) and ammonia (11 ml). The obtained colloidal silica particles were diluted with isopropanol (1:1 volume ratio) and deposited on material via dip coating method, without previous drying nor separation.

To reverse the negative charge and enable efficient coating the reference cellulose was immersed in solution of 1% wt of PDDA (positive electrolyte) in aqueous 0.5 M solution of NaCl for 15 minutes.

To hydrophobize the surface, in the second step of the modification the material was exposed to the 1H,1H,2H,2H-perfluorooctyl triethoxysilane (FOTS) solution in ethanol with addition of water (the volume ratio of used components FOTS:EtOH:H<sub>2</sub>O was equal to 1:100:2). The treatment was conducted by immersing the silica coated cellulose in the solution for 6 hours at ambient temperature. At the end of treatment the material was dried in oven at 120°C for 2 hours [3]. The scheme of the cellulose surface modification and chemical structure of fluorosiloxane is given in Fig. 1.

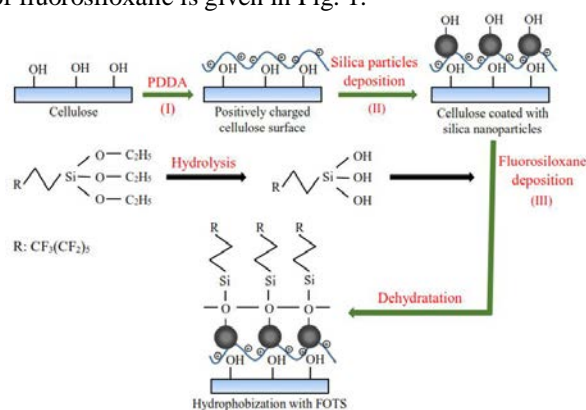


Fig.1 Scheme of cellulose surface modification: (I) changing the cellulose surface charge, (II) deposition of silica particles, (III) bonding fluorosiloxane on inorganic surface.

## IV. Results and discussion

As a result of Stober reaction a stable suspension of colloidal silica spheres was obtained. The concentration of particles was about 34 mg/cm<sup>3</sup> and their zeta potential at pH=9 was  $-49.1 \pm 1.5$  mV, which confirms stability of colloidal system. In the Fig. 2 the SEM image of synthesized silica particles (after solvent evaporation) is presented.

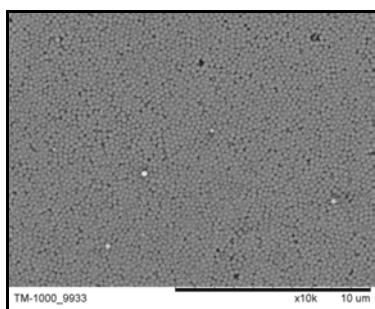


Fig.2 SEM image of silica particles with average size of  $301.6 \pm 1.4$  nm (by number).

In the modification procedure the hydroxyl groups of cellulose play an important role in adhering of silica nanoparticles. They create interfacial C-O-Si bonds with the Si-O groups of silica formed as a result of TEOS hydrolysis. However, the deposition of fluorosiloxane directly onto cellulose was possible due to self-condensation of siloxane followed by hydrolysis (black arrows path in Fig. 1). The different morphologies of cellulose fibres after modification are shown in Fig. 3.

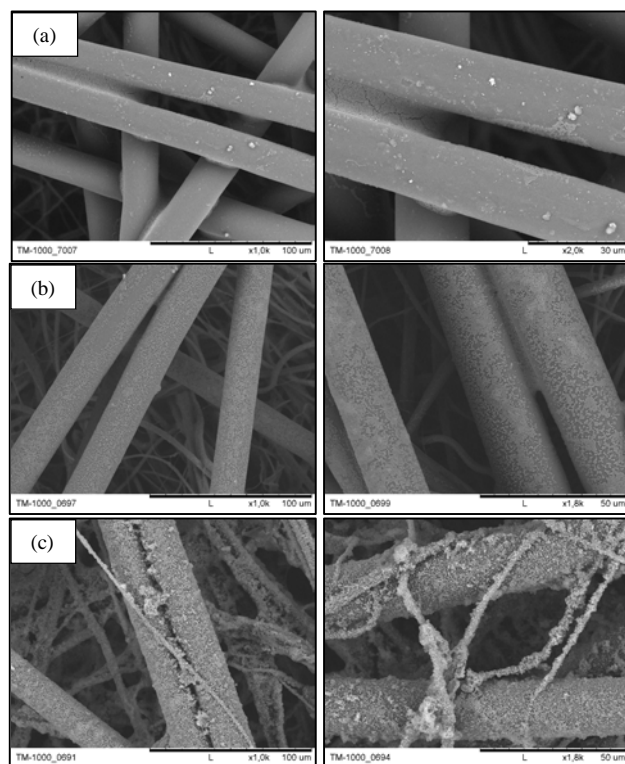


Fig.3 SEM images showing the surface morphology of cellulose fibers: (a) without changing negative charge of cellulose, (b) and (c) single or twice repeated deposition procedure of silica particles respectively, with previous changing surface charge of cellulose for positive (magnification: 1000x i 1500x).

The small amount of silica particles (Fig. 3a) is due to skipping the step of changing cellulose charge in modification procedure. In such case repulsive forces between negatively charged silica particles and the cellulose surface hindered the fiber coating process.

In Fig. 3b and 3c the silica particles appear well dispersed at the cellulose surface, which makes its roughness rather homogeneous. When the particle deposition procedure was repeated, the higher amount of silica particles on cellulose fibers was present, as shown in the Fig. 3c. However, no multilayer coating has been observed.

In Table I results of wettability expressed by values of contact angles and sliding angles of water for obtained materials after modification are presented.

TABLE 1

CHARACTERIZATION OF SURFACE PROPERTIES OF TESTED MATERIALS

Material	Water contact angle (CA), °	Water sliding angle ( $\alpha_{50}$ ), °
Cellulose, without modification	$125.5 \pm 5.1$	$44.0 \pm 1.8$
Cellulose + FOTS	$134.0 \pm 4.1$	$45.5 \pm 2.4$
Cellulose + silica particles 1x + FOTS	$136.8 \pm 6.2$	$44.7 \pm 2.1$
Cellulose + silica particles 2x + FOTS	$139.3 \pm 4.3$	$47.4 \pm 6.2$

The significant increase of water contact angle as a result of fluorosiloxane deposition was noticed. However, introducing the silica particles lead to an increase of water contact angle only by few degrees. The reduction of water sliding angle of water was not achieved in this case. Obtained results can be explained by application of silica particle with a very uniform size, which did not allow to create a hierarchical structure. In literature the best results of surface roughness were obtained for silica particles diameter about 600 nm [3], where sodium silicate layers were applied to create hierarchical roughness.

## Conclusion

The presented approach constitutes a promising method to increase hydrophobicity of cellulose material. The best results were obtained for the filter covered with silica particles (procedure repeated twice) and fluorosiloxane (FOTS) comparing to the reference structure (before modification). Additionally, the necessity of changing cellulose surface charge before silica deposition step was confirmed to be critical to obtain an effective and uniform coating.

## References

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