

Effect of walnut shells and silanized walnut shells on the mechanical and thermal properties of rigid polyurethane foams

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ABSTRACT

In the study walnut shells (WS) and silanized walnut shells (S_WS) were used as cellulosic fillers for novel polyurethane (PU) composite foams. The impact of 1, 2 and 5 wt% of WS and S_WS on the foaming parameters, mechanical and thermo-mechanical properties of obtained materials were evaluated. The results have shown that compared to untreated WS filler, the application of S_WS leads to PU foams with more regular structure and improved physico-mechanical behavior of PU materials. For example, compared to controlled WS_0 foam, PU foams enhanced with 1 wt% of the S_WS exhibited better mechanical properties, such as higher compressive strength (~15% of improvement), better impact strength (~6% of improvement), and improved tensile strength (~9% of improvement). The addition of S_WS improved the thermomechanical stability of PU foams. This work provides a better understanding of a relationship between the surface modification of the walnut shell filler and the mechanical, insulating and thermal properties of the PU composites. Due to these positive and beneficial effects, it can be stated that the use of WS and S_WS as natural fillers in PU composite foams can promote a new application path in converting agricultural waste into useful resources for creating a new class of green materials.

1. Introduction

Polyurethanes (PUs) are one of the most versatile polymers that have been successfully used in many fields such as foams, coatings, thermoplastic elastomers, adhesive, and composites [1]. PU foam is the largest product segment in the total PU market and its global market that was valued at 46.8 billion in 2014 is expected to reach 72.2 billion by 2021 [1]. Rigid polyurethane (PU) foams are widely used mainly due to their low cost, low pollution impact and high insulation properties (0.018–0.025 W m⁻¹K⁻¹). Due to their exceptional thermal insulating properties, they are commonly used in the production of thermal insulation materials [2–4].

The main disadvantage of PU foams is their relatively low mechanical strength. To improve the mechanical strength of PU foams, many additives such as nanoparticles or fibers have been used as reinforcement. Besides several inorganic fillers, such as nanoclay [5], expandable graphite [6], silica [7], talc [8] or polyhedral oligosilsesquioxanes (POSS) [9], production of PU composite foams with bio-based fillers from natural resources has attracted attention due to their environmentally friendly character [10,11]. Incorporating bio-based fillers into

PU foams improves their mechanical properties as well as provides reactive groups to react with isocyanates. In the literature, many different agricultural waste fillers have been examined [12–19]. For example, Zhou et al. [16] have reported on the synthesis of semi-rigid PU foams based on palm-oil polyol and reinforced with cellulose nanocrystals (0.25–1 wt%). Compared to the unmodified foams, PU composites with improved compressive strength, superior dimensional stability as well as greater water uptake were obtained. Paberza et al. [20] prepared PU composite foams based on tall oil amide and reinforced with wheat straw lignin in the amount of 0–6.3 wt%. Increasing the concentration of lignin in PU foams improved thermal insulation and the maximum value of compressive strength. Zieleniewska et al. [17] synthesized PU foams with eggshells as a natural filler (5–25 wt%). The eggshells filler increased apparent density and compressive strength in the orientation parallel to the foam growth direction. The composites exhibited also low water absorption, low friability and high dimensional stability in aqueous media.

Among different bio-based fillers, the chemical composition of walnut shells has a great potential as sustainable reinforcements for a novel PU composite foams [21]. Walnut is an important crop that is cultivated

