

PHYSICAL CHEMISTRY 2022

16th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume II

September 26-30, 2022
Belgrade, Serbia

Title: PHYSICAL CHEMISTRY 2022, 16th International Conference on Fundamental and Applied Aspects of Physical Chemistry (Proceedings) **ISBN** 978-86-82475-41-5

Volume II: ISBN 978-53-82475-43-9

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, Ilije Đuričića 19, Belgrade, 200 Copies

Number of pages: 6+320, Format A4, printing finished in December 2022

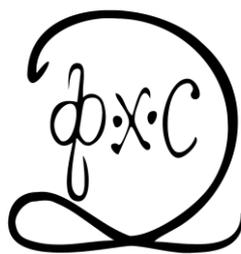
Text and Layout: "Jovan"

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

<i>Volume II</i>	
<i>Organizer</i>	IV
<i>Comittes</i>	V
<i>Sponsors</i>	VI
<i>Material Science</i>	321
<i>Photochemistry, Radiation Chemistry, Photonics</i>	391
<i>Macromolecular Physical Chemistry</i>	395
<i>Environmental Protection, Forensic Sciences, Geophysical Chemistry, Radiochemistry, Nuclear Chemistry</i>	437
<i>Phase Boundaries, Colloids, Liquid Crystals, Surface-Active Substances</i>	513
<i>Complex Compounds</i>	517
<i>Food Physical Chemistry</i>	535
<i>Pharmaceutical Physical Chemistry</i>	565
<i>Index</i>	633



PHYSICAL CHEMISTRY 2022

*16th 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. Cvjetičanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), A. Ivanović-Šašić (Serbia), D. Jovanović (Serbia), N. Jović-Jovičić (Serbia), M. Kuzmanović (Serbia), S. Maćešić (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović Bijelić (Serbia), B. Simonović (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. Azizoglu (Turkey), R. Cervellati (Italy), A. Clayton (Australia), A. Cristina Silva (Portugal) G. Ćirić-Marjanović (Serbia), V. Dondur (Serbia), R. Faria (Brasil), M. Fronczak (Poland), I. Grinvald (Russia), P. Humpolíček (Czech), M. Jeremić (Serbia), I. Kiss (USA), E. Kiš (Serbia), A.V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), T. Kowalska (Poland), G. Kyzas (Greece), G. Lente (Hungary), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), N. Ostrovski (Serbia), V. Parmon (Russia), J. Pérez-Mercader (USA) 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), Zs. Szakacs (Romania), Z. Šaponjić (Serbia), Á. Tóth (Hungary), M. Trtica (Serbia), H. Varela (Brasil), V. Vasić (Serbia), Nadezda Vasilyeva (Russia), D. Veselinović (Serbia), V. Vukojević (Sweden), A. De Wit (Belgium)

Local Executive Committee

- Chairman:** S. N. Blagojević
Vice-chairman: A. Ivanović-Šašić
Members: M. Ajduković, I. N. Bujanja, D. Dimić, J. Dostanić, D. Drakulić, S. Jovanović, Z. Jovanović, D. Lončarević, J. Krstić, B. Marković, J. Maksimović, S. Marinović, D. Milenković, T. Mudrinić, M. Pagnacco, N. Potkonjak, B. Stanković, I. Stefanović, A. Todorović, M. Vasić, F. Veljković, M. Pejčić, G. Stevanović, H.Šalipur.K. Milošević, S. Pavlović, V. Kostić, B. Milovanović.

THE INFLUENCE OF TiO₂ NANOPARTICLES ON VISCOELASTIC PROPERTIES AND THERMO-OXIDATIVE STABILITY OF POLYURETHANE NETWORK

J. V. Džunuzović^{1,2}, I. S. Stefanović², E. S. Džunuzović³, S. J. Brzić⁴ and C. Marega⁵

¹University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Center of Excellence in Environmental Chemistry and Engineering, Njegoševa 12, 11000 Belgrade, Serbia.

²University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia. (ivan.stefanovic@ihm.bg.ac.rs)

³University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11100 Belgrade.

⁴Military Technical Institute, Ministry of Defense, Ratka Resanovića 1, 11000 Belgrade.

⁵University of Padova, Department of Chemical Sciences, via Marzolo 1, 35131 Padova, Italy.

