ORIGINAL SCIENTIFIC PAPER OPEN ACCESS

The effect of silica nanoparticles obtained from different sources on mechanical properties of polyurethane nanocomposites

Milan P. Nikolić[1*], Slobodanka Stanojević - Nikolić[1], Vladimir B. Pavlović[2], Vladimir V. Srdić[3]

[1] University of Kragujevac, Faculty of Agronomy, Čačak, Serbia
[2] University of Belgrade, Faculty of Agriculture, Belgrade, Serbia
[3] University of Novi Sad, Faculty of Technology, Novi Sad, Serbia

ARTICLE INFO

[*] **Correspondence:** milanik@kg.ac.rs

DOI: 10.5937/engtoday2400006N

UDC: 621(497.11) **ISSN:** 2812-9474

Article history: Received 19 April 2024; Revised 20 May 2024; Accepted 22 May 2024

ABSTRACT

Spherical silica particles were synthesized from two different sources, tetraethyl orthosilicate (TEOS) and sodium silicate obtained from wheat straw ash, respectively. In the first case, monodispersed and microporous silica particles with average particle size of 400 nm were prepared by hydrolysis and condensation of TEOS.In the second case, the silica particles were generated from supersaturated sodium silicate solution. The extraction of silicate solution from wheat straw ash (WSA) was performed by the multi-step sequential extraction using 2,5 mol/L NaOH. WSA silica particles were polydispersed and contain the primary silica particles with average size of ~250 nm and agglomerates obtained by aggregation of primary silica particles, with average size of ~1.5 µm and 5 µm. The silica particles obtained from WSA have the average pore size of 28.3 nm, total pore volume of 0.1638 cm^3/g and average surface area of 23.131 m^2/g. Flexible polyurethane/silica composites with my(TEOS silica and WSA silica) and different filler concentration were synthesized. Dispersion of silica fillers in polyol system preceded the mixing with isocyanate resulted in formation of cavities in polyurethane-silica composite. On the other hand, dispersion of TEOS silica filler into isocyanate which preceded the mixing with polyol system resulted in homogenous and compact composite. The application of silica filler obtained from TEOS at filler concentration of 4 wt.% increased Young's modulus for 20% relative to that of polyurethane without filler. On the other side, the application of WSA silica filler resulted in reduced Young' s modulus probably due to large silica aggregates.

KEYWORDS

Silica, Agricultural waste, Mesoporous materials, Polyurethane, Nanocomposites, Mechanical properties.

1. INTRODUCTION

Organic–inorganic nanocomposites combine the advantages of organic polymers (flexibility, ductility, dielectric strength, etc.) and those of inorganic materials (rigidity, high thermal stability, UV-shielding property, and high refractive index, etc.) [1]. There are many polymer nanocomposites, especially containing nano-silica particles which due to their excellent properties, such as adjustable size, morphology and porosity, chemical stability, biocompatibility and non-toxicity, contribute improved properties of polymer composites [1,2]. Silica particles were mainly synthesized using two different precursors, tetraethylorthosilicate (TEOS) [3] and sodium silicate[4]. Sodium silicate is about

© Faculty of Mechanical and Civil Engineering in Kraljevo. All rights reserved

four times less expensive than TEOS, but contains sodium ions and gives less homogeneous gels. However, conventional silica synthesis from sodium silicate solution requires the heating of sodium carbonate with quartz sand at a temperature of about 1300°C, resulting in the formation of sodium silicate, which then reacts with sulfuric acid. This process consumes a large amount of energy and contributes to global warming due to the large amount of carbon dioxide emitted from this process. Typically, 0.23 tons of carbon dioxide, 0.74 tons of sodium sulfate, and 20 tons of wastewater are released per ton of silica produced, all of which contribute to causing significant environmental problems [5].

Agricultural waste (AW) is one of the primary sources of environmental pollution.It is estimated that more than 3,300 megatons of waste biomass from the main crops are produced annually [6]. The burning of biomass is a huge environmental concern, especially in agricultural countries. This leads to deteriorated air quality, haze conditions, and serious repercussions on the health of humans [7].It was found that 730 gigatonnes of biomass is burned in Asia in a typical year from both anthropogenic and natural causes [8]. In this case, 33,4% was comprised of open-field burning.Having this in mind, reutilization of agro-industrial waste is an important strategy for long-term manner to achieve sustainable cycles in the industry [9].The synthesis of nanomaterial from waste is considered an effective way to treat and recycle waste which adheres to the concepts of minimum waste generation and waste-to-wealth mission [9]. Some of the possible industrial waste application, including the biomass from the main crops is their reutilization for silica synthesis.

Herein, we report some discoveries about the synthesis of silica particles from two silica sources. In the first case, silica particles were obtained by hydrolysis and condensation of TEOS. In the second case, the silica particles were generated from sodium silicate solution obtained from wheat straw ash. Both particles were used as the filler of polyurethane materials. The effect of filler type and synthesis procedure on mechanical properties of polyurethane composites was examined.