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throughout the world's temperate regions for its edible nuts [22]. Walnuts are mainly cultivated in order to obtain the kernels, and other parts of fruit such as the shell and husk are produced as waste crops during the fruit processing [23,24]. Since walnut shells comprise 67% of the total weight of the walnut kernel, around 1.5 million tons of walnut shells are left behind each year all over the world. A great amount of walnut shell is available after fruit processing in walnut kernel production centers, yet only a limited amount has been used in the industry [25]. In fact, most of it is discarded as waste material or used as fuel for burning applications [26]. But this causes pollution of the environment, and it also has low utility value. Therefore, it is necessary to find other, better uses for walnut shells. The chemical composition of walnut shells includes hemicellulose (24.4%), α -cellulose (23.9%) and lignin (50.3%) (Fig. 1) [23,27]. As evidenced in the literature each ingredient plays an important role in the properties of the final polymeric product. High lignin content increases the brittleness of the material, while cellulose causes a lowering of that parameter. Moreover, cellulose and hemicellulose contain a large number of polar hydroxyl groups, which are able to initiate interaction between the filler and polymeric matrix. Besides these main components, walnut shells also contain extractives such as tannins, pectins, fats, waxes, gums, essential oils, volatile materials, and ash [28,29]. Walnut shells offer many advantages, such as sufficient reactive functional groups, high carbon content, compatibility with diverse industrial chemicals, good stability, mechanical properties due to the presence of aromatic rings, good rheological and viscoelastic properties making it a potential candidate to be used as a reinforcing material in polymer composites. It has been well documented that walnut shells [30–37] can be employed in different industries as low-cost materials [30,35,36].

The main disadvantage of natural fillers is their hydrophilic character that limits their compatibility with hydrophobic polymer matrices and leads to composites having high water sorption capacity, which ultimately reduces their applicability [38]. In addition to this, pectin and waxy substances cover the reactive functional groups of the fillers and act as a barrier to interlock with the matrix. This results in weakening of the bonding strength at the interface, which in turn leads to dimensional instability, matrix cracking and poor mechanical properties of the composites. Therefore, the removal of moisture from fibers is an essential step for the preparation of composites. Various investigations have been taken out on the modifications of natural fillers to improve their compatibility with the polymeric matrix [39–42]. Several authors have reported different surface modifications for lignocellulosic fillers, which involve chemical modifications, such as acetylation [43], alkalinization [44], benzylation [45], grafting [45] and silane treatment [46].

To the best of our knowledge, walnut shells as a filler in the PU foams have not been used to date. Keeping in view the outstanding properties of the polymeric composites filled with walnut shells, it seems logical to use walnut shells as a reinforcing filler for the new bio-based PU composite foams. The preparation of novel materials from walnut shells products may improve the mechanical properties of the PU materials as well as possibly solve the problem of its waste disposal. This part of the work will be a comprehensive investigation of the effect of chemical

modification of walnut shells on the interfacial phenomena and the properties of PU composite foams. It is expected that the results will permit a better understanding of a relationship between the surface modification of the walnut shell filler and the mechanical and thermal properties of the PU composite foams. To achieve this information, the effect of the walnut shells' treatment on the properties of the PU composites must be clearly defined.

2. Experimental

2.1. Materials

Aromatic polyester polyol with the trade name STEPANPOL PS-2352 with a hydroxyl value of 250 mg KOH/g and functionality of 2.0 was supplied by Stepan Company. Polymeric diphenylmethane-4,4'-diisocyanate (pMDI) containing 31% of isocyanate groups was supplied by Purinova Sp. z o.o. Kosmos 75 and Kosmos 33 produced by Evonik Industries AG were used as catalysts. Silicone surfactant with a trade name TEGOSTAB B8513 was provided by Evonik Industries AG. Pentane and cyclopentane (used in a volume ratio of 50:50 v/v) supplied by Merck KGaA were used as a blowing agent. 3-aminopropyl (diethoxy)methylsilane was provided by Sigma-Aldrich Corporation. Walnut shells (WS) were supplied by a local company from Poland.

2.2. Chemical treatment of WS and preparation of the rigid PU foams

Before adding to the PU system the walnut shells (WS) were mechanically grounded in the laboratory mixer and powdered following by sieving through a sieve with a mesh diameter of 0.01 mm. The ground filler was subsequently dried (100 °C, 24 h) to remove any traces of water contained in the filler. The moisture content (determined by removing moisture and then by measuring weight loss) was maintained at 2–2.5%.

Ethanol/distilled water solution was prepared according to ratio 80:20 by weight. 5 wt% of silane solution was prepared by adding 0.1 g of 3-aminopropyl (diethoxy) methylsilane into the ethanol/distilled water solution for hydrolysis. 10 g of grounded walnut shells were added into silane solution (silane-filler ratio 1:100) and the solution was then stirred continuously for 1 h. The walnut shells were soaked in a silane solution for another 3 h. Then, the treated walnut shells were dried in an oven maintained at 80 °C for 24 h.

