

# PHYSICAL CHEMISTRY 2016

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Physical Chemistry*

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## IMPACT OF THE TiO<sub>2</sub> NANOPARTICLES ON THE PROPERTIES OF URETHANE-SILOXANE COPOLYMERS

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### ABSTRACT

Rutile/anatase TiO<sub>2</sub> was incorporated in different amounts (1, 2, 3 and 5 wt.%) in relative to the polyurethane-siloxane (PUS) matrix in order to investigate the influence of nano-fillers on the hydrophobicity, thermal properties and morphology of the PUS. A series of PUS nanocomposites (PUSN) based on  $\alpha,\omega$ -dihydroxy-ethoxypropyl-poly(dimethylsiloxane) (EO-PDMS) as the soft segment (SS) and 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) as the hard segment (HS), was prepared via two-step polyaddition reaction in solvent mixture. Prepared PUSNs were characterized using FTIR spectroscopy, thermogravimetric analysis, water absorption, water contact angle and AFM analysis. In summary, the synthesized PUSNs and especially PUSN with 2 wt.% of TiO<sub>2</sub> had better water resistivity and nonwettability, higher thermal stability, and more pronounced surface morphology that can be potentially used as protective coatings.

### INTRODUCTION

The recent decades have seen an increase in developing novel organic/inorganic materials for different applications (protecting coatings, elastomers, adhesives, etc). These materials often incorporate colloidal inorganic nanoparticles into an organic matrix yielding physical features superior than conventional polymer [1]. Generally, PUS copolymers have good thermal and oxidative stability, elasticity, hydrophobicity, chemical and UV resistance, etc. Interaction of TiO<sub>2</sub> nanoparticles with components in the PUS matrix enables improvement of the mentioned properties. To date, plenty research have been focused on the usage of TiO<sub>2</sub> with proper dispersion and enhanced compatibility with the polymer matrix [2]. The goal of this research was to synthesize TiO<sub>2</sub>-PUS nanocomposites and to

investigate the influence of different loadings of TiO<sub>2</sub> nanoparticles on thermal, barrier and surface properties of PUS matrix.

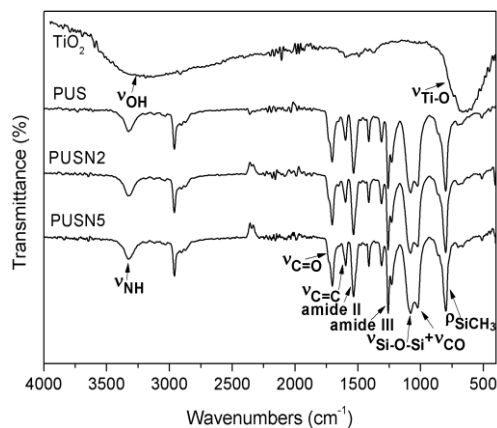
## EXPERIMENTAL

$\alpha,\omega$ -Dihydroxy-ethoxypropyl-poly(dimethylsiloxane) (EO-PDMS) ( $M_n = 1000 \text{ g mol}^{-1}$ ) was dried over molecular sieves before use. 4,4'-Diphenylmethane diisocyanate (MDI) was used as received. 1,4-Butanediol (BD) was purified with distillation before use. Tetrahydrofuran (THF) and *N,N*-dimethylacetamide (DMAc) were purified with distillation before use. Stannous octoate (Sn(Oct)<sub>2</sub>) was used as a diluted catalyst solution in THF/DMAc. AEROXIDE<sup>®</sup> TiO<sub>2</sub> P 25 (anatase/rutile=80/20) was supplied from Evonic Industry. The PUSNs with 20 wt.% of HS, were synthesized with addition of TiO<sub>2</sub> nanoparticles by *in situ* two-step polyaddition process in solvent mixture (THF/DMAc; 1/1 v/v). The last number in the name of the PUSN represents the weight percent of the TiO<sub>2</sub> nanoparticles. The initial reaction mixture and final polymer solution were sonicated on ultrasonic bath for a period of 1 hour. Synthesis was carried out as follows: firstly, the isocyanate terminated prepolymer was synthesized by the reaction between the EO-PDMS and MDI in solvent mixture at 40 °C for 30 min under N<sub>2</sub> atmosphere, and with presence of Sn(Oct)<sub>2</sub> solution used as a catalyst. Then, in the second phase of reaction, dilute solution of BD was drop-wise added and the reaction was continued at 50 °C for 10 hours. From the final polymer solutions were prepared PUSN films that had been used for characterization. The synthesized PUSNs were characterized by means of infrared spectroscopy (ATR-FTIR), atomic force microscopy (AFM) and thermal gravimetric analysis (TGA). Water absorption (WA) was performed at room temperature by immersion of PUSNs in phosphate buffers (pH = 7.4). Water contact angles (WCA) were measured on Krüss DSA 100 instrument using the sessile drop method. Measurements were performed at room temperature, 30 s after placing the single drops on the surface of the films.

