CHANGE OF SURFACE PROPERTIES OF MATERIALS FOR VARIOUS APPLICATIONS

BENKOCKÁ Monika[1], LUPÍNKOVÁ Simona[1], MATOUŠEK Jindřich[1], KOLSKÁ Zdeňka[1]

[1]*J. E. Purkinje University in Usti nad Labem, Faculty of Science, Usti nad Labem, Czech Republic, EU*
BenkockaMonika@seznam.cz

Abstract

Many materials, like polymers, silicates, glass, play crucial role in many areas of industry, medicine or our common life due to their properties. But their surface properties can limit their further use in some areas. Physical or chemical modification of these surfaces can change their chemical composition and subsequent better adhesion of grafted compounds, cells or antimicrobial activities. We can use this for development of new materials for electronics, optics or bio application. We have modified surfaces of selected materials by physical or chemical methods and we studied the changes of surface properties. The surface properties of the modified materials changed significantly and were studied using various techniques. Some antimicrobial tests have been applied on selected samples.

Keywords: Polymer, piranha solution, compounds grafting, electrokinetic analysis, X-ray photoelectron spectroscopy

1. INTRODUCTION

Natural and synthetic polymers play crucial role in many areas of our life. Also silicates or glass have a wide range of usage. Using these materials can be limited to certain applications because of the surface properties (e.g. chemistry, surface charge, morphology). Modification of many of these materials has expanded their potential for application greatly. Many modification approaches have been developed to change and improve surface properties by the physical or chemical methods. [1-15]

The chemical structure of surface, morphology, [16] surface chemistry or biological composition of these interfaces, together with surface pattern (distribution and dimensions of the pattern, ranging from the macro- through the micro- to the nano-scale [17] has ability to strongly influence the behaviour, biocompatibility and response of the surface.

We have modified surfaces of different substrates (polymers, glass, and phyllosilicates) by plasma, UV irradiation or by chemical methods to activate these surfaces. Subsequently we grafted variable chemical compounds (aminocompounds, thiols, PEG, borane compounds, etc.). After individual steps we studied the changes of surface properties by a wide range of available techniques. [18-22]

2. EXPERIMENTAL

2.1. Used materials and chemicals

In this work we studied silicate powder montmorillonite (MMT, $(Na_{0,25}K_{0,07}Ca_{0,10}(Si_{4,0})(Al_{1,45}Fe^{3+}{}_{0,21}Mg_{0,24}Ti_{0,01})O_{10}(OH)_2)$, microscopy glass (20 x 20 mm, Deck Glaser, VWR, Germany) and different polymer foils, polytetrafluoroethylene (PTFE, thickness 50 µm, Goodfellow, UK) or high density polyethylene (HDPE, thickness 50 µm, Goodfellow, UK).

For activation of surfaces there were used various Piranha solutions. Piranha solution is a mixture of acid and hydrogen peroxide in proportion 3:1. We used (i) sulfuric acid (H_2SO_4, 96%, Lach-Ner, s.r.o., Neratovice) or (ii) phosphoric acid (H_3PO_4, 96%, Lach-Ner, s.r.o., Neratovice), hydrogen peroxide (H_2O_2, 30%, Lach-Ner, s.r.o., Neratovice).

The activated surface was grafted by 10% aqueous solution of (i) cysteamine ($HS(CH)_2)_2NH_2$, 98%, Sigma Aldrich), (ii) ethylenediamine ($NH_2(CH_2)_2NH_2$, MERCK) or (iii) chitosan (85%, deacetylated powder, Alfa Aesar) and subsequently with selected boron compounds synthetized according to the procedure in literature [23,24,25]. These chemical grafting have been described earlier. [18-22]

2.2. Surface modification

The samples were firstly activated by Piranha solutions for one hour at room temperature. Then they were rinsed with distilled water and put into aqueous solution of selected amino compounds (cysteine, ethylene diamine, chitosan). After twenty-four hours the samples were rinsed with distilled water and dried. Some of samples were also inserted to the selected borane solutions for twenty-four hours.

2.3. Used analytical methods

The changes of surface properties were studied by various analytical methods, such as X-ray photoelectron spectroscopy, electrokinetic analysis, goniometry, UV-Vis spectroscopy, some samples were tested for antimicrobial activity.

