

Preparation and characterization of poly(urethane-siloxane)/titanium-dioxide nanocomposites

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Abstract

This work is focused on preparation of poly(urethane-siloxane)/titanium-dioxide nanocomposites (PUSNs) with enhanced features. PUSNs were prepared by the *in situ* polymerization reaction using titanium-dioxide as a nano-filler in different amounts (1, 2, 3 and 5 wt.%) with respect to the poly(urethane-siloxane) (PUS) matrix. PUS copolymer was based on α,ω -dihydroxy-ethoxypropyl-poly(dimethylsiloxane), 4,4'-methylenediphenyldiisocyanate and 1,4-butanediol. In order to investigate the influence of TiO₂ content on the structure, UV resistance, thermal properties, hydrophobicity and morphology of the prepared PUSNs, FTIR spectroscopy, UV-Vis diffuse-reflectance spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), contact angle measurements, surface free energy (SFE) analysis, water absorption, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed. The PUSNs showed excellent UV resistance, high hydrophobicity, low surface free energy and also higher thermal stability and rougher surface and cross-section relief structure as compared to the pure PUS copolymer. Based on the obtained results it can be concluded that prepared PUSNs could be potentially used as protective coatings.

Keywords: polyurethanes; poly(dimethylsiloxanes); titanium-dioxide; nanocomposites, thermal properties; morphology

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1. INTRODUCTION

Segmented polyurethanes (PU) are linear multi-block copolymers containing hard (HS) and soft segments (SS). The thermodynamic incompatibility between them results in microphase separation, which predominantly determines the final properties of the PUs. Properties of the PUs also depend on the chemical structure of the segments, molecular weights, HS/SS ratio, crystallizability of segments, physical crosslinking, etc. [1,2]. Introducing poly(dimethylsiloxane) (PDMS) as SS leads to the improvement of the oxidative and thermal stability, UV resistance and hydrophobicity of the PUs. In literature, there are many studies related to poly(urethane-siloxane) (PUS) copolymers with different PDMS macrodiols as a part of SS [3-7].

Polymer nanocomposites, containing different inorganic nano-fillers, are recognized as one of the possible solutions for the constant demand for new materials and materials with enhanced properties. The use of titanium-dioxide (TiO₂) as a filler in PUS nanocomposites (PUSN) has attracted a lot of interest. Properties of TiO₂ nanoparticles are a function of crystal structure, anatase/rutile ratio, size and particle morphology [8]. Due to its broad UV-absorption spectrum and high refractive index, the addition of TiO₂, can improve UV resistance of polyurethane coatings [9,10]. Due to high photostability, environmentally friendly nature, chemical inertness and high photocatalytic activity, TiO₂ is one of the most suitable compounds to be used as a nano-filler. Moreover, the addition of TiO₂ nanoparticles in PUs can improve their mechanical, thermal and optical properties and expand their potential applications in many fields [11,12].

A drawback of using inorganic oxide nanoparticles as nano-fillers is their tendency to segregate when dispersed in predominantly hydrophobic polymers such as polyurethanes based on PDMS. Moreover, the use of conventional

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synthetic methods can often lead to formation of TiO₂ agglomerates and their inhomogeneous dispersion inside the PUS matrix due to extremely large surface to volume ratio of TiO₂ nanoparticles [13]. Sonication, during the synthesis process, can be used to overcome these problems and to ensure preparation of PUSNs with improved thermal, mechanical, barrier and optical properties [14].

According to our knowledge, there are only few studies related to the preparation of PUSNs with incorporated TiO₂ nanoparticles. Silva *et al.* [15] prepared PUSNs based on poli(ϵ -caprolactone) ($M_n = 2000 \text{ g mol}^{-1}$) and 1,6-diisocyanatohexane with different TiO₂ contents (0.5, 1.0, 2.0, 3.0, 5.0 and 10.0 wt.%) by *in situ* polymerization reaction. The prepared PUSNs showed higher degradation temperature and improved mechanical properties as compared to the neat polyurethane polymer. Moreover, scanning electron microscopy (SEM) analysis confirmed that even though some agglomeration occurred in the PUSN matrix, it was possible to achieve good nano-filler dispersion without any treatment of TiO₂ nanoparticles. In the work of Sabzi *et al.*, better nano-filler dispersion and increased interactions between TiO₂ nano-filler and polyurethane matrix were obtained by modifying the surface of TiO₂ with amino propyl trimethoxy silane [16]. Besides obtaining better nanoparticles dispersion, the prepared urethane coatings showed improved mechanical properties and UV resistance. González-Garsía *et al.* [17] reported obtained PUSN hybrid materials based on polyurethanes/TiO₂ by a sol-gel process and investigated their potential applications in bone tissue regeneration. Prepared PUSNs represent biodegradable and non-cytotoxic hybrid materials, where the incorporated nano-filler enhanced thermal and mechanical features and promoted bioactivity.

In the present paper, poly(urethane-siloxane)/titanium-dioxide nanocomposites were prepared by a conventional *in situ* polymerization process. Sonication of the reaction mixture, before and after polymerization, was performed in order to obtain good dispersion of TiO₂ nanoparticles in the PUS matrix. The content of TiO₂ used as a nano-filler was optimized in order to obtain improved thermal, surface and morphological properties, as well as high hydrophobicity and UV resistance.

2. EXPERIMENTAL

2. 1. Materials

α,ω -Dihydroxy-ethoxypropyl-poly(dimethylsiloxane) (EO-PDMS) was supplied from ABCR, Germany (purity > 95 %) and dried over molecular sieves (0.4 nm) before the use. The number average molecular weight ($M_{n,NMR}$) of the EO-PDMS was 1000 g mol^{-1} and the degree of polymerization of the PDMS-block was 9.95. 4,4'-Methylenediphenyl diisocyanate (MDI) (Aldrich, Germany, purity 98 %) was used as received. 1,4-Butanediol (BD) (Aldrich, Germany, purity 99 %) was distilled and dried over molecular sieves before the use. *N,N*-Dimethylacetamide (DMAc) (Acros, USA, purity 99 %) was dried for 2 h over calcium hydride and distilled under reduced pressure before use. Tetrahydrofuran (THF) (J. T. Baker, USA, purity 99.99 %) was dried over lithium aluminum hydride and distilled before use. Stannous-octoate (Sn(Oct)₂) (Aldrich, USA, purity 95 %) was used as a dilute solution in an anhydrous mixture of THF/DMAc (1/1, v/v). *N,N*-Dimethylformamide (Macron, Germany, purity 99.8 %), formamide (Merck, Germany, purity > 99 %) and diiodomethane (UCB, Belgium, purity 98 %) were used as received. A commercially available TiO₂, Aeroxide P25 (80 % anatase and 20 % rutile, surface area $52 \text{ m}^2 \text{ g}^{-1}$, mean diameter $\sim 30 \text{ nm}$) was supplied from Evonik Degussa GmbH (Germany).

