Mechanical Resistance of Hydrophobic Inorganic-Organic Nanolayers with Antifouling Effect

Vojtěch Miller[1], Totka Bakalova[2], Petr Exnar[1], Irena Lovětinská Šlamborová[1], Petr Louda[2]
[1]Faculty of Science, Humanities and Education, Department of Chemistry, Technical University of Liberec, Studentska 2, 461 17 Liberec, Czech Republic. E-mail: vojtech2miller@gmail.com, petr.exnar@tul.cz, irena.slamborova@tul.cz
[2]Faculty of Mechanical Engineering, Department of Material Science, Technical University of Liberec, Studentska 2, 461 17 Liberec, Czech Republic. E-mail: totka.bakalova@tul.cz, petr.louda@tul.cz

This paper deals with the preparation, composition and mechanical resistance of inorganic-organic nanolayers with built-in hydrophobic groups through sol-gel synthesis. The components of the nanolayers are 3-(trimethoxysilyl)propyl methacrylate, tetraethyl orthosilicate and hydrophobic chains – hydrocarbon chains in the range of 8 to 16 carbons. The study is aimed at evaluating the mechanical properties of prepared nanolayers with different hydrophobic chains compared to a reference sample without any hydrophobic groups. An abrasion resistance test was performed on several selected nanolayers with the best hydrophobic and antifouling properties. In the framework of the research, nanolayers prepared with polymerization achieved by heating at 85 °C or 150 °C were compared. The best mechanical properties and hydrophobicity of prepared nanolayers was AF12 with a hexadecyl hydrocarbon chain polymerized at 150 °C. These nanolayers are suitable for marine, underwater or any other hydrophobic application results from performed research.

Keywords: Sol-gel synthesis, Polymerization, Abrasion resistance, Hydrophobicity, Antifouling properties

1 Introduction

The term "nano" has gained increasing public awareness in recent years. This is proof of the growing interest in this topic, its utilization and further research. According to the European Chemicals Agency (ECHA) nanomaterials are defined as tangible structures, which have dimensions of between 1 and 100 nm in either of three directions. This is also the boundary where quantum effects begin occur [1, 2]. Enhancing mechanical resistance or changing the optical properties of materials has become increasingly common in industries dealing with layers and nanolayers. Most of these layers are based on oxides, such as titan oxide or its mixtures with other metal oxides. New types of nanolayers for several different applications include inorganic-organic nanolayers consisting of silicon dioxide and alkylalkoxysilanes.

Examples of processes of preparing nanolayers and thin layers are chemical deposition, which further includes the sol-gel process, chemical vapor deposition (CVD), atomic layer deposition (ALD) and physical deposition. Most of these physical methods can be classified as physical vapor deposition (PVD) [3].

What makes nanolayers so different to common layers (coatings) is their surface to volume ratio, whereby their surface properties outweigh their bulk volume properties.

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

The principle of the sol-gel process rests in the preparation of a sol – mainly from alkoxides. Firstly, it is required to prevent moisture entering the system to stop the uncontrolled hydrolysis of alkoxides, and also it is applied to a substrate. Evaporation of the remaining solvent and placing the sol in contact with air leads to an exponential increase in hydrolysis and the rapid transformation of the sol into a gel and further to xerogel. In the case of hybrid inorganic-organic materials, the final step is to polymerize the coating material either by heat or by UV light if there are photo-initiators built into the nanolayer [4-6].

There are several techniques for applying sol prepared through the sol-gel process, including dip coating and spin coating:

- *Dip coating* – this method is based on the steady removal of a substrate sunk into a sol. After the substrate with the applied nanolayer emerges from the sol, gelation of the sol occurs due to it being in contact with air and evaporation of the solvent;
- *Spin coating* – this method is based on the application of a sol to the centre of a rotating substrate, which is spread evenly over the substrate due to centrifugal force. The thickness of the applied nanolayer is inversely proportional to the angular speed of the substrate [7, 8].

The research that includes undertaken experiments in this paper targets the development of hydrophobic coating for the different kinds of surfaces (metal, glass, plastics) for the suppression of the effects that water solutions have on these surfaces and mainly to limit the biological contamination of these surfaces in the real water environment i.e. antifouling (ships, water cleaning plants etc.) [8-10]. The purpose of the study is to improve the utility properties and the abrasion resistance of the studied nanolayers.