For surface elemental analysis there was used X-ray photoelectron spectroscopy (Omicron Nanotechnology ESCA Probe spectrometer, Omicron Nanotechnology GmbH, Germany). [18]

Electrokinetic analysis (zeta potential determination) was performed for the planar samples of polymer foil on the device SurPass (Anton Par, Austria). Two samples of the same surface were fixed on two brackets, size of the samples was 2x1 cm. Measurements were carried out in a cell with adjustable gap (about 100 µm), at room temperature, atmospheric pressure and constant pH 6.5. For determination of zeta potential the streaming current method was used and the Helmholtz-Smoluchowski equation to calculate zeta potential. [18,19]

Surface wettability was determined by measuring the contact angle at room temperature using the SEE system (Surface Energy Evolution System). A drop of water of a volume 8.0 µl was applied using automatic pipette on a surface immediately after activation or chemical modification. This drop was photographed and evaluated.

For determining the effect of fluorescence after borane compounds grafting on the surfaces the UV-Vis spectroscopy was used. Fluorescence is the emission (in the transition from the lowest vibrational level in the ground state), the radiation of the substance which absorbs light or other electromagnetic radiation. This phenomenon occurs when an electron that has been excited into an excited state relaxes when returning to the ground state photon. The best known and the most striking example is the absorption of the fluorescence agent in the ultraviolet region and the subsequent emitted light is in the visible. [18,22]

2.4. Antimicrobial tests

Some of samples have been tested also for antimicrobial activity by an inhibition of algae Desmodesmus quadricauda growth tests. This test was performed on selected samples. Size of the samples was 3x1 cm2. On the surfaces of samples was added a solution of algae (volume 1.5 ml). Counting of algae cells was carried out in a counting chamber under the light microscope (1, 2 and 24 h after seeding).

2. RESULTS AND DISCUSSION

It is clear from results of individual employed characterization methods that all steps of surface activation or chemical grafting lead to changes in surface chemistry and therefore other surface properties. **Figure 1** presents changes in surface chemistry and charge of glass after surface activation by Piranha solution and subsequent grafting of tested amino compounds (cysteamine, ethylenediamine and chitosan) and subsequent grafting of borane compound. As it is clear from **Figure 1**, all modification steps change surface chemistry and charge. Activation with Piranha solution created the reactive sites on a surface so there are changes in chemical composition and the polarity of a surface. [18-21]. These changes are compared to the unmodified sample. After grafting tested compounds with amine- group (cysteamine, ethylenediamine and chitosan) the surface became „less negative“. [18,21] Grafting of boron compounds causes negative charged surface.

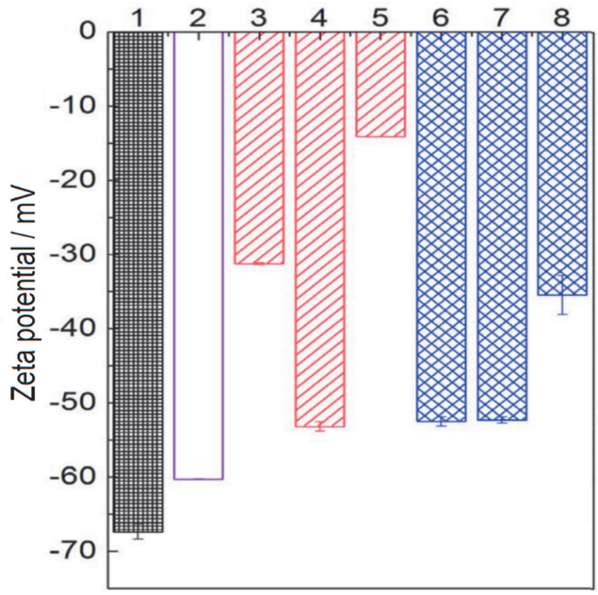

Figure 1 Electrokinetic analysis (zeta potential) of glass before and after individual modification steps: Sample 1: unmodified glass; 2: activated by the Piranha solution; 3 to 5: grafted in solutions of cysteamine (3), ethylenediamine (4) or chitosan (5); 6 to 8: subsequently grafted by borane compound after cysteamine (6), ethylenediamine (7) or chitosan (8)

Also **Figure 2** indicates surface properties changes before and after surface activation and chemical modification. On the left we can see wettability and contact angle of unmodified PTFE surface and its comparison with wettability and contact angle of PTFE surface activated by Piranha solution and grafted by cysteamine and subsequently with borane compound. Wettability of a surface has an influence on the surface cytocompatibility or antimicrobial activity.