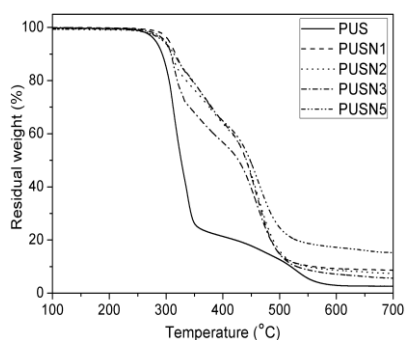
## RESULTS AND DISCUSSION

The chemical structures of the prepared PUSNs, initial PUS copolymer and TiO<sub>2</sub> nanoparticles were confirmed by FTIR spectroscopy (Figure 1). Characteristic bands of PUS and PUSN samples appeared at 3330 cm<sup>-1</sup> ( $\nu_{\text{N-H}}$ ), 2960 and 2900 cm<sup>-1</sup> ( $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  of -CH<sub>2</sub>-), 1705 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$ ), 1535 cm<sup>-1</sup> and 1260 cm<sup>-1</sup> (amide II and amide III bands), 1020 cm<sup>-1</sup> and 1080 cm<sup>-1</sup> ( $\nu_{\text{Si-O}}$  and  $\nu_{\text{C-O}}$ ), 1600 and 1410 cm<sup>-1</sup> ( $\nu_{\text{C=C}}$ <sub>arom</sub>), 800 cm<sup>-1</sup> ( $\rho_{\text{SiCH}_3}$ ). In the FTIR spectra of TiO<sub>2</sub> nanoparticles two wide absorption bands appeared from 3630 to 2300 cm<sup>-1</sup> (hydroxyl groups on the surface of TiO<sub>2</sub>) and one absorption band at about 600 cm<sup>-1</sup> ( $\nu_{\text{Ti-O}}$ ).

Thermal degradation of the PUSN samples, i.e.  $T_{5\%}$  values, started between 294 and 305 °C in comparison to initial PUS that started to degrade at 281 °C (Table 1). It can be observed that thermal stability of PUSNs was improved for ~ 15 to 25 °C, while the temperature of 50% weight loss,  $T_{50\%}$  values, are improved for ~ 110 °C compared to the initial PUS. Moreover, TGA curves (Figure 2) also show that thermal stability of PUSN copolymers was significantly improved with increasing the content of TiO<sub>2</sub> nanoparticles.



**Figure 1.** FTIR spectra of the initial PUS and PUSN copolymers with 2 and 5 wt.% of TiO<sub>2</sub>



**Figure 2.** TGA curves of the prepared PUSNs and initial PUS

**Table 1.** Thermal properties, water absorption (WA) and water contact angle (WCA) values of the prepared PUSNs and initial PUS

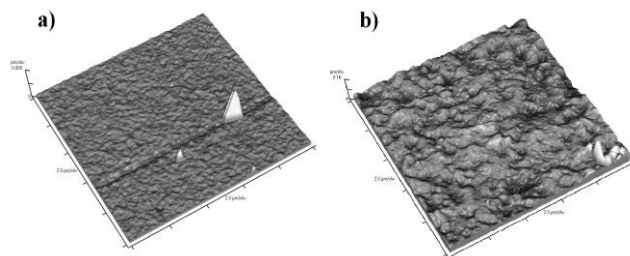
Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	$T_{85\%}$ (°C)	WA <sup>a)</sup> (%)	WCA (°)
PUS	281	327	478	1.2	94.4
PUSN1	305	441	499	0.8	101.6
PUSN2	296	442	503	0.5	108.7
PUSN3	298	427	499	0.6	104.9
PUSN5	294	448	>700	0.8	104.0

a) measured after 48 hours

Water absorption and water contact angle values (Table 1) show that addition of TiO<sub>2</sub> nanoparticles leads to decrease of amount of absorbed water and increase of water contact angles. These obtained values indicate improvement of hydrophobicity of the PUSN samples.



AFM images presented in Figure 3 showed that the surface morphology of PUS copolymer is significantly changed and becomes rougher after incorporation of TiO<sub>2</sub> nanoparticles. With incorporation of 2 wt.% of TiO<sub>2</sub>, the resulting PUSN exhibited a high uniformity of nanoparticles dispersion with minimal agglomeration giving more pronounced surface morphology.



**Figure 3.** 3D AFM images of the surface of films of a) initial PUS and b) PUSN with 2 wt.% of TiO<sub>2</sub> (scan area 10 × 10 μm<sup>2</sup>)

## CONCLUSION

In this work, series of PUSN were prepared from PUS copolymers, synthesized via two-step polyaddition reaction in solvent mixture, and with incorporation of different percentages of TiO<sub>2</sub> nanoparticles. The structure of PUSNs and presence of the TiO<sub>2</sub> nanoparticles were confirmed by FTIR spectroscopy. TGA analysis showed that incorporation of the TiO<sub>2</sub> led to significant increase of thermal stability of PUSNs. The introduction of TiO<sub>2</sub> led to a noticeable increase in hydrophobicity and nonwettability of the PUSNs. Moreover, homogenous TiO<sub>2</sub> dispersion on the surface results in pronounced surface morphology of the PUSNs. Therefore, the prepared PUSN copolymers with TiO<sub>2</sub> nanoparticles led to significant improvement of investigated features and potentially can be applied as protective coatings.

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