2. MATERIALS AND METHODS

2.1. Preparation of silica particles from TEOS

Silica particles were synthesized by hydrolysis and condensation of TEOS, dissolved in anhydrous ethanol, with distilled water under basic condition (25% NH3, Merck). The sample was prepared using a molar ratio TEOS:H2O:NH4OH = 1:40:2 and TEOS concentration of 0.25 mol/L. After feeding, the product suspension was continuously stirred at room temperature for 1 h. The white precipitated powder was centrifuged and washed with distilled water until the effluent was free of NH4 groups, and finally dried at 120 C for 1 day.

2.2. Preparation of silica from sodium silicate solution derived from wheat straw ash

Wheat straw ash undergoes alkaline treatment to form a Na_2SiO_3 solution. 20 g of ash was dissolved in 200 mL of 2,5 mol/L NaOH. The solution was magnetically stirred at 80°C for 5 hours. After the time has expired the ash was separated from the liquid phase by centrifugation and obtained supernatant was used for the next cycle of extraction adding new amount of ash (20 g). As it was shown in Fig. 1, the process has been repeated five times.

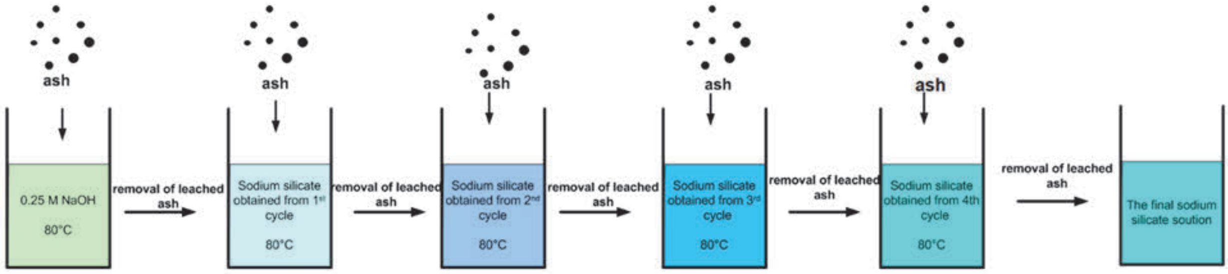

Figure 1: Scheme of preparation of aqueous sodium silicate solution by alkaline treatment of wheat straw ash

The obtained final sodium silicate solution was left in flask. After seven days the clear solution of sodium silicate obtained from straw ash started to coalescence and became milky indicating on spontaneous precipitation of silica. The precipitation followed for the next 10 days at room temperature. The obtained precipitate was washed with water and dried at 100 °C for 10 hours.

2.3. Preparation of silica-polyurethane composite

To remove the bound water, the as-synthesized silica particles were firstly dried at 250°C for three hours and then three hours at 450°C. Before use,the dried powder was kept at exicator. Silica particles were used as a filler for polyurethane material which is obtained by mixing two components: polyol system (which represents a mixture of two polyols: 75 wt% of polyether polyol (molecular weight 5000 g/mol) and 25 wt% of 1,4-butanediol) and diphenylmethane-4,4'-diisocyanate (DESMODUR PA 50, Bayer). The measured hydroxyl number in polyol system was 350 mg (KOH)/g. The polyurethane was prepared by mixing silica-polyol system with diphenylmethane-4,4'-diisocyanate (DESMODUR PA 50, Bayer) at mix ratio 100:77 by weight.The silica content in polyurethane composite was set on 2 and 4 wt.% (Table 1). Before mixing the polyol system and isocyanate, dispersion of silica particles was carried out either in polyol system or isocyanate. The mixture was well stirred for 30 seconds and then poured into aluminium mold for the production of tensile test specimens (Figure 2). The dimensions of molds for production of tensile test specimens are according ASTM E 646-98 specifications [10]. Aluminium mold was put on 50° Cheating plate to provide low gradient temperature profile within the sample in the mold (Figure 2). The sample was kept in the mold for four hours.

Table 1: Sample notation and synthesis conditions for polyurethane composites

Sample notation	Silica source	Silica filler concentration (wt.%)	Dispersion of silica in isocyanate	Dispersion of silica in polyol system
PU*	-	-	-	-
PU-T_{iz}-2%	TEOS	2	YES	NO
PU-T_{ps}-2%	TEOS	2	YES	NO
PU-T_{iz}-4%	TEOS	4	YES	NO
PU-S_{iz}-2%	Sodium silicate solution	2	NO	YES
PU-S_{ps}-2%	Sodium silicate solution	2	NO	YES

*PU represent notation for polyurethane materials without silica fillers

Figure 2: Aluminium mold for the production of tensile test specimens filled with polyurethane-silica sample

2.4. Characterization of materials

The size and morphology of the silica particles and silica-polyurethane composites were examined using a scanning electron microscope (SEM, JSM-6390 LV JEOL, operating at 30 kV) coupled with energy dispersive x-ray spectroscopy (EDS) (Oxford Instruments X-MaxN). Prior to SEM imaging, the samples were sputtered with gold. The particle size was measured by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments, United Kingdom).Adsorption-desorption measurements of silica powder were conducted on a MicrotracBelsorp MiniX apparatus at 77 K using nitrogen as the adsorption gas. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore diameter distributions were derived from the adsorption branch by the Barrett-Joyner-Halenda (BJH) method. Automated potentiometric determination of the hydroxyl number of polyols was measured following the standard DIN EN ISO 4629-2:2016 using Eco Titrator (Metrohm) equipped with electrode for non-aqueous titrations (Solvotrode easy Clean, Merochm).

