HYDROPHOBIC AND ANTIBACTERIAL TREATMENT OF TEXTILES USING ORGANIC-INORGANIC HYBRID LAYERS PREPARED BY SOL-GEL

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Abstract: *The sol-gel method allows the preparation of organic-inorganic layers with the possibility of adjusting the resulting properties to a relatively wide range. Potentially very interesting treatments are hydrophobic or antibacterial layers that can be applied to practically all types of textiles. Their main advantage is, in addition to their excellent adhesion to the fabric surface, their high resistance to both mechanical and chemical attack. On non-polar textiles, the increase in layer adhesion is supported by surface plasma treatment. Resistance of layers on fabrics has been confirmed by functionality even after repeated washing.*

Keywords: *Sol-gel method, hydrophobicity, antibacterial layer, textile, organic-inorganic hybrid material, plasma treatment.*

1 INTRODUCTION

The sol-gel process is a chemical method for preparing nanolayers and is mainly used in the synthesis of the oxidic layers. Its utilization increases due to its universality and simplicity, without the need for expensive laboratory equipment for the vacuum processes. Other advantages include cleanliness and homogeneity of the final product.

The principle of the sol-gel process rests in the preparation of the sol – mainly from the alkoxides. Prepared sol is afterwards applied onto the surface of the substrate (by wetting, spraying, etc.). Evaporation of the remaining solvent and placing the sol in contact with the air humidity leads to an exponential increase in hydrolysis and rapid transformation of the sol into a gel and further to a xerogel. In the case of hybrid inorganic-organic materials, the final step is to polymerize the coating material either by the heat or by the UV light if there are any photo-initiators built into the nanolayer [1-3].

The research that includes the undertaken experiments in this paper targets the development of hydrophobic or antibacterial coating for the textile materials.

2 EXPERIMENTAL

2.1 Materials

Pure cotton (further referred as Ba) and pure polyester (further referred as PE) were chosen for the first series of experiments that compares microbiological behavior of the textiles with antibacterial or hydrophobic (also antifouling) layers.

AMANDA (100% PE), CARLTON (100% Ba) and TAURUS (mixed Ba/PE 50/50) textiles were chosen for the second series of the experiments that deals with the optimization of the hydrophobic coating.

Monofils for the medical hernia nets Bard Mesh (polypropylene monofil, further referred as PP monofil), manufacturer C. R. Bard, Inc. and Parietex Hydrophobic 3-Dimensional Mesh (PE monofil), manufacturer Covidien were chosen for the third series of the experiments that test possibilities of the treatment of the medical materials.

Preparation of sols and their application

All of the sols for the surface treatment of the tested textiles were prepared by the sol-gel method from 3-(trimethoxysilyl)propyl methacrylate and tetraethoxy-silane in the isopropyl alcohol solvent by an acid catalysis.

The sol marked as AD30 was used for the antibacterial treatment – bounded cations of silver, copper and zinc were added to the basic composition and the acid catalysis was secured by adding a small amount of nitric acid. Composition of this sol and its preparation are protected by patents [4-6].

Hydrophobic treatments were applied by the sol AE10 and further by the sols from series AF (AF8-2, AF10-2 and AF12-2), all of them with added catalytic

amount of a hydrochloric acid. As a hydrophobic agent in sols AE10, AF10-2 and AF12-2 was used trialkoxyalkylsilane with alkyl-hexadecyl in this case. The sols AE10 and AF10-2 were different only in the details of the preparation. The sol AF12-2 had enhanced volume of hexadecyl groups. The hexadecyl was substituted with a dodecyl in the sol AF8-2. The detailed process of synthesis of the hydrophobic sols is described in publication [7].

All of the layers are characterized by an excellent chemical resistance against all organic solvents and water solutions except highly concentrated alkali hydroxides and hydrofluoric acid. The thickness of the layers can be adjusted from 80 to 200 nm according to the dilution of the sols and the way of the application of the sol.

All of the samples of the textiles were cleaned by repeated soaking into the isopropyl alcohol or by a plasmatic treatment (in the case of the hernia nets) prior to the application of the sols. The application of the sols onto the surface of the tested textiles was done by foulard (pressure 5 bars, velocity of cylinders 3 m/min). The application of the sols onto the hernia nets was done by soaking the nets in the sol followed by pulling out – this process was chosen due to the structure of the material – knitwear. The application of the sols was followed by the heat polymerization, which was done in 85°C/3 h (in the case of materials with PE or PP) or in 150°C/2 h (in the case of pure Ba).