2. 2. Preparation of the PUSNs

The complete synthesis procedure and preparation of PUS copolymers based on EO-PDMS are described in our previous papers [18,19]. In the present work, PUSNs were prepared using EO-PDMS macrodiol as SS and MDI-BD as HS, with addition of titanium-dioxide as a nano-filler.

The PUSNs were prepared by *in situ* polymerization technique in a solvent mixture. A series of PUSNs was prepared with a constant content of HS (20 wt.%) and different contents of TiO₂ nanoparticles (1, 2, 3 and 5 wt.%). A control PUS sample was prepared without TiO₂ addition. For homogenous dispersion of TiO₂ nanoparticles, the initial reaction mixture was firstly sonicated in an ultrasonic bath for a period of 1 hour. Polymerization reaction was carried out in a four-neck round-bottom flask equipped with a mechanical stirrer, an inlet for dry argon, a reflux condenser and a dropping funnel. MDI (4.2 g, 16.8 mmol) was added to the initial reaction mixture, containing the adequate amount of TiO₂ dispersed by sonication in 72 mL of the solvent mixture DMAc/THF (1/1, v/v) and 8.0 g (8.00 mmol) of EO-PDMS. The homogeneous mixture was then heated up to 40 °C under an inert atmosphere. The polymerization started by introduction of 0.78 mL of the catalyst solution in DMAc/THF (4.86 mg, $1.2 \times 10^{-5} \text{ mol}$). First phase of the polymerization was carried out at 40 °C for 30 min under continuous stirring, to prepare the NCO-terminated prepolymer, i.e. until the theoretical -NCO content was attained (5.6 wt.%) [20]. In the second polymerization stage, the chain extension was achieved by dropwise addition of a dilute solution of BD (0.72 g, 8.0 mmol) in 6.0 mL of DMAc/THF. This phase lasted for 10 h at 50 °C. The final polymer concentration was approximately 15 wt.%. The reaction mixture was also sonicated after polymerization for a period of 30 min and then casted onto Teflon® dishes. The solvent evaporation was achieved

in a force-draft oven over 48 h at 40 °C, after which the obtained PUSN films were dried in a vacuum oven at 40 °C for 24 h until the constant weight. The prepared polymer nanocomposites are denoted as PUSNX, where X designates the weight percent of the incorporated TiO₂ nanoparticles.

2. 3. Characterization

FTIR spectra of the prepared PUSNs, pure PUS and TiO₂ nanoparticles were recorded using a Nicolet 6700 FTIR spectrometer (USA) operating in attenuated total reflection (ATR) mode. The measurements were performed in the scanning range from 400 to 4000 cm⁻¹ at the resolution of 2 cm⁻¹ and 64 scans were done for each sample.

Reflectance measurements were performed using an integrating sphere spectrophotometer (Thermo Nicolet Evolution 500, USA) to measure diffuse-reflectance of examined samples in approximately UV-Vis wavelength range.

Differential scanning calorimetry (DSC) was carried out by using a Q1000V9.0 Build 275 thermal analyzer (TA Instruments, USA). The DSC scans were recorded under nitrogen flow at the rate of 50 mL min⁻¹. The temperature range of recording was between -90 and 230 °C at heating and cooling rates of 10 and 5 °C min⁻¹, respectively. The weight of the samples was ~10 mg.

Thermal stability was determined by using a simultaneous thermogravimetry and differential thermogravimetry (TG-DTG) instrument (Setsys 2400, SETARAM Instrumentation, France) in the temperature range from 25 to 700 °C, under the argon flow of 20 mL min⁻¹ and at the heating rate of 20 °C min⁻¹ in an Al₂O₃ pan.

Static contact angles of the prepared PUSNs were measured by a sessile drop method at room temperature, using a contact angle analyzer (Krüss DSA100, Germany). Single drop of tested liquid (20 µL) was deposited on the film surface and contact angles were measured immediately. Contact angles for each sample were calculated as the average value of three measurements. From the measured values of contact angles of water, formamide and diiodomethane in contact with the surface of PUSN films, the surface free energies were calculated using the acid-base theory for solids according to the Oss-Chaudhury-Good approach [21], as described previously [22].

Water absorption (WA) of polymer films was investigated by sample immersion in phosphate buffered saline (PBS, pH 7.4) at 37 °C. The weight of immersed specimens was measured after 1, 2 and 3 days. Before weighing, the samples were blotted with filter paper to remove excess of water. The average value of three measurements for each sample was used. The weight percent of the water absorption was calculated as:

$$WA = \frac{w_w - w_{wo}}{w_{wo}} 100 \quad (1)$$

where, w_w is the weight of the immersed sample at each time point and w_{wo} is the initial dry sample weight.

The cross-sectional morphology was analyzed by field emission scanning electron microscopy (SEM) by using a JEOL JSM-6460LV instrument (Japan), at a working distance of *ca.* 14 mm and the accelerating voltage of 20 kV. Samples were cryo-fractured in liquid nitrogen and coated with a thin layer of gold prior to the measurements.

AFM images were obtained by the atomic force microscope AutoProbe CP-Research SPM (TM Microscopes-Veeco, USA). Veeco Phosphorus (n)-doped silicon contact metrology probes model MPP-31123-10 with the Al-reflective coating and symmetric tip were used. Measurements were performed under ambient conditions using the noncontact AFM mode at the scan size 20 × 20 µm², with the resolution of 256 × 256 data points per image.

3. RESULTS AND DISCUSSION

Steps in the reaction procedure used and possible interactions between HS and SS of PUSN with TiO₂ nanoparticles are presented in Figure 1. These interactions have influence on the obtained microphase separation of the prepared PUSNs.