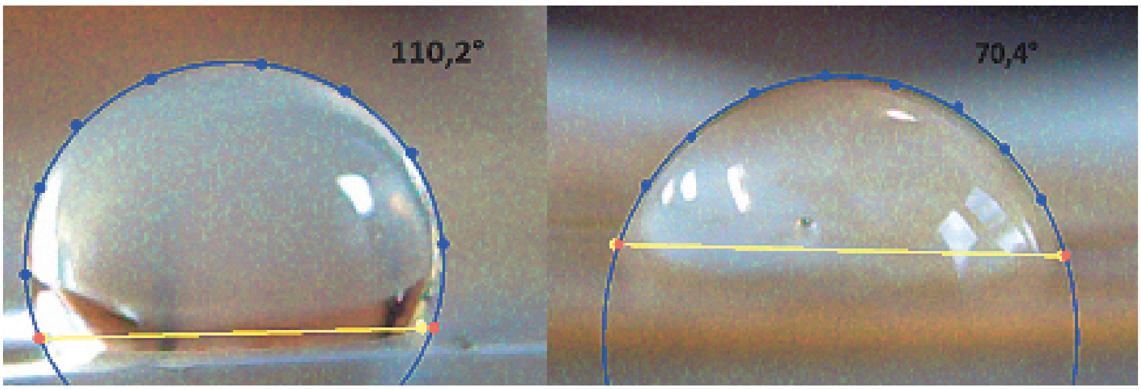

Figure 2 Contact angle of PTFE before and after modification with cysteamine and borane compound

Changes in surface chemistry were detected by XPS analyses. Results of chemical composition are presented in **Table 1**. It is clear, activation by Piranha solution consisting of HNO_3 and H_2O_2 leads to presence of oxygen and nitrogen in surface chemistry. After grafting of individual amino compounds increase the amount of nitrogen groups and in case of cysteamine also presence of sulphurs it is obvious.

Table 1 Element concentration in atmospheric % for HDPE after individual steps of activation by Piranha solution and subsequent grafting of cysteamine, ethylenediamine or chitosan

Sample	Element	C 1s	O 1s	N 1s	S 2p
Pristine		100.0	-	-	-
Piranha (HNO_3 + H_2O_2)		94.0	4.5	1.5	-
Piranha/ cysteamine		91.0	4.4	2.8	1.8
Piranha/ ethylenediamine		92.0	4.6	3.4	-
Piranha/ chitosan		72.0	21.8	6.2	-

Results of antimicrobial test for HDPE activated by Piranha solution consisting of sulphuric acid and peroxide in range of H_2SO_4:H_2O_2=3:1 and subsequently grafted by ethylenediamine (DIA), cysteamine (CYS) and chitosan (CHI) are presented in **Figure 3**. It is obvious that the algae growth was inhibited at all samples, especially after 24 h in comparison with cell numbers after 1 h with exception of CYS, which is a good surrounding for cell adhesion and proliferation.

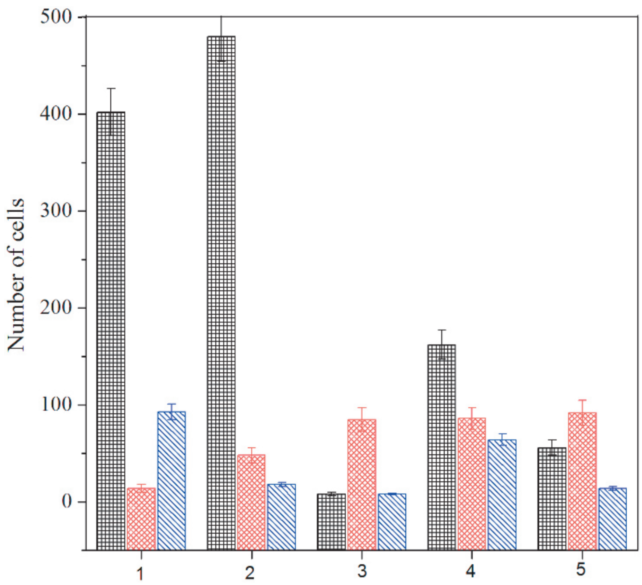

Figure 3 Number of algae Desmodesmus quadricauda on studied samples 1 (black columns), 2 (red columns) and 24 h (blue columns) after seeding on unmodified HDPE (1), activated by Piranha solution (2), grafted by cysteamine (3), ethylenediamine (4) and chitosan (5)

These materials of changed surfaces chemistry can be employed in many fields, for preparation of new luminophores on the base of silicates, glass or polymers, [18-22] for tissue engineering, [20] or for surfaces with antimicrobial activities.

