PHYSICAL CHEMISTRY 2021

15th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume II

The Conference is dedicated to the

30th Anniversary of the founding of the Society of Physical Chemists of Serbia

and

100th Anniversary of Bray-Liebhafsky reaction

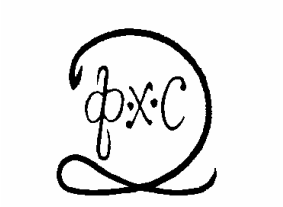
September 20-24, 2021
Belgrade, Serbia

Title: Physical Chemistry 2021 (Proceedings) **ISBN** 978-86-82475-40-8
Volume II: ISBN 978-86-82475-39-2
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: ″Jovan″, <Printing and Publishing Company, 200 Copies
Number of pages: 6+388, Format A4, printing finished in December 2021

Text and Layout: ″Jovan″

200 - *Copy printing*

CONTENT



PHYSICAL CHEMISTRY 2021

15th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by

The Society of Physical Chemists of Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of Russian Academy of Sciences

and

University of Belgrade, Serbia:

Faculty of Physical Chemistry
Institute of Chemistry, Technology and Metallurgy
Vinča Institute of Nuclear Sciences
Faculty of Pharmacy

and

Institute of General and Physical Chemistry, Belgrade, Serbia

International Organizing Committee

Chairman: S. Anić (Serbia)
Vice-chairman: M. Gabrovska (Bulgaria)
A. A. Vedyagin (Russia)
S. N. Blagojević (Serbia)

Members: N. Cvjetićanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), D. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), M.Stanković (Serbia), B. Šljukić (Serbia), G. Tasić (Serbia), S. Veličković (Serbia), N. Vukelić (Serbia)

International Scientific Committee

Chairman: Ž. Čupić (Serbia)
Vice-chairman: V. Bukhtiyarov (Russia)
S. Todorova (Bulgaria)
B. Adnađević (Serbia)

Members: S. Anić (Serbia), A. Antić-Jovanović (Serbia), A. Azizoğlu (Turky), R. Cervellati (Italy), G. Ćirić-Marjanović (Serbia), V. Dondur (Serbia), I. I. Grinvald (Russia), R. Jerala (Slovenia), M. Jeremić (Serbia), G. N. Kaluđerović (Germany), E. Kiš (Serbia), A.V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), U. Kortz (Germany), T. Kowalska (Poljska), A. Lemarchand (France), G. Lente (Hungary), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), N. Ostrovski (Serbia), V. Parmon (Russia), Z. Petkova Cherkezova-Zheleva (Bulgary), M. Plavšić (Serbia), J. Savović (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech), L. Schreiberova (Czech), D. Stanisavljev (Serbia), N. Stepanov (Russia), M. Stojanović (USA), E. Szabó (Slovakia), Zs. Szakacs (Romania), Z. Šaponjić (Serbia), Á. Tóth (Hungary), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia), V. Vukojević (Sweden)

Local Executive Committee

Chairman: S. N. Blagojević
Vice-chairman: A. Ivanović-Šašić
N. Jović-Jovičić
A. Stanojević

Members: M. Ajduković, I. N. Bubanja, A. Dobrota, J. Dostanić, D. Dimić, S. Jovanović, Z. Jovanović, D. Lončarević, M. Kragović, J. Krstić, B. Marković, S. Maćešić, J. Maksimović, S. Marinović, D. Milenković, T. Mudrinić, M. Pagnacco, N. Potkonjak, B. Stanković, I. Stefanović, G. Stevanović, A. Stoiljković, M. Vasić

CELL ADHESION CHARACTERISTICS OF POLYURETHANE-MESOPOROUS SILICA NANOPARTICLE COMPOSITE MATERIALS

M. V. Pergal [1], J. Brkljačić [2], G. Tovilović-Kovačević [2], M. Špirkova [3], I. D. Kodranov [4], D. D. Manojlović [4] and N. Ž. Knežević [5]

[1] *University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia. (marijav@chem.bg.ac.rs)*
[2] *Department of Biochemistry, Institute for Biological Research "Siniša Stanković", National Institute of Republic of Serbia, University of Belgrade, 142 Despot Stefan Blvd, 11060 Belgrade, Serbia.*
[3] *Institute of Macromolecular Chemistry CAS (IMC), Heyrovsky Sq. 2, 16206 Prague 6, Czech Republic.*
[4] *Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia.* ikodranov@gmail.com
[5] *BioSense Institute, University of Novi Sad, Dr Zorana Djindjica 1, Novi Sad 21000, Serbia. (nknezevic@biosense.rs)*

ABSTRACT

Surface characteristics and biocompatibility of new nanocomposites based on polyurethane network and mesoporous silica nanoparticles (PUMSNs) were investigated. Surface topography and roughness coefficient were studied by AFM. Biocompatibility with endothelial cells and cytotoxicity of the PUNs were assessed using MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl-tetrazolium bromide) and cell adhesion assays. The addition of MSNs into polyurethane network led to improvement of surface properties, as well as exhibited promising characteristics regarding adhesion of cells, toward potential application in coating for medical devices.