3. 1. FTIR analysis

Chemical structure of the PUS and PUSNs was investigated by ATR-FTIR spectroscopy. In Figure 2, FTIR spectra of the prepared PUSNs with 2 and 5 wt.% of TiO₂ nanoparticles are presented. Moreover, spectra of the pure PUS copolymer and TiO₂ powder are also presented for comparison. In the FTIR spectrum of TiO₂, bands that are characteristic for stretching and bending vibrations of -OH groups are visible at 3230 and 1380 cm⁻¹, respectively, and stretching vibration of Ti-O band that is characteristic for anatase crystalline form (in the range from 400 to 880 cm⁻¹), can be observed.

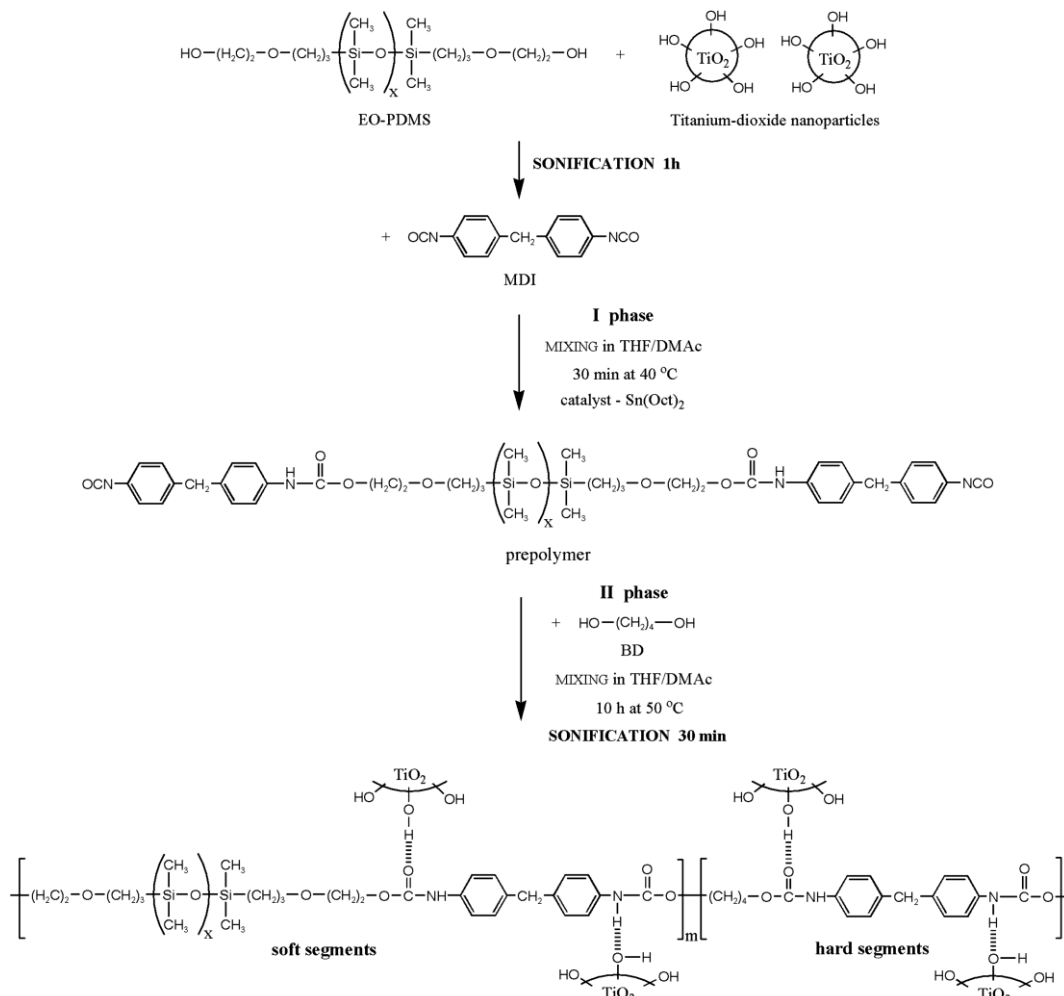


Figure 1. In situ polymerization and titanium-dioxide interaction with the poly(urethane-siloxane) matrix

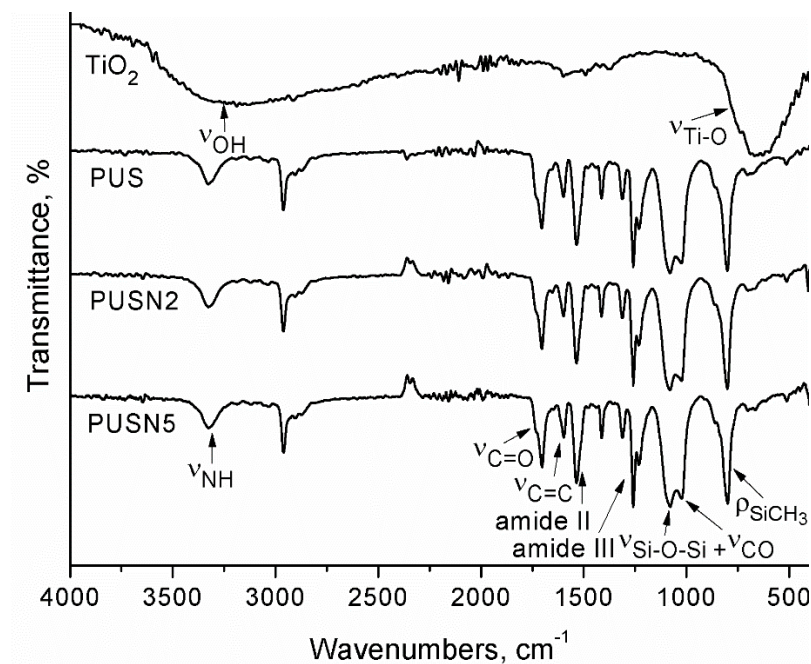


Figure 2. ATR-FTIR spectra of the TiO₂ nanoparticles, pure PUS copolymer and PUSNs with 2 and 5 wt.% of TiO₂ nanoparticles

Positions of characteristic bands in the spectrum of pure PUS and corresponding bands in PUSNs spectra differed negligibly. Bands characteristic for stretching vibrations of –NH groups (3330 cm^{-1}), stretching vibrations of the amide II and amide III groups (1535 cm^{-1} and 1260 cm^{-1} , respectively), stretching vibrations of the carbonyl absorption band (1705 cm^{-1}), overlapped bands of stretching vibrations of Si-O-Si and C-O groups (1020 cm^{-1} and 1080 cm^{-1} , respectively) symmetric and asymmetric stretching vibrations of –CH₂– and –CH₃ groups (2900 and 2960 cm^{-1} , respectively), aromatic bands (1410 and 1600 cm^{-1}) and rocking vibrations of the SiCH₃ groups (800 cm^{-1}) can be observed in the FTIR spectra of PUSNs. The absence of stretching vibrations of Ti-O bands in the FTIR spectra of PUSNs is due to small quantities of TiO₂ nanoparticles within the polymer matrix and overlapping of these bands with more intensive bands of the PUS matrix.