ABSTRACT

In this study, unmodified TiO₂ nanoparticles (NPs) and TiO₂ NPs surface modified with lauryl gallate were incorporated into polyurethane (PU) network, based on Boltorn[®] aliphatic hyperbranched polyester of the second pseudo generation (BH-20) as crosslinking agent and polycaprolactone (PCL) as soft segment (SS). The influence of the applied TiO₂ NPs on viscoelastic properties and thermo-oxidative stability of the prepared PU/TiO₂ nanocomposites (NCs) were investigated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), respectively. DMA results revealed that addition of unmodified and modified TiO₂ NPs led to the increase of glass transition temperature of SS, decrease of the glass transition temperature of hard segments and crosslinking density of PU network. According to the obtained results, PU/TiO₂ NC loaded with TiO₂ NPs surface modified with lauryl gallate has better thermo-oxidative stability than pure PU and PU/TiO₂ NC prepared with unmodified TiO₂ NPs.

INTRODUCTION

Nano-sized TiO₂ is one of the most versatile materials, often applied as filler for the preparation of polymer based NCs. This metal oxide NPs have become increasingly intriguing because of their excellent chemical and physical stability, nontoxicity, low cost, high specific surface area, high reactivity, unique electro-chemical and photocatalytic properties, and are therefore widely used as UV-resistant material and in the field of chemical fiber production, plastics, printing ink, coatings, self-cleaning ceramics, antibacterial materials, foods packing material, chemical industry, cosmetics, etc. [1]. The main goal for designing PU/TiO₂ NCs is to create stable material with excellent multiple performances, such as improved thermal, mechanical, barrier, dielectric and antimicrobial properties compared to the pure PU matrix. Therefore, the influence of unmodified and modified TiO₂ NPs on the properties of environmentally friendly polyurethane network was investigated in this work.

METHODS

Titanium dioxide NPs (P25, size 25 nm) were obtained from Degussa, while lauryl gallate (LG) and acetonitrile (AN) were purchased from Sigma-Aldrich. TiO₂ NPs were surface modified with lauryl gallate by adding 2 g of TiO₂ in 100 cm³ solution of LG in AN (concentration 0.01 mol dm⁻³). After placing the obtained mixture in ultrasonic bath for 10 min and leaving to rest overnight, TiO₂ NPs surface modified with LG (TiO₂-LG) were precipitated in centrifuge, washed twice with AN and dried till constant weight in vacuum oven at 40 °C. For the synthesis of pure PU network, based on PCL, BH-20 and isophorone diisocyanate (IPDI), with soft segment (PCL) content of 30 wt.%,

procedure published elsewhere was applied [2]. The stoichiometric ratio between –NCO and –OH groups was 1.1. The synthesis of NCs was performed in the same manner, by addition of 1.0 wt.% (based on the total weight of PCL, BH-20 and IPDI) of unmodified or modified TiO₂ NPs, dispersed in small amount of THF using ultrasonic bath, during the first step of the reaction.

Density of samples, ρ , was determined at room temperature, using pycnometer and distilled water. The average of three measurements was taken.

Dynamic-mechanical analysis (DMA) of samples was performed using Modular Compact Rheometer MCR-302 (Anton Paar GmbH). Measurements were conducted in a torsion rectangular mode from -80 °C to 180 °C, at strain amplitude of 0.1% and angular frequency of 1 Hz, within the linear viscoelastic region. The crosslinking density of samples, ν , was calculated using the following equation:

$$\nu = \frac{G'}{RT} \quad (1)$$

where G' represents storage modulus, R is the universal gas constant and T is the absolute temperature. The number average molecular weight of polymer chain between crosslinks, M_c , was calculated as follows:

$$M_c = \frac{\rho_{PU}}{\nu} \quad (2)$$

Thermogravimetric analysis (TGA) of samples was done on a TA Instrument SDT 2960 simultaneous TG/DSC system, under an air atmosphere (flow 130 mL/min), from room temperature to 700 °C, with a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

The influence of TiO₂ NPs on viscoelastic properties of PU network was investigated with DMA. Temperature dependences of storage modulus, G' , and $\tan \delta$ of the pure PU and prepared NCs are given in **Figure 1**.