The tensile properties of the samples were measured using an Autograph AGS-X plus (Shimadzu, kyoto, Japan) tensile testing machine equipped with a 500 N Shimadzu load cell, a contact extensometer, and the TRAPEZIUM X computer software (Shimadzu, Kyoto, Japan), operated at a constant crosshead speed of 50 mm/min. Measurements were performed at room temperature with a gauge length of 60 mm. Standard tensile testing specimen is according to the ASTM E 646-98. The tensile modulus, tensile strength, and elongation at break of the materials were determined.

3. RESULTS AND DISCUSSIONS

SEM micrographsat different magnifications (×10,000 and ×50,000)of silica particles obtained by hydrolysis and condensation of TEOS are shown on Figure 3. The obtained particles are monodispersed and spherical with average particle size of 0.4 µm.

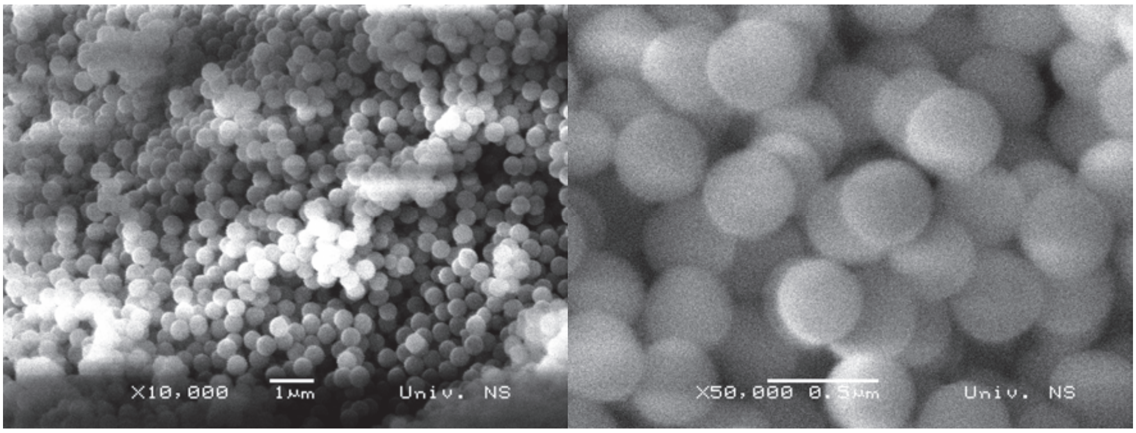

Figure 3: SEM micrographs of silica particles obtained by hydrolysis and condensation of TEOS

SEM micrograph with EDS spectrum of wheat straw ash is shown on Figure 4. The wheat straw ash exhibits particles with irregular shapes and size below 10 µm. EDS analysis of wheat straw ash presents a high level of silicon of 11.4 wt. %. Elemental composition of wheat straw ash obtained by EDS is shown on Table 2.

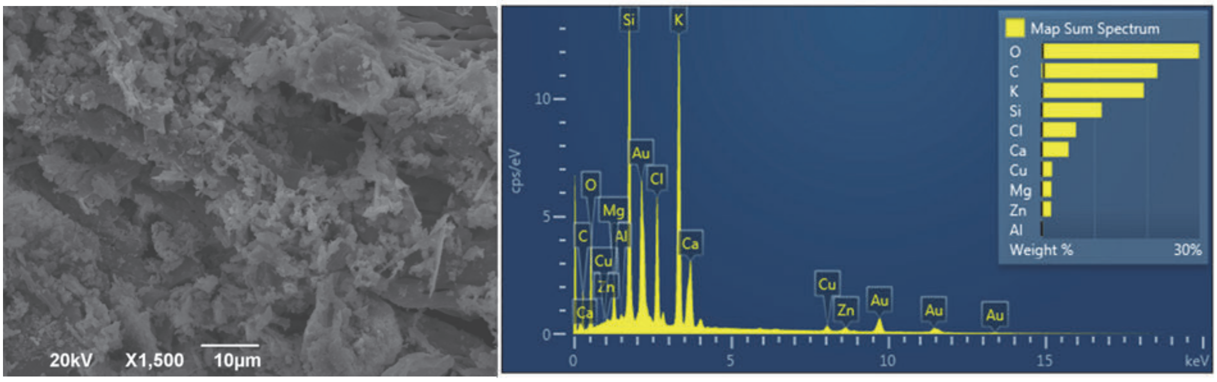

Figure 4: SEM micrograph and EDS spectrum of wheat straw ash

Table 2: Elemental composition of wheat straw ash

Element	O	C	Si	Mg	Ca	Cu	Zn	Cl	K	Al
Concentration of element in wheat straw ash (wt%)	29.89	21.94	11.4	1.86	5.1	1.94	1.75	6.51	19.41	0.21

Photographs of wheat straw ash and extracted silica powderare shown on Fig. 5. Dried silica powder obtained by precipitation from sodium silicate solution appeared as a fine and white powder (Fig. 5-right).

