Modification of Polyurethane-Coated Fabrics by Sol–Gel Thin Films

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ABSTRACT: Sol–gel derived silica and hybrid films from tetraethoxysilane (TEOS) and 3-glycidyloxypropyltrimethoxysilane (GLYMO) were deposited by dip-coating, in order to find the best treatment. GLYMO-based treatments preserved textile feel of the material. The coatings were characterized by infrared spectroscopy (IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and water contact angle measurement. IR spectra confirmed the existence of silicate network and successfully conducted modification for both precursors. DSC and TGA showed that the conditions of hydrolysis had greater influence on TEOS than GLYMO-based treatments. Both treatments shifted the degradation onset to higher temperatures. SEM images showed that polyurethane surface and pores were completely covered and filled by silica or hybrid thin films forming a composite organic–inorganic coating. Hydrophobic effect was preserved for all the samples, except for a single treatment of the GLYMO, due to its polar epoxy group. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39914.

INTRODUCTION

Requirements for new, better and multifunctional textile materials in the course of the last century have provoked widespread attention for the nanostructured materials in the field of the textile technology. Sol–gel process is an innovative approach to surface modification of textiles and other materials and has been one of the most important discoveries for several past decades.[1,2] In the field of textile engineering, the number of published papers dealing with the sol–gel technology has increased in the last fifteen years.[3–11] The sol–gel technology offers great opportunities in terms of design and creation of new surface properties for textiles. The sol–gel modification of textiles was investigated on various textile substrates (cotton, regenerate cellulose, cotton/polyester, polyester, polyamide, flax and polyacrylonitrile fabrics, aramide nonwoven textile, etc.) most often with the aim to improve flame retardancy, resistance to surface wetting, color change, UV-absorption, antimicrobial properties, with or without nanoparticles.[1,3–11] Most often used precursor for sol–gel modification of textile materials has been tetraethoxysilane (TEOS), although there are numerous other precursors as well [tetramethoxysilane (TMOS), methyl trimethoxysilane (MTMS), 3-aminopropyltriethoxy silane (APTES), etc.]. Organically modified precursor 3-glycidyloxypropyltrimethoxysilane (GLYMO)

has been used only rarely. The advantage of an organically modified precursor, in comparison with TEOS, is that they introduce functional organic groups to the sol–gel derived coating, which enables tuning of such properties as surface wetting and better immobilization of auxiliary nanoparticles and nanopowders. The number of alkoxy groups of GLYMO and TEOS is also important: while the first has three, the second has four alkoxy groups, which leads to the formation of stiffer inorganic networks and therefore a more brittle coating.[12]

In the sol–gel chemistry, reactions of hydrolysis and condensation are highly complex and the structures of hybrid materials obtained are extremely sensitive to the conditions occurring during preparation. To obtain reproducible hybrid materials, parameters and conditions of the process should be kept strictly unchanged. Main parameters are: the existence of covalent bonds between the phases, the type of catalyst used, the concentration and purity of the reactants, the type of alkoxy group and organic substitution, solvent, temperature and the manner of mixing.

Textile materials are characterized by their complex structures and the sol–gel process is highly complex too. The knowledge of textile chemistry and materials, as well as the familiarity with the mechanisms of reactions of hydrolysis and condensation are

needed to obtain hybrid textile materials with desired structure. The sol–gel process is highly suitable for the modification of textile materials, because of its versatility and possibility to obtain an inorganic phase at a low reaction temperature (usually under 100°C). This is very important, to avoid degradation of sensitive compounds.

Different ratios of the precursor to water, temperature, pH value, types of catalysts and solvent have been selected in most of the papers in the field of textile engineering. In the work presented here, wide range of ratios, duration of hydrolysis and temperature were used to perform numerous experiments. Approximately 2100 samples were coated to select the best treatment for the chosen sample. All the important parameters were covered in these experiments, giving a complete overview of their influence. The aim of this research was to investigate the influence of the precursor used (TEOS or GLYMO), as well as the impact of the conditions of hydrolysis and deposition of sol on textile substrate, on the properties of treated textiles. The main idea was finally to choose the best treatment, with the additional requirements related to the retention of the textile character of the newly created protective textile material. The best treatment was intended to be used as the solution for the addition of silver nitrate ($AgNO_3$), in this work, aimed at achieving antimicrobial properties on the polyurethane coated textiles.

Silver has been used for centuries to prevent and treat a variety of diseases, most notably infections. Silver ions appear to kill microorganisms instantly by blocking the respiratory enzyme system (energy production), as well as altering microbe DNA and the cell wall, while having no toxic effect on human cells *in vivo*.[13]

The number of textiles with an antimicrobial activity has increased considerably over the last few years. Together with the increase of new antimicrobial fibers and fabrics technologies in the health sector (hygienic and medical applications) and the food stuffs industry.

The sol–gel process has several advantages, but the most important is the possibility to incorporate additives such as silver into the first stage of the sol preparation without inhibiting formation of the silica network. For antimicrobial activity of textiles, very important is that the silver is not removable from fibers, fabrics, coatings, etc. As long as no silver released, there should be no toxic risks.[14] The sol–gel process is unique in comparison with other antimicrobial agents given that silver ions must be sufficiently anchored in the silica network to provide durable antimicrobial properties.

EXPERIMENTAL

Preparation of Sols and Textile Materials

Hydrochloric acid (37%, Aldrich Chemicals) and ammonia (30%, Aldrich Chemicals) were chosen as catalysts for the hydrolysis, since these are volatile substances and can be removed from sol by evaporation before or during condensation. TEOS (98%, Aldrich Chemicals) and GLYMO (98%, Aldrich Chemicals) were hydrolyzed with aqueous solutions of hydrochloric acid as an acidic catalyst, or ammonium hydroxide as a base catalyst, as well as distilled water with no catalyst added.

For all the ratios used, the influence of the duration of hydrolysis (1 or 4 h) and temperature (20 or 60°C) was also investigated. With all this combinations, important parameters for the sol–gel properties (precursor, types of catalysts and solvent, molar ratio of precursor to solvent, pH value, and temperature) were also included.

The sol was stirred magnetically for all molar ratios of TEOS and GLYMO to water. In the first step, the solution of distilled water, ethanol (1.6 mol L^{-1}) and catalyst (0.1 mol L^{-1}) was thoroughly mixed. Then, TEOS or GLYMO was added drop by drop to this solution, raising the speed of mixing. The process was carried out under continuous magnetic stirring until a homogeneous solution was obtained.

In the second step, the samples 5×5 cm^2 in size were dip-coated on a custom-made apparatus with the predetermined drawing speed of 0.5, 1, 1.5, and 2 mm s^{-1} to obtain a thin coating. Modified samples were left to gel at room temperature for 24 h, and were then dried at 100°C for 1 h.

For the antimicrobial treatment, $AgNO_3$ (Aldrich, 99.9%) was chosen, and added to sol without a catalysts, for the GLYMO : water ratio of 1 : 3. Two mass concentrations of $AgNO_3$ (10 and 20 g dm^{-3}) were chosen. $AgNO_3$ was carefully added to the sol in small amounts, under higher speed of mixing. The process was carried out under continuous magnetic stirring until a homogeneous solution was obtained. Samples were then dip-coated as described above.

Some samples treated with $AgNO_3$ were additionally treated with simulated urine, consisting of 9 g L^{-1} solution of sodium chloride in Grade 3 water, conforming to standard, with the surface tension of 70 ± 2 mN m^{-1} at 20 ± 2°C.[15,16] Antimicrobial treated samples were submerged in the simulated urine solution in Petri dishes and left for 30 min at room temperature. Treated antimicrobial samples were left to dry at room temperature for 24 h.

