DOI 10.7251/ZRPIM2001002P

ORIGINAL SCIENTIFIC PAPER – ORIGINALAN NAUČNI RAD

NOVEL POLYCARBONATE-BASED POLYURETHANE NANOCOMPOSITES: SYNTESIS AND CHARACTERIZATION

Jelena Pavličević[1], Milena Špírková[2], Ayse Aroguz[3], Dejan Kojić[4], Katalin Mészáros Szécsényi[5], Jaroslava Budinski-Simendić[1]

[1]University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, 21 000 Novi Sad, Serbia, jelenapavlicevic@gmail.com
[2]Institute of Macromolecular Chemistry AS CR v.v.i., Heyrovského nám. 2, 162 06 Prague, Czech Republic
[3]Istanbul University, Engineering Faculty, İstanbul Ünv. Avcılar Kampüsü No:2, 34320 Avcılar, Istanbul, Turkey
[4]University PIM, Technical Faculty, despota Stefana Lazarevića bb, 78 000 Banja Luka, Bosnia and Herzegovina
[5]University of Novi Sad, Faculty of natural sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

ABSTRACT

All aliphatic starting reactants were used to prepare two series of polycarbonate-based polyurethane (PC-PU) composite films: 1) with a low amount of titanium dioxide nanoparticles (0.5, 1.0 and 2.0 wt%) by one-step technique and 2) PC-PU hybrid materials by addition of submicron amorphous SiO_2 Sidistar T120 particles (0, 1, 2, 5 and 10 wt%) using prepolymerization method. The study of the influence of different filler distribution on the structure of obtained elastomers composites was performed using FT-IR and AFM. TGA analysis was carried out to investigate the effect of inorganic fillers on thermal stability and degradation of synthesized PC-PU materials. The impact of silica and titania on the glass transition temperature and melting of obtained polyurethane systems was studied by DSC and MDSC. Based on obtained results, the synthesized polyurethane materials showed improved thermal stability and enhanced thermal properties.

Keywords: polycarbonate, polyurethane, nanocomposites, synthesis, characterisation.

INTRODACTION

Modern research in the polymers fields significantly pays attention to study of novel thermoplastic segmented polycarbonate-based polyurethanes (PUs) that are characterized by good biostability, biocompatibility, melt-processability and rubber like behavior at the service temperature (Zhu et al., 2016; Poręba et al., 2015; Špírková et al., 2015; Špírková et al., 2011; Kim et al., 2014). These materials, due to their phase separated structure can find various application in medicine as well as coatings, building materials, etc (Ding et al., 2020; Touchet, & Cosgriff-Hernandez, 2016; Serkis et al., 2016; Kim et al., 2020; Mi et al., 2014; Asensio et al., 2019). The hard segments behave as physical crosslinkers and they are responsible for good mechanical properties. They originate from diisocyanates and are linked by a short chain extender (Pavličević et al., 2018; Špírková et al., 2020). The soft segments enable the flexibility of thermoplastic polyurethanes and they are made from macrodiol component with low glass transition temperature (Kultys, Rogulska, & Głuchowska, 2011).

An adequate selection of starting components (all aliphatic: macrodiol, diisocyanate and a chain extender), the choice of polyurethanes preparation procedure, as well as filler type is very significant for designing the elastomeric materials with desired end-used properties.

In the recent years, many researches were focused on the use of silica (SiO_2) as potential nanofiller, in order to the heat resistance, mechanical, thermal and electrical characteristics of the polyurethane materials (Seyfi et al., 2015; Zhang et al., 2011; Saha et al., 2020). The homogenous distribution of silica nanofillers into polyurethane matrix enables hydrogen bonding increase and higher phase separation.

From environmentally point of view, non-toxic titanium dioxide (TiO_2) nanoparticles are, also, one of the most promising inorganic fillers with a great potential of improvement of various polyurethanes properties such as electrical, thermal, optical and mechanical (Stefanović et al., 2019; Dahl, Liu, & Yin, 2014; Chen, Wang, & Jiao,2018; Charpentier et al., 2012).

The aim of this research is to study the influence of preparation procedure as well as the filler choice (SiO_2 and TiO_2) and content on the structure, morphology, phase separation degree, thermal stability and degradation, and thermal properties of prepared PU-SiO_2 and PU-TiO_2 elastomeric hybrids.

