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″

Neither this book nor any part may be reproduced or transmitted in any form or by any means, including photocopying, or by any information storage and retrieval system, without permission in writing from the publisher.

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

THERMAL CHARACTERIZATION OF POLYURETHANE/SILVER FERRITE NANOCOMPOSITES

M. V. Pergal [1], B. P. Dojčinović [1], I. D. Kodranov [2], S. Ostojić [3], M. Ognjanović [4], D. Stanković[2] and B. Antić [4]

[1] *University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia. (marijav@chem.bg.ac.rs)*
[2] *Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia.* ikodranov@gmail.com
[3] *Institute of General and Physical Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia.*
[4] *The Vinca Institute of Nuclear Sciences, University of Belgrade, POB 522, Belgrade, Serbia.*

ABSTRACT
The novel polyurethane composite films were prepared using *in situ* polymerization method in the presence of silver ferrite nanoparticles (1 wt.%). Preparation, structure, and thermal characterization of polyurethane/silver ferrite nanocomposites (PUFNCs) were investigated. The study of the effect of soft segment content (from 30 to 60 wt.%) on the structure and thermal properties was performed using FTIR, DSC, TGA and TEM analyses. The higher thermal stability was detected for PUFNCs with higher soft segment content. The glass transition of the hard segment (T_{gHS}) of PUFNCs increased with decreasing soft segment content due to higher crosslinking density.

INTRODUCTION

Polyurethane nanocomposites (PUNCs) have received widespread attention due to their improved physicochemical properties compared with the pure polyurethane (PU) [1]. It is currently accepted that attractive interactions between the PU and the nanoparticles may promote homogeneous dispersion [1]. The most challenging task in construction of PUNCs is to achieve a good dispersion of nanoparticles into a PU matrix, as these tend to agglomerate [1]. Surface modification is one of the pathways to reduce the agglomeration tendency of the nanoparticles. Ferrite nanoparticles possess unique properties, such as uniform size distribution, less agglomeration, good biocompatibility, and stability in the biological medium. The good mechanical properties and blood compatibility of PUNCs, moreover, have made them major candidates for medical devices [2]. Poly(dimethylsiloxane) (PDMS) has been incorporated into PUs to produce a non-cytotoxic materials with enhanced degradation resistance and *in vivo* biostability [2]. PUs based on PDMS are particularly suitable for the development of cardiovascular implants, such as vascular grafts, catheters, artificial heart-assisting devices, etc [2]. However, bacterial colonization on the medical device surface often occurs, frequently causing bloodstream infections in patients [3]. Several metal ions show antimicrobial activity due to their ability to affect bacterial protein synthesis by the coordination of protein active site residues or by binding to bacterial ribosomal subunits. Silver has been widely employed as an effective non-resistance-inducing agent able to prevent medical device-related infections when incorporated in polymers [3]. Conventional approaches mainly consist of the deposition of metallic silver on the polymer surface, or direct incorporation of silver ions, the active species of silver into the polymer [3].

In this paper, preparation, structure, and thermal properties of novel polyurethane/ferrite composites (PUFNCs) using low amount of silver ferrite (1 wt.%) as fillers were studied. The synthesized PUFNCs have a great deal of attention from scientific community, due its unique properties (good thermal, mechanical and surface properties) and applications (as coatings for medical devices and implants).

METHODS

Polyurethane nanocomposites based on polyurethane network and silver ferrite were prepared by *in situ* polymerization method as previously described [4]. PUFNCs were prepared using α,ω-dihydroxy-poly(dimethylsiloxane) (PDMS; ABCR; M_n = 1000 g/mol), 4,4′-methylenediphenyl diisocyanate (MDI; Sigma-Aldrich) as monomers and hyperbranched polyester of the second pseudo generation as crosslinking agent (BH-20; Polymer Factory; M_n = 1780 g/mol) [4]. The soft PDMS segment was varied from 30 to 60 wt.%. Silver ferrite was used as the nanofillers in the concentration of 1 wt.% in nanocomposites. The silver ferrite ($AgFeO_2$) nanoparticles modified with poly(ethylene oxide) was prepared by co-precipitation/microwave hydrothermal method.
FTIR spectra were recorded on ATR Nicolet 380 FTIR spectrometer. Differential scanning calorimetry (DSC) was carried out on a TA DSC Q1000 thermal analyzer. The DSC scans were recorded under a dynamic nitrogen atmosphere (50 cm^3/min), in the temperature range from -90 to 260 °C, at a heating and cooling rate of 10 and 5°C/min, respectively (two scans were run for each sample). The thermal stability was determined by thermogravimetric (TG) analysis, using TA TGA Q500 instrument in nitrogen atmosphere, at heating rate of 10 ºC/min.

RESULTS AND DISCUSSION

FTIR analysis was performed to study the structure of the obtained PUFNC films. The FTIR spectra of the selected PUFNCs are displayed in Fig. 1. The absence of unreacted isocyanate absorption peaks at 2270 cm^{-1} relieved that the presence of silver ferrite nanoparticles did not negatively affect the formation of the urethane groups.

The characteristic stretching frequencies of the prepared PUFNCs appeared at 3320−3450 cm^{-1} (ν_{N-H}), 2960, 2945, and 2865 cm^{-1} (ν_{sym} and ν_{asym} of C−H), 1645−1735 cm^{-1} ($\nu_{C=O}$), 1535 and 1260 cm^{-1} (ν_{C-N} + δ_{N-H}, i.e., amide II and amide III bands), 1016 and 1080 cm^{-1} ($\nu_{Si-O-Si}$ and ν_{C-O-C}), 1597 and 1415 cm−1 ($\nu_{(C=C)arom}$), and 790 cm^{-1} (ρ_{C-H} in $SiCH_3$). In FTIR spectra of PUFNCs, two bands at lower frequency range i.e., one strong band at ~450 cm^{-1} and one very week band at ~510 cm^{-1}. An FTIR band at ~450 cm^{-1} could be assigned to stretching vibration of Ag–O, while the appeared FTIR band at ~510 cm^{-1} could be ascribed to stretching vibration of Fe–O [5].