3. CONCLUSION

Obtained results confirmed our methods of surface activation and modification can lead to changes in surface chemistry and other surface properties. These changes can help us to develop new materials for different usage, for luminophores, for materials applicable in tissue engineering, for materials of antimicrobial activities, etc.

The surface properties of studied material changed significantly after individual steps of surface activation and chemical modification and these changes were proved using various methods. It was proved the successful grafting of selected chemical compounds on the surfaces of different substrates, silicates, glass, polymers.

Piranha activation and grafting by tested chemical compounds changed surface charge, chemistry, polarity and wettability.

ACKNOWLEDGEMENT

This work was supported by the Czech Science Foundation (GA CR) under the project no. 13-06609S, by the Grant Agency of Health Ministry under project no. 15-33018A and by the internal grant of the J. E. Purkinje University in Ústí nad Labem in the Czech Republic (SGA project no. 5351815000801).

The authors acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under project No. LM2015073.

REFERENCES

[1] GODDARD J. M., HOTCHKISS J. H.: Polymer surface modification for the attachment of bioactive compounds. *Prog. Polym. Sci*., 2007, vol. 32, pp. 698.

[2] MERRET K., CORNELIUS R.M., MCCLUNG W.G., UNSWORTH L.D. Surface analysis methods for characterizing polymeric biomaterials. *J. Biomater. Sci. Polymer Edn*. 2002, vol. 13, no. 6, pp. 593.

[3] SLEPICKA P., CHALOUPKA A., SAJDL P., HEITZ J., HNATOWICZ V., SVORCIK V.: Angle dependent laser nanopatterning of poly(ethylene terephthalate) surfaces. *Applied Surface Science*, 2011, vol. 257, pp. 6021-25;

[4] LI L., HONG M., SCHMIDT M., ZHONG M., MALSHE A., HUIS P., VELD B.: Laser nano-manufacturing - State of the art and challenges, *CIRP Annals: Manufacture Technology*, 2011, vol. 60, pp. 735-55;

[5] BAUER S., SCHMUCKI P., von der MARK K., PARK J.: *Engineering biocompatible implant surfaces: Part I: Materials and surfaces*. *Progress Materials Science*, 2013, vol. 58, pp. 261-326.

[6] ASHLEY K. M., MEREDITH J. C., AMIS E., RAGHAVAN D., KARIM A.: Combinatorial investigation of dewetting: Polystyrene thin films on gradient hydrophilic surfaces. *Polymer,* 2003, vol. 44, pp. 769.

[7] SAVARAM K., KALYANIKAR M., PATEL M., BRUKH R., FLACH C. R., HUANG R., KHOSHI M. R., MENDELSON R., WANG A., GARFUNKEL E., HE H.: Synergy of oxygen and a piranha solution for eco-friendly production of highly conductive graphene dispersions. *Green Chemistry,* 2015, vol. 17, pp. 869.

[8] SIEGEL J., REZNICKOVA A., CHALOUPKA A., SLEPICKA P., SVORCIK V.: Ablation and water etching of plasma-treated polymers. *Radiat. Eff. Def. Sol*., 2008, vol. 163, pp. 779.

[9] REISINGER B., FAHRNER M., FRISCHAUF I., YAKUNIN S., SVORCIK V., FIEDOROWICZ H., BARTNIK A., ROMANIN C., HEITZ J.: EUV micropatterning for biocompatibility control of PET. *Appl. Phys*., 2010, vol. 100, pp. 511.

[10] SHIFANG W., JUAN L., JINPING S., TIANZHI L.: Surface modification of porous poly(tetrafluoraethylene) film by a simple chemical oxidation treatment. *Appl. Surf. Sci*., 2010, vol. 256, pp. 2293-2298.

[11] KWASNIAK P., PURA J., ZWOLINSKA M., WIECINSKI P., SKARZYNSKI H., OLSZEWSKI L., MARCZAK J., GARBACZ H., KURZYDLOWSKI K. J.: Laser and chemical surface modifications of titanium grade 2 for medical application. *Appl. Surf. Sci*. 2015, vol. 336, pp. 267-273.