EXPERIMENTAL PART

Two soft segments, PCDL T5651 and T4671, deriving from the aliphatic polycarbonate diol with molecular mass of about 1000 g/mol), are kindly provided by Asahi Kasei Chemical Corporation. The detailed specification of chosen diols (Špirkova et al., 2011). The diisocyanate component (1,6- diisocyanatohexane), the chain extender (1,4-butanediol) and the catalyst (dibutyltin dilaurate) were supplied by Fluka Chemical Corporation. One of the used nanofiller, hydrophilic fumed titanium (IV) oxide nanoparticles (Aeroxide TiO_2 PF2) from Evonik Industries, Germany, was used (average nominal diameter of 20 nm and specific surface area in the range of 45–70 m^2/g). Second used filler was silica submicron (spherical and amorphous) Sidistar T120 particles, obtained from Elkem, with average particle size of 140 nm and surface are of 25 m^2/g.

Preparation of PU-TiO_2 and PU-SiO_2 polyurethane hybrids

A series of segmented aliphatic hybrid materials was prepared by addition of different nanosilica and using during prepolymerization procedure. Throughout the synthesis, hexamethylene-diisocyanate was in a slight excess (NCO to total OH group ratio was 1.05), while the hydrogen group ratio, *R*, attributed to the ratio of OH groups of macrodiol and the chain extender was kept fixed ($R = 1$). In the first step of prepolymerization, SiO_2 nanoparticles (0, 1, 2, 5 and 10 wt. %) were added to the polycarbonate diol T5651 previously dissolved in tetrahydrofuran solvent (THF), and briefly stirred at the ambient temperature, using the magnetic stirrer for 72 h, and additionally, in the ultrasonic bath for 2 h, in order to obtain the homogeneous distribution of SiO2 in macrodiol. Then, the catalyst solution (0.05 wt. %) and hexamethylene-diisocyanate (drop by drop) were added and the reactive mixture was stirred for 24 h. In the second stage, a short chain component (1,4-butane diol) was put as the last constituent, and mixed, during 15 min, with previously obtained reaction mixture. The solvent removal and the reaction of chain extender with previously prepared pre-polymer lasted 24 h at room temperature in the inert atmosphere

PU-TiO_2 polyurethane hybrids were synthesized by one step preparation procedure. The appropriate mass of the starting components was calculated on the basis of equal ratio of hydrogen-donor groups from the chain extender and macrodiol, respectively. The hexamethylene-diisocyanate was added in a small excess ($NCO/OH_{total} = 1.05$). Primary, TiO_2 nanoparticles in different mass fraction (0.0, 0.5, 1.0 and 2.0 %) were dispersed in the polycarbonate diol T5671, using magnetic stirrer for 2 h, and additionally in ultrasonic bath for 20 minutes. Then, the chain extender was added to the mixture.

The final mixture for both series of polyurethane nanocomposite samples was spread on the polypropylene sheet using a ruler with a slot-width of 300 μm, and left in the oven for 24 h at 90 °C in order to obtain polyurethane films. Obtained samples were all transparent, containing 30±3.9 wt. % of hard segments. The codes of synthesized polyurethane hybrids contain the type of used filler as well as its content (e.g., sample with 1 wt% of silica is marked as PU-SiO_2-1).

Fourier transform infrared spectroscopy (FT-IR)

The structure study of PU-TiO_2 and PU-SiO_2 polyurethane hybrids as well as investigation of the influence of different nanooxides on the hydrogen bonding was performed by The Fourier transform infrared spectroscopy (Thermo Nicolet Nexus 670 FTIR-ATR). FT-IR spectra of the prepared nanocomposites were scanned after averaging 40 scans in a transmittance mode, in the wavenumber range between 4000 and 500 cm^{-1}.

Atomic Force Microscopy (AFM)

Commercial atomic force microscope (Dimension Icon, Bruker), equipped with the SSS-NCL probe Super Sharp SiliconTM-SMP-Sensor (NanosensorsTMSwitzerland); spring constant 35 Nm^{-1}, resonant frequency ≈ 170 kHz) was applied for the investigation of the microphase-separated structure and topography of PU-SiO_2 and PU-TiO_2 hybrids. The measurements of pure PU and nanocomposite surfaces were performed at room temperature, in the tapping mode AFM technique. The surface size of obtained square scans was in the range from 1 to 2500 μm^2.

Thermogravimetric analysis (TGA)

The study of effect of SiO_2 and TiO_2 nanoparticles on the thermal stability and decomposition of synthesized polyurethane nanocomposites was carried out by means of Q50 TGA, TA Instruments'. The measurements were performed under nitrogen atmosphere with a flowing rate of 50 cm^3/min, from ambient temperature to 800 °C, at the heating rate of 10 °C/min. The sample masses were about 3.0 mg.