Antimicrobial treated samples were also washed according to standards in the automatic washing machine, with non phosphate ECE reference detergent A.[17] Delicate machine cycle and 41 ± 3°C washing temperature were chosen. Washed samples were left to dry at room temperature for 24 h.

Commercially available coated textile material, code MAP 4 220, made by Čateks d.d. for medical program (covers for mattresses, pillows, sheets, etc. in hospitals and nursing homes) was used. Before the treatment, some basic characteristics of the textile were defined according to international standards.

Sensory Evaluation of Samples with the Interaction of Touch and Vision

Modified samples were evaluated by visual and tactile examination to select the treatment that would retain textile character of the sample. The organization AATCC (American Association of Textile and Chemist and Colourists) has published guidelines for the subjective fabric assessment and we mostly accepted them, as applicable for small sample size we used.[18]

For better and easier comparison of treatments, maps of modified samples were made. The maps of modified samples were

prepared according to the precursor, catalysts, time and temperature of treatment. An unmodified sample was observed as a reference sample.

Treatments which resulted in sample surface rigid to touch were discarded. The attributes used for tactile and visual-tactile examination were:

1. uniformity of coating (thickened or thinned places, any unevenness of coating, etc.),
2. touch (smooth or rough),
3. shine,
4. flexibility (whether the coating cracked in bending),
5. any observation that reduced the textile character of the sample.

Instrumental Methods

FTIR spectra of the samples were recorded on Bruker Vertex 70 instrument equipped with the attenuated total reflection (ATR) unit, in 400–4000 cm^{-1} interval. Surface structure, morphological characteristics and thickness of the coated textiles were investigated by scanning electron microscope (SEM) TESCAN, VEGA TSS136LS, with the operating voltage of 30 kV and secondary electron detector. Chemical analysis of the surface was performed by energy dispersive X- ray spectroscopy (EDS) analysis, using EDS detector manufactured by Oxford Instruments in the detection range of 20 keV.

Differential scanning calorimetry (DSC) measurements were carried out on Netzsch DSC 200, from room temperature to 300°C, at the heating rate of 10 K min^{-1}, with sample size ~2.5 mg. DSC investigation was done under stationary air atmosphere.

Thermogravimetric analysis (TGA) was performed on Netzsch thermoanalyzer STA 409. Samples weighing ~17.0 mg were heated from room temperature to 1000°C at the heating rate of 10 K min^{-1}, in a synthetic air flow of 30 cm^3 min^{-1}.

Degradation onset temperature both from DSC and DTG (Derivative thermogravimetry) curves was determined using Netzsch proprietary software NETZSCH Proteus—Thermal Analysis version 4.8.0.

Contact Angle Measurements

Contact angles were measured using OCA 20 optical contact angle system (DataPhysics Instruments GmbH, Germany). Surface tension ($\gamma = 72.8$) and its dispersive ($\gamma^d = 21.8$) and polar ($\gamma^p = 51.0$) components of test liquid—water ($\lambda = 1.33$ mL cm^{-1}) were used for contact angle measurement.

Small strips (5×1 cm^2) of the treated samples were cut for contact angle measurements. Contact angles were measured immediately (10–30 s) after placing a 2 μL drop of one of the test liquids on the surface of the material, and the calculations of contact angles were made from screen images of the drops, measuring their maximum height and width, assuming a spherical profile in accordance to the Young-Laplace equation. Five drops were used for each sample, averaging the values for our final contact angle value. Standard deviation of the results

obtained was below 2°. The measurements were done at the temperature of 23 ± 0.2°C.

Antimicrobial Activity

Determination of antibacterial activity was performed by agar diffusion plate test.[19] *Staphylococcus aureus* (ATCC 292 13) as a gram positive strain and *Escherichia coli* (ATCC 11229) as a gram negative strain were used. Test specimens were circular, with the diameter of 25 ± 5 mm. They were prepared in accordance with the standard and then tested in a certified laboratory. Inhibition zone in mm as an effect of the antibacterial treatment was measured. Contact zone under the specimens was also tested for bacterial growth.

Evaluation of the action of microfungi was done in accordance with the standard, method B2: Antimycotic activity.[20] *Aspergillus niger van Tieghem* (ATCC 6275) was used as a test strain. Circular test specimens of 30 mm were cut and prepared in accordance with the standard and tested in accordance with the standard in a certified laboratory. Inhibition zone in mm and the growth in agar was determined and then evaluated in accordance with the standard.

To test the durability to washing, samples were tested after 1 and 10 washings. The antimicrobial activity of samples treated in a solution was also tested.

RESULTS AND DISCUSSION

Results of the Preparation of Sols and Textile Materials

The molar ratio of GLYMO to water was chosen based on results obtained, where it was determined that 1 : 1.5 is the stoichiometric ratio for total condensation of the alkoxide groups and 1 : 3 is the stoichiometric ratio for total hydrolysis of the alkoxide groups.[12] Substoichiometric molar ratio for GLYMO (1 : 0.5) was also investigated, and the exact ratio was chosen in the preliminary investigation.

Substoichiometric molar ratio for GLYMO (1 : 0.5) was investigated as well. It was chosen in the preliminary investigation from among a large number of molar ratios, because of its uniformity of coating, smooth touch, shine and flexible surface without cracking, which was associated with the retention of the textile character as the main feature for textiles.

Molar ratio of TEOS to water was chosen based on the criteria of stoichiometric ratio for condensation and hydrolysis (1 : 2, 1 : 4), and some additional ratios (1 : 6, 1 : 0.25, 1 : 0.5) were chosen in preliminary investigations. The molar ratios of TEOS and GLYMO to water are given in Table I.

The composition of the sample was determined in accordance with the ISO 1833.[22] The sample was composed of a layer, i.e., coated polymer (polyurethane) and substrate, i.e., backing fabric (polyester). Polyurethane is aromatic and between layer and the substrate is a one-component aromatic polyether as a connective agent.

The textile material in question was treated during the production with antifungal and inflammable flame additives, known only to the producer. Mass per unit was determined in

Table I. Process Conditions and Variations of the Molar Ratio of TEOS and GLYMO to Water with the Aim of Selecting the Best Treatment[21]

Precursor	Alkoxide : water ratio	Temperature	Time
TEOS	Acid: 1 : 2, 1 : 4, **1 : 6**	20°C	1 h
	Base: **1 : 0.25**, 1 : 0.5		
	No catalyst: **1 : 2**		
GLYMO	Acid: 1 : 0.5, 1 : 1.5, **1 : 3**	60°C	4 h
	Base: 1 : 0.5, **1 : 1.5**, 1 : 3		
	No catalyst: **1 : 1.5**, 1 : 3		

Best treatments are bolded.

accordance with the ISO 2286-2 and found to be 186.7 g m^{-2}.[23] No preparatory process on the textile substrate before dip-coating was performed (scouring, bleaching, etc.).

Results of the Sensory Evaluation of Samples with the Interaction of Touch and Vision

Visual and tactile examination served to select the treatments that offered the feel and look similar to, if not the same as, unmodified sample.

It should be noted that almost every treatment based on GLYMO was acceptable. However, to select only the best ones (acid: 1 : 3, base: 1 : 1.5, no catalyst: 1 : 1.5), decisive details in choosing were scrutinized, such as the best touch and flexibility, and visually almost unnoticeable differences of the modified surface in comparison with the unmodified sample. Hydrolysis with pure water at 20°C for GLYMO : water ratio 1 : 3 was especially effective, as it had almost identical visual and tactile characteristics to those of the unmodified sample, so that it was hard to distinguish which sample was modified and which was not.