Thermogravimetric curves of the selected PUFNC films are given in Fig. 2 and results are presented in Table 1. Thermal stability increased with increasing soft (PDMS) segment content. DTG curves of PUFNC films are characterized with three steps (Table 1; 5th column). The first one, DTG peak, is more pronounced, and belongs to the degradation of hard domains (the urethane links scission), while the second and third process (shoulders in DTG curves) are assigned to the decomposition of ester and soft segments (PDMS).

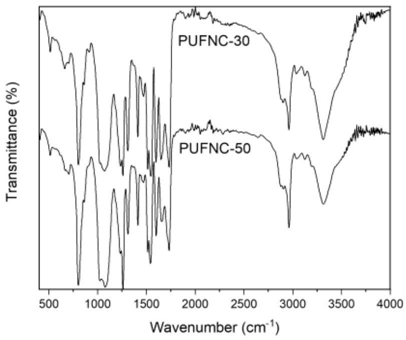

Figure 1. FTIR spectra of PUFNCs.

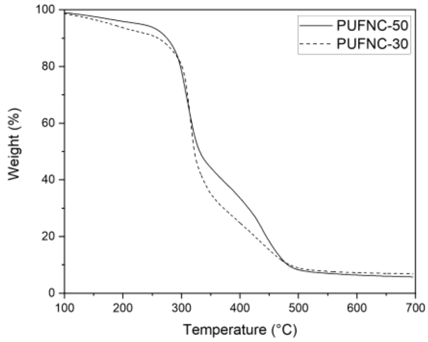

Fig. 2ure TGA of the selected PUFNCs.

Thermal characteristics of PUFNCs were investigated by DSC. The first heating DSC curves of PUFNC films show glass transition temperature of the hard (MDI-BH20) segment (T_{gHS}). The T_{gHS} values ranged from 49 to 56 °C (Table 1) and increased with decreasing soft segment content. The obtained results are attributed to the higher of cross-linking density in materials with lower soft segment content, that cause more restricts the molecular motion of the polymer chains and leads to the increase in T_{gHS}.

Table 1. The soft segments content (SSC), characteristic temperatures of thermal degradation, and glass transition temperature of the hard segment (T_{gHS}), determined by DSC, of PUFNC films

Sample	SSC, wt.%	T_{10}, ºC	T_{50}, ºC	T_{max}, ºC	T_{gHS} (DSC), ºC
PUFNC-30	30	260	322	316/343//445	56
PUFNC-40	40	265	324	314/352/450	54
PUFNC-50	50	275	332	309/357/440	52
PUFNC-60	60	270	343	308/326/452	49

Incorporation of PEG coated $AgFeO_2$ nanoparticles in PU was examined by High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) using a JEOL ARM 200CF electron microscope equipped with JEOL Centurio EDXS and Quantum ER Gatan GIF dual-EELS systems. A micrograph of PUFNC-30 composite is shown in the Fig. 3. Bright spots indicate that nanoparticles of $AgFeO_2$ are a few nanometer is size, spherical shape and random distributed in polymer.

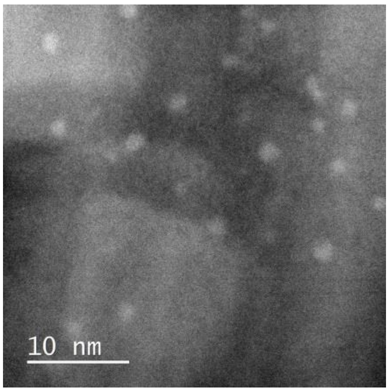

Figure 3. HAADF/STEM images of PUFNC-30.

CONCLUSION

A series of novel PU nanocomposites with different soft segment content was successfully obtained by addition of 1 wt% of silver ferrite nanoparticles using *in situ* polymerization method. The thermal stability increased with increasing soft segment content. The T_{gHS} values increased with decreasing soft segment content due to higher crosslinking density. The obtained results confirmed the existence of interaction between the silver ferrite nanoparticles and hard segments of PUFNCs.

Acknowledgement

The authors would like to thank the Ministry of Education, Science and Technological Development (Grant No: 451-03-9/2021-14/200026). We thank Prof. Goran Drazic for performing HAADF/STEM measurements.

REFERENCES

[1] M. V. Pergal, I. S. Stefanović, R. Poręba, M. Steinhart, P. Jovančić, S. Ostojić, M. Špírková, Ind. Eng. Chem. Res., 2017, 56, 4970-4983.

[2] R. Vermette, H. J. Griesser, G. Laroche, R. Guidoin, Biomedical Applications of Polyurethanes; Landes Bioscience, Austin, TX, 2001.

[3] I. Francolini, L.D ’Ilario, E. Guaglianone, G. Donelli, A. Martinelli, A. Piozzi, Acta Biomater., 2010, 6, 3482-3490.

[4] M. V. Pergal, J. V. Džunuzović, R. Poręba, S. Ostojić, A. Radulović, M. Špírková, Prog. Org. Coat., 2013, 76, 743-756.

[5] S. M. Hosseini, H. Hosseini-Monfared, V. Abbasi, M. R. Khoshroo, Inorg Chem Commun., 2016, 67, 72–79.