Modulated Differential Scanning Calorimetry (MDSC)

The investigation of effect of TiO_2 and SiO_2 on the thermal characteristics of obtained hybrids was done using modulated differential scanning calorimeter (MDSC Q1000 TA Instruments). The sample masses were about 3 mg. The experiments were carried out under nitrogen atmosphere, between –80 ºC and 180 ºC, with a heating rate of 10 ºC/min.

RESULTS AND DISCUSION

Material structure analysis

The influence of SiO_2 and TiO_2 nanoparticles on the structure and hydrogen bonding formation was investigated by means of attenuated total reflection Fourier transform infrared spectroscopy. The addition of nanooxide particles did not have influence on the formation of urethane groups since no unreacted isocyanate and alcohol absorption peaks were detected in all FTIR spectra. As an example of obtained FTIR spectra for both series, Figure 1 shows the characteristic bands of free and hydrogen-bonded carbonyl and amine groups depending on SiO_2 content, with 1-4 wavenumber regions, interesting for detailed study.

The absorption region 1, observed between 3322 and 3369 cm^{-1}, is related to urethane groups and its intensity increased with the presence of low silica content. Achieved good nanoparticles distribution enabled additional hydrogen bonding formation. On the other hand, the intensity of peak 1 for elastomers with higher silica loading (PU-SiO_2-5 and PU-SiO_2-10) compared to the analogous pure (PU-SiO_2-0), due to poor SiO_2 dispersion that caused no additional hydrogen bonding and phase separation decrease. The absorbance area 2, detected between 2927 and 2941 cm^{-1}, and from 2857 to 2869 cm^{-1}, is related to -CH_2 asymmetrical and symmetrical stretching of polycarbonate macrodiol. The absorbance area 3, detected from 1600 and 1850 cm^{-1}, corresponds to the carbonyl groups. The absorption peak 4, registered at 1245 cm^{-1}, origins from C-O-C asymmetrical stretching of polycarbonate diol. Its surface area enhanced with low silica loading. On the other hand, agglomerates, present in PU-SiO_2-5 and PU-SiO_2-10 decreased fillers distribution. The similar trend related to the influence of low TiO2 content on the structure and hydrogen bonding formation is found, based on FTIR spectra of PU-TiO_2 samples: a good filler distribution enabled additional hydrogen bonding formation and the phase separation degree increment and achievement of interaction between the soft phase and homogeneously dispersed nanoparticles.

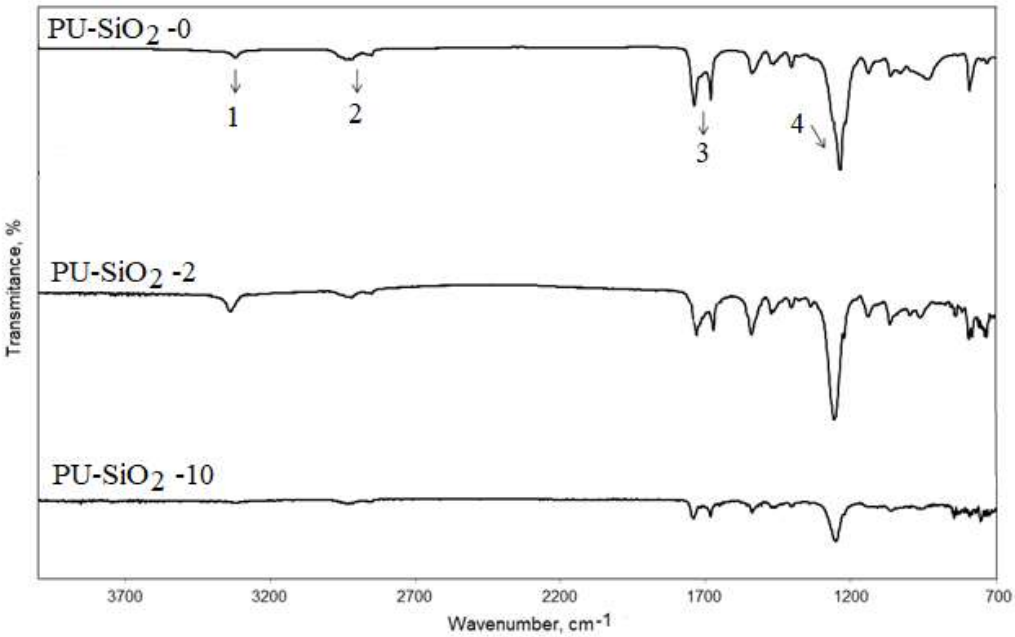

Fig. 1. FTIR spectra of PU-SiO_2 hybrids with different silica loading (0, 2 and 10 wt%).