Sensory evaluation showed that time and temperature of hydrolysis, as well as drawing speed, had no significant influence on the tactile feel of the samples, i.e., there was no significant difference in their surface properties.

Comparing the sol–gel coatings based on TEOS and GLYMO, it was noted that the samples modified with GLYMO:

1. were softer in comparison to the ones coated with TEOS,
2. remained undistorted after gelling,
3. had a shinier coat,
4. were unnoticeable to touch.

Most of the samples modified with TEOS showed the following characteristics:

1. distortion after gelling,
2. being harder to touch,
3. brittleness of coating (cracking with lightest bending).

From the theory it is known that hybrids can vary from soft and flexible to brittle and hard, depending on the chemical structure of organic components and the overall ratio of organic to inorganic phase.[24] If we apply this to the results of sensory

evaluation, then listed characteristics are the reflection of the number of alkoxy groups of GLYMO and TEOS: while the first has three, the second has four alkoxy groups, which leads to the formation of stiffer inorganic networks and therefore more brittle coatings.12

Obviously, GLYMO coating leads to less brittle coatings and softer feel, as the organic chains offer higher flexibility and softness to GLYMO coating.

For the purpose of further investigation employing instrumental methods (FTIR-ATR, DSC and TGA, SEM and EDS, contact angle measurement), three conditions for every alkoxide were selected, representing every type of the hydrolysis (acid, base and no catalyst). These treatments are marked in bold in Table I. Hydrolysis at 20°C for 1 h at the drawing speed of 1 mm s^{-1} was carried out.

Results of Infrared Spectroscopy

The sol–gel coatings were characterized by infrared spectroscopy to determine chemical modification and the presence or formation of bonds characteristic for sol–gel processes. These are primarily Si—O and Si—C vibrations, stretching of Si—O bonds and in particular Si—O—C and Si—O—Si bridges. Due to the large number of overlapping bands, it is sometimes difficult to determine which bonds appear and which disappear. Therefore, this analysis should be performed very cautiously.

The assignments of bands were taken from the literature.[12,25] In the spectra of sol–gel coatings, the presence of strong —OH bands or the loss of CH$_3$— bands was taken as the evidence of rapid and complete hydrolysis. The other bands included:

1. Si—O ($\sim$1200–1000 cm^{-1})—an area of stretching Si—OC and Si—O—Si (bands are overlapping but they were the evidence of silicate networks),
2. Si—C band ($\sim$1260 cm^{-1}),
3. Si—OH ($\sim$910 cm^{-1}),
4. C—H ($\sim$2920 cm^{-1}),
5. C—O ($\sim$1110 cm^{-1}), etc.

Three treatments based on TEOS were used for further analysis by infrared spectroscopy (Table I). The impacts of the time and temperature of hydrolysis were also studied, and it was noted that these parameters did not influence the shape of the infrared spectra. For this reason, further investigation was limited to the samples modified by TEOS, hydrolyzed at 20°C for 1 h, as shown in Figure 1.

All the spectra showed the formation of silanol groups (reflected in the appearance of —OH bands at 3652 cm^{-1} and 1500 cm^{-1}), and the decrease in the band at 2920 cm^{-1}, attributed to C—H bonds.

The bands in this region were of lowest intensity after coating with acid sol, which was expected since acid catalysis favors hydrolysis, and the water : TEOS ratio was the highest for this sample. Lower amounts of water used for the other two TEOS treatments probably did not allow complete hydrolysis. Basic sol showed a decrease in C—H band similar to the neutral one, in
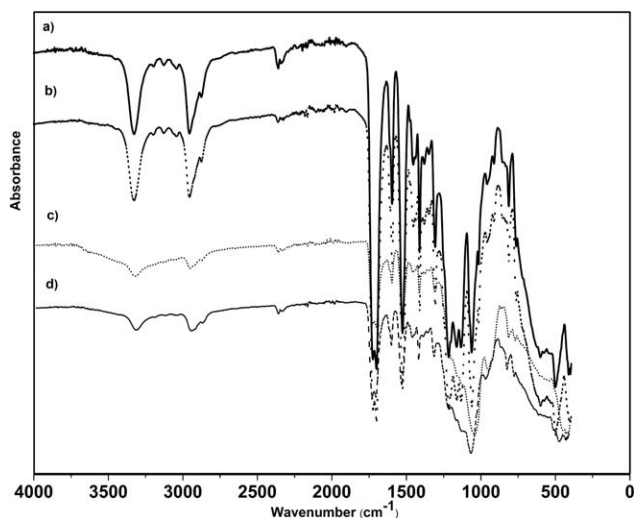
Figure 1. FTIR spectra of TEOS-based treatments: (a) unmodified, (b) P : H$_2$O, 1 : 2, 20°C, (c) HCl, 1 : 6, 1 h, 20°C, and (d) NH$_4$OH, 1 : 0.25, 1 h, 20°C.

Figure 2. FTIR spectra of GLYMO-based treatments: (a) unmodified, (b) P : H$_2$O, 1 : 1.5, 1 h, 20°C, (c) HCl, 1 : 3, 1 h, 20°C, and (d) NH$_4$OH, 1 : 1.5, 1 h, 20°C.

spite of much lower water content, probably due to catalytic effect of the base.

All the spectra showed a wide band at 1200–1000 cm^{-1} which indicated the existence of the silicate network and successfully conducted modification. Bands of the polyurethane substrate were clearly visible in all the spectra (3333, 2961, 1696, 1529, 1228, 1148, 1050, and 511 cm^{-1}), but their relative intensity decreased in the following order: unmodified > neutral treatment > base treatment > acid treatment. This could be taken as an indication of the thickness of the inorganic layer formed.

As was the case with TEOS-based treatments, time and temperature of GLYMO hydrolysis did not affect the spectra of sol–gel coating. Therefore, all further observations were of the treatments where GLYMO was hydrolyzed at 20°C for 1 h.

To compare the conditions of hydrolysis, three GLYMO-based treatments were selected (Figure 2):

1. the addition of acidic catalyst (ratio of precursor to water— 1 : 1.5),
2. the addition of base catalyst (ratio of precursor to water—1 : 1.5),
3. no catalyst (ratio of precursor to water—1 : 3).

The spectra of GLYMO-based treatments (Figure 2) showed the characteristic Si—O bands at 1100–1000 cm^{-1}, which indicated the presence of silica network and successfully completed modification.

Irrespective of the catalyst used, the conversion of methoxide groups of GLYMO (i.e. the reduction of bands at 2870 cm^{-1}) was comparable, although the hydrolysis should have been faster in the acid-catalyzed system. GLYMO-treated samples also showed the decrease in the characteristic polyurethane bands, in the following order: unmodified > neutral treatment > acid treatment > basic treatment. It can be assumed that the "coverage" was better for basic GLYMO-treatment (when com-
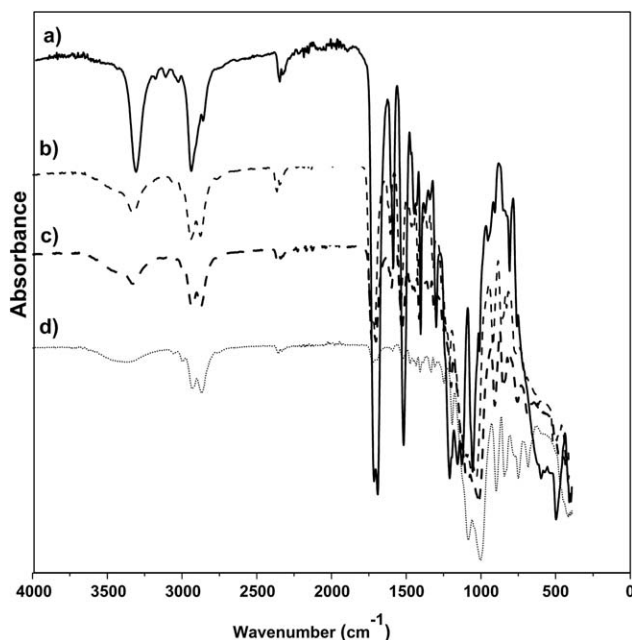
pared to basic TEOS-treatment) because of higher water : alkoxide ratio. The treated samples also showed a sharp Si—C band at 1200 cm^{-1} and the epoxy ring band at 904 cm^{-1}, which confirmed the formation of a hybrid film on the surface of the fabric.