Presence of a shoulder in the C=O band indicates the presence of three different regions related to different types of hydrogen bonding. Carbonyl groups that are involved in hydrogen bonding are observed at 1704 cm^{-1} , carbonyl groups associated with hydrogen bonding in disorder (amorphous) domains are observed at 1714 cm^{-1} , whereas free carbonyl groups are observed at 1730 cm^{-1} [18].

Degree of the phase separation (DPS) (Table 1) in the PUS copolymer and the influence of added TiO₂ nanoparticles on the DPS in the prepared PUSNs were determined according to:

$$DPS = \frac{A_{1704} + A_{1714}}{A_{1704} + A_{1714} + A_{1730}} \quad (2)$$

where, A_{1704} , A_{1714} and A_{1730} are areas of deconvoluted FTIR maxima for the C=O band at the particular wavenumber.

Table 1. TiO₂ content, curve fitting results of the C=O regions from FTIR spectra, the degree of phase separation (DPS) and degree of hydrogen bonding (HI) determined using a deconvolution technique of the pure PUS copolymer and PUSNs

Sample	TiO ₂ content, wt. %	Area, %			DPS	HI
		C=O H-bonded at 1704 cm^{-1}	C=O Disorder at 1714 cm^{-1}	C=O Free at 1730 cm^{-1}		
PUS	0	65	10	25	75	1.9
PUSN1	1	66	14	20	80	1.9
PUSN2	2	67	13	20	80	2.0
PUSN3	3	69	12	19	81	2.2
PUSN5	5	70	12	18	82	2.3

The obtained DPS values for all examined samples are listed in Table 1. It can be observed that DPS values of PUSN samples are higher than DPS value of pure PUS and increase with the increase of TiO₂ content in PUSNs. Therefore, it can be concluded that incorporation of TiO₂ nanoparticles enhances the microphase separation of the PUS matrix.

Addition of TiO₂ resulted also in slightly higher intensities of –NH and H-bonded C=O bands and a slight shift of these bands towards lower wavenumbers, indicating additional hydrogen bonding between polymer chains and TiO₂ nanoparticles in prepared PUSNs. The degree of hydrogen bonding (HI) [23] was calculated by using the equation:

$$HI = \frac{A_{1704}}{A_{1730} + A_{1714}} \quad (3)$$

The obtained values of HI (Table 1) indicate that addition of TiO₂ nanoparticles increases the level of hydrogen bonding inside the polymer matrix. This additional hydrogen bonding may arise between urethane bonds within hard and soft segments and TiO₂ nanoparticles (Figure 1).

3. 2. DR/UV-Vis analysis

Diffuse-reflectance UV-Vis spectra of the samples are presented in Figure 3. The obtained spectra show that the PUSNs have a higher diffuse reflectance as compared to the pure PUS copolymer, due to the reflectance arising from TiO₂ nanoparticles. Among the prepared samples, PUSN3 and PUSN5 that contain the highest TiO₂ contents, exhibit similar and the highest UV light reflection. The same results were obtained by Silva *et al.* [15].

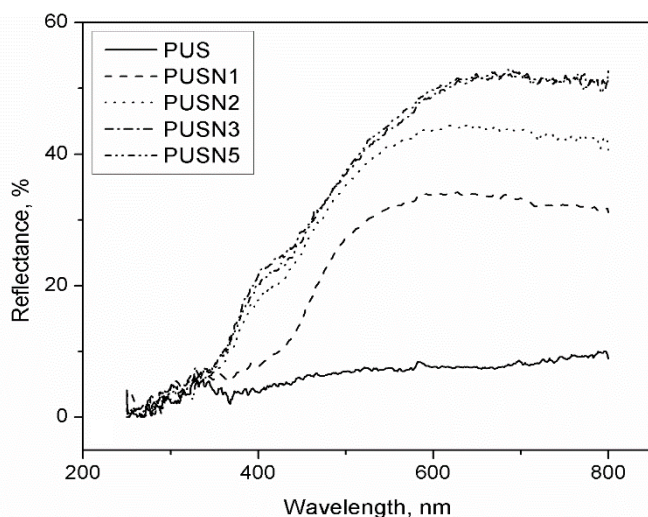


Figure 3. UV-Vis diffuse-reflectance spectra of the prepared pure PUS and PUSNs

3. 3. DSC analysis

Thermal properties of the prepared pure PUS and PUSNs were investigated by DSC measurements (Table 2). DSC curves during the second heating run and cooling run are presented in Figure 4. It can be observed that prepared PUS and PUSNs exhibit the glass transition temperature (T_{gHS}), melting temperature (T_{mHS}) and the crystallization temperature (T_{cHS}) of the hard segments. The enthalpy of melting (ΔH_m), the total degree of crystallinity (X_c) and degree of crystallinity of hard segments (X_c^{HS}) for the pure PUS copolymer and PUSNs were also determined (Table 2).

In DSC thermograms, the T_{gHS} values of the prepared PUSNs were observed in the range from 52.5 to 57.4 °C, while T_{gHS} of the pure PUS was 50.2 °C. The obtained T_{gHS} values are lower than the T_g value of high molecular weight HS ($T_{gMDI-BD} = 110$ °C), because of the obtained short length of the HS (degree of polymerization of the HS is 1.4, determined by quantitative ^{13}C NMR spectroscopy) [18,19]. T_{gHS} values of prepared PUSNs are higher than that of the pure PUS copolymer, due to reduction of polyurethane HS chains mobility after incorporation of TiO_2 nanoparticles. The obtained increase in T_{gHS} values is most pronounced for samples PUSN1 and PUSN2.