Figure 5: Photographs of samples during the silica powder preparation from wheat straw ash: wheat straw ash (left); extracted silica powder (right)

SEM micrographs of silica powder obtained from sodium silicate solution derived from wheat straw ash show silica particles with globular shape (Figure 6).The lack of a regular geometry indicates the product's amorphous nature. The average size of primary particles is between 160 and 235 nm. However, there is a presence of aggregated primary silica particles with average size between 400 and 1040 nm.

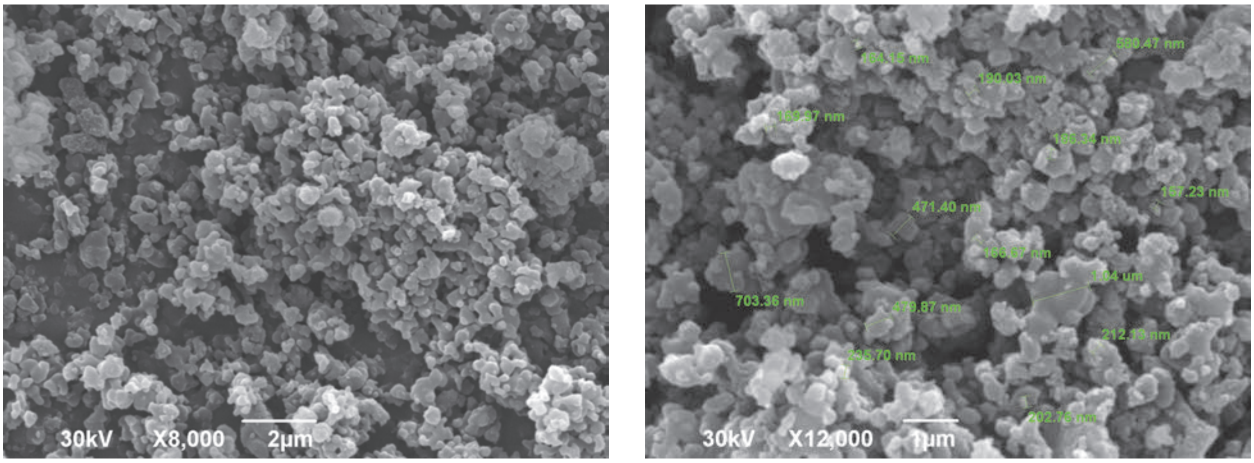

Figure 6: SEM micrographs at different magnifications (×8,000 and ×12,000) of silica particles generated by precipitation from sodium silicate solution obtained from wheat straw ash

Figure 7 shows particle size distributions of silica particles obtained from TEOS (a, b) and sodium silicate solution (c, d) expressed as number and volume distributions, respectively. On the other hand, Table 3 and Table 4 shows averagevalues of particle size, the percentage that each size class occupies of the overall distribution (either when calculated as a percentage of the total volume of particles or number of particles) and standard deviations for silica particles obtained from TEOS and sodium silicate solution, respectively.Silica particles obtained from TEOS show unimodal size distribution for both number and volume distributions with average particle size of 476 and 559 nm, respectively. However, there is a trimodal size distribution of the silica particles obtained from sodium silicate solution. The smallest particles with average particle size of 250 nm represent primary silica particles. The larger aggregates were obtained by aggregation of the primary silica particles and have the average particle size of 1550 and 4800 nm, respectively. The number-based size distribution of silica particles obtained from sodium silicate solution shows that 81.7%, 17.4 and 0.8% of the total number of particles have a size of 250, 1300 and 4725 nm, respectively. On the other hand, the volume-based size distribution of silica shows that 0,9%, 34.8% and 64.3% of the total volume of particles is occupied by the particles with average size of 274, 1884 and 4931 nm, respectively.