[12] RIMPELOVA S., SLEPICKOVA KASALKOVA N., SLEPICKA P., LEMEROVA H., SVORCIK V., RUML T.: Plasma treated polyethylene grafted with adhesive molecules for enhanced adhesion and growth of fibroblasts: *Mat.Sci and Engine.:C*, 2013, vol. 33, pp. 1116-1124.

[13] MORACZEWSKI K., RYTLEWSKI P., MALINOWSKI R., ZENKIEWICZ M.: Comparison of some effects of modification of a polylactide surface layer by chemical, *Plasma and laser methods*, 2015, vol. 346, pp. 11-17.

[14] SIMOR M., CREYGHTON Y., WYPKEMA A., ZEMEK J.: The Influence of Surface DBD Plasma Treatment on the Adhesion of Coatings to High-Tech Textiles, *Journal of Adhesion Science and Technology*, 2012, vol. 24, pp. 77-97.

[15] YOSHIDA S., HAGIWARA K., HASEBE T., HOTTA A.: Surface modification of polymers by plasma treatments for the enhancement of biocompatibility and controlled drug release, *Surface and Coatings Technology*, 2013, vol. 233, pp. 99-107.

[16] FENG CH. L., ZHANG D., SCHONHERR H.: The investigation of cell adhesion on nano-patterned biointerfaces of block copolymer films by reactive microcontact printing approach. *Journal of Controlled Relase*, 2011, vol. 152, pp. 201-202.

[17] VASUDEVAN R., KENNEDY A. J., MERRITT M., CROCKER F. H., BANEY R. H.: Microscale patterned surfaces reduce bacterial fouling-microscopic and theoretical analysis. *Colloids Surface B*, 2014, vol. 117, pp. 225-232.

[18] KOLSKA Z., MAKAJOVA Z., KOLAROVA K., KASALKOVA SLEPICKOVA N., TROSTOVA S., REZNICKOVA A., SIEGEL J., SVORCIK V.: Electrokinetic potential and other surface properties of polymer foils and their modifications. *Polymer Science*. (Ed. Dr. FarisYılmaz), In Techd.o.o., Rijeka, Croatia, 2013, pp. 203-228 ISBN: 978-953-51-0941-9

[19] KOLSKA Z., SLEPICKOVA KASALKOVA N., SIEGEL J., SVORCIK V.: Electrokinetic Potential for Characterization of Nanostructured Solid Flat Surfaces. *J. Nano Res.*, 2013, vol. 5, pp. 31-39.

[20] KOLSKA Z., REZNICKOVA A., NAGYOVA M., SLEPICKOVA KASALKOVA N., SAJDL P., SLEPICKA P., SVORCIK V. Plasma activated polymers grafted with cysteamine for bio-application. *Polym. Degrad. and Stabil.* 2014, vol. 101, pp. 1-9.

[21] KOLSKA Z., MATOUSEK J., CAPKOVA P., BRABOREC B., CERNA H., BENKOCKA M., LONDESBOROUGH M.G.S. A luminescent montmorillonite/borane nanocomposite. *Appl. Clay Sci.*, 2015, vol. 118, pp. 295.

[22] BENKOCKA M., KNAPOVA T., BRABOREC J., MATOUSEK J., CERNA H., LONDESBOROUGH M. G. S., SVORCIK V., KOLSKA Z. Chemically Activated and Grafted Substrates and Their Analyses. *Chem. Listy*, 2015, vol. 109, no. 12, 960.

[23] PITOCHELLI A. R., HAWTHORNE M. F.: Preparation of a new boron hydride B18H22. *J. Am. Chem. Soc.*, 1962, vol. 84, pp. 3218.

[24] SAURI V., OLIVA J. M., HNYK D., BOULD J., BRABOREC J., MERCHAN M., KUBAT P., CISAROVA I., LANG K., LONDESBOROUGH M. G. S.: Tuning the Photophysical Properties of anti-B18H22: Efficient Intersystem Crossing between Excited Singlet and Triplet States in New4,4'-(HS)2-anti-B18H22. *Inorg.Chem.* 2013, vol. 52, pp. 9266.

[25] LI Y., SNEDDON L. G.: Improved Synthetic Route to *n*-$B_{18}H_{22}$. *Inorg. Chem.*, 2005, vol. 45, pp. 470.