Plasmatic treatment of hernia nets

For enhancing adhesion of antibacterial layers onto the hernia nets and similar substrates it was necessary to treat the surface by plasma with a vacuum aperture by application of the oxygen plasma (device LA400, flow of oxygen 200 sccm with pressure 100 Pa, 10 s for PP monofil, 60 s for PE monofil) in the company SurfaceTreat Turnov. The adhesion of the applied layers especially onto the PP monofil without this treatment was insufficient. There was also tested an atmospheric plasma treatment of the surfaces but the results were inconvenient (worse adhesion of the layers with the low intensity, destruction of monofils with higher intensity).

2.2 Methods

Determining of antibacterial properties

Following pathogenic bacterial strains from the Czech collection of microorganisms of Masaryk University Brno were used to test the antibacterial properties.

1. *Escherichia coli* (E.C.) - CCM 2024 (ATCC 9637), gram-negative bacteria (G-).

2. *Staphylococcus aureus* (S.A.) - CCM 2260 (ATCC 1260), gram-positive bacteria (G+).

AATCC Test Method 147-2016 [8]

This method is qualitative, tentative and it should be done prior to the method AATCC 100-2012. The antibacterially treated sample is placed on the agar which is standardly applied with the bacterial inoculum in several lines. A modification of this method was used in this case where the bacterial inoculum was applied to the whole surface of the agar. After 24 hours of incubation there was rated grow of the bacteria under the tested sample as well as the inhibitory (halo) zone around the sample.

Specific conditions of the tests: There was cut a square sample of 18x18 mm (according to the norm). 1 ml of the bacterial inoculum with a concentration of 10^5 CFU/ml was inoculated individually on a Petri dish with the blood agar. Tested sample was put in the middle of the dish and firmly pressed to the agar. The incubation took place in a thermostat with 37°C for 24 hours. After the specified incubation there was the halo zone rated (its area) and the inhibition of bacteria under the sample (place of a sample).

AATCC Test Method 100-2012 [9]

This method is quantitative and there is rated a reduction factor which states the reduction (in percent) of the inoculated concentration of the bacteria due to the effect of the sample. The result is a number of survivor bacteria colonies (CFU) and from this number there is calculated inhibition degree (in %). It is always necessary to compare the treated sample with an untreated one (standard).

Specific conditions of the tests: There was cut a square sample of 18x18 mm which was placed into a sterile container. There was applied 100 µl of the respective bacterial strain with a concentration of 10^5 CFU/ml. Incubation took place in the thermostat with 37°C for 24 hours. After incubation there was added 10 ml of a physiological solution. After vortexing there was pipetted 1 ml and it was inoculated on the Petri dish with the blood agar (there were inoculated triplets from each sample). The result is a sum of number of colonies on all three dishes.

Determination of hydrophobicity

Krüss Drop Shape Analyser DSA30 device in Surface Treat Turnov was used to determine the wetting angles of water. The wetting angle was measured by measuring a small exactly-defined drops placed on the surface of the textile, with a defined volume of 3 µl. The results are calculated as the average of the 10 measurements with the corresponding standard deviation.

3 RESULTS AND DISCUSSION

3.1 Microbiological behavior of textiles with layers

The sol AD30 was used as an antibacterial treatment for the tested textiles (pure cotton Ba and pure polyester PE). Next to the antibacterial treatment based on the effect of cations Ag, Cu and Zn in the active layer there was also tried a treatment of the textiles with the hydrophobic sol AE10 where it was assumed an antifouling effect will take place [10-11]. The antifouling effect restricts the adhesion and the number of bacteria and subsequent creation of the biofilm on the surface of the textile.

The details about the used sols and their application on the tested textile are mentioned in the paragraph 2.1. Testing of the antibacterial properties on the prepared samples of the textiles together with the untreated samples was done both by the qualitative AATCC Test Method 147-2016 and by the quantitative AATCC Test Method 100-2012. The results are summarized in Tables 1 and 2.

Table 1 The results of the antibacterial testing of the textiles by the AATCC Test Method 147-2016

Bacterial strain	Sample	Inhibition zone, inhibition
Escherichia coli	Ba - US	0% inhibition zone, 0% inhibition under the sample
	PE - US	0% inhibition zone, 0% inhibition under the sample
	Ba - AE10	0% inhibition zone, 0% inhibition under the sample
	PE - AE10	0% inhibition zone, 0% inhibition under the sample
	Ba - AD30	Inhibition zone d = 1.3 mm, 100% inhibition under the sample
	PE - AD30	Inhibition zone d = 2.9 mm, 80% inhibition under the sample
Staphylococcus aureus	Ba - US	0% inhibition zone, 0% inhibition under the sample
	PE - US	0% inhibition zone, 0% inhibition under the sample
	Ba - AE10	Inhibition zone d = 5.5 mm, 100% inhibition under the sample
	PE - AE10	0% inhibition zone, 0% inhibition under the sample
	Ba - AD30	0% inhibition zone, 100% inhibition under the sample
	PE - AD30	Inhibition zone d = 5.5 mm, 100% inhibition under the sample

US – untreated standard

According to the acquired results it is visible that the effects on the used bacterial strains differ in partial parameters. In both cases it can be said that the results are greatly positive.