The study of SiO_2 and TiO_2 impact on phase separation degree (*PSD)* values was performed by investigating the carbonyl group in detail, applying deconvolution of that absorbance region of obtained polyurethane hybrids, using Gaussian transformation (Fig.2). Fig. 2a shows deconvoluted carbonyl absorbance group for the sample PU-SiO_2-1, containing of four peak areas, observed at 1662, 1684, 1714 and 1741 cm^{-1}. Fig. 2b presents four deconvoluted carbonyl carbonyl peak areas for the sample PU-TiO_2-1, with peak registered at 1655, 1682, 1715 cm^{-1} and 1742 cm^{-1}. The peak areas marked with 1-3 in carbonyl region belong hydrogen bonded carbonyl groups (in soft segments, in ordered hard segments and in the amorphous region, respectively). The deconvoluted C=O peak area 4, with the maximum at 1742 cm^{-1}, is ascribed to the free carbonyl group of the aliphatic carbonate.

Determining the surface of each registered absorbance band in the wavenumber region from 1600 to 1850 cm^{-1}, it is possible to calculate the degree of phase separation, using the following equation 1 (Pavličević, et al., 2014):

$$PSD,\ \% = \frac{A_1 + A_2 + A_3}{A_1 + A_2 + A_3 + A} \cdot 100 \qquad (1)$$

In case of PU-SiO_2 samples, the uniform distribution of SiO_2 fillers, achieved for the samples with low silica content (PU-SiO_2-1 and PU-SiO_2-2) caused the increase of phase separation degree in regard to analogous *PSD* of unfilled elastomer (from 80.5 % for PU-SiO_2-0 to 83.1 % and 85.4 % for PU-SiO_2-1 and PU-SiO_2-2, respectively). The agglomerates existence in the structure of PU-SiO_2-10 remarkably decreased *PSD* value, by 10 %.

In case of PU-TiO_2 samples, the positive effect of nanofiller addition on *PSD* values was noticed. Namely, the addition of titania fillers increased *PSD* values of pure sample (72.4 % for PU-TiO_2-0) to 83.5% for the elastomer filled with 2 % of TiO_2 (PU-TiO_2-0). The obtained results confirmed the absence of TiO_2 agglomerates in the structure of PU-TiO_2 nanocomposites.

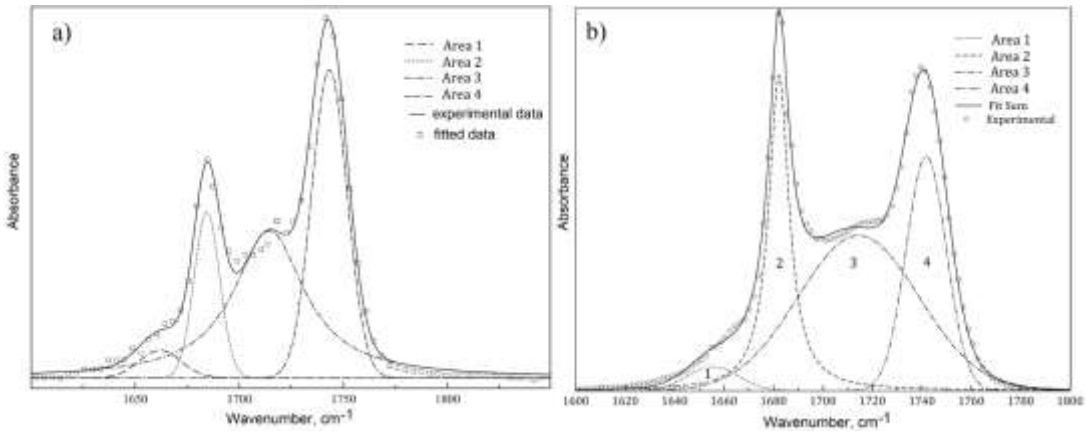

Fig.2 Deconvoluted FT-IR spectra of the carbonyl group absorbance region for polyurethane nanocomposite: a) containing 1 wt. % SiO_2 and b) containing 1 % of TiO_2.