Thermal Properties

Figure 3 shows the results of DSC measurements, and Figure 4 shows the results of TGA measurements. Since the DSC curve of core polyester fabric (PES) showed large endothermal melting maximum at 250°C, all the measurements were performed on polyurethane (PUR) coating removed from the modified samples [Figure 3(a)]. PUR showed initial exothermal degradation at ~225°C. Small residual melting maximum of PES remained visible with some of the samples, indicating incomplete separation of the coating from the core fabric. TEOS-based and GLYMO-based treatments offered quite different impacts on the properties of PUR coating. While the influence of TEOS-based treatment varied greatly with the conditions of hydrolysis [Figure 3(b)], GLYMO-based treatments showed very little influence on the shape of the DSC curve [Figure 3(c)]. Key parameters from the DSC curve are summarized in Table II.

Acid-catalyzed TEOS-based treatment completely inhibited the initial degradation of PUR, which was evident from the appearance of the sample after measurement: while all the other samples were melted and black, this one retained its shape and showed only slight browning. This indicated the presence of a homogeneous inorganic coating that prevented diffusion of oxygen into PUR, thus slowing down the reaction of degradation. Base-catalyzed treatment, on the other hand, showed additional reaction at lower temperatures (possibly degradation of non-hydrolyzed ethoxide groups in TEOS), while neutral treatment showed almost no impact.
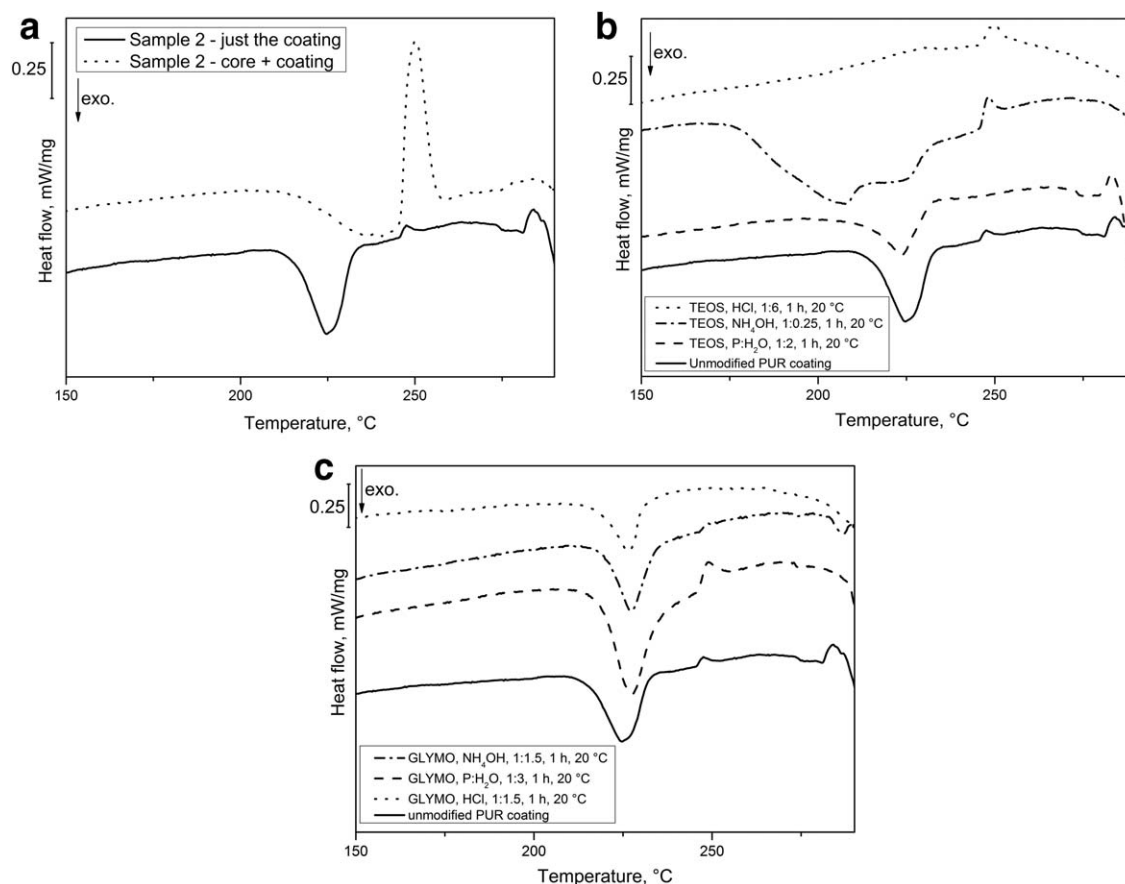
Figure 3. DSC curves of (a) core and coating of the unmodified fabric; (b) PUR coating with TEOS-based treatments; (c) PUR coating with GLYMO-based treatments. Curves have been shifted for clarity.

All GLYMO-based treatments shifted the degradation temperature several degrees higher. The influence on reaction enthalpy was small as well, and could be attributed to the combined influence of increased inorganic content (decreased enthalpy) and exothermal reaction of etherification of epoxy groups of GLYMO at higher temperatures (increased enthalpy). Both effects could also explain somewhat improved resistance to degradation. Unlike acid-catalyzed TEOS-based treatments, none of GLYMO-treatments formed an impenetrable coating on surface of the PUR.

TGA measurements were also made on PUR coatings alone. Regardless of the treatment, all the coatings lost mass in two

separate degradation steps: the first one at ~290°C and the second one at ~375°C, as illustrated in Figure 4. The exothermal degradation reaction, as determined by DSC, did not involve any mass loss. All the parameters extracted from TGA and DTG curves are summarized in Table III. Both TEOS and GLYMO-based treatments shifted the onset of degradation to somewhat higher temperatures. The effect was again most pronounced for the acid-catalyzed TEOS-treatment, which also exhibited the largest shift in temperature maximum of the first degradation step. Other TEOS-treatments showed very little influence on the temperature of degradation. GLYMO-treatments all showed a

Table II. Onset Temperature, t_{onset}, Maximum Temperature, t_{max}, and Enthalpy, Δh, of PUR Degradation, as well as Melting Enthalpy of PES at 250°C, $\Delta_{\text{m}}h$, as Determined by DSC