Table 2. Glass transition (T_{gHS}), melting (T_{mHS}) and crystallization temperatures (T_{cHS}) and the enthalpy of melting (ΔH_m), total degree of crystallinity (X_c) and degree of crystallinity of hard segments (X_c^{HS}), determined by the DSC analysis of the pure PUS copolymer and PUSNs:

Sample	T_{gHS} / °C	T_{mHS} / °C	T_{cHS} / °C	ΔH_m / J g ⁻¹	X_c / % ^a	X_c^{HS} / % ^b
PUS	50.2	163.4	135.5	4.4	4.8	22.1
PUSN1	57.3	171.6	140.6	3.8	4.2	19.1
PUSN2	57.4	171.9	143.5	2.3	2.5	11.6
PUSN3	52.5	171.2	142.8	3.0	3.3	15.1
PUSN5	53.9	172.0	147.4	2.4	2.6	12.0

^a $X_c = \Delta H_m / \Delta H_m^0$; where $\Delta H_m^0 = 91.2$ J g⁻¹ is the enthalpy of melting for perfectly crystalline MDI-BD homopolymer

^b $X_c^{HS} = X_c / w_{HS}$; where $w_{HS} = 21.8$ wt.% is the weight fraction of the HS determined by 1H NMR spectroscopy [19]

Prepared PUS and PUSNs showed a wide endothermic peak in the range from 163.4 to 172.0 °C, which is associated with the melting temperature of the short HS [18] (Figure 4a). The values of T_{mHS} slightly increased with increasing the content of TiO_2 nanoparticles, indicating that TiO_2 addition causes slightly better ordering of hard segments. Values of ΔH_m , X_c and X_c^{HS} for the pure PUS copolymer were 4.4 J g⁻¹, 4.8 % and 22.1 %, respectively. Values of ΔH_m for the prepared PUSNs were in the range from 2.3 to 3.8 J g⁻¹, lower than the values determined for the pure PUS. Values of X_c and X_c^{HS} for the prepared PUSNs were in the range from 2.5 % to 4.2 % and 11.6 % to 19.1 %, respectively. In both cases, it was shown that addition of TiO_2 nanoparticles caused a reduction in the total crystallinity of the PUSNs and crystallinity of the HS, indicating interactions between TiO_2 and HS.

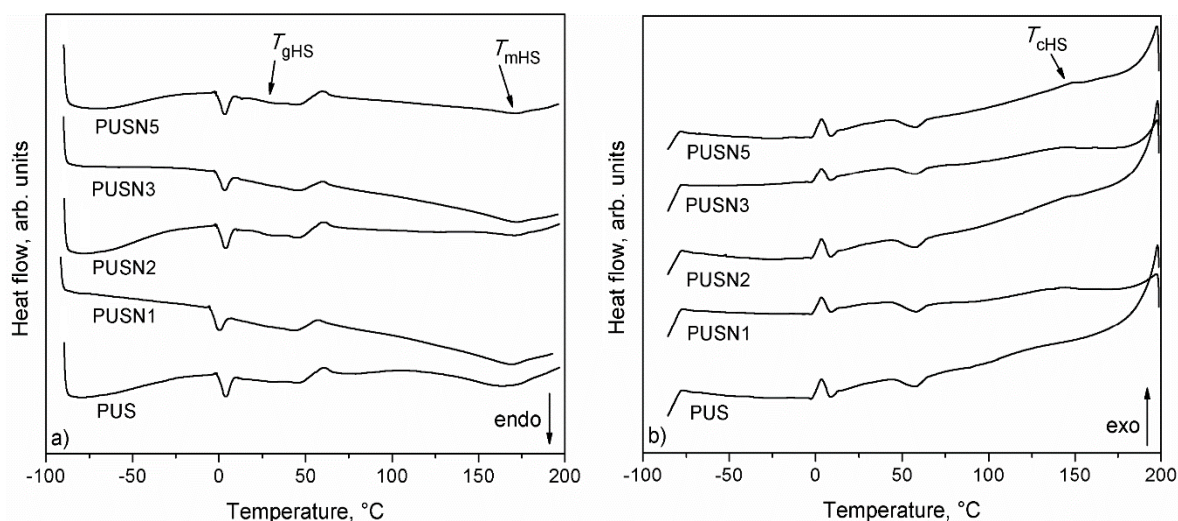


Figure 4. DSC thermograms recorded during a) the second heating and b) the cooling run, of the pure PUS copolymer and PUSNs

Values of T_{CHS} of the prepared PUS and PUSNs were in the range from 135.5 to 147.4 °C, and they generally increased with increasing the nanoparticle content in PUSNs. According to the obtained results, it can be concluded that differences in T_{gHS} , T_{mHS} , T_{CHS} values between those of the pure PUS and the prepared PUSNs, originate from interactions between incorporated TiO_2 nanoparticles and hard segments. In Figures 4a and 4b one endothermic and one exothermic peak, respectively, are visible all around 3 and 4 °C in all samples that arise from relaxation of the mixed phase of HS/SS [24,25].

3. 4. TGA analysis

TGA and DTG curves of the pure PUS and PUSN samples are presented in Figure 5 and data are summarized in Table 3. The results show that thermal degradation, *i.e.* $T_{5\%}$ values, of the prepared PUSNs started between 294 and 305 °C in comparison to the pure PUS copolymer that started to degrade at 281 °C. Values of the temperature of 50 % weight loss, $T_{50\%}$, of the prepared PUSNs ranged between 427 and 448 °C in comparison to the value of 327 °C determined for the pure PUS copolymer. According to the obtained results, it can be concluded that thermal stability of the prepared PUSNs was significantly improved with addition of TiO_2 nanoparticles. Moreover, TGA curves show that thermal stability of PUSN1 sample is better than that of the other PUSN samples in temperature ranges up to $T_{50\%}$ values. On the other side, PUSN5 sample has shown the best thermal stability above $T_{50\%}$ values that is due to the larger amount of TiO_2 . A similar observation that TiO_2 nanoparticles enhance heat resistance of epoxy resin/polyurethane composites was reported in literature [26].

Furthermore, due to the large specific surface area of TiO_2 , the contact area between nanoparticles and the polymer matrix is significant. The best dispersion of TiO_2 nanoparticles was achieved in the sample containing the smallest TiO_2 content (1 wt.%) and the obtained Nano effect led to the improvement of thermal stability of PUSNs as also reported in literature [26]. The increase in the content of incorporated TiO_2 nanoparticles leads to increased aggregation due to higher nanoparticle interaction forces, resulting in poorer dispersion within the polymer matrix.