The influence of nanosilica on the heterogeneity and surface topography of aliphatic polyurethane hybrid materials

The information on used fillers and their content on the surface topography were obtained by study of AFM phase images of obtained PU-SiO_2 and PU-TiO_2 hybrids (Fig. 3). The soft domains were anticipated to give dark contrast in the phase imaging, whereas bright areas present the hard segments.

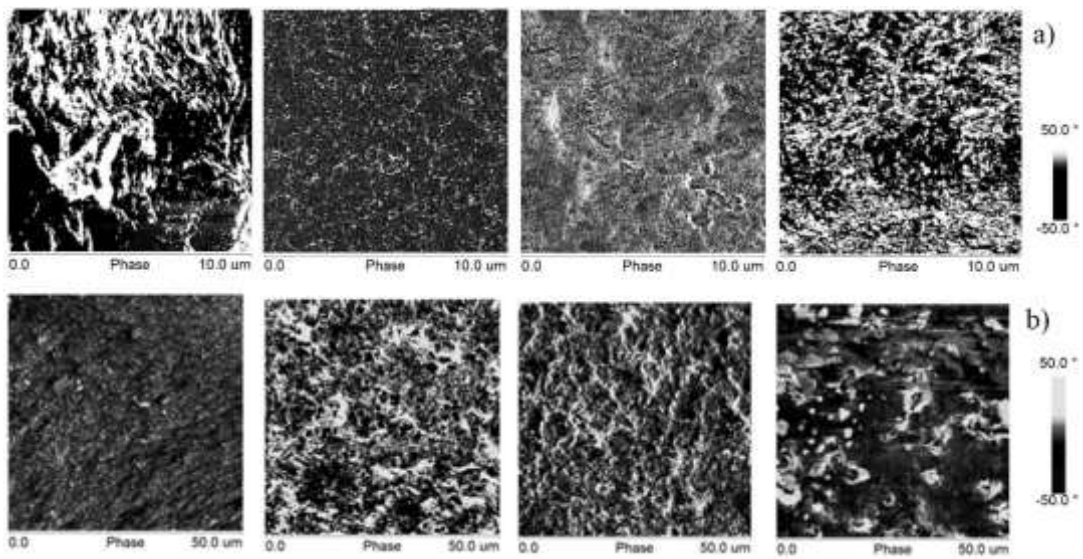

Fig. 3. AFM phase images of the freeze-fractured surfaces of two PU hybrid seria with different fillers content: a) 0; 1; 2 and 5 wt% of SiO_2; b) 0; 0,5; 1 and 2 wt% of TiO_2.

Based on Fig. 3a, PU-SiO_2 samples with low silica loading are not definite as they are visible for the pure sample, (Fig. 3a), In this case, low SiO_2 content is acting as dispersive agent in soft phase based on polycarbonate diol. On the opposite, higher segmentation was registered for PU-SiO_2-5 sample. On the basis of Fig. 3b, it can be seen that pure sample (PU-TiO_2-0) has very smooth surface and highest homogeneity. The surface roughness and phase separation of PU-TiO_2 samples increased by increasing titania amount.

The thermal stability and decomposition of PU-SiO_2 and PU-TiO_2 hybrids

As an example of results obtained by TGA analyses of both series of polyurethane materials, derivative thermogravimetric curves of the samples containing different silica filler loading (0,2 and 10 wt%) is shown in Fig. 4. The positions of onset temperatures (T_{onset}), the temperature of maximum decomposition (T_{max}) as well as temperature registered as a shoulder (T_{sh}) on DTG curves are marked.

It can be noticed that different SiO_2 content affects decomposition pattern of prepared polyurethane nanocomposites distribution. Moreover, this impact is most pronounced for the sample containing nanoparticles agglomerates (PU-SiO_2-10). However, the agglomerates positively affected T_{onset}, that its highest value is determined at 314 °C for the sample with highest silica loading (PU-SiO_2-10). Decomposition path of the samples with low SiO_2 filler content is taking place as two parallel processes: degradation of hard domains and while the the decompositon of soft segments (characterized by T_{sh}) (Pavličević et al., 2010). The maximum temperature of degradation (T_{max}) has been significantly increased by addition of silica nanoparticles (by about 20 °C and 25 °C, for samples PU-SiO_2-5 and PU-SiO_2-10).