2 Experimental procedure

The first step in the experimental procedure was to

prepare and clean the glasses that the nanolayers were applied on. Glasses were deeply cleaned to remove any grease and impurities from the surface of the glass so the nanolayers can properly adhere to it. The cleaning was performed in ten individual steps:

- 1x rinsed in technical acetone; 1x rinsed in acetone p.a.; 2x rinsed in demi water; 10 mins in diluted nitric acid 1:1 at 70-80 °C; 2x rinsed in demi water; 2 mins in demi water in an ultrasonic bath; 1x rinsed in demi water; 1x rinsed in isopropyl alcohol (IPA) p.a.; 3 mins in IPA p.a.; stored in a beaker with IPA p.a.

The glasses were cleaned in IPA vapours immediately prior to applying the nanolayers onto the surface of the glass. Inorganic-organic nanoparticles prepared by the sol-gel process were applied to the prepared substrates. The composition of the layer labelled AF12 is described below in Table 1.

Tab. 1 *Composition of sol AF12 (50 ml)*

Chemicals	Abbrev.	Supplier	Quantity
Isopropyl alcohol (0.03 % H_2O)	IPA	Lach:ner	48.0 ml
Tetraethyl orthosilicate (≥ 99 %)	TEOS	Sigma Aldrich	---
3-(Trimethoxy silyl)propyl methacrylate ≥ 98 %	TMSPM	Sigma Aldrich	1.0 ml
Hexadecyltrimethoxysilane; Technical ≥ 85 % (GC)	HDTMS	Sigma Aldrich	0.8 ml
Benzoyl peroxide (Luperox; 75 %)	BPO	Sigma Aldrich	0.03 g
Chloride acid; c = 2 mol/dm^3 prepared from HCl 35 % p.a.	HCl	Lach:ner	0.1 ml
Demi water	H_2O		0.1 ml

The sols were aged for three to seven days. After aging, the sols were applied to the cleaned glasses. Nanolayers were applied by dip-coating. Each glass was sunk into the corresponding sol and slowly removed at a speed of 6 cm/s. After application of the sol, the nanolayers were polymerized in a furnace. Two nanolayers per specific sol were prepared. One nanolayer was polymerized at 85 °C and the other at 150 °C. It should be noted that polymerization through heating is not practical for industrial use in certain cases. Therefore, it is possible to polymerize the sol with UV light, whereby the catalyst (BPO) is substituted with a UV catalyst.

The preparation process this work was based on is as follows:

- Fill the apparatus with approximately 60 % of IPA. After reflow with argon add TEOS, TMSPM and HDTMS.
- Fill the apparatus with BPO and stir for 30 mins until the BPO dissolves.
- Prepare a solution in an Erlenmeyer's flask from the remaining IPA with HCL dissolved in water (c = 2 mol/dm^3) and add the remaining water according to the calculated composition.
- After the BPO dissolves, pour the contents of the Erlenmeyer's flask into the apparatus for 30 seconds. Stir for the next 30 min.
- Boil the sol in the apparatus for 35 mins in a reflux condenser. Subsequently, cool to ambient temperature.

In the framework of the research, a number of measurements were performed on several selected samples. The samples were labelled as follows:

- AF00 – a reference sample with no hydrophobic component;
- AF08 – the best sample from the hydrophobic nanolayers with dodecyl as the hydrophobic component; AF08-2– a sample prepared from the newly prepared AF08 sol to gain an insight into repeatability
- AF12 – the best sample from the hydrophobic nanolayers with hexadecyl as the hydrophobic component; AF12-2 – a sample prepared from the newly prepared AF12 sol to gain an insight into repeatability.

The above-mentioned samples were polymerized at 85 °C and 150 °C.

3 Results

3.1 Characteristics of the studied layers - hydrophobicity

Measurement of the wetting angle was carried out at SurfaceTreat a.s. based in Turnov, Czech Republic using a drop shape analyser (DSA). The method used for calculating the free surface energy (internal software verified by independent calculation) was the static Owens, Wendt, Rabel and Kaelble (OWRK) method. The wetting angle was measured by measuring small exactly-defined drops placed on the surface of the glass with nanolayers, with a defined volume of 3 µl. The results are calculated as the average of the 10 measurements with the corresponding standard deviation (Table 2, 3 and Fig. 1). This method requires two different liquids, one polar – deionized water and one non-polar – diiodomethane (Sigma Aldrich).