The qualitative method with the hydrophobic treatment of AE10 with the bacterial strain *Escherichia coli* has not showed any inhibitory effect in any of the materials used. On the other hand, with the bacterial strain *Staphylococcus aureus* there has been noted an inhibition zone and 100% inhibition under the sample on the cotton sample. This means that the treatment on the cotton limits the adhesion and the growth of the bacteria *Staphylococcus aureus.* There has been no inhibitory effect noted on the polyester samples.

Table 2 The results of the antibacterial testing of the textiles by the AATCC Test Method 100-2012

Bacterial strain	Sample	Result	% of inhibition
Escherichia coli	Ba - US	UQ	0
	PE - US	UQ	0
	Ba - AE10	28	100
	PE - AE10	300	99.9
	Ba - AD30	2	100
	PE - AD30	2	100
Staphylococcus aureus	Ba - US	UQ	0
	PE - US	450	Sample stops compact growth of test strain
	Ba - AE10	1	100
	PE - AE10	0	100
	Ba - AD30	2	100
	PE - AD30	0	100

US – untreated standard; UQ – unreadable quantity

The quantitative method with the antibacterial treatment of AD30 showed the inhibition under the samples (that means the treatment stopped the growth of the bacteria under the material with a treatment) for both materials (Ba, PE) and there also appeared inhibition zones which indicates that the components of the final layer (cations Ag, Cu and Zn) partially release themselves into the surroundings and inhibit the bacterial strain.

The quantitative method proved excellent or very good inhibitory effect to all of the tested samples with layers. The number of cultivated bacterial colonies of *Escherichia coli* on the materials with the hydrophobic treatment AE10 has been larger than on the other treated samples. Nevertheless, even these results can be rated as good when compared with the standards.

The really important aspect is a stability of the antibacterial layer on the textile substrate which has been verified by repeated washing of cotton socks with the layer AD30. Still suitable antibacterial properties have been observed even after 50th washing by a standard washing cycle [2].

3.2 Hydrophobic treatment of textiles

The hydrophobic treatment of the textiles is interesting for a number of practical uses, mainly for outdoor finishes of sportswear and working cloth. Next to stopping the liquid water penetration, great penetration of water vapors and a long-term preservation of mechanical and utility properties of textiles it has also important ecological aspect. In contrary to commonly used impregnations with the addition of fluorine compounds nor the tested sols nor the final layers contain any ecologically problematic components while keeping all

the necessary requirements for the outdoor usage. Table 3 summarizes the results of test with three different test sols. As you can see in the results all of the textiles with the treatment have outstanding hydrophobic properties and there are basically no differences between the tested sols.

Table 3 The results of the water wetting angle measurement on the treated textiles (n = 10)

Textile	Sol	Water	
		Angle [°]	s_x [°]
AMANDA (PE)	US	Soaking	
AMANDA (PE)	AF8-2	124.5	4.0
AMANDA (PE)	AF9-2	125.8	2.5
AMANDA (PE)	AF12-2	126.3	2.6
CARLTON (Ba)	US	Soaking	
CARLTON (Ba)	AF8-2	122.8	5.3
CARLTON (Ba)	AF9-2	124.1	4.1
CARLTON (Ba)	AF12-2	124.0	3.2
TAURUS (Ba/PE)	US	Soaking	
TAURUS (Ba/PE)	AF8-2	135.3	4.1
TAURUS (Ba/PE)	AF9-2	132.5	3.0
TAURUS (Ba/PE)	AF12-2	135.1	4.6

s_x – standard deviation; US – untreated standard

3.3 Hernia nets

The hernia implants (nets) are used for a surgical solution of hernias which is a bag-like exit of a peritoneal cavity where part of the abdominal organs moves to. Although there is applied the latest knowledge and used modern materials in the surgical solution, one of the post-operative complication is an inflammation. In the material which are the hernia nets made of can occur so called hiding of the microorganisms from the effects of the immune system and persistence of inflammation or delay of break out in the range from several months to several years [12].