Rigid PU foams were synthesized by mixing two-components system. Firstly, polyol, catalysts, surfactant and blowing agents were mixed for 60 s at 4500 RPM. The obtained component A was modified with 1, 2 and 5 wt% of walnut shells (WS) or silanized walnut shells (S_WS). Then, the mixture was additionally mixed for 60 s at 4500 RPM. After that, the isocyanate (component B) was added to component A, and the mixture was intensively mixed for 60 s at 4500 RPM. Finally, the mixture was poured into an open mould and foamed in the vertical direction. All samples were conditioned for 24 h at a temperature of 22 °C and relative humidity of 50%. After that, the samples were cut according to the selected standards and tested. The selected amounts of raw materials for the preparation of PU foams modified with WS and S_WS are presented in Table 1. The stages of foams synthesis are shown in Fig. 2.

2.3. Testing methods

The average size of WS and S_WS was determined by the Dynamic Light Scattering (DLS) method using a Zetasizer NanoS90 instrument (Malvern Instruments Ltd, UK). The dispersion of the WS particles in a polyol dispersion was prepared (0.04 g l⁻¹). The measurement was evaluated at 5 min intervals.

The viscosity of the polyol premixes modified with WS and S_WS was determined according to ISO 2555 using a Viscometer DVII+ (Brookfield, Germany). The measurement was performed in the function of a shear rate (10–100 rpm) in ambient temperature.

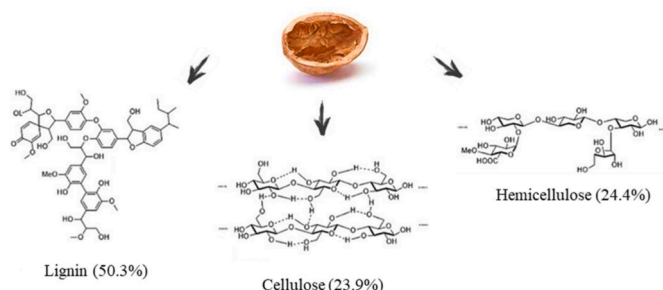


Fig. 1. Chemical composition of walnut shells [23,27].

Table 1
Composition of PU foams modified with WS and S_WS.

| Component | Raw materials | WS_0 | WS_1 | WS_2 | WS_5 | S_WS_1 | S_WS_2 | S_WS_5 |
|--------------------------|-------------------------|--------------------------|------|------|------|--------|--------|--------|
| | | Amount, wt% ^a | | | | | | |
| Component A | STEPANPOL PS-2352 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | Kosmos 75 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| | Kosmos 33 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| | Tegostab B8513 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| | Water | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | Pentane/cyclopentane | 11 | 11 | 11 | 11 | 11 | 11 | 11 |
| Component B | PUROCYN B | 160 | 160 | 160 | 160 | 160 | 160 | 160 |
| Amount, wt% ^b | Filler | | | | | | | |
| | Walnut shells | 0 | 1 | 2 | 5 | 0 | 0 | 0 |
| | Silanized walnut shells | 0 | 0 | 0 | 0 | 1 | 2 | 5 |

^a Parts by weight.

^b In relation to the weight of Component A.