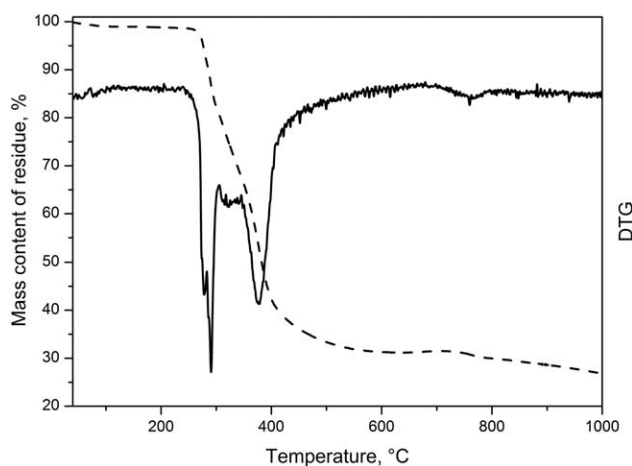| Treatment	t_{onset} (°C)	t_{max} (°C)	Δh (J g^{-1})	$\Delta_{\text{m}}h$ (J g^{-1})
TEOS, HCl, 1 : 6, 1 h, 20°C	–	–	–	2.6
TEOS, NH$_4$OH, 1 : 0.25, 1 h, 20°C	175.6	208 + ~225	~ −100	3.3
TEOS, P:H$_2$O, 1 : 2, 1 h, 20°C	212.8	223.8	−23	–
GLYMO, HCl, 1 : 3, 1 h, 20°C	218.2	226.7	−20	–
GLYMO, NH$_4$OH, 1 : 1.5, 1 h, 20°C	217.1	227.4	−24	–
GLYMO, P:H$_2$O, 1 : 1.5, 1 h, 20°C	218.9	227.4	−28	3.8
Unmodified	215.5	224.7	−26	0.8

Figure 4. TGA (dashed) and derived DTG (full) curves of the degradation of PUR coating.

similar effect on the first degradation step, regardless of the hydrolysis conditions, similar to the influence on DSC curves. It can be concluded that the morphology of GLYMO-coating did not change significantly with the conditions of hydrolysis. The second degradation step was not influenced by the treatments. Final mass residue of the treated samples was actually lower than that for the unmodified PUR coating (with the exception of acid-catalyzed TEOS-treatment). This was quite unexpected, since the inorganic modification should result in higher ash content. Since the samples did not combust completely at 1000°C (~26% char, black in appearance), it can be assumed that the presence of inorganic network led to the formation of less compact char, which ensured easier combustion at higher temperatures.

Results of Surface Structure and Morphological Characteristics

Treatments with the potential to serve as a base for the addition of $AgNO_3$ were chosen for SEM and EDS characterization:

Treatment I. GLYMO as a precursor, acid catalyst (HCl), the stoichiometry ratio of precursor and water—1 : 1.5, processing time 1 h, 20°C, closed reaction system,

Treatment II. GLYMO as a precursor, without catalyst, i.e., the hydrolysis was carried out with distilled water, the stoichiometry

ratio of precursor and water—1 : 3, the processing time 1 h, 20°C, closed reaction system.

Two chosen treatments were compared with TEOS treatment (acid catalysis, 1 : 6) and the untreated sample.

The images of coating surface by SEM (Table IV) showed the modification of polyurethane coatings. Polyurethane surface was not only covered with silica or hybrid thin films, the surface pores were also completely filled, forming a composite organic–inorganic coating. The samples modified by GLYMO-based treatments showed homogenous coating, with the Treatment I providing noticeably more complete coverage of the polyurethane. This may be explained by higher degree of hydrolysis in this acid-catalyzed system, resulting in more hydroxyl groups being able to from hydrogen bonds with the polyurethane. TEOS-based treatment resulted in the presence of cracks all the way to the microscale, thus confirming brittleness of this type of treatment, and its unsuitability for the modification of textiles.

The differences observed in the SEM can be explained by the differences in solid content and probably the viscosity of the sols. However, main interest of this work is successful modification, and particularly surface structure and its relation to the feel of the textile material treated. Detailed research of solid content and viscosity will be of more interest in some future work.

The results of chemical element microanalysis on the surface of the coatings are shown in Table V. The area $25 \times 25 \ \mu m^2$ in size in the centre of every sample was used to collect the EDS information. The presence of Si as an indicator of the existence of silicate network was confirmed on all the modified samples.
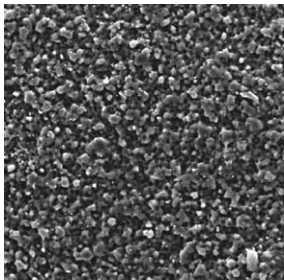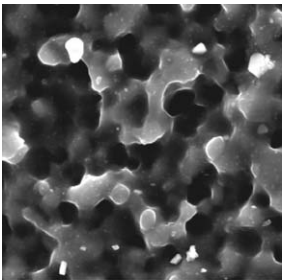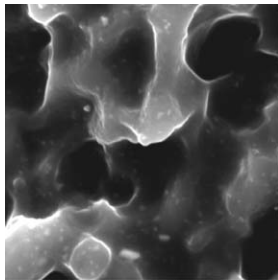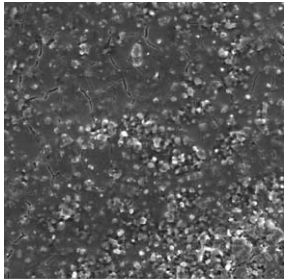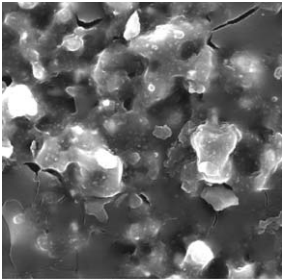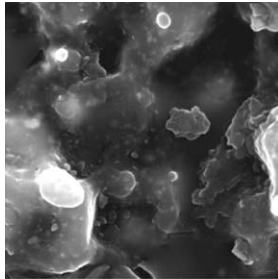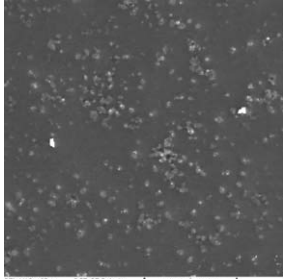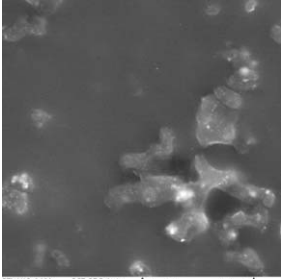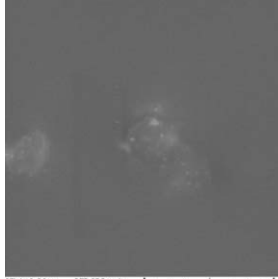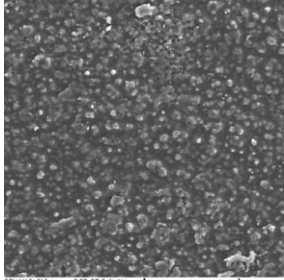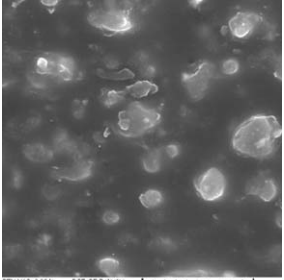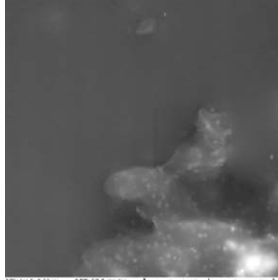
The Treatment I of GLYMO exhibited highest Si content, and the ratios of elements were very close to that of the fully hydrolyzed and condensed GLYMO-based coating ($RSiO_{3/2}$, where R stands for the organic chain of GLYMO). This matched the results of SEM observation, showing almost complete coverage of the surface with a smooth hybrid film.

For the Treatment II, the covering was poorer, as shown by smaller Si : O and Si : C ratios. C : O ratio decreases for all the modified samples, since organic polyurethane chains were covered by silica or hybrid films. The decrease was most pronounced for silica film (TEOS treatment), since it contained no organic components of its own.