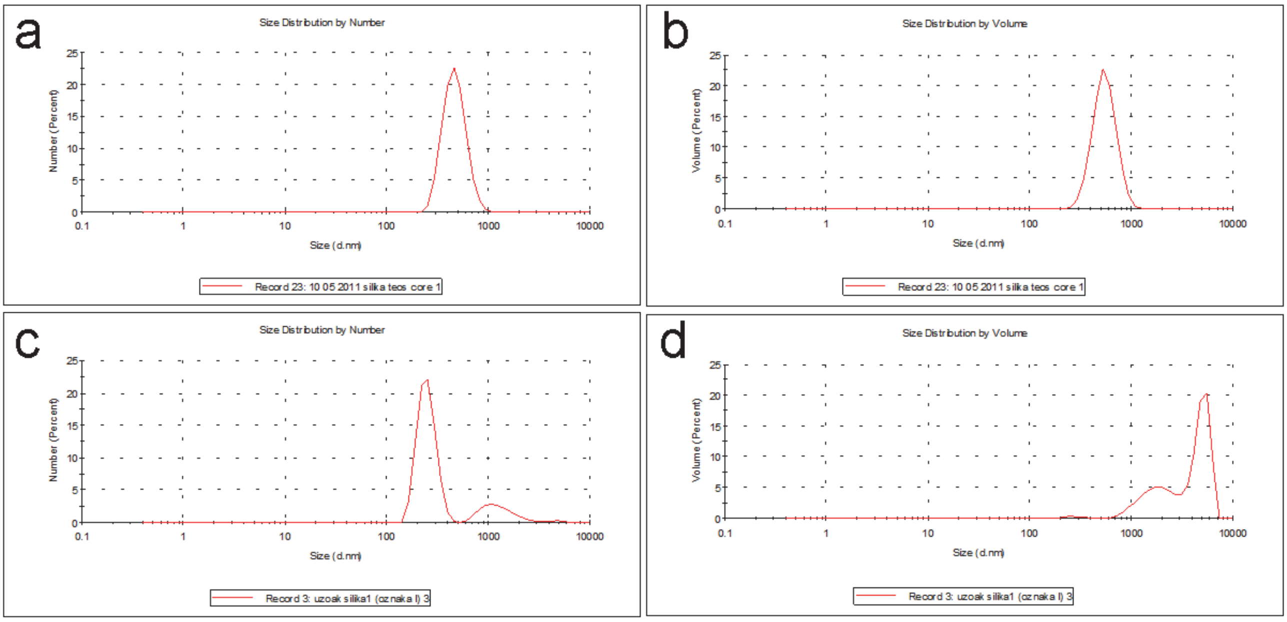

Figure 7: Particle size distribution of silica particles: number distribution of silica particles obtained from TEOS (a); volume distribution of silica particles obtained from TEOS (b); number distribution of silica particles obtained from sodium silicate solution (c);volume distribution of silica particles obtained from sodium silicate solution (d)

Table 3: Particle size distribution of silica particles obtained from TEOS

The average particle size from number distribution (nm)	Number %	Standard deviation (d. nm) for number distribution	The average particle size from volume distribution (nm)	Volume %	Standard deviation (d. nm) for number distribution
476	100	121.7	559	100	144

Table 4: Particle size distribution of silica particles obtained from sodium silicate solution.

The average particle size from number distribution (nm)	Number %	Standard deviation (d. nm) for number distribution	The average particle size from volume distribution (nm)	Volume %	Standard deviation (d. nm) for number distribution
1300	17.4	531.5	1884	34.8	658.9
4725	0.8	850	4931	64.3	910.7
250	81.7	50.79	274	0.9	55.25

The adsorption–desorption isotherms and pore size distributions of the silica particles were measured by low-temperature nitrogen adsorption, and shown on Fig. 8. The adsorption–desorption isotherm of silica particles obtained from TEOS (Fig. 8a) belongs to a typical type I indicating the microporous structure of silica particles obtained from TEOS. On the other hand, the adsorption–desorption isotherm of silica particles obtained from supersaturated sodium silicate solution belongs to a type II isotherm and type H3 hysteresis (Fig. 8a), indicating that silica particles have meso- and macro-porous structures [11]. At high relative pressure there is no saturation which indicates that macropores are not completely filled with nitrogen. On the other hand, desorption isotherm abruptly closes to the adsorption isotherm probably due to cavitation phenomena. The pore size distribution obtained by BJH method for silica particles obtained from TEOS (Fig. 8b) shows pore with an internal width of less than 2 nm. On the other hand, silica particles obtained from sodium silicate solution have multimodal pore distribution in the range between 5 and 100 nm and pores with average size of ~30 nm dominate the sample (Fig. 8c). The additional information, such as average pore size, total pore volume and specific surface area, are also shown in Table 5. The average surface area and total pore volume of silica particles obtained from TEOS are 324 m^2 and 0,186 cm^3/g, respectively. The average pore size, average surface area and total pore volume of silica particles obtained from sodium silicate solution are 28.33 nm, 23 m^2/g and 0.1638 cm^3/g, respectively. The relatively low surface area and pore volume can be related to high concentration of monomer silica which speeds up the condensation reactions and almost complete closing of small pores [12].

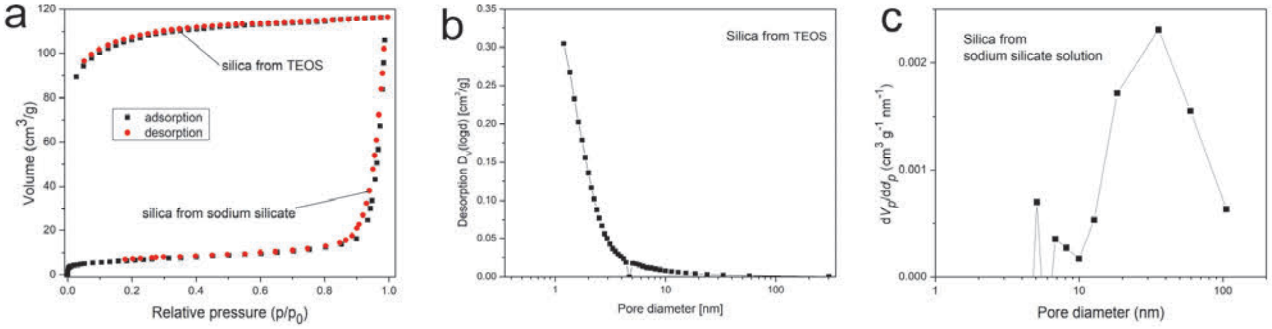

Figure 8 :Adsorption–desorption isotherm (a) and pore size distribution (b, c) of silica particles obtained from TEOS and sodium silicate solution