Table 3. Thermogravimetric analysis (values of temperature of 5, 10, 50 and 85 % weight loss, $T_{5\%}$, $T_{10\%}$, $T_{50\%}$, $T_{85\%}$, respectively, degradation maxima temperatures and residual weights at 700 °C), of the pure PUS copolymer and PUSNs:

Sample	$T_{5\%}/^{\circ}\text{C}$	$T_{10\%}/^{\circ}\text{C}$	$T_{50\%}/^{\circ}\text{C}$	$T_{85\%}/^{\circ}\text{C}$	$T_{\text{max}}(\text{DTG})/^{\circ}\text{C}$	Residual weight at 700 °C, %
PUS	281	293	327	478	310/338/530	2.7
PUSN1	305	317	441	499	316/360/459	8.7
PUSN2	296	309	442	503	313/360/461	7.4
PUSN3	298	309	427	499	312/362/464	5.7
PUSN5	294	314	448	>700	318/363/462	15.3

Thermal degradation of the prepared pure PUS and PUSNs is carried out as a three-step process. In the first degradation step, in the range from 310 to 318 °C, urethane bonds in the HS begin to break up. In the second degradation step in the temperature range from 338 to 363 °C EO-PDMS segments are decomposed. The last degradation step in the temperature range from 459 to 530 °C comprises decomposition of aromatic rings. The residual weight at 700 °C, of the pure PUS was 2.7 %, while residual weights of the prepared PUSNs were in the range from 5.7 to 15.3 %. It can

be observed that the experimentally obtained values of residual weights are higher than the theoretically determined. The residual weight of the pure PUS and PUSNs mainly originated from the MDI-BD fraction [19]. The highest residual weight determined for the PUSN5 sample is a result of the highest content of TiO₂ nanoparticles, which contribute to the residual component of thermal degradation of PUSNs [27,28].

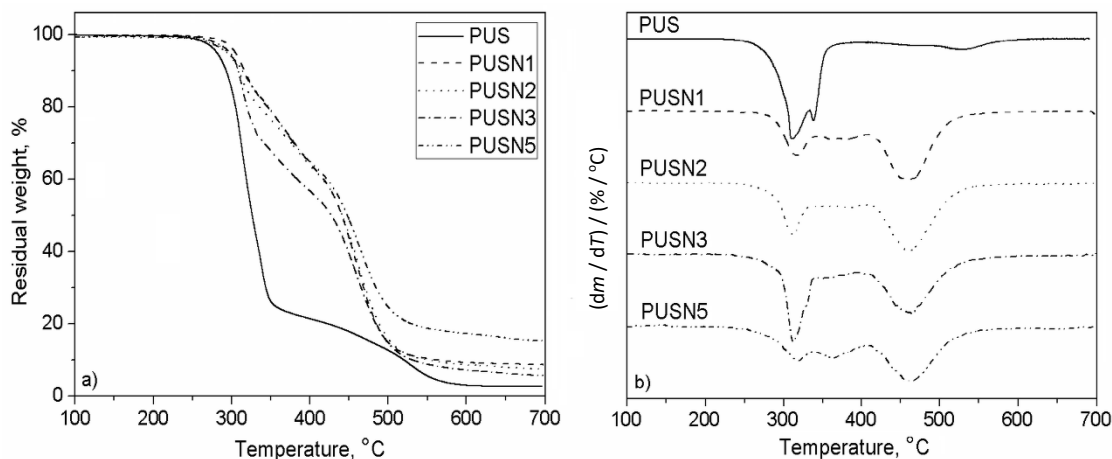


Figure 5. Thermal stability study of the pure PUS copolymer and PUSNs: a) TGA and b) DTG curves

3. 5. Contact angles, water absorption and surface free energies

Wettability and hydrophobicity of the pure PUS and PUSNs were investigated by contact angle measurements using different liquids, as well as by water absorption analysis and by determination of the surface free energies. Table 4 presents summarized values of the water contact angle (WCA), formamide contact angle (FCA), diiodomethane contact angle (ICA), water absorption values after 1, 2 and 3 days and determined surface free energy, γ_s , for the pure PUS and PUSNs.

Table 4. Static contact angles with water (WCA), formamide (FCA) and diiodomethane (ICA), values of the surface free energy, γ_s , water absorption results and root-mean-square roughness coefficient (R_q) values of the pure PUS copolymer and PUSNs

Sample	WCA, ° ^a	FCA, ° ^a	ICA, ° ^a	γ_s / mJ m ⁻² ^b	Water absorption, %			R_q / nm ^c
					1 day	2 days	3 days	
PUS	94.4±1.4	84.4±1.5	73.2±2.2	23.86	1.02	1.22	1.23	3.3
PUSN1	101.6±1.7	89.8±2.1	84.5±2.3	19.61	0.76	0.83	0.84	13.3
PUSN2	108.7±0.6	100.3±0.8	87.6±1.7	16.81	0.48	0.51	0.51	27.7
PUSN3	104.9±0.8	95.1±0.4	87.1±1.2	15.14	0.44	0.58	0.56	21.3
PUSN5	104.0±1.0	90.7±1.2	82.5±1.5	18.47	0.65	0.79	0.78	10.3

a - values are expressed as a mean ± standard error; b - determined by the van Oss-Chaudhury-Good method; c - values obtained from AFM studies

All prepared PUSNs show higher WCA, FCA and ICA values as compared to the pure PUS copolymer, indicating higher hydrophobicity and non-wettability by the investigated liquids. Among prepared samples, PUSN2 has shown the highest contact angle values, indicating the highest hydrophobicity and non-wettability. According to the AFM analysis (Section 3. 7.), the best dispersion of TiO₂ nanoparticles at the nanocomposite surface was obtained for the sample PUSN2, which is probably the reason for its highest hydrophobicity and non-wettability.

Li *et al.* [29] measured WCA values of 142.5 and 152.3 ° for a pure polyurethane/PDMS film and for the film with added TiO₂ nanoparticles, respectively. Superhydrophobic PDMS-TiO₂ coated polyurethanes sponge were prepared by sol-gel growth of TiO₂ nanoparticles on the surface of a PU sponge by *in situ* polymerization of PDMS [30]. These materials reached a WCA value of 154° due to the rough surface and hydrophobic groups constructed by TiO₂ particles and PDMS, while the WCA value for the pure PU-PDMS sponge without TiO₂ was 140°.