Tables 2 and 3 show the measured data for the wetting

angles and the calculated values of the different parts of the free surface energy for the tested nanolayers with different terminal groups depending on the different volume ratios versus total volume of the nanolayers. The volume of the hydrophobic part is the relative volume of the terminal hydrophobic groups (dodecyl or hexadecyl).

Tab. 2 *Data for nanolayers polymerized by 85 °C*

Sample identification	AF00 85 °C	AF08 85 °C	AF12 85 °C	AF08-2 85 °C	AF12-2 85 °C
Wetting angle of H_2O [°]	75.1 ± 1.1	92.2 ± 0.5	99.2 ± 1.3	89.0 ± 0.9	96.4 ± 0.8
Wetting angle of diiodomethane [°]	50.3 ± 1.3	49.7 ± 0.6	46.5 ± 1.6	53.2 ± 1.1	47.7 ± 4.3
Free surface energy FSE [mN/m]	40.8 ± 1.2	35.6 ± 0.4	36.3 ± 1.0	34.6 ± 0.8	35.9 ± 2.6
Disperse part of energy DP [mN/m]	34.1 ± 0.7	34.4 ± 0.3	36.2 ± 0.9	32.5 ± 0.6	33.4 ± 2.4
Polar part of energy PP [mN/m]	6.7 ± 0.5	1.1 ± 0.1	0.1 ± 0.1	2.1 ± 0.2	1.5 ± 0.2
Volume of hydrophobic part [%]	0	34.3	40.9	34.3	40.9
Hydrophobic part	None	$-C_{12}H_{25}$	$-C_{16}H_{33}$	$-C_{12}H_{25}$	$-C_{16}H_{33}$

Tab. 3 *Data for nanolayers polymerized by 150 °C*

Sample identification	AF00 150 °C	AF08 150 °C	AF12 150 °C	AF08-2 150 °C	AF12-2 150 °C
Wetting angle of H_2O [°]	75.6 ± 0.4	91.4 ± 1.0	93.7 ± 1.3	91.6 ± 1.2	90.9 ± 0.7
Wetting angle of diiodomethane [°]	48.5 ± 0.9	50.4 ± 0.9	48.0 ± 2.0	47.8 ± 1.8	51.5 ± 1.8
Free surface energy FSE [mN/m]	41.3 ± 0.7	35.4 ± 0.7	36.2 ± 1.3	36.3 ± 1.3	35.0 ± 1.2
Disperse part of energy DP [mN/m]	35.1 ± 0.5	34.0 ± 0.5	35.4 ± 1.1	35.5 ± 1.0	33.4 ± 1.0
Polar part of energy PP [mN/m]	6.2 ± 0.2	1.4 ± 0.2	0.8 ± 0.2	1.1 ± 0.3	1.5 ± 0.2
Volume of hydrophobic part [%]	0	34.3	40.9	34.3	40.9
Hydrophobic part	None	$-C_{12}H_{25}$	$-C_{16}H_{33}$	$-C_{12}H_{25}$	$-C_{16}H_{33}$