Table 5:The average pore size, total pore volume and specific surface area of silica particles

Sample name	Average pore size (nm)	Total pore volume (cm^3/g)	Average surface area (m^2/g)
Silica particles obtained from TEOS	< 2 nm	0.186	324
Silica particles obtained from sodium silicate solution	28.333	0.1638	23.131

Figure 9 shows SEM micrographs of the cross-sectional area of silica-polyurethane composite obtained by using silica filler obtained from TEOS (Fig. 9-left) and sodium silicate solution (Fig. 9-right) (samples PU-T_{ps}-2% and PU-S_{ps}-2%). In both samples there is a presence of the cavities with average size in the range between 200 and 500 µm. However, the number and size of cavities is more pronounced for composite with silica filler obtained from sodium silicate solution. If moisture is present in the mixture, the water reacts with isocyanate to create carbamic acid that is not stable and dissociates into amine and carbon dioxide thus resulting in foaming [13]. Strongly bound water molecules can exist at the surfaces of mesoporous silica [14], so this water can react with isocyanate and induce formation of cavities.

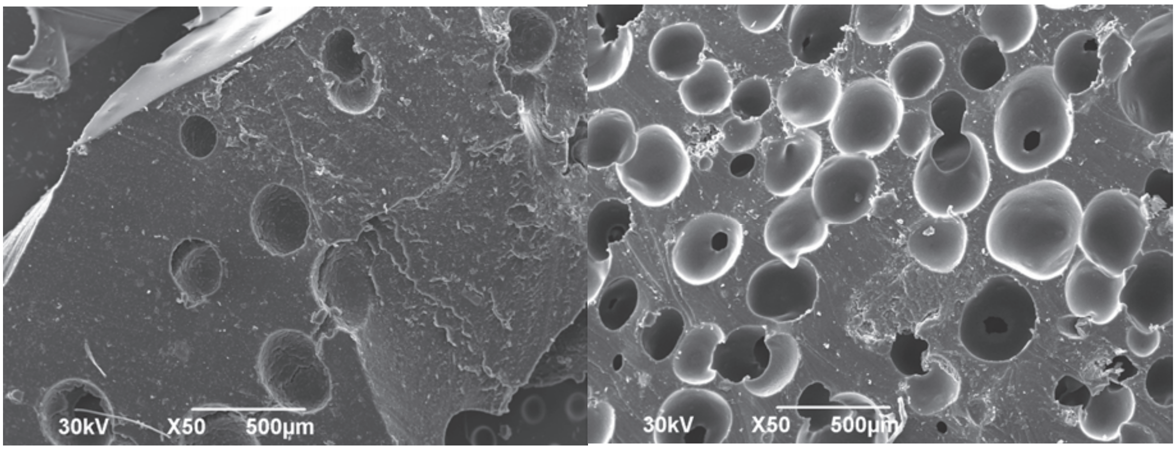

Figure 9: SEM micrographs of the cross-sectional area of silica-polyurethane composite: silica filler obtained from TEOS (left); silica filler obtained from sodium silicate solution (right).

The Energy Dispersive X-ray analysis (chemical mapping) of the cross-sectional area of polyurethane composite filled with silica filler obtained from sodium silicate solution at concentration of 2 wt.% is shown on Fig. 8. Chemical mapping shows uniformly distributed silicon atoms in polyurethane materials indicating that silica particles had a uniform distribution in the polymer matrix.

