



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"

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CONTENT

<i>Volume II</i>	
<i>Organizer</i>	IV
<i>Comittes</i>	V
<i>Organic Physical Chemistry</i>	345
<i>Material Science</i>	367
<i>Macromolecular Physical Chemistry</i>	487
<i>Environmental Protection, Forensic Sciences, Geophysical Chemistry, Radiochemistry, Nuclear Chemistry</i>	519
<i>Phase Boundaries, Colloids, Liquid Crystals, Surface-Active Substances</i>	633
<i>Complex Compounds</i>	643
<i>General Physical Chemistry</i>	655
<i>Pharmaceutical Physical Chemistry</i>	669
<i>Food Physical Chemistry</i>	679
<i>Physico-Chemical Analysis</i>	703
<i>Index</i>	725



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*15th International Conference on
Fundamental and Applied Aspects of
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Organized by

*The Society of Physical Chemists of
Serbia*

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

*Borekov Institute of Catalysis Siberian Branch of
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and

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THERMAL PROPERTIES OF POLYURETHANE-CLAY NANOCOMPOSITES

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ABSTRACT

Two samples of poly(urethane-siloxane) nanocomposites (PUNs), based on 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) as the comonomers of the hard segments (HS) and α,ω -dihydroxyethoxy propyl poly(dimethylsiloxane) (EO-PDMS) as the part of the soft segments (SS), were prepared by *in situ* polymerization. HS content of the prepared PUN samples were 10 and 20 wt%. Organomodified montmorillonite clay (Cloisite 30B[®]) was used as nanofiller (1 wt%) for poly(urethane-siloxane)s. Prepared PUNs have good thermal stability, and they represent semicrystalline polymers.

INTRODUCTION

Segmented polyurethanes (PUs) are polymers constructed of alternating flexible polyol parts that represent soft segments and rigid urethane parts which represent hard segments. By careful selection of diisocyanates, as well as polyols and chain extenders, it is possible to obtain PUs with a wide range of physical and chemical features that are quite important for a variety of applications [1]. Moreover, properties of PUs are also affected by the utilized composition of HS and SS, their chemical structure and obtained molecular weight. Although these PUs have significant number of advantages, it is still unsatisfactory when it comes to their heat resistance and thermal properties. In order to improve these properties, PUN can be prepared by using poly(dimethylsiloxane) (PDMS) as polyol and different clay nanoparticles as nanofillers [2].

EXPERIMENTAL

Two samples of PUNs based on α,ω -dihydroxyethoxy propyl poly(dimethylsiloxane) (EO-PDMS) (ABCR, $M_n = 1000$ g/mol) and organically modified montmorillonite clay (Cloisite 30B[®]), with different HS content (10 and 20 wt%, samples PUN10 and PUN20, respectively), were prepared by *in situ* two-step polyaddition reaction in THF/DMAc solution (1/1, v/v). In the first step, MDI, PDMS and delaminated clay were mixed in order to prepare -NCO-prepolymer with addition of catalyst dibutyltin dilaurate, and in the second step BD was added to the reaction mixture at 60 °C for 6 h. The PUN films were prepared by placing reaction mixtures in the Teflon[®] dishes, followed by their drying in air and vacuum oven for 24h at 50 °C and 24h at 40 °C, respectively.

The thermogravimetric analysis (TG) was carried out on a TA SDT 2960 instrument that was calibrated with Curie temperature standard materials (with well-known Curie temperatures) and melting point standards (Ni and Zn). The TG measurements were recorded under N₂ and air atmosphere, in the range from 25 to 700 °C and at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC6 thermal analyzer. The DSC measurements were performed under N₂ flow, using weighted samples (~5 mg) in Al pans and in the temperature range from -20 to 220 °C, at a heating and cooling rate of 10 °C/min.

RESULTS AND DISCUSSION

The thermal stability of the prepared PUNs was investigated by TG analysis under nitrogen and air atmosphere. The obtained TG and derivative TG (DTG) curves are shown in Figure 1, while characteristic degradation temperatures are listed in Table 1.

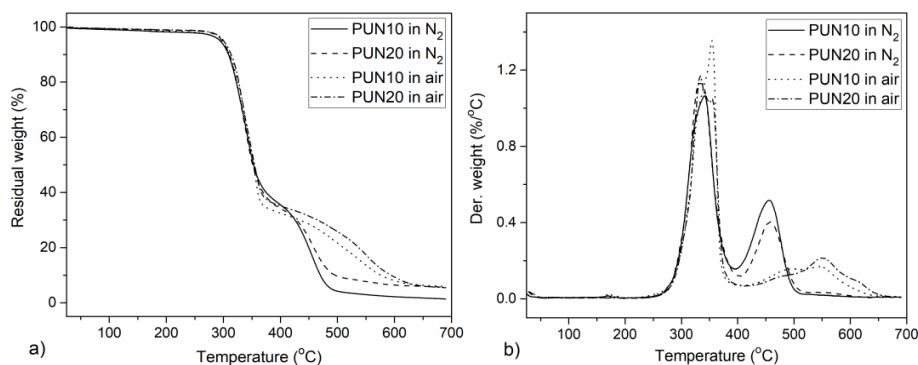


Figure 1. a) TG and b) DTG curves of the prepared PUNs in nitrogen and air atmosphere.