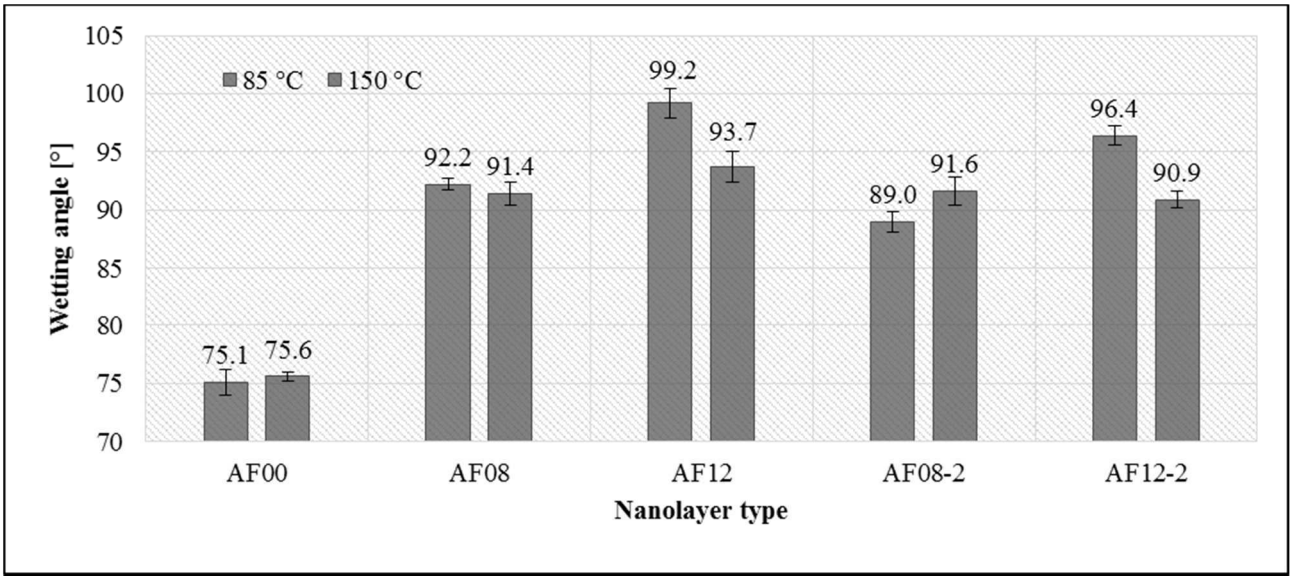

Fig. 1 *Overview of the wetting angles of water*

In terms of the hydrophobic terminal groups, the hexadecyl terminal groups were found to be better than the dodecyl terminal groups, and both hydrophobic terminal groups were significantly better than nanolayers without any added hydrophobic terminal groups. This is in accordance with data from the literature that assign great hydrophobic properties to hydrocarbon chains with lengths greater than eight carbons. Figure 1 shows that the nanolayers significantly improve after the addition of hydrocarbon chains to the base inorganic-organic matrix. Nanolayer AF12 has the best properties from all of the measured nanolayers. Nanolayers AF08-2 and AF12-2

were prepared separately with their own new sol after measuring nanolayers AF08 and AF12 to gain an insight into the reproducibility of these nanolayers as they are known to be influenced by temperature, humidity and other properties of their surroundings.

3.2 Mechanical properties of the layers

The roughness of the surface was evaluated at three different sites on the surfaces of the studied layers. The measurements were made using a confocal microscope (according to the ISO 25178 standard) over different areas of 113.34 x 94.58 μm^2 for each layer.

Figure 2 shows the surface roughness of samples AF12 and AF12-2, respectively after polymerization at 85 °C.

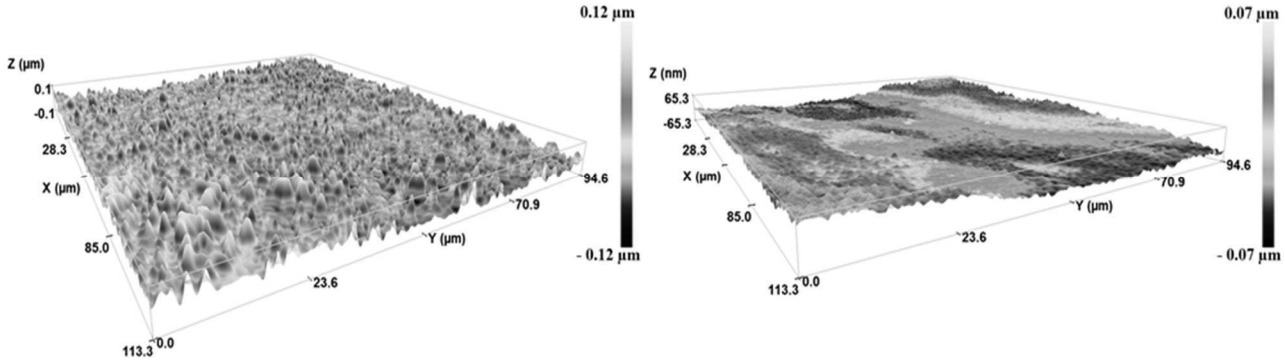

Fig. 2 *Surface roughness of sample AF12 (on the left) and of sample AF12-2 (on the right) after polymerization at 85 °C*