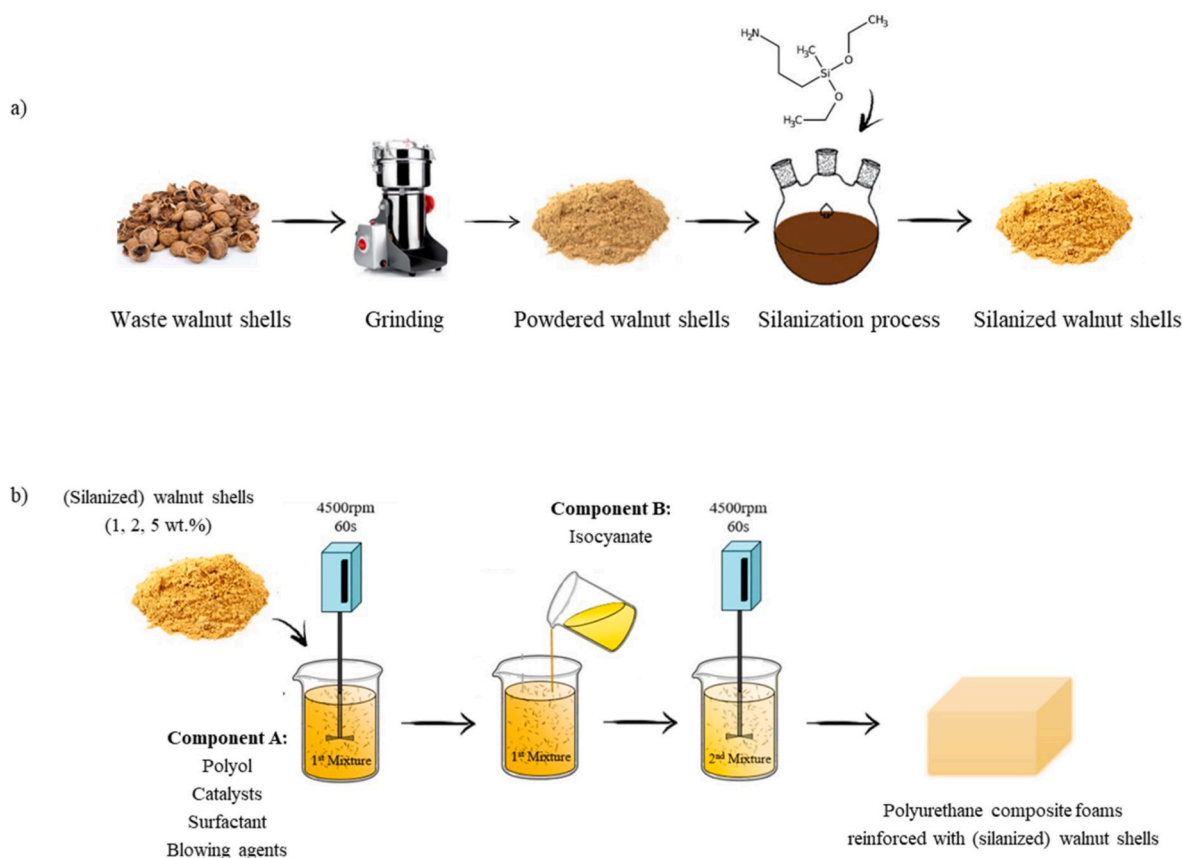


Fig. 2. Schematic representation for the preparation of a) silanized walnut shells and b) PU foams modified with WS and S_WS.

The chemical structure of WS and S_WS was determined by Fourier-transform infrared spectroscopy (FTIR) using Nicolet iS50 FTIR Spectrometer with DGTS/KBr detector (Thermo Fisher Scientific, USA). The measurement was performed for the wavelength range from 3500 to 400 cm^{-1} with a maximum resolution of 4 cm^{-1} . FTIR was performed with a DGTS/KBr detector. The presented FTIR spectrum is an average of 64 individual scans.

The morphology of PU foams was determined by JEOL JSM-5500 LV scanning electron microscopy (JEOL Ltd., USA). The samples were scanned in the free-rise direction at the accelerating voltage of 10 kV and magnification of 50 μm . Statistical analysis of the size distribution of the PU foam cells was calculated based on SEM images using *ImageJ* software (Media Cybernetics Inc. USA).

The apparent density of PU foams was determined as the ratio of sample weight to its volume following ISO 845 standard.

The porosity of PU foams was determined following ISO 4590 standard.

Compressive strength ($\sigma_{10\%}$) of PU composite foams was measured according to ISO 844 standard using Zwick Z100 Testing Machine (Zwick/Roell Group, Germany) at a constant speed of 2 mm min^{-1} and load cell of 2 kN–10% of deformation. PU foams were tested perpendicular and parallel to the foam rise direction.

Flexural strength (ϵ_f) of PU foams was measured according to ISO 178 standard using Zwick Z100 Testing Machine (Zwick/Roell Group, Germany) at a constant speed of 2 mm min^{-1} .