From the obtained TG results, thermal degradation of the PUN10 starts after 294 and 295 °C, in nitrogen and air atmosphere, respectively. $T_{10\%}$ values were 309 °C for PUN10 and 311 °C for PUN20 in nitrogen, and 311 °C for PUN10 and 314 °C for PUN20 in air atmosphere. From these results, it is concluded that PUNs exhibit slightly greater thermal stability in air than in a nitrogen atmosphere. Moreover, sample with higher content of HS exhibit greater thermal stability. According to the DTG curves (Figure 1b), thermal degradation occurs as a three- or four-step process in nitrogen and air atmosphere, respectively. In the first step, in the range from 332 to 341 °C and from 354 to 355 °C in nitrogen and air atmosphere, respectively, the urethane bonds start to decompose. In the second step, in the range from 457 to 458 °C and from 483 to 493 °C in nitrogen and air atmosphere, respectively, ether bonds inside PDMS start to break down. In the third step, the decomposition of the aromatic rings occurred in the range from 553 to 557 °C and from 547 to 549 °C in nitrogen and air atmosphere, respectively [3]. Degradation of the PUNs in the air atmosphere is more complex due to the one more additional peak-shoulder at ~ 600 °C, which originates from oxidation of the PDMS and creation of complex silicate structures.

Table 1. TG results of the prepared PUNs in nitrogen and air atmosphere.

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	DTG _{max} (°C)
PUN10 ^{a)}	294	309	353	470	341/457/553
PUN20 ^{a)}	298	311	351	495	332/458/557
PUN10 ^{b)}	295	311	353	576	354/493/547/603
PUN20 ^{b)}	301	314	355	594	355/483/549/604

a) Recorded under nitrogen atmosphere

b) Recorded under air atmosphere

In order to investigate thermal properties of the prepared PUNs, differential scanning calorimetry (DSC) was performed. The obtained DSC curves are shown in Figure 2. The glass transition (T_g), melting (T_m) and crystallization (T_c) temperatures, as well as the enthalpy of melting (ΔH_m) and crystallization (ΔH_c), were determined and summarized in Table 2.

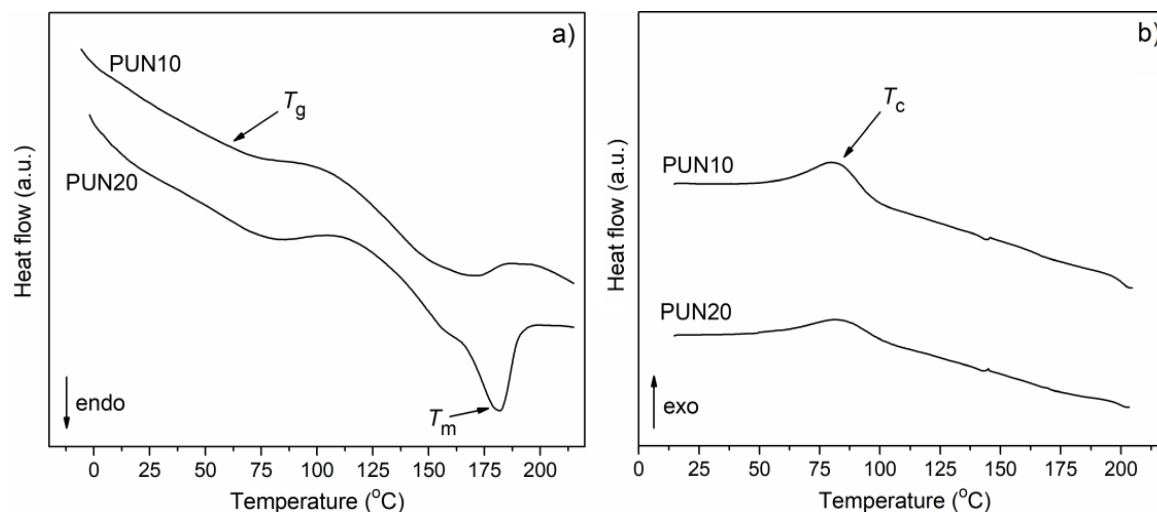


Figure 2. DSC curves of the prepared PUNs recorded during a) the second heating and b) cooling run.

DSC curves of PUNs have only one peak which appeared during the heating and cooling run, corresponding to the melting and crystallization, respectively, of the HS (MDI-BD). Also, PUNs have one T_g that belongs to the HS and obtained T_g values are higher than values reported for the neat copolymer, resulting from the addition of clay nanoparticles [3]. According to the results presented in Table 2, all values, except ΔH_c , increased with increasing HS content in the prepared PUNs. This was caused by better ordering of the hard domains which are formed from the longer MDI-BD units. The crystallinity degrees (X_c and X_{cHS}) were calculated based on the group contribution method [4]. Total crystallinity degrees (X_c) are lower than theoretical values, which indicates that these HS could not crystallize completely, partly because of the addition of clay nanoparticles and partly due to the incorporation of HS into the amorphous phase.

Table 2. DSC results (glass transition (T_g), melting (T_m) and crystallization (T_c) temperatures, the enthalpy of melting (ΔH_m) and crystallization (ΔH_c), total crystallinity degree (X_c) and crystallinity degree of the HS (X_{cHS})) of the prepared PUNs.

Sample	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)	X_{cHS} (%)
PUN10	41.4	162.9	82.8	3.54	2.46	3.88	17.81
PUN20	54.1	181.4	84.3	10.20	1.99	11.18	30.47

CONCLUSION

Two PUN samples with different HS content, based on MDI, PDMS, BD and clay Cloisite 30B[®], were successfully prepared. TG analysis showed that these PUNs have good thermal stability, while DSC analysis showed that they are semicrystalline polymers.

Acknowledgement

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants No. 451-03-9/2021-14/200026).

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