Table III. Onset Temperature, t_{onset}, Temperatures of Two Degradation Maxima, t_{max1} and t_{max2}, and Residual Mass Content, as Determined by TGA and DTG

Treatment	t_{onset} (°C)	$t_{max,1}$ (°C)	$t_{max,2}$ (°C)	Residue (%)
TEOS, HCl, 1 : 6, 1 h, 20°C	299.1	307.1	375.5	26.9
TEOS, NH_4OH, 1 : 0.25, 1 h, 20°C	278.1	292.7	374.2	23.6
TEOS, P : H_2O, 1 : 2, 1 h, 20°C	270.2	288.0	375.1	22.5
GLYMO, HCl, 1 : 3, 1 h, 20°C	285.2	298.1	374.9	20.9
GLYMO, NH_4OH, 1 : 1.5, 1 h, 20°C	286.5	299.5	375.2	22.1
GLYMO, P:H_2O, 1 : 1.5, 1 h, 20°C	290.4	300.7	374.7	25.0
Unmodified	270.0	290.8	376.8	26.8

Table IV. Surface of Unmodified Samples and Samples Modified with TEOS and GLYMO at Magnification 500×, 3000×, and 7000×

500×	3000×	7000×
Unmodified sample		
TEOS–Treatment (catalyst HCl, 1 : 6)		
GLYMO—Treatment I (catalyst HCl, 1 : 1.5)		
GLYMO—Treatment II (without catalyst, 1 : 3)		

To determine the influence of the treatment on polyurethane coating thickness, sample cross-cuts were inspected by SEM, and the results are shown in Table VI. Since the investigation was performed at a limited number of locations on the sample, it is possible that the results are not fully representative.

Coating thickness after GLYMO Treatment I was comparable with the unmodified sample, while the other two treatments resulted in decreased thickness. The siloxane film formed was expected to be denser in the case of TEOS (with four alkoxide groups compared to three of GLYMO)

Table V. Number Ratios of Elements on the Surface of Coatings as Determined by EDS; Comparison with Fully Hydrolyzed Precursor Molecules

Sample	C : O	Si : O	Si : C
Unmodified	2.38	0.00	0.00
GLYMO treatment I	1.87	0.30	0.16
GLYMO treatment II	2.10	0.06	0.03
TEOS treatment	1.73	0.12	0.07
Hydrolyzed GLYMO	1.20	0.20	0.17
Fully condensed GLYMO	1.71	0.29	0.17
Hydrolyzed TEOS	0.00	0.25	–
Fully condensed TEOS	0.00	0.50	–

and in the case of higher pH of hydrolysis and condensation.

Water Contact Angle Results

Contact angle results for the untreated and treated samples are shown in Table VII. Depending on contact angle results, the droplet is characterized as completely wetting, non-wetting or completely non-wetting. It is well known that water wettability of materials is governed by both their chemical composition and geometric microstructure of the surface. Wettability strongly depends on two properties—surface free energy and surface roughness. Surface free energy is an intrinsic property of the material that can be controlled by chemical modification such as fluorination and other hydrophobic coatings.[26]

The results of contact angle obtained indicated significant changes between the treatments (TEOS and GLYMO) and

Table VI. Polyurethane Coating Thickness of the Unmodified Sample and the Samples Modified with TEOS and GLYMO at the Magnification of 500×
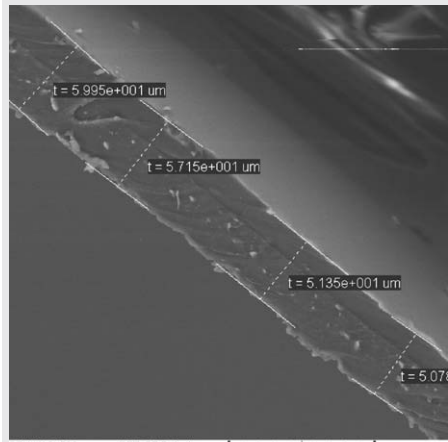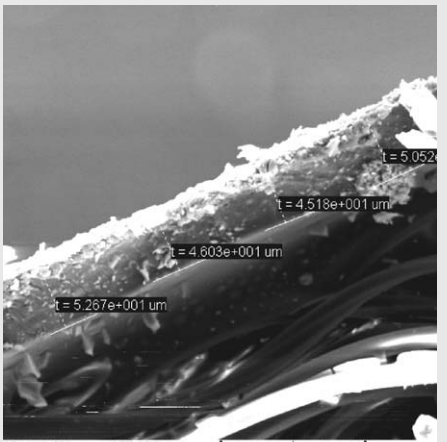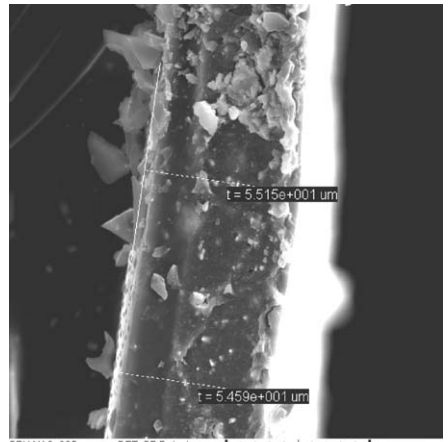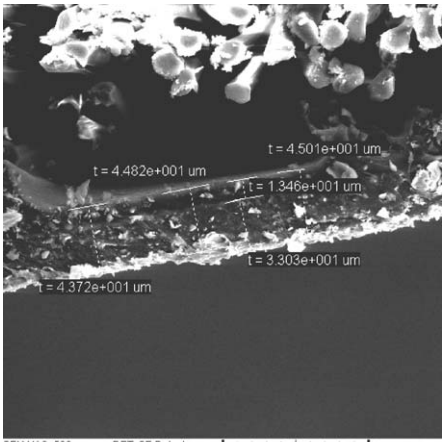
Unmodified sample (500×)	TEOS (500×)—Treatment (catalyst HCl, 1 : 6)
D (μm): 59.95; 57.15; 51.35, 50.73 = Σ **54.80 μm**	D (μm): 50.52; 45.18; 46.03; 52.67 = Σ **48.60 μm**
GLYMO—Treatment I (catalyst HCl, 1 : 1.5) (500×)	GLYMO—Treatment II (without catalyst, 1 : 3) (500×)
D (μm): 55.15; 54.59 = Σ **54.87 μm**	D (μm): 43.72; 44.82; 45.01 = Σ **45.72 μm**

Table VII. Water Contact Angles for the Untreated and Treated Samples

| | | Treatment | | | | | |
| | | TEOS (20°C, 1 h) | | | GLYMO (20°C, 1 h) | | |
No.	Untreated	HCl, 1 : 6	NH$_4$OH, 1 : 0.25	P : H$_2$O, 1 : 2	HCl, 1 : 3	NH$_4$OH, 1 : 1.5	P : H$_2$O, 1 : 1.5
1	115.48	100.07	111.39	117.61	91.91	100.89	86.77
2	114.22	101.44	113.84	114.74	90.62	99.76	90.84
3	114.83	101.19	112.91	112.58	90.22	100.26	89.68
4	111.76	99.01	110.72	114.56	90.79	101.11	86.67
5	110.28	99.55	108.48	105.06	89.91	103.34	85.16
Average (°)	**113.32**	**100.25**	**111.47**	**112.91**	**90.69**	**101.072**	**87.83**
σ (°)	1.971	0.933	1.850	4.240	0.683	1.229	2.101
V (%)	1.74	0.93	1.66	3.75	0.75	1.22	2.39

between the untreated sample and treatments with the GLYMO. The contact angle for the untreated sample was 113.32°, while with the treatments based on TEOS it decreased to 100.25° for acid-catalyzed TEOS-treatment, and as low as from 87.83° to 101.07° for the treatments based on GLYMO. Super hydrophobic effect was not achieved and GLYMO (P:H$_2$0, 1 : 1.5) exhibited the lowest hydrophobic values. Increased hydrophilicity of the treated fabrics was to be expected, since hydrolysis formed polar silanol (Si—OH) groups and GLYMO additionally posses polar epoxy groups.