Surface hydrophobicity of PU foams was measured using contact angle goniometer OEC-15EC (DataPhysics Instruments GmbH, Germany) with software module SCA 20.1 μL of water was dropped on the surface of PU samples using a micrometer syringe with a steel needle. The average of 10 measurements was evaluated.

The thermal properties of PU foams were determined by thermogravimetric analysis (TGA) using STA 449 F1 Jupiter Analyzer (Netzsch Group, Germany). The measurement was performed for samples of 10 mg. Samples were heated in an argon atmosphere up to 600 °C. The initial decomposition temperatures, such as $T_{2\%}$, $T_{10\%}$, $T_{50\%}$ and $T_{80\%}$ of mass loss were determined.

Water absorption of PU foams was performed according to ISO 2896. Samples were weighed (m_0) and immersed in distilled water for 24 h (water depth of 1 cm). After this time, PU foams were removed from the water and the excess of water was absorbed by filter paper. PU samples were weighed again (m) and the water absorption was calculated according to equation (1).

$$WA = \frac{m - m_0}{m_0} \quad (1)$$

3. Results and discussion

3.1. Rheological behavior

Particle size is an important parameter that determines the proper dispersion of particles in the polymer matrix. Too small particles tend to agglomerate, forming large aggregates in the PU matrix [47]. On the other hand, too large particles can disturb the foaming process leading to the formation of materials with a heterogeneous structure [48]. The particle size of the fillers was measured in a polyol dispersion (1 g/100 g of polyol). The measurements were done with the time interval between every measurement. The particle size distribution of the sample measured after 3, 6, 9, 12 and 15 min of ultrasonic mixing are given in Fig. 3. The results presented in Fig. 3a indicates that the particles of WS tend to agglomerate. After the 15 min, the size of WS particles increases from 700 nm to 3 μm . The intensity of the peak decreases from 27 to 21% indicating a lower content of particles. Different behavior is observed for S_WS (Fig. 3b). No difference between the particle size is observed after 3 and 15 min. The particle size ranges from 600 nm to 3 μm . This indicates that the silanization of WS can improve the dispersion of filler particles in the polyol system and prevent their agglomeration.

The dynamic viscosity of the PU mixture affects the foaming process and further properties of PU foams [49]. The results of the dynamic viscosity of PU systems containing WS and silanized WS are presented in

Table 2. In both cases, the dynamic viscosity increases significantly as the filler content increases from 1 to 5 wt%. This effect is more prominent in the case of the PU system modified with WS. It can be seen that the dynamic viscosity of the PU system with non-treated WS particles is almost twice as high as that with silanized WS. It indicates that the effect of the filler on the pseudo-plasticity behavior becomes more significant for systems modified with non-treated WS, leading to highly non-Newtonian behavior. The difference between the dynamic viscosity of the modified systems indicates that the silanization of WS particles breaks the formation of larger agglomerates and distributes the filler particles more evenly in the PU system. The dynamic viscosity of all modified systems decreases dramatically at the beginning of the shearing. Once the filler molecules reach the best possible arrangement, the value of viscosity becomes relatively stable. Such dependence is typical for non-Newtonian fluids and is well known for PU systems modified with different kinds of organic and inorganic fillers [50,51].

The schematic representation of the silane treatment of WS is shown in Fig. 4. The FT-IR spectra of WS and S_WS are presented in Fig. 5. Bands at 837, 1030, 1460 and 2950 cm^{-1} are selected as stable bands of cellulose and lignin of WS filler and they correspond to C-H vibration of the aromatic nucleus [52]. Bands at 740, 1230, 1090, 1330 and 3340 cm^{-1} are selected as characteristic bands for silanized WS [53]. As a result of WS silanization, new bands at ~ 740 and ~ 1230 cm^{-1} assigned to Si-CH₃ vibration are appeared [53]. The occurrence of the aforementioned peaks confirms the formation of chemical bonds between WS and selected silane. The silanization reaction is confirmed by the presence of a band at 1330 cm^{-1} which is assigned to Si-O-Si stretching vibration. An intense peak at 1090 cm^{-1} is assigned to Si-O vibration.