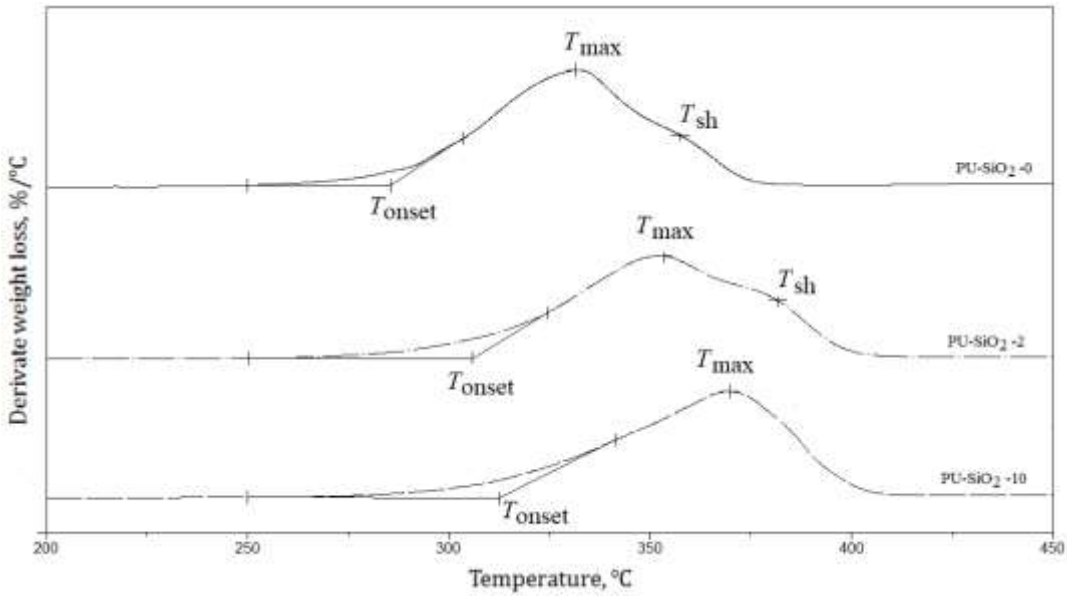

Fig. 4. DTG curves of PU-SiO_2 hybrids with different silica loading (0, 2 and 10 wt%)

On the basis of DTG results obtained for PU-TiO_2 nanocomposites, it is assessed that also PU-TiO_2 nanocomposites show two-step decomposition. The addition of TiO_2 filler positively affected onset temperature. Also, the addition of higher titania amount caused the significant increase of T_{max} values (from 355 °C PU for PU-TiO_2-0.5 to 388 °C for the sample containing 2 % of nanoparticles (PU-TiO2-2), in regard to analogous T_{max} value for unmodified elastomer, registered at 342 °C.

Thermal behavior of PU-SiO_2 and PU-TiO_2 hybrids

The temperatures interesting to be discussed for study of influence of SiO_2 and TiO_2 addition on thermal behavior of polyurethane elastomers are glass transition temperature (T_g), temperature of relaxation of soft segments (T_{rel}) and temperatures of melting mechanism (T_{mel1}, T_{mel2} and T_{mel3}, each assigned for multi-step endothermic melting event) are summarized in Table 1.

Table 1. The values of glass transition temperature, temperature of relaxation of soft segments and temperatures of melting mechanism of polycarbonate-based polyurethanes with different TiO_2 content

Sample code	T_g (°C)	T_{rel} (°C)	T_{mel1} (°C)	T_{mel2} (°C)	T_{mel3} (°C)
PU-SiO_2-0	-36	53	116	134	150
PU-SiO_2-1	-36	54	124	135	152
PU-SiO_2-2	-37	56	129	143	156
PU-SiO_2-5	-38	56	131	145	160
PU-SiO_2-10	-38	56	133	-	-
PU-TiO_2-0	-36	50	117	134	151
PU-TiO_2-0.5	-36	51	121	152	-
PU-TiO_2-1	-37	51	125	168	-
PU-TiO2-2	-37	52	132	172	-

On the basis of obtained DSC results, it can be noticed that the glass transition temperature was not significantly affected by the presence of used nanofillers, which is in accordance with previous results. Temperature of relaxation of soft segments for the samples based on T5651 polycarbonate diol increased by addition of higher silica amount. The melting og PU-SiO2 series consists of three endothermic peaks and the presence of silica particles did not affect the melting mechanism of obtained hybrids, except of 10 wt% SiO_2 addition (one-step melting is detected for sample PU-SiO_2-10). The melting temperatures (Tmel1, Tmel2 and Tmel3 (°C) significantly increased by increment of silica, indicating achievement of polyurethane matrix-SiO_2 system homogeneity. On the other hand, the low content of TiO_2 resulted in two-step melting of prepared hybrids in regard to three-step of physical crosslinking disruption, observed for unmodified polyurethane (PU-TiO_2-0). The increase of melting temperatures by increase of titania loading is also detected.