This increase is in contrast with the potentially desirable objective, i.e., ultrahydrophobic surface ("lotus effect"). Since these surfaces are obtained by nanopatterning the surface, increased hydrophobicity may be achieved by adding different nanoparticles.

Results of Antibacterial Activity
Treated fabric showed significant differences in antibacterial effects against _Staphylococcus aureus_ and _Escherichia coli_ in com-

parison with the untreated sample. The untreated fabric did not show any antibacterial activity. The results of determination of antibacterial activity to the _Staphylococcus aureus_ (ATCC 292 13) as a gram positive strain are shown in Table VIII and to the _Escherichia coli_ (ATCC 11229) as a gram negative strain are shown in Table IX.

The results show that different drawing speeds did not significantly affect the results of the antimicrobial activity for both strains.

A good effect, i.e., antibacterial resistance and highest assessment according to the standard were shown by all the samples, except for the washed ones. They exhibited no antibacterial effect and at 20 times magnification under microscope showed the growth of bacteria in the nutrient medium under the specimen.

Two different mass concentrations of the silver nitrate exhibited the same antibacterial effect. However, higher mass concentration was not enough to get a better effect after washing. This behavior indicated that standard detergents were too aggressive and that signifi-

Table VIII. The Results of the Antibacterial Effect to a _Staphylococcus aureus_

| | | _Staphylococcus aureus_ | |
Test code	Treatment (GLYMO : H$_2$O = 1 : 3)/drawing speed	Inhibition zone—H (mm)	Assessment
B1	10 g dm^{-3} AgNO$_3$ 0.5 mm s^{-1}	1	Good effect
B2	1 mm s^{-1}	1	
B3	1.5 mm s^{-1}	1	
B4	2 mm s^{-1}	1	
B5	1 mm s^{-1}—washed	0	Insufficient effect
B5-10×	1 mm s^{-1}—10× washed	0	
B6	0.5 mm s^{-1}—urine	1	Good effect
B7	20 g dm^{-3} AgNO$_3$ 0.5 mm s^{-1}	1	Good effect
B8	1 mm s^{-1}	1	
B9	1.5 mm s^{-1}	1	
B10	2 mm s^{-1}	0.75	
B11 B11-10×	1 mm s^{-1}—washed 1 mm s^{-1}—10× washed	0 0	Insufficient effect
B12	0.5 mm s^{-1}—urine	0.2	Good effect

Table IX. The Results of the Antibacterial Effect on *Escherichia coli*

Test code	Treatment (GLYMO : H$_2$O = 1 : 3)/drawing speed		*Escherichia coli* Inhibition zone—H (mm)	Assessment
B1	10 g dm^{-3} AgNO$_3$	0.5 mm s^{-1}	1	
B2		1 mm s^{-1}	1	
B3		1.5 mm s^{-1}	1	
B4	2 mm s^{-1}	1		
B5		1 mm s^{-1}—washed	0.25	
B5-10×		1 mm s^{-1}—10× washed	0.20	
B6		0.5 mm s^{-1}—urine	0.2	Good effect
B7	20 g dm^{-3} AgNO$_3$	0.5 mm s^{-1}	1	
B8		1 mm s^{-1}	1	
B9		1.5 mm s^{-1}	1	
B10		2 mm s^{-1}	1	
B11		1 mm s^{-1}—washed	0.25	
B11-10×		1 mm s^{-1}—10× washed	0.24	
B12		0.5 mm s^{-1}—urine	0.2	

cant loss of Ag$^+$ occurred during the process, or that the mass concentration of AgNO$_3$ and with that Ag$^+$ was too low to kill gram positive strain *Staphylococcus aureus* which belongs to the most resistant group of bacteria. All the samples showed a good effect for *Escherichia coli*, including the washed ones (1× and 10×).

The comparison of the antibacterial activity against two often investigated strains, *Staphylococcus aureus* and *Escherichia coli,* with other similar textile products on the market was preformed to check the modification. There were no significant differences between modified samples and commercial antibacterial textile samples. Only the washed samples (1× and 10×) exhibited insufficient effect against *Staphylococcus aureus*. This was not expected, since the same mass concentration of AgNO$_3$ was enough against gram negative strain *Escherichia coli.*

Results of the Evaluation of the Action of Microfungi

The untreated fabric did not show any antifungal activity. The action of microfungi was evaluated by visual assessment and measuring inhibition zone in millimeters.

Results of evaluation of the action of microfungi on the *Aspergillus niger van Tieghem* (ATCC 6275) are shown in Table X.

The visual examination (microscope with the magnification 50×) of the test specimen on the side facing agar (agar side) showed a reduction of fungal colonies. All the samples showed good effect in terms of inhibiting the growth of fungi and creating a satisfactory inhibition zone.

Different drawing speeds had no significant affect on the results of antifungal activity but higher silver nitrate mass concentration showed better results. Washed and urine samples had lower inhibition zone but still showed satisfactory results. The samples exhibited stronger and faster action against microfungi *Aspergillus niger van Tieghem* than against bacteria (*Staphylococcus aureus, Escherichia coli*).

One of the aims of this work was to find universal solutions (antibacterial and antifungal efficacy) to reduce production costs. The modification was practical and proved promising since it could simultaneously affect three types of microbes with one treatment.

Our results showed a good effect regarding the quality of the antifungal activity against *Aspergillus niger van Tieghem*, including the washed samples (1× and 10×). Silver ions were sufficiently anchored in the silica network and provide durability of antifungal properties. During the agar plate diffusion, test samples were compared with the samples of antifungal socks. The results were quite similar. Generally, the activity was higher, which indicated that the modification was performed properly.

Antifungal and antibacterial polyurethane-coated fabrics prepared by sol–gel method in this work were found to have satisfying textiles quality rating and the antimicrobial effects. From a hygienic point of the view, modified samples were fit for their purpose for a medical program (covers for mattress, pillows, sheets, etc. in hospitals and nursing homes). They were not in direct contact with human skin but they prevent colonization, infection and reinfection of bacteria and fungi. In this way, the cumulative costs of therapy were limited to the initial cost of the silver-polyurethane-coated fabrics. Silver-polyurethane-coated fabrics could not be correlated with clinical efficacy. They were designed as a support, by eliminating microorganism without disturbing so called wound-healing process. Modified samples could withstand 10 processes of washing cycles with a stable antimicrobial effect but after that they should be retreated, as the results of our work indicated.

CONCLUSION

The authors investigated the influence of the precursor used (TEOS or GLYMO), the conditions of hydrolysis, and the deposition of sol on textile substrate, on the properties of treated textile.