Table 2

Dynamic viscosity of PU systems modified with WS and S_WS.

| | Dynamic viscosity η [mPa·s] | | | | |
|--------|----------------------------------|--------|--------|--------|---------|
| | 10 RPM | 20 RPM | 30 RPM | 40 RPM | 100 RPM |
| WS_0 | 650 | 330 | 270 | 160 | 120 |
| WS_1 | 1050 | 820 | 750 | 550 | 450 |
| WS_2 | 1540 | 1090 | 960 | 840 | 510 |
| WS_5 | 1990 | 1450 | 1080 | 950 | 760 |
| S_WS_1 | 690 | 520 | 360 | 190 | 130 |
| S_WS_2 | 890 | 830 | 740 | 660 | 320 |
| S_WS_5 | 1050 | 1010 | 990 | 840 | 540 |

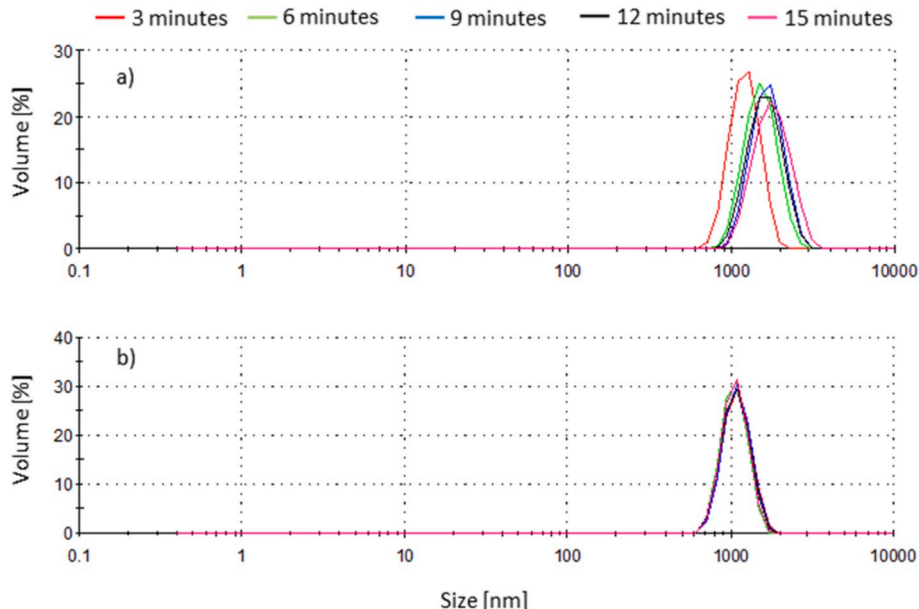


Fig. 3. The particle size distribution of a) WS and b) S_WS measured after 3, 6, 9, 12 and 15 min of ultrasonic mixing.

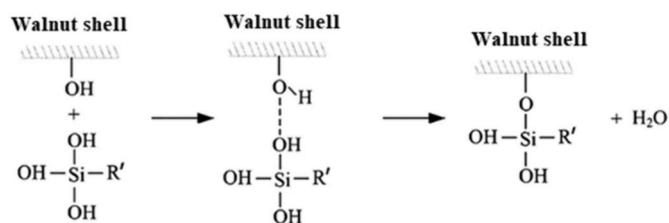


Fig. 4. Schematic representation of silane treatment of WS.

The intense band at 3340 cm^{-1} may be attributed to the hydroxyl group of silanized WS [53,54].

3.2. Foaming characteristics of PU foams

The influence of different contents of WS on the foaming process was investigated by measuring characteristic times, such as start, growth and tack-free time. The results presented in Table 3 indicate that the addition of WS and S_WS affects the foaming kinetics of PU foams. Compared to controlled WS_0, the addition of each amount of WS and S_WS increases the start and extension times, which can be explained by different factors. Previous studies have stated that nano- and micro-sized particles can act as nucleating centers during the nucleation process resulting in the formation of a greater number of air bubbles. Moreover, the reactive groups of filler, such as hydroxyl groups can react with highly reactive isocyanate groups and affects the proper stoichiometry of polyurethane synthesis [6,55–57]. Due to this, the number of isocyanate groups remaining to react with water is reduced and the amount of produced CO_2 is reduced. On the other hand, further growth and expansion of formed cells are additionally limited by increased viscosity of modified PU systems. The mobility of the molecules is reduced, which affects the polymerization kinetic of PU synthesis. The rate of isocyanate conversion at the early stage of the reaction is decreased leading to prolonged cream and growth times [58,59]. Comparing PU systems modified with WS and S_WS, the highest values of processing times are observed for PU systems modified with un-treated WS. This indicates that the silanization of WS affects the chemical interaction between silanized WS and isocyanate during the foaming step. Similar results have been also reported in previous studies [60,61].