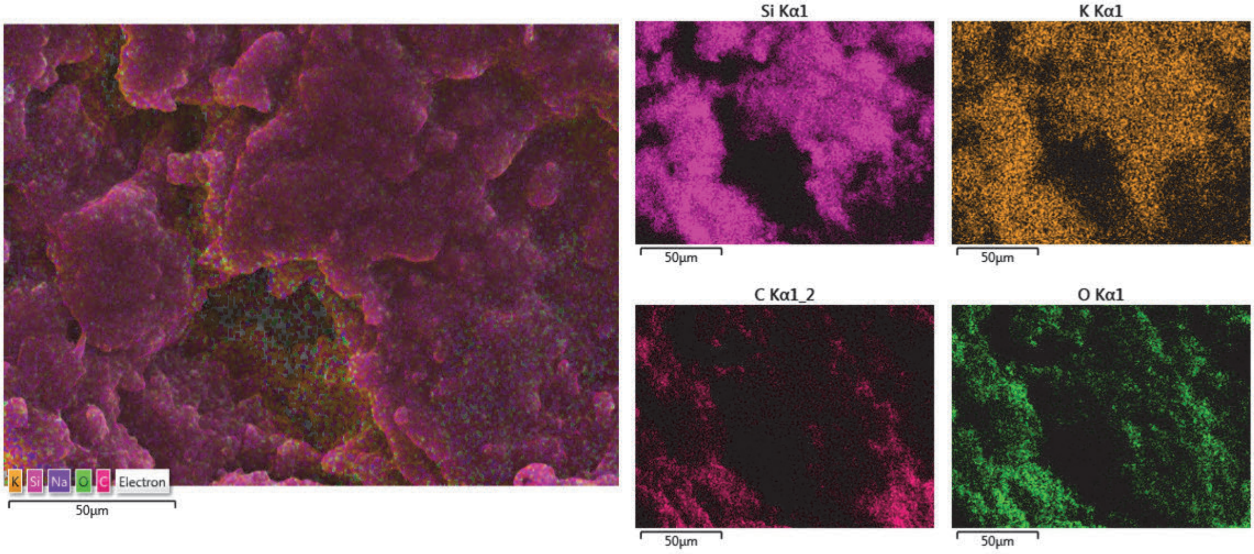

Figure 10: EDS mapping images of the cross-sectional area of silica-polyurethane composite

The effect of synthesis conditions and silica filler type on tensile modulus, tensile strength and elongation at break of polyurethane/silica composite is shown on Table 6. Tensile modulus of polyurethane-silica composite samples (PU-T_{iz}-2, PU-T_{iz}-4% and PU-S_{iz}-2%) obtained by dispersion of silica filler into isocyanate before mixing with polyol system was higher than that obtained by dispersion of silica filler in polyol system (PU-T_{ps}-2%, PU-S_{ps}-2%). This indicates that dispersion of silica filler in isocyanate prevents formation of cavities obtained by released carbon dioxide which is obtained by the reaction of bound water inside silica skeleton with diphenylmethane-4,4'-diisocyanate. Reducing of tensile modulus by dispersion of silica particles into polyol system relative to that obtained by dispersion in diphenylmethane-4,4'-diisocyanate is more pronounced for silica particles obtained from sodium silicate solution (samples PU-S_{ps}-2% and PU-S_{iz}-2%, respectively) relative to samples obtained by using silica from TEOS (samples PU-T_{ps}-2% and PU-T_{iz}-2%, respectively).This indicates that silica particles obtained from sodium silicate solution contain larger amount of bound water. It can also be assumed that mesoporous structure, characteristic of silica obtained from sodium silicate solution, improves diffusion of water in contrast to microporous structure (characteristic of silica from TEOS). After preventing foaming effects caused by water by dispersion of silica particles into diphenylmethane-4,4'-diisocyanate, it can also be noticed reduced tensile modulus of polyurethane-silica composites obtained by application of silica particles from sodium silicate solution (PU-S_{iz}-2%) relative to that obtained by using silica particles obtained from TEOS (PU-T_{iz}-2%). It is probably due to the presence of larger aggregates in the silica particles obtained from sodium silicate solution which causing weak binding between the polymer matrix and aggregated silica filler particles. On the other hand, the incorporation of 4 wt% silica filler obtained from TEOS (PU-T_{iz}-4%) increased tensile modulus by ~20% relative to polyurethane material without silica filler (sample PU).

Table 6: The effect of synthesis conditions and silica filler type on tensile modulus, tensile strength and elongationat break of polyurethane/silica composite

Sample	Tensile modulus (N/mm^2)	Tensile strength (N/mm^2)	Elongation at break (mm)
PU	33.5875	5.14023	23.6285
PU-T_{iz}-2%	33.1013	7.45002	55.4285
PU-T_{ps}-2%	29.4611	4.52602	41.2035
PU-T_{iz}-4%	40.0703	7.45474	38.7202
PU-S_{iz}-2%	11.8127	4.56136	93.8118
PU-S_{ps}-2%	6.95099	2.68040	57.1285

4. CONCLUSIONS

Silica particles were derived from two sources. The first source is expensive chemical compounds tetraethyl orthosilicate (TEOS). On the other hand, the second source is cheap and represent sodium silicate solution obtained by alkaline treatment of wheat straw ash. Monodispersed and spherical silica particle obtained by hydrolysis and condensation of tetraethyl orthosilicate (TEOS) were monodispersed and spherical with average particle size of 0,4 µm. Silica particles obtained from the supersaturated sodium silicate solution extracted from the wheat straw ash were polydispersed with small volume fraction of particles with average size of 270 nm and larger aggregates with volume fraction of 34.8 and 64.3 with average particle size of about 670 and 910 nm, respectively. Silica particles obtained from TEOS have microporous structure. On the other hand, silica particles obtained from the sodium silicate solution were mesoporous and macroporous. Both particles were used as a filler for polyurethane materials.Preventing of foaming effect was performed by dispersion of silica particles into diphenylmethane-4,4'-diisocyanate followed by mixing with polyol system. Polyurethane composites with silica fillers derived from TEOS showed improved tensile modulus. On the other hand, polyurethane composites with silica fillers obtained from the sodium silicate solution displayed reduced tensile modulus probably due to the presence of larger aggregates causing weak binding between the polymer matrix and aggregated silica filler particles and also formation of non-homogenoussystem with internal defects. The further investigations will be focused on the development of monodispersed and non-aggregated silica particles derived from the wheat straw ash which will allow the of cheaper polyurethane composites with uniformly dispersed silica fillers resulting in improved mechanical properties.