INTRODUCTION

In recent years, polyurethane (PU) has shown strong potential for biomedical applications due to its adjustable design of chemical structures and appropriate mechanical properties [1]. Poly(dimethylsiloxane) (PDMS) has been widely used in biological and chemical research, owing to its chemical inertness, optical transparency, biocompatibility, nontoxicity, permeability to gases and rapid prototyping capabilities [1]. To improve the properties of conventional PU coatings, a newer approach has been developed to manipulate the coating properties by modifying the macromolecular architecture using branched polymer, such as hyperbranched polymers, as precursors [2]. These polymers show unique physical properties like low melt and solution viscosity, low degree of chain entanglement and high solubility, due to their high branching, large number of end group functionalities, compact and globular structure. Polyurethane nanocomposites (PUN), with excellent mechanical properties and biocompatibility, are good candidates for use as coatings on medical devices and implants. Also, mesoporous silica nanoparticles (MSNs) have specific properties, such as good biocompatibility, large specific surface area, uniform pore size distribution, ability for various surface functionalization, excellent thermal stability and strength, meaning they are useful for biomedical applications [3]. Recent expansion in research on new biomaterials has contributed to the ability to create PU materials with desired physical, chemical and biological properties for specific purposes, thanks to the knowledge of how these polymers' structures influence their properties. Most physiologically relevant interactions between material and biological system occur at the interface, so crucial requirement for every biomaterial is biocompatibility of its coating [4]. The enhancement of physicochemical properties and biocompatibility of PU materials as medical implants remains an

important challenge. In the present study, new nanocomposites based on crosslinked polyurethane and MSNs (PU-MSNs) were prepared through *in situ* two-step polymerization method. Surface properties of PU-MSNs and their interaction with endothelial cells were evaluated for potential biomedical applications.

METHODS

Nanocomposites based on polyurethane network and MSNs with 50 wt.% PDMS segment were prepared by *in situ* two-step polymerization in solution (NMP/THF) using α,ω-dihydroxy-ethylene oxide-poly(dimethylsiloxane)-ethylene oxide (PDMS; abcr GmbH; M_n = 1000 g/mol), 4,4′-methylenediphenyl diisocyanate (MDI; Sigma-Aldrich) as monomers and hyperbranched polyester of the second pseudo generation (BH-20; Polymer Factory; M_n = 1780 g/mol). The synthesis procedure for nanocomposite films is analogous to our previously published procedure [4]. Non-functionalized and surface-functionalized (with 3-(trihydroxysilyl)propyl methylphosphonate (PHMSN) and 2-[methoxy(polyethyleneoxy)6-9propyl]trimethoxysilane (PEOMSN)) MSNs were used as the nanofillers in the concentration of 1 wt.% in the PU-MSN materials. The study of microphase-separated structure and topography of prepared PU-MSN films was carried out by a commercial atomic force microscope (Dimension Icon, Bruker), equipped with the SSS-NCL probe Super Sharp SiliconTM-SMP-Sensor (NanosensorsTMSwitzerland); spring constant 35 Nm^{-1}, resonant frequency ≈ 170 kHz). The measurements were done at ambient temperature, in the tapping mode AFM technique. Endothelial cell adhesion on the surface of PU-MSN films was examined by a computer-based Carl Zeiss Axiovision microscope as previously described by Pergal et al. [4]. Briefly, different concentrations of EA.hy926 cells were seeded into 96-microwell plate and 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl-tetrazolium bromide (MTT) test was performed 48 h post-seeding. The results were presented as percent of the control value obtained from cells grown without sample film, taken as 100%.

RESULTS AND DISCUSSION

AFM images of the surface topology were used to characterize the PU nanocomposites with different types of MSNs and AFM image of selected PU-PHMSN film is presented in Fig. 1a. Surface roughness values increase in order PU-PHMSN (R_q = 60 nm), PU-MSN (R_q = 118 nm), and PU-PEOMSN (R_q = 192 nm). The samples with higher R_q values showed a rougher surface of the prepared nanocomposites.