CONCLUSION

Two series of aliphatic polyurethane elastomeric hybrids, based on TiO_2 and SiO_2 addition were prepared. The different polycarbonate diol, particle type, size and content as well as preparation procedure were used in order to compare their influence on the structure, thermal stability and thermal behavior of synthesized nanocomposites. FTIR results revealed that all samples were homogenous and characterized by phase separation degree, except of one with the highest filler content (10 wt% of silica). The thermal stability both synthesized series of polyurethanes was significantly improved by the presence of used nanoparticles, independently on the fillers dispersion. The thermal decomposition pattern of all prepared samples, found affected by the filler presence, consists of two processes: breakage of urethane linkages and degradation of soft segments. The maximum degradation temperature (assigned to hard domains degradation) as well as temperature related to soft chains decomposition increased by addition of nanoparticles, for both PU series. On the basis of obtained TGA results, all synthesized polyurethanes were thermally stable up to 285 °C, which is significant for their potential applicatin under high temperature conditions. Onset temperatures of prepared polyurethane nanocomposites, based on different polycarboate diols, increased by the presence of both fillers.

The addition of two types of inorganic particles and the use of two different polycarbonate diols did not affect the glass transition temperature of obtained polyurethane elastomers, determined at 37.3±1 °C for all samples. The melting of PU-SiO_2 systems with low silica content was characterized with three endothermic minima, while the melting of sample with agglomerates (PU-SiO_2-10) is described with only one endotherm. Nevertheless, the three-step melting temperatures polyurethane hybrids were remarkably shifted to higher values by the low content of homogenously dispersed silica particles. The addition of TiO_2 nanoparticles caused two-step physical crosslinking disruption in regard to triple melting of unmodified polyurethane. The starting of physical disruption of prepared PU-TiO_2 systems is also significantly shifted to higher values by the increase of titania loading.

Acknowledgement

The authors wish to thank for the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 451-03-68/2020-14/200134.). The author from Prague would like to acknowledge to the Czech Science Foundation, project No. 18-03932S.

LITERATURE

Asensio, M., Costa, V., Nohales, A., Bianchi, O., & Gómez, C. M. (2019). Tunable Structure and Properties of Segmented Thermoplastic Polyurethanes as a Function of Flexible Segment. *Polymers*, *11*(12), 1910.

Charpentier, P.A., Burgess, K., Wang, L., Chowdhury, R.R., Lotus, A.F., & Moula, G. (2012). Nano-TiO_2/polyurethane composites for antibacterial and self-cleaning coatings. *Nanotechnology*, *23*(42), 425606.

Chen, X., Wang, Y., & Jiao, C. (2018). Influence of TiO_2 particles and APP on combustion behavior and mechanical properties of flame-retardant thermoplastic polyurethane. *Journal of Thermal Analysis and Calorimetry*, *132*(1), 251-261.

Dahl, M., Liu, Y., & Yin, Y. (2014). Composite titanium dioxide nanomaterials. *Chemical reviews*, *114*(19), 9853-9889.

Ding, X., Wang, X., Zhang, H., Liu, T., Hong, C., Ren, Q., & Zhou, C. (2020). Preparation of waterborne polyurethane-silica nanocomposites by a click chemistry method. *Materials Today Communications*, *23*, 100911.

Kim, H.J., Kang, M.S., Knowles, J.C., & Gong, M.S. (2014). Synthesis of highly elastic biocompatible polyurethanes based on bio-based isosorbide and poly (tetramethylene glycol) and their properties. *Journal of biomaterials applications*, *29*(3), 454-464.

Kim, B.K., Shin, Y.J., Cho, S.M., & Jeong, H.M. (2000). Shape-memory behavior of segmented polyurethanes with an amorphous reversible phase: The effect of block length and content. *Journal of Polymer Science Part B: Polymer Physics*, *38*(20), 2652-2657.

Kultys, A., Rogulska, M., & Głuchowska, H. (2011). The effect of soft-segment structure on the properties of novel thermoplastic polyurethane elastomers based on an unconventional chain extender. *Polymer international*, *60*(4), 652-659.