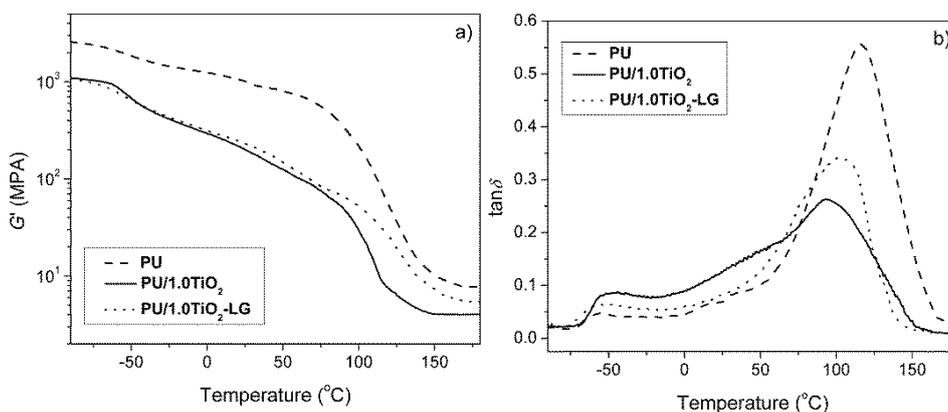


Figure 1. Temperature dependences of a) storage modulus, G' and b) $\tan \delta$ of the pure PU and prepared NCs.

Obtained results show that all samples have glass transition temperature of the soft, T_{gS} , and hard segments, T_{gH} , due to the presence of microphase separated morphology (Table 1). However, the incorporation of unmodified and surface modified TiO₂ NPs increased T_{gS} , decreased T_{gH} , and, according to the results given in Table 1, also reduced crosslinking density and simultaneously increased M_c value. It can be concluded that the presence of TiO₂ NPs resulted in enhanced segmental mobility of PU. Unmodified TiO₂ NPs have greater effect on viscoelastic properties of PU matrix than TiO₂ NPs surface modified with LG. Also, $\tan \delta$ peak corresponding to the T_{gH} of

sample PU/1.0TiO₂ is much broader, indicating existence of higher degree of network structure heterogeneity.

Table 1. Values of glass transition temperatures, T_{gS} and T_{gH} , determined as $\tan \delta$ peak position, storage modulus in the rubbery plateau (at $T_{gH} + 60$ °C), G'_{RP} , density, ρ , values of the crosslinking density, ν , and number average molecular weight of polymer chain between crosslinks, M_c , of pure PU and NCs

Sample	$(T_{gS})_{\tan \delta}$ (°C)	$(T_{gH})_{\tan \delta}$ (°C)	G'_{RP} (MPa)	ρ (g/cm ³)	$\nu \times 10^3$ (mol cm ⁻³)	M_c (g mol ⁻¹)
PU	-55	116	7.7	1.011 ± 0.010	2.06	490
PU/1.0TiO ₂	-50	94	4.0	1.024 ± 0.015	1.13	910
PU/1.0TiO ₂ -LG	-53	103	5.5	1.030 ± 0.018	1.52	680

Thermo-oxidative stability of pure PU and prepared NCs was investigated using TGA under air atmosphere. TG curves of the examined samples are given in Figure 2, while characteristic temperatures of thermo-oxidative degradation T_5 , T_{10} , T_{50} and T_{90} (at 5, 10, 50 and 90% weight loss, respectively) and temperatures at which maximum thermal degradation rate occurred are listed in Table 2. The obtained results show that the incorporation of TiO₂-LG NPs in PU network leads to the slight increase of thermo-oxidative stability, indicating that TiO₂ NPs surface modified with LG are involved in inhibition of some thermo-oxidative degradation stages of PU network. According to the literature, during thermo-oxidative degradation oxygen can be adsorbed on the surface of TiO₂-LG, reducing in this manner the amount of oxygen that can reach PU matrix, which further leads to the slower thermo-oxidative degradation than in the case of pure PU [3]. Thermo-oxidative stability of pure PU is somewhat better than for PU/1.0TiO₂, probably due to the reduced crosslinking density after incorporation of unmodified TiO₂ NPs in PU matrix.

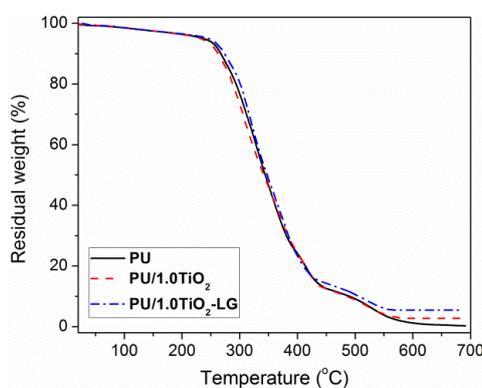


Figure 2. TG curves of the pure PU and NCs, obtained at a heating rate of 10 °C/min, in air.