Prepared PUSNs exhibited lower surface free energy values, γ_s , in the range from 15.14 to 19.61 mJ m⁻², than that of the pure PUS copolymer amounting to 23.86 mJ m⁻². The γ_s values generally become lower as the TiO₂ nanoparticle content in the prepared PUSNs increased, indicating enhancement of hydrophobic properties.

Water resistance of the prepared PUSNs was confirmed by water absorption values in the range from 0.51 to 0.83 % (after 2 days), indicating again the hydrophobic nature of the surface of nanocomposites. Water absorption slightly increased over time and maximal water uptake values were obtained after 2 days of immersion. Among prepared samples, PUSN2 has shown the lowest water absorption and the highest hydrophobicity, which is in accordance with the highest WCA value obtained for this sample.

3. 6. SEM analysis

Scanning electron microscopy was used to investigate morphology of cross-sections of the pure PUS and PUSN samples (Figure 6). The micrographs clearly show a difference in the morphology of PUSNs in comparison to the pure PUS copolymer. Surface of the pure PUS copolymer is smooth and uniform, without any relief structures, while it becomes rougher and more irregular with increasing the TiO₂ nanoparticle content within the prepared PUSNs. In addition, the cross-section micrographs reveal homogeneous dispersion of TiO₂ nanoparticles within the poly(urethane-siloxane) structure. Addition of TiO₂ nanoparticles led to a more pronounced difference between brighter and darker domains (that represent hard and soft segments, respectively), which indicates the increase in the phase separation in PUSNs. The obtained results are in accordance with the results obtained by the FTIR analysis.

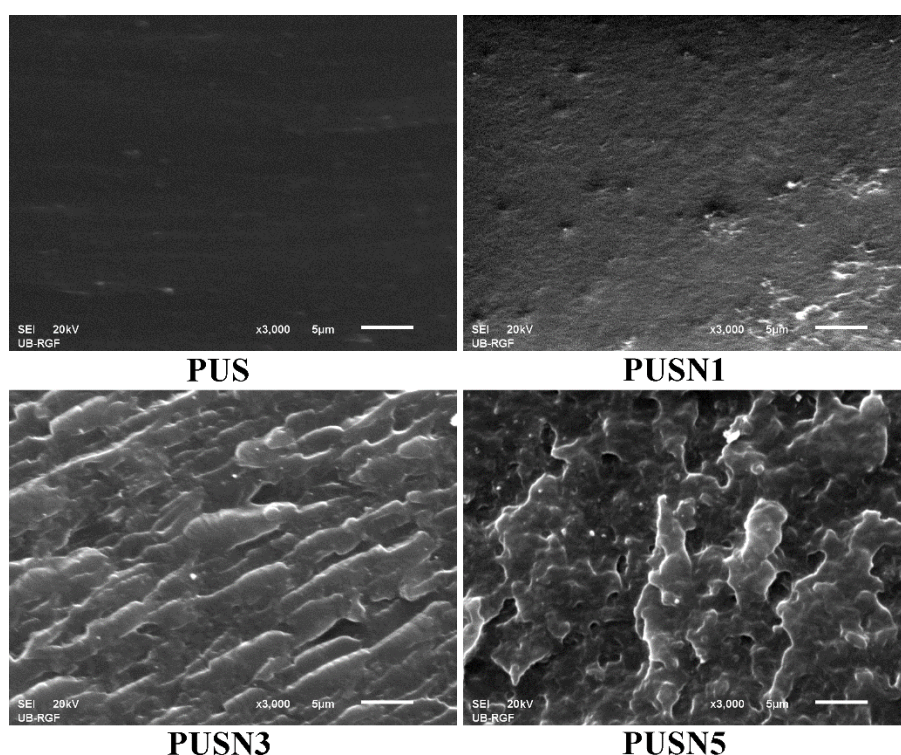


Figure 6. SEM micrographs of cross-sections of the pure PUS copolymer and PUSNs with 1, 3 and 5 wt. % of the TiO₂ nanoparticles (PUSN1, PUSN3 and PUSN5, respectively; scale bar = 5 μm)

3. 7. AFM analysis

Surface morphology of the pure PUS copolymer and PUSNs was studied by AFM. 2D phase and 3D AFM images of the prepared PUS and PUSNs (scan area 20 × 20 μm²) are presented in Figure 7. According to the literature data, brighter regions represent HS domains, while darker regions represent SS domains [31].

As compared to the pure PUS copolymer, the surface morphology of PUSNs is significantly changed and became rougher after incorporation of TiO₂ nanoparticles. A high uniformity of nanoparticles dispersion could be observed. The root-mean-square roughness coefficient (R_q) varied between PUSN samples having different TiO₂ contents (Table 4). The R_q values for prepared PUSNs are in the range from 10.3 to 27.7 nm, with the highest value obtained for the PUSN2 sample. The increased surface roughness of this sample could be the reason for the highest hydrophobicity and non-wettability as suggested in literature [28,30]. Moreover, prepared PUSNs exhibit much higher R_q values than that of the pure PUS copolymer (3.3 nm). Decreased roughness of the PUSN5 sample can be explained by the tendency of TiO₂ nanoparticles to aggregate due to the higher content of TiO₂ in this sample.