The average values of the measured surface parameters and standard deviations are described in Tables 4 and 5. The used parameters are as follows: *Sa* is the average arithmetic height (average surface roughness); *Sz* is the maximum height (height between the lowest recesses and the highest projection); *Sq* is the standard deviation of the distribution of heights (root mean square roughness); and *Sp* is the maximum height of the protrusion (height between the median plane and the highest projection). [11, 12]

Monitoring of parameters of surface roughness (Sa and Sz) indicated that nanolayers AF08, AF12 and AF08-2 polymerized at 85 °C had a rougher surface than when polymerized at 150 °C. For nanolayers AF00 and AF12, the surface roughness of the two polymerizations remained the same.

Tab. 4 *The average values of the measured surface parameters and standard deviations for nanolayers polymerized at 85 °C*

Parameters	AF00 85 °C	AF08 85 °C	AF12 85 °C	AF08-2 85 °C	AF12-2 85 °C
Sa [nm]	17.6 ±0.4	25.4 ±4.0	30.3 ±0.9	23.2 ±0.5	19.0 ±0.7
Sz [nm]	102.8 ±0.1	269.1 ±12.9	204.2 ±3.0	133.8 ±4.7	103.4 ±5.7
Sq [nm]	21.1 ±0.3	35.0 ±6.6	37.8 ±1.1	29.5 ±2.1	22.7 ±1.0
Sp [nm]	61.4 ±0.9	220.6 ±12.6	125.5 ±1.4	86.9 ±2.0	60.9 ±3.9

Tab. 5 *The average values of the measured surface parameters and standard deviations for nanolayers polymerized at 150 °C*

Parameters	AF00 150 °C	AF08 150 °C	AF12 150 °C	AF08-2 150 °C	AF12-2 150 °C
Sa [nm]	18.1 ±0.4	17.3 ±1.1	17.9 ±2.1	17.9 ±0.1	19.1 ±0.1
Sz [nm]	99.9 ±4.5	94.5 ±2.9	113.8 ±14.4	97.5 ±2.7	99.8 ±1.6
Sq [nm]	21.4 ±0.5	20.6 ±1.1	22.0 ±2.4	21.0 ±0.1	24.6 ±2.3
Sp [nm]	59.3 ±3.4	55.0 ±2.1	64.2 ±10.0	54.9 ±0.2	59.6 ±2.9

The glasses with the applied nanolayers were placed in a CETR UMI multi-specimen test system to measure the abrasion resistance. The lowest normal load that the machine allowed was used i.e. 2 N. The machine made reverse movements during the measuring. The distance of the path taken was set to 10 mm. One cycle consisted of two runs over a defined path i.e. a ball was moving across the surface of a glass with the applied nanolayer. The speed of movement of the ball (from made from ceramic material Si_3N_4) on the surface of the layer was set to 2 mm/s and the number of repetitions was set to 40. A frictional ball was firmly fixed into a hanger so it could not rotate. The specific resistance of the material during the abrasive resistance test corresponded to sliding friction not rolling friction. Friction in time intervals of 400 seconds was evaluated.

Figure 3 shows the surface wear of samples AF12 and AF12-2, respectively after polymerization at 85 °C.