Table X. The Results of the Evaluation of the Action of *Aspergillus niger van Tieghem*

| Test code | Treatment (GLYMO : H$_2$O = 1 : 3)/drawing speed | | Aspergillus niger van Tieghem | |
			Inhibition zone—H (mm)	Fungal growth
G1	10 g dm^{-3} AgNO$_3$	0.5 mm s^{-1}	6	
G2		1 mm s^{-1}	6	
G3		1.5 mm s^{-1}	6	
G4		2 mm s^{-1}	6	
G5		1 mm s^{-1}—washed	2.5	
G5-10×		1 mm s^{-1}—10× washed	2.2	
G6		0.5 mm s^{-1}—urine	3.5	No growth on test specimens and in the agar medium
G7	20 g dm^{-3}AgNO$_3$	0.5 mm s^{-1}	7.5	
G8		1 mm s^{-1}	7.5	
G9		1.5 mm s^{-1}	7.5	
G10		2 mm s^{-1}	7.5	
G11		1 mm s^{-1}—washed	2.5	
G11-10×		1 mm s^{-1}—10× washed	2.5	
G12		0.5 mm s^{-1}—urine	4	

All the spectra of TEOS and GLYMO show a wide band at 1200–1000 cm^{-1} which indicates the existence of a silicate network and successfully performed modification. Bands of polyurethane substrate in TEOS treatments are clearly visible, but their relative intensity decreases in the following order: unmodified > neutral treatment > base treatment > acid treatment. This can be taken as an indication of the thickness of the inorganic layer formed.

GLYMO-treated samples also show the decrease in the characteristic polyurethane bands, in the following order: unmodified > neutral treatment > acid treatment > basic treatment. We suppose the "coverage" is better for the basic treatment (when compared to basic TEOS-treatment) because of higher water : alkoxide ratio.

Both TEOS and GLYMO-based treatments shift the onset of degradation to somewhat higher temperatures. The effect is most pronounced for acid-catalyzed TEOS-treatment, while other TEOS-treatments show very low impact on the temperature of degradation. GLYMO-treatments all show similar effects on the first degradation step, regardless of the hydrolysis conditions.

Polyurethane surface is covered by silica or hybrid thin films and the surface pores are also completely filled, forming a composite organic–inorganic coating, as shown by SEM. Hydrophobic effect was preserved for all the samples, except for a single treatment of the GLYMO, due to its polar epoxy group. Based on the results of sensory evaluation and instrumental characterization, two treatments on the basis of GLYMO have a good potential to serve as the base for the addition of AgNO$_3$:

Treatment I. GLYMO as a precursor, acid catalyst (HCl), the stoichiometry ratio of precursor and water—1 : 1.5, processing time 1 h, 20°C, closed reaction system,

Treatment II. GLYMO as a precursor, no catalyst, i.e., the hydrolysis is carried out with distilled water, the stoichiometry ratio of precursor and water—1 : 3, processing time 1 h, 20°C, closed reaction system.

Polyurethane fabrics treated with Treatment II and AgNO$_3$ were tested for antimicrobial activity and offered good antibacterial and antifungal performance. From a hygienic point of the view, the samples modified by sol–gel process were fit for their purpose for a medical program. They were not in direct contact with human skin but they prevent colonization, infection and reinfection of bacteria and fungi. They were designed as a support by eliminating microorganisms without disturbing so-called wound-healing process. Modified samples could withstand 10 washing cycles with a stable antimicrobial effect against *Escherichia coli* and *Aspergillus niger van Tieghem*. However after that they should be retreated as the results of our work indicated.

REFERENCES

1. Mahltig, B.; Textor, T. Nanosols and Textiles; World Scientific Publishing Co. Pte. Ltd.: Singapore, **2008**; Preface, p IX.

2. .Web of Knowledge, Sol-gel process in textile. Available at: http://apps.webofknowledge.com/summary.do?SID=P2eMcO9I47CcBLgigEm&product=WOS&doc=163&qid=3&search_mode=Refine, accessed January 2012.

3. Mahltig, B.; Haufe, H.; Böttcher, H. *J. Mater. Chem.* **2005**, *15*, 4385.

4. Mahltig, B.; Knittel, D.; Schollmeyer, E.; Böttcher, H. *J. Sol-Gel Sci. Technol.* **2004**, *31*, 293.

5. Yaman, N. *Fibers Polym.* **2009**, *10*, 413.

6. Lobnik, A.; Gutmaher, A.; Sitar, D.; Majcen Le Marechal, A. In 5th World Textile Conference AUTEX; Majcen Le Marechal, A., Ed.; Portorož, Slovenia, Maribor, June 27–29, **2005**.

7. Sfiligoj Smole, M.; Stakne, K.; Bele, M.; Jamnik, J.; Hribernik, S.; Veronovski, N.; Stana Kleinschek, K.; Ribitsch, V. In 3rd International Textile, Clothing & Design Conference—Magic World of Textiles; Dragčević, Z., Ed.; University of Zagreb Faculty of Textile Technology: Zagreb, Dubrovnik, Croatia, October 8–11, **2006**.

8. Tomšić, B.; Orel, B.; Jovanovski, V.; Jerman, I.; Simončić, B. In 4th International Textile, Clothing & Design Conference—Magic World of Textiles; Dragčević, Z. Ed.; University of Zagreb Faculty of Textile Technology: Zagreb, Dubrovnik, Croatia, October 5–8, **2008**.

9. Farouk, A.; Textor, T.; Schollmeyer, E.; Tarbuk, A.; Grancarić, A. *AUTEX Res. J.* **2009**, *9*, 114.

10. Mahltig, B.; Fiedler, D.; Fischer, A.; Simon, P. *J. Sol-Gel Sci. Technol.* **2010**, *55*, 269.

11. Mahltig, B.; Knittel, D.; Schollmeyer, E.; Böttcher, H. *J. Sol-Gel Sci. Technol.* **2004**, *31*, 293.

12. Macan, J. Sol-gel synthesis of hybrid materials for coating application. Ph.D. Thesis, University of Zagreb, Zagreb, Croatia, June **2006**.

13. .ACTICOATTM. A unique nanocrystalline silver delivery system for burns and wounds. Available at: www.eplasty.com/images/PDF/Acticoat.pdf, accessed January, 2013.

14. Kramer, A.; Guggenbichler, P.; Heldt, P.; Jünger, M.; Ladwig, A.; Thierbach, H.; Weber, U.; Daeschlein, G. In Biofunctional Textiles and the Skin; Burg, G., Eds.; Karger, Basel, **2006**; Vol. *33*, pp 78–109.

15. ISO 9073-11:**2002**, Textiles—Test methods for nonwovens—Part 11: Run-off.

16. ISO 3696:**1987**, Water for analytical laboratory use—Specification and test methods.

17. ISO 6330:**2012**, Textiles—Domestic washing and drying procedures for textile testing.

18. AATCC Technical Manual. AATCC Evaluation Procedure 5, Fabric Hand: Guidelines for the Subjective Evaluation of. **2006**, 81, 384.

19. ISO 20645:2004, Textile fabrics—Determination of antibacterial activity—Agar diffusion plate test.

20. EN 14119:**2003**, Testing of textiles—Evaluation of the action of microfungi.

21. Somogyi, M. Modification of coated fabrics for personal protection by sol-gel synthesis. Ph.D. Thesis, University of Zagreb, Zagreb, Croatia, August 2010..

22. ISO 1833:**1977**, Textiles—Binary fibre mixtures—Quantitative chemical analysis.

23. ISO 2286-3:**1998**, Rubber- or plastics-coated fabrics—Determination of roll characteristics—Part 2: Methods for determination of total mass per unit area, mass per unit area of coating and mass per unit area of substrate.

24. Brinker, C. J.; Scherer, G. W. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing; Academic Press. Inc.: San Diego, CA, **1990**; Chapter 2, pp 53–59.

25. Kovačić, T. Structure and Properties of Polymers. University course notes, University of Split, **2010**.

26. Ramaratnam, K.; Iyer, S. K.; Kinnan, M. K.; Chumanov, G.; Brown, P. J.; Luzinov, I. *J. Eng. Fibers Fabrics* **2008**, *3*, 1.