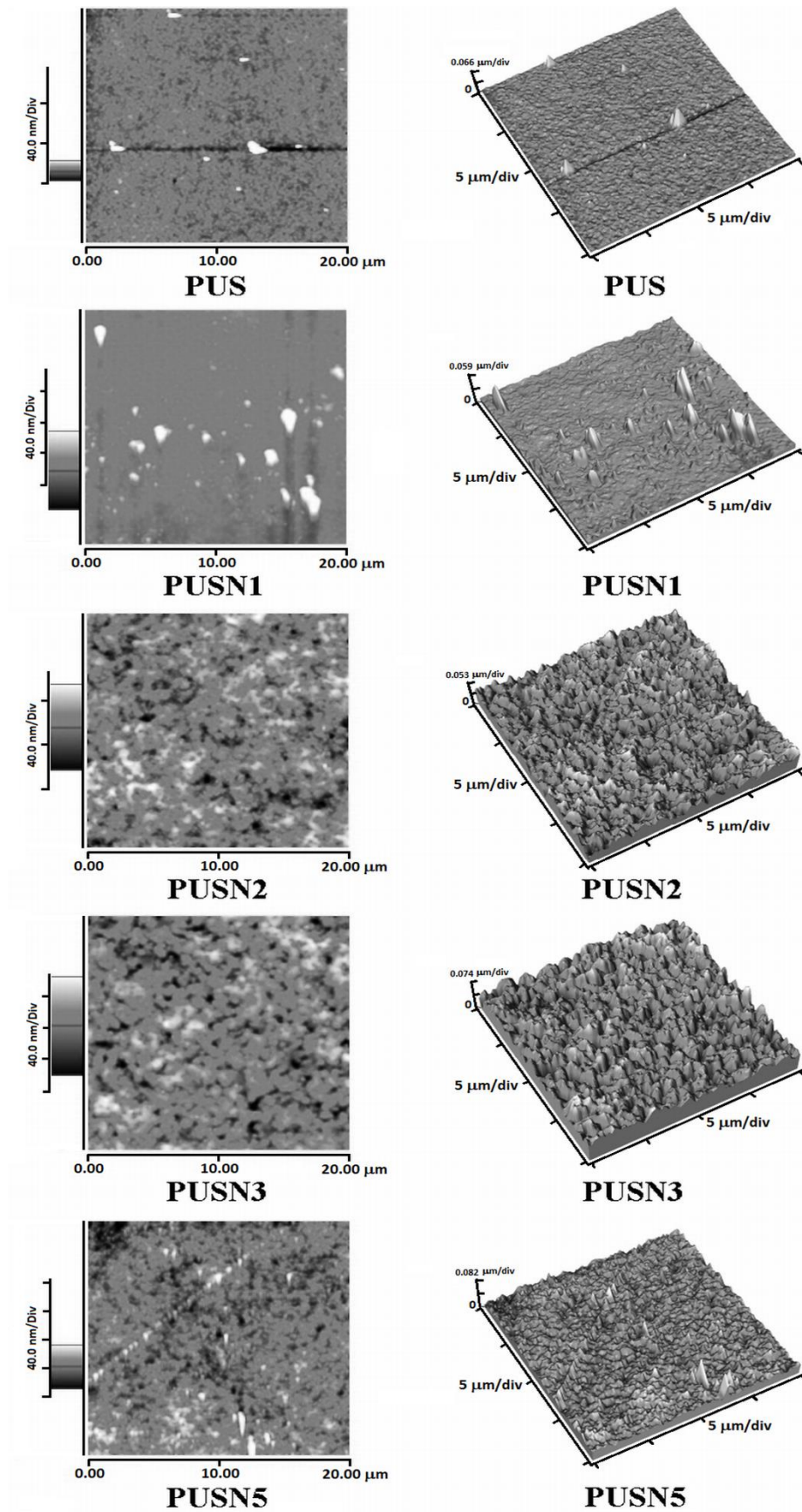


Figure 7. 2D phase and 3D AFM images of the pure PUS copolymer and PUSNs, scan area $20 \times 20 \mu\text{m}^2$

4. CONCLUSIONS

In this work, a series of novel PUSNs with different percentages of TiO₂ nanoparticles were prepared by *in situ* polymerization. Additional hydrogen bonding in the prepared PUSNs was found between urethane bonds within hard and soft segments and TiO₂ nanoparticles. The increase in the TiO₂ content led to higher UV light reflection. DSC analysis revealed that glass transition, melting and crystallization temperatures are higher, while enthalpies of melting and degrees of crystallinity are lower for the PUSNs than those determined for the pure PUS copolymer. The results also show that incorporation of TiO₂ nanoparticles led to a significant increase in thermal stability of the prepared PUSNs relative to the pure PUS copolymer.

Introduction of TiO₂ nanoparticles also led to a noticeable increase in hydrophobicity, non-wettability and reduced surface free energy of the PUSNs. Moreover, homogenous TiO₂ dispersion on the surface as well as within the polymer matrix, resulted in rougher surface and cross-sectional relief structure of the prepared PUSNs. Therefore, the PUSNs with different TiO₂ nanoparticle contents (especially with 1 and 2 wt.%), exhibited significant improvements of investigated features and potentially can be applied as waterproof and UV protective coatings.

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SAŽETAK

Priprema i karakterizacija poli(uretana-siloksana)/titan-dioksida nanokompozita

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Ovaj rad je fokusiran na pripremu poli(uretana-siloksana)/titan-dioksida nanokompozita (PUSN) sa poboljšanim svojstvima. PUSN nanokompoziti su bili pripremani postupkom *in situ* polimerizacije koristeći titan-dioksid kao nanopunilac u različitim količinama (1, 2, 3 i 5 mas.%) u odnosu na poli(uretana-siloksansku) (PUS) matricu. PUS kopolimer je bio na bazi α,ω -dihidroksi-etoksi-propil-poli(dimetilsiloksana), 4,4'-metilendifenildiizocijanata i 1,4-butandiola. Sa ciljem da se ispita uticaj sadržaja TiO₂ na strukturu, UV otpornost, termička svojstva, hidrofobnost i morfologiju dobijenih PUSN nanokompozita, primenjene su sledeće tehnike: FTIR spektroskopija, UV-Vis difuzna-refleksna spektroskopija, diferencijalna skenirajuća kalorimetrija (DSC), termogravimetrijska analiza (TGA), merenje kontaktnih uglova, određivanje slobodne površinske energije (SFE), određivanje apsorpcije vode, skenirajuća elektronska mikroskopija (SEM) i mikroskopija atomskih sila (AFM). Dobijeni PUSN uzorci su pokazali izuzetnu otpornost na UV zračenje, visoku hidrofobnost, nisku slobodnu površinsku energiju i takođe poboljšanu termičku stabilnost i hrapaviju površinsku i unutrašnju reljefnu strukturu u odnosu na čist PUS kopolimer. Na osnovu dobijenih rezultata zaključeno je da se dobijeni PUSN nanokompoziti mogu potencijalno koristiti kao zaštitni premazi.

Ključne reči: poliuretani, poli(dimetilsiloksani), titan-dioksid, nanokompoziti, termička svojstva, morfologija