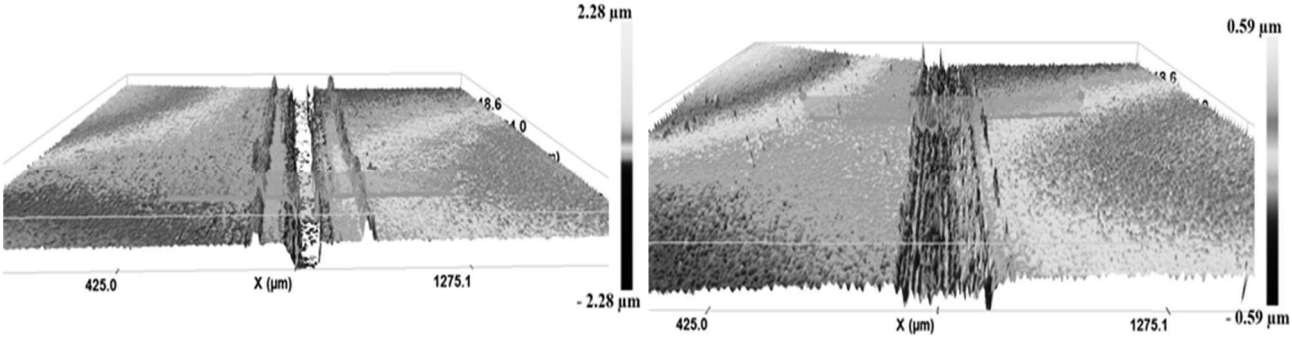

Fig. 3 *Surface wear of sample AF12 (on the left) and of sample AF12-2 (on the right) after polymerization at 85 °C*

After the abrasion test, it was found that the AF12 nanolayer was completely damaged and it is possible to observe the substrate material – glass (see Fig. 3 left). Only slight damage was observed on the surface of the AF12-2 nanolayer while maintaining the same abrasion resistance parameters (see Fig. 3 right). The counterpart (a ball of ceramic material Si_3N_4) did not get through the AF12-2 nanolayers.

Tab. 6 *Friction coefficient values (layers polymerized at 85 °C) and time until layer damage*

Layer	Coefficient of friction CoF [-]	Standard deviation CoF	Time until layer damage [s]
AF00 85 °C	0.39	0.07	10
AF08 85 °C	0.20	0.02	20
AF12 85 °C	0.14	0.06	52
AF08-2 85 °C	0.25	0.07	49
AF12-2 85 °C	0.24	0.06	47

Tab. 7 *Friction coefficient values (layers polymerized at 150 ° C) and time until layer damage*

Layer	Coefficient of friction CoF [-]	Standard deviation CoF	Time until layer damage [s]
AF00 150 °C	0.23	0.09	58
AF08 150 °C	0.24	0.07	89
AF12 150 °C	0.25	0.10	162
AF08-2 150 °C	0.44	0.09	226
AF12-2 150 °C	0.28	0.10	251

According to the results of the abrasion resistance tests, the nanolayers showed constant abrasion the substrate material (glass) was reached below. Tables 6 and 7 show the data and standard deviation for the friction coefficients as well as the time needed to rub through the nanolayers. Table 6 contains data for nanolayers polymerized at 85 °C, whereas Table 7 contains data for nanolayers polymerized at 150 °C.

The mechanical resistance of the inorganic-organic nanolayers unexpectedly showed an improvement when a hydrophobic part is included in the matrix of the nanolayer. Furthermore, when a hydrophobic nanolayer consists of longer hydrocarbon chains it further improves the mechanical resistance. This can be seen in Tables 6 and 7 (as stated above) where nanolayers AF08 (AF08-2) and AF12 (AF12-2) are compared. There is a large difference in the measured data for nanolayers AF08-2 and AF12-2 versus the original nanolayers. Further work should include a complex experiment with a larger set of samples in order to carry out a statistical analysis.

When the data form the nanolayers polymerized at 85 °C are compared with those from the nanolayers polymerized at 150 °C there is a significant improvement in the nanolayers polymerised at 150 °C. Trends between these nanolayers remain the same for the nanolayers polymerized at 85 °C.

3.3 Antifouling properties of the nanolayers

The final test to be performed was a test for antifouling properties. Two bacteria were tested: *Escherichia coli (E. C.)* – CCM 2024 (ATCC 9637) – gram positive bacteria and *Staphylococcus aureus (S. A.)* – CCM 2260 (ATCC 1260) – gram negative bacteria. Both of the nanolayers AF08 and AF12 showed similar properties. *Escherichia coli* was not inhibited but *Staphylococcus aureus* was greatly inhibited by both nanolayers – the concentration of the colony forming units (CFU) was ten times lower than on a standard sample (pure glass).

4 Conclusion

From the results of the wetting angle measurements, it can be concluded that the prepared nanolayers were almost purely non-polar at the surface, which leads to great hydrophobic properties. It is clear that the more carbons in the terminal hydrocarbon chains, the better the wetting properties. With growing wetting angles up to 100°, the water free surface energy decreases to a minimum of 34.6 mN/m. The best nanolayer from the prepared nanolayers was AF12 with a hexadecyl hydrocarbon chain serving as the hydrophobic part.