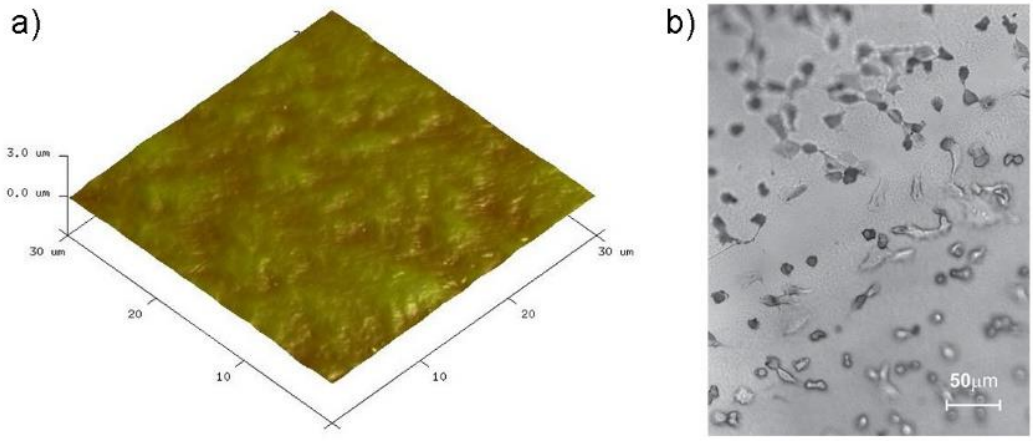


Figure 1. PU-PHMSN: a) 3D AFM image and b) photograph of cell attachment

To assess biocompatibility of novel PU-MSNs, cell viability and cell adhesion tests were carried out using human EA.hy926 cell line (Fig. 1b). Influence of incubation with nanocomposites on cell viability was evaluated by MTT assay. The reduction in cell viability (41.0±8.1% for PU-PHMSN; 51.4±9.4% for PU-MSN and 56.3±4.7% for PU-PEGMSN) can indicate a lower number of cells on the surface of investigated materials in relation to the control surface (polystyrene; cell viability on control sample was 100%), probably as a consequence of moderate EA.hy926 cells attachment on the surface of PU-MSN films. Although MTT test was not sensitive enough to show differences between the prepared materials, probably because of the high respiratory activity of cells grown around the films, the micrographs detected subtle distinction in cell attachment among investigated films. The cell adhesion and growth appeared to depend on the microphase separation and surface roughness. The prepared PU-MSNs with higher microphase separation and surface roughness showed enhanced endothelial cells attachment. In addition, cell morphology was preserved on the surface of PU-MSN films. The density of adhered cells was the highest on PU-PEOMSN (2345±615 cells/mm^2) followed by PU-MSN (1645±301 cells/mm^2) and PU-PHMSN (1500±518 cells/mm^2). The level of the endothelial cell attachment on PU-MSNs films was in the range from 47.0 (for PU-PHMSN) to 55.1% (for PU-PEOMSN), which is higher as compared to some commercial PU i.e. ElastEon^{TM} (31.4%). Prepared nanocomposites indicated improved endothelial cell attachment as compared to PU based on tri-block pre-polymer poly(ε-caprolactone)-*block*-poly(dimethylsiloxane) macrodiol [4].

CONCLUSION

A series of polyurethane nanocomposites with different type of MSNs was successful prepared. The PUMSN materials with higher surface roughness values showed enhanced endothelial cells attachment. Prepared nanocomposites favored endothelial cells adhesion and growth, indicating good biocompatibility. The results of this study indicate that prepared PUMSN materials can be considered as biocompatible materials with potential applications in biomedical fields, in particular as a new coating for medical implants.

Acknowledgement

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia within Serbian-French Bilateral Project No. 337-00-8/2020-04 (2020-2021) and Ministry of Foreign Affairs of the Republic of France. The authors would like to thank the Ministry of Education, Science and Technological Development (Grant No: 451-03-9/2021-14/200026; 451-03-9/2021-14/200358; 451-03-9/2021-14/200168; 451-03-9/2021-14/200007) and the Czech Science Foundation (No: 18-03932S).

REFERENCES

[1] R. Vermette, H. J. Griesser, G. Laroche, R. Guidoin, Biomedical Applications of Polyurethanes; Landes Bioscience, Austin, TX, 2001.
[2] M. V. Pergal, J. V. Džunuzović, R. Poręba, M. Steinhart, M. M. Pergal, V. V. Vodnik, M. Špírková, Ind. Eng. Chem. Res. 2013, 52, 6164-6176.
[3] N. Knežević, N. Ilić, V. Đokić, R. Petrović, Đ. Janaćković, ACS Appl. Mater. Inter. 2018, 10, 20231−20236.
[4] M. V. Pergal, V. V. Antić, G. Tovilović, J. Nestorov, D. Vasiljević-Radović, J. Djonlagić, J. Biomater. Sci. Polym. E. 2012, 23, 1629-1657.