Mi, H.Y., Jing, X., Salick, M.R., Turng, L.S., & Peng, X.F. (2014). Fabrication of thermoplastic polyurethane tissue engineering scaffold by combining microcellular injection molding and particle leaching. *Journal of Materials Research*, *29*(8), 911.

Pavličević, J., Špirkova, M., Strachota, A., Szécsényi, K.M., Lazić, N., & Budinski-Simendić, J. (2010). The influence of montmorillonite and bentonite addition on thermal properties of polyurethanes based on aliphatic polycarbonate diols. *Thermochimica Acta*, *509*(1-2), 73-80.

Pavličević, J., Špírková, M., Bera, O., Jovičić, M., Pilić, B., Baloš, S., Budinski-Simendić, J. (2014). The influence of ZnO nanoparticles on thermal and mechanical behavior of polycarbonate-based polyurethane composites. *Compos Part B-Eng*, *60*, 673-679.

Pavličević, J., Špirková, M., Bera, O., Jovičić, M., Kojić, D., Szécsényi, K.M., & Budinski-Simendić, J. (2018). Uticaj nanočestica silicijum (IV) oksida na termička i mehanička svojstva nanokompozita na bazi alifatičnih poliuretana. *Chemical Industry/Hemijska Industrija*, *72*(4).

Poręba, R., Kredatusová, J., Hodan, J., Serkis, M., & Špírková, M. (2015). Thermal and mechanical properties of multiple-component aliphatic degradable polyurethanes. *Journal of Applied Polymer Science*, *132*(16).

Saha, C., Bahera, P.K., Raut, S.K., & Singha, N.K. (2020). A Thermoplastic Polyurethane/Nanosilica Composite via Melt Mixing Process and its Properties. *SILICON*. https://doi.org/10.1007/s12633-020-00487-1

Serkis, M., Špírková, M., Hodan, J., & Kredatusová, J. (2016). Nanocomposites made from thermoplastic waterborne polyurethane and colloidal silica. The influence of nanosilica type and amount on the functional properties. *Progress in Organic Coatings*, *101*, 342-349.

Seyfi, J., Jafari, S. H., Khonakdar, H. A., Sadeghi, G. M. M., Zohuri, G., Hejazi, I., & Simon, F. (2015). Fabrication of robust and thermally stable superhydrophobic nanocomposite coatings

based on thermoplastic polyurethane and silica nanoparticles. *Applied Surface Science*, *347*, 224-230.

Stefanović, I.S., Dostanić, J., Lončarević, D., Vasiljević Radović, D., Ostojić, S., Marković, S., & Pergal, M.V. (2019). Preparation and characterization of poly (urethane-siloxane)/titanium-dioxide nanocomposites. *Hemijska industrija*, *73*(1), 13-24.

Špírková, M., Pavličević, J., Strachota, A., Poreba, R., Bera, O., Kaprálková, L., Baldrian, J., Šlouf, M., & Budinski-Simendić, J. (2011). Novel polycarbonate-based polyurethane elastomers: Composition–property relationship. *European Polymer Journal*, *47*(5), 959-972.

Špírková, M., Machová, L., Kobera, L., Brus, J., Poręba, R., Serkis, M., & Zhigunov, A. (2015). Multiscale approach to the morphology, structure, and segmental dynamics of complex degradable aliphatic polyurethanes. *Journal of Applied Polymer Science*, *132*(10).

Špírková, M., Pavličević, J., Aguilar Costumbre, Y., Hodan, J., Krejčíková, S., & Brožová, L. (2020). Novel waterborne poly (urethane-urea)/silica nanocomposites. *Polymer Composites*, *41*(10), 4031-4042.

Touchet, T.J., & Cosgriff-Hernandez, E.M. (2016). Hierarchal structure–property relationships of segmented polyurethanes. In *Advances in polyurethane biomaterials* (pp. 3-22). Woodhead Publishing.

Zhang, X.C., Chen, Y.Z., Yu, J., & Guo, Z.X. (2011). Thermoplastic polyurethane/silica nanocomposite fibers by electrospinning. *Journal of Polymer Science Part B: Polymer Physics*, *49*(23), 1683-1689.

Zhu, R., Wang, Y., Zhang, Y., Ma, D., Wang, X. (2016). Synthesis of polycarbonate urethane elastomers and effects of the chemical structures on their thermal, mechanical and biocompatibility properties. *Heliyon*, *2*(6):e00125