Testing of the mechanical properties showed a similar progress as the hydrophobic properties. Adding a hydrophobic component to the inorganic-organic matrix led to an increase in the mechanical resistance of the nanolayers. At the same time, we can state that the nanolayers polymerized at 150 °C showed much better mechanical resistance than the nanolayers polymerized at 85 °C. This means that the nanolayers polymerized at 150 °C would be significantly better for applications where mechanical resistance plays a major role.

The nanolayers also showed an antifouling effect, which was observed on bacteria *Staphylococcus aureus*. On the other hand, *Escherichia coli* was resistant to the nanolayers. Further testing of mixed bacteria simulating an environment of the target application needs to be performed.

Acknowledgement

This publication was written at the Technical University of Liberec as part of the project "The study and evaluation of the material structures and properties" with the support of the Specific University Research Grant, provided by the Ministry of Education, Youth and Sports of the Czech Republic in the year 2018, by the Ministry of Education, Youth and Sports of the Czech Republic and the European Union - European Structural, Investment Funds in the frames of Operational Programme Research, Development and Education - project Hybrid Materials for Hierarchical Structures (HyHi, Reg. No. CZ.02.1.01/0.0/0.0/16_019/0000843) and by the project TAČR TH02020145 "Hydrophobic UV-lacquers and nano-layers protecting substrates against bio-attack".

References

[1] IKHMAYIES, S. J. (2014) Characterization of Nanomaterials. *Journal of the Minerals*, Metals & Materials Society, 66(1), pp. 28–29.

[2] NANOMATERIÁLY - ECHA [online], [2018-03-22], https://echa.europa.eu/cs/regulations/nanomaterials.

[3] Thin film [online], [2018-02-27], https://en.wikipedia.org/w/index.php?title=Thin_film&oldid=817961308.

[4] EXNAR, P. (2006), Sol-gel method. Liberec, *Technical University of Liberec*, ISBN 978-80-7372-063-6.

[5] FICAI, D., GRUMEZESCU, A. (2017) Nanostructures for novel therapy: synthesis, characterization and applications. Amsterdam, Netherlands, *Elsevier*, ISBN 978-0-323-46142-9.

[6] SVOBODOVA, J., KRAUS, P., CAIS, J., LATTNER, R. (2016). Research of Chemical Pretreatment Created by Sol-gel Process on the Polished Surface of Aluminium Substrate. *Manufacturing technology*, 16 (1), pp. 259 – 264.

[7] DANGLAD-FLORES, J., EICKELMANN, S., RIEGLER, H. (2018), Deposition of polymer films by spin casting: A quantitative analysis. *Chemical Engineering Science*, 179, pp. 257–264.

[8] MILLER, V. (2018) Příprava a vlastnosti hydrofobních nanovrstev (Preparation and properties of hydrophobic nano-layers). Bachelor thesis, *Technical University of Liberec*, Faculty of Mechatronics, Informatics and Interdisciplinary Studies, 2018-06-13.

[9] FLEMMING, H.-C. (ed.) et all. (2009), Marine and industrial biofouling. Berlin: *Springer*, ISBN 978-3-540-69794-7.

[10] HNATIUC, B., EXNAR, P., SABAU, A., SPATENKA, P., DUMITRACHE, C.L., HNATIUC, M., GHITA, S. (2016) Biofouling development on plasma treated samples versus layers coated samples. *Proceedings of SPIE - The International Society for Optical Engineering*, 10010, ID 100103C. DOI: 10.1117/12.2243145.

[11] BAKALOVA, T., et al. (2014). The Use of Optical Microscopy to Evaluate the Tribological Properties, *Manufacturing technology*, 14(3), pp. 256 – 261.

[12] BAKALOVA, T., PETKOV, N., CHOLAKOVA, T., KAVÁN, F., BAHCHEDZHIEV, H., (2016). Mechanical Properties of Titanium-Aluminium Base Nanomultilayer Coatings. *Manufacturing technology*. 16(4), pp. 657 – 662.

10.21062/ujep/177.2018/a/1213-2489/MT/18/5/781