The most promising strategy in the present is the usage of an implant material with added antibacterial properties which stops the bacterial adhesion and creates a biofilm on its surface. The design of these resistant implants [13] is based on a modification of their surface by anti-adhesive substance, antimicrobial agents, antiseptic, antibiotic, metals or their ions or inhibitors of bacterial adherence coatings. These treatments should be nontoxic in the case of releasing controllably-degradable non-affecting original biomechanical properties of the material and non-obstructing integration of the implant to the organism.

Currently there are no hernia nets with the antimicrobial treatment which would meet all the requirements of the nontoxicity. Greatly promising treatment is the applied layer summarized below which contains ions of Ag, Cu, and Zn and very effectively stops growth of the pathogenic bacteria. The results of the testing in this work are summarized in Table 4.

Table 4 The results of antibacterial testing of the hernia nets by the AATCC Test Method 147-2016

Sample	*Escherichia coli*	*Staphylococcus aureus*
PP monofil-US	0% inhibition under the sample	0% inhibition under the sample
PE monofil-US	4% inhibition under the sample	2% inhibition under the sample
PP monofil-AD30	25% inhibition under the sample	100% inhibition under the sample
PE monofil-AD30	100% inhibition under the sample, inhibition zone d=2 mm	100% inhibition under the sample, inhibition zone d=1.5 mm

US – untreated standard

The applied antibacterial treatment to the surface of hernia implants enhanced their antibacterial effect in the comparison with the standards. Even the standard PE monofil proved inhibition under the sample for both the bacterial strains but after the application of the sol the inhibition improved and showed itself as inhibition zones with the material PE. This effect is, especially in the case of the hernia nets, requested because it will not only kill the bacteria in the application spot but also in the near surroundings and prevent creation of the inflammation which could appear as an after-effect of an operation.

4 CONCLUSIONS

The organic-inorganic hybrid layers based on 3-(trimethoxysilyl)propyl methacrylate and tetraethoxysilane prepared by the sol-gel method have great adhesion and long-term durability on the surface of the polar textiles. When the application to the non-polar textile is needed it is necessary to treat the surface of the textile with the low-pressure oxygen plasma.

Significant modification of the properties of the prepared layers can be achieved by adding the proper additions (nitrates of Ag, Cu and Zn for the antibacterial layers, trialkoxyalkylsilanes with alkyl with 12 to 16 carbons for the hydrophobic layers) to the basic composition of the sols.

By using the both standardized methods it was confirmed the antibacterial effectiveness of the layer AD30 on all of the tested textiles and the hernia nets. According to the achieved results it is noticeable that the effects on the used bacterial strains differ in partial parameters but in all of the cases, it can be said that the results are quite positive.

The really important aspect is a durability of the antibacterial layer on the textile substrate which has been verified by repeated washing of the cotton socks with the layer AD30. Still suitable antibacterial properties have been observed even after 50th washing by a standard washing cycle.

In the case of the hydrophobic layer AE10 there have been anticipated just a lesser antifouling effect during the antibacterial tests. The expectation has

been confirmed. The qualitative method on the bacterial strain *Escherichia coli* did not show any inhibition effect on neither of the tested materials. On the other hand, the bacterial strain *Staphylococcus aureus* on the cotton showed the inhibition zone plus 100% inhibition under the sample. That means the treatment on the cotton limits the adhesion and the growth of bacteria *Staphylococcus aureus.* There was no inhibitory effect observed on the polyester. The quantitative method on the other hand showed excellent or great inhibitory effect on all of the samples with the hydrophobic layers AE10. The number of the bacterial colonies of *Escherichia coli* on the materials with this treatment has been larger than on the other treated samples. Nevertheless, even these samples can be classified as great when compared with the untreated samples.

The measuring of the water wetting angles on the textiles with all of the types of hydrophobic treatments confirmed that all the textiles with treatment have excellent hydrophobic properties and among both the used sols and the textiles there were no real differences.

The antibacterial treatments of the textiles (both the classical and the hernia nets) are greatly perspective for a medical usage. This treatment causes antibacterial effect that leads to the death of tested bacteria. The hydrophobic treatment had significantly lower effectiveness during antibacterial tests. Still, for a number of usages in common life is it enough to stop adhesion and further bacterial growth (bacterial-static effect).

The hydrophobic treatment of the textiles is interesting for a number of practical uses, mainly for the outdoor finishes of sportswear and working cloth. In contrary to the commonly used impregnations with addition of fluorine compounds nor the tested sols nor the final layers contain any ecologically problematic components while keeping all the necessary requirements for the outdoor usage.

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