Table 2. Characteristic temperatures of thermal degradation T_5 , T_{10} , T_{50} and T_{90} (at 5, 10, 50 and 90% weight loss, respectively) and temperatures at which maximum thermal degradation rate occurs of the pure PU and NCs, in air atmosphere

Sample	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	T_{sh1} (°C)	T_{max1} (°C)	T_{max2} (°C)	T_{sh2} (°C)	T_{max3} (°C)
PU	237	267	344	490	275	325	356	413	528
PU/1.0TiO ₂	233	262	342	485	268	308	368	412	523
PU/1.0TiO ₂ -LG	246	274	347	506	279	324	375	412	524

From differential TG (DTG) curves of pure PU and NCs, given in Figure 3, and results listed in Table 2 it can be observed that all samples have three decomposition steps in air. The first DTG peak ($T_{\max 1}$) is associated to the degradation of the urethane bonds of the hard segments, which represents the weakest link in PU [2,4]. The second and third DTG peak ($T_{\max 2}$) and ($T_{\max 3}$) corresponds to the thermo-oxidative degradation of soft segments. It can be observed that incorporation of TiO_2 NPs in PU matrix led to visible splitting of the first and the second DTG peak, which are in DTG curve for pure PU overlapped. The first and the second DTG peak each have one shoulder, the first on its left side (T_{sh1}) corresponding to the thermal degradation of HS, and the second on its right side (T_{sh2}), assigned to the thermal degradation of PCL.

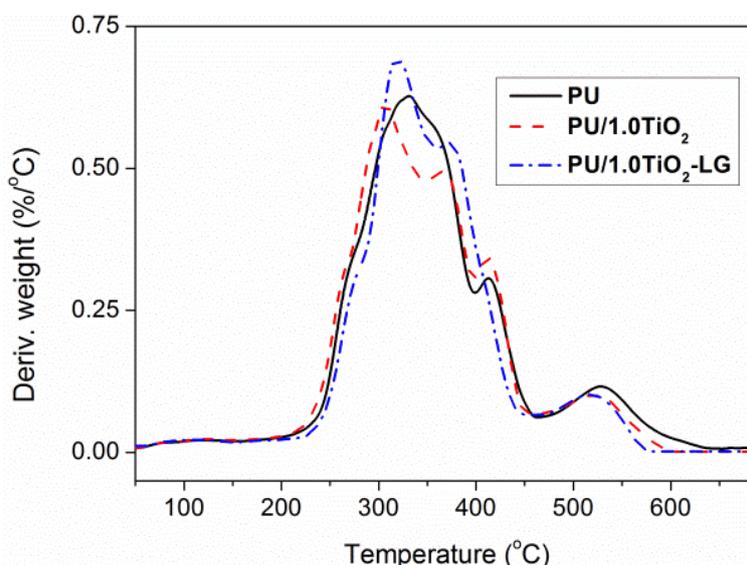


Figure 3. DTG curves of the pure PU and NCs, determined at a heating rate of 10 °C/min, in air.

CONCLUSION

Viscoelastic properties and thermo-oxidative stability of PU matrix are changed after incorporation of unmodified TiO_2 NPs and TiO_2 NPs surface modified with LG. Value of T_{gS} is higher, while T_{gH} and crosslinking density of prepared NCs are lower than for pure PU, while thermo-oxidative stability of PU network was improved by incorporation of TiO_2 -LG NPs.

Acknowledgment

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant no 451-03-68/2022-14/200026 and 451-03-68/2022-14/200135).

REFERENCES

- [1] X. Chen, S. S. Mao, Chem. Rev., 107 (2007) 2891.
- [2] J. V. Džunuzović, I. S. Stefanović, E. S. Džunuzović, A. Dapčević, S. I. Šešlija, B. D. Balanč, G. C. Lama, Prog. Org. Coat., 137 (2019) 105305.
- [3] E. S. Džunuzović, J. V. Džunuzović, A. D. Marinković, M. T. Marinović-Cincović, K. B. Jeremić, J. M. Nedeljković, Eur. Polym. J., 48 (2012) 1385.
- [4] D. K. Chattopadhyay, D. C. Webster, Prog. Polym. Sci., 34 (2009) 1068.