ACKNOWLEDGEMENTS

This work is financially supported by the United Nations Development Programme under the project “Biosilica fillers and biopolyols derived fromagricultural and industrial wastes for circular production of new eco-friendly adhesives”, project ref. number 00123168/01-10. This work is also supported by the Ministry of Science, Technological Development and Inovations of the Republic of Serbia, Project No. 451-03-66/2024-03/200088.

REFERENCES

[1] Y. Chen, S. Zhou, H. Yang and L. Wu, “Structure and properties of polyurethane/nanosilica composites”, Journal of Applied Polymer Science, Vol. 95(5), pp. 1032-1039, http://dx.doi.org/10.1002/app.21180, (2005)

[2] X. Ding, X. Wang, H. Zhang, T. Liu, C. Hong, Q. Ren and C. Zhou, “Preparation of waterborne polyurethane-silica nanocomposites by a click chemistry method”, Materials Today Communications, Vol 23, p. 100911, https://doi.org/10.1016/j.mtcomm.2020.100911, (2020)

[3] W. Stöber, A. Fink and E.Bohn,"Controlled growth of monodisperse silica spheres in the micron size range" Journal of Colloid and Interface Science, Vol 26(1), pp. 62-69, https://doi.org/10.1016/0021-9797(68)90272-5, (1968)

[4] M-S. Tsai, "The study of formation colloidal silica via sodium silicate", Materials Science and Engineering: B, Vol 106(1), pp. 52-55, http://dx.doi.org/10.1016/j.mseb.2003.08.052, (2004)

[5] V. Zarei, M. Mirzaasadi, A. Davarpanah, A. Nasiri, M. Valizadeh and M.J.S. Hosseini,"Environmental method for synthesizing amorphous silica oxide nanoparticles from a natural material", Processes, Vol 9(2) 334, pp. 1-9, https://doi.org/10.3390/pr9020334, (2021)

[6] E. Commission, A sustainable Bioeconomy for Europe: strengthening the connection between economy, society and the environment. Publications Office of the European Union, Brussels, Belgium, Updated Bioeconomy Strategy, (2018)

[7] H. Zhao, X. Zhang, S. Zhang, W. Chen, D. Tong and A. Xiu, "Effects of agricultural biomass burning on regional haze in China: A review", Atmosphere, Vol 8(88), pp. 1-9, https://doi.org/10.3390/atmos8050088, (2017)

[8] D.G. Streets, K.F. Yarber, J.H. Woo and G.R. Carmichael, "Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions", Global Biogeochemical Cycles, Vol 17(4), http://dx.doi.org/10.1029/2003GB002040, (2003)

[9] N.A.A. Razak, N. H. Othman, M.S.M Shayuti, A. Jumahat, N. Sapiai and W.J. Lau,"Agricultural and industrial waste-derived mesoporous silica nanoparticles: A review on chemical synthesis route", Journal of Environmental Chemical Engineering, Vol 10(2), p. 107322, https://doi.org/10.1016/j.jece.2022.107322, (2022)

[10] R. G. Narayanan and G. S. Kumar, "Prediction of tensile and deep drawing behaviour of aluminium tailor-welded blanks", in Recent Trends in Processing and Degradation of Aluminium Alloys, Z. Ahmad, Ed. Rijeka: IntechOpen, https://doi.org/10.5772/22687, (2011)

[11] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol and K.S.W. Sing, "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)", Pure and Applied Chemistry, Vol 87(9-10), pp.1051-1069, https://doi.org/10.1515/pac-2014-1117, (2015)

[12] R. Filipović, Z. Obrenović, I. Stijepović, Lj. Nikolić and V. V. Srdić, "Synthesis of mesoporous silica particles with controlled pore structure", Ceramics International, Vol 35(8), pp.3347-3353, https://doi:10.1016/j.ceramint.2009.05.040, (2009)

[13] D. S. Kaikade and A.S. Sabnis, "Polyurethane foams from vegetable oil-based polyols: A review", Polymer Bulletin, Vol 80, pp. 2239-2261, https://doi.org/10.1007/s00289-022-04155-9, (2023)

[14] B. Grünberg, T. Emmler, E. Gedat, I. Shenderovich, G. H. Findenegg, H-H. Limbach, and G. Buntkowsky. "Hydrogen bonding of water confined in mesoporous silica MCM-41 and SBA-15 studied by ^{1}H solid-state NMR", Chemistry - A European Journal, Vol 10(22), pp. 5689-5696, https://doi.org/10.1002/chem.200400351, (2004)