The results of processing times are also in agreement with the results of maximum temperature during the PU synthesis. Based on the results presented in Table 3, the incorporation of WS and S_WS decreases the reactivity of the PU system. For example, the value of T_{max} decreases from 125 to 105 and $116\text{ }^\circ\text{C}$ with the addition of 5 wt% of WS and S_WS, respectively. Previous studies have shown that such a decrease in the case of PU foams modified with the addition of organic filler, may be related to the fact that fillers can absorb some of the heat generated during the synthesis of PU materials [62–65]. A similar explanation may be found in our research.

3.3. Cellular structure and apparent density of PU foams

The cellular structure of PU foams modified with WS and S_WS is shown in Fig. 6 and Fig. 7. As observed in Fig. 6a, the structure of WS_0 is nearly uniform and high content of closed-cells is observed. The incorporation of WS leads to the formation of a more inhomogeneous structure with a greater number of open-cells. As presented in Fig. 6b and c the incorporation of 1 and 2 wt% of WS do not affect the structure of PU foams, however, with the addition of 5 wt% of WS the structure becomes less uniform and the number of open cells is increased. The porosity of PU foams decreases from 90.8 to 87.5% as the WS content increases from 1 to 5 wt% (Table 4). The possible explanation of structure disintegration may be found in interphase interaction between WS and PU matrix which disrupts the foaming process and results in the formation of a more defective structure [66]. Moreover, as presented in Fig. 7, WS particles are not completely built in the PU matrix, but, some bigger aggregates are located in empty cells. This indicates poor interfacial adhesion between the WS surface and the PU matrix, which in turn leads to cell collapse and the formation of open pores in the foam structure [8]. PU foams modified with S_WS are characterized by a more regular structure with a lower number of open cells comparing to PU foams modified with un-treated WS. The overall structure of PU foams modified with S_WS in each amount seems to be similar to the structure of WS_0. It can be concluded that the silanization of WS can enhance the formation of more homogenous cells. It can be also seen that the modification of the rigid PUR foams with S_WS does not affect the porosity and all PU foams are characterized by a high value of this parameter (*ca.* 90%). This indicates that the silanization of WS improves the interfacial adhesion between WS particles and PU matrix leading to more effective formation of PU structure. The higher cross-linking degree of PU foams modified with S_WS may prevent disruption of the cells during the foaming process. On the other hand, the incorporation of compatible S_WS can form new edges which can encapsulate blowing agents as well as volatile substances released from the filler, thereby increasing the content of closed cells.

In both cases, the incorporation of WS and S_WS reduces the cell size of PU foams. Previous studies have shown, that during the foaming process, micro and nano-sized particles can act as additional centers,

Table 3
Foaming parameters of PU foams modified with WS and S_WS.

| Sample | Temperature [°C] | Cream time [s] | Extension time [s] | Tack-free time [s] |
|--------|------------------|----------------|--------------------|--------------------|
| WS_0 | 125 | 43 ± 4 | 270 ± 10 | 340 ± 12 |
| WS_1 | 120 | 50 ± 2 | 330 ± 10 | 335 ± 11 |
| WS_2 | 116 | 57 ± 1 | 358 ± 11 | 270 ± 10 |
| WS_5 | 105 | 68 ± 2 | 380 ± 10 | 270 ± 10 |
| S_WS_1 | 122 | 48 ± 2 | 312 ± 12 | 320 ± 10 |
| S_WS_2 | 120 | 51 ± 4 | 345 ± 10 | 265 ± 11 |
| S_WS_5 | 116 | 54 ± 3 | 360 ± 10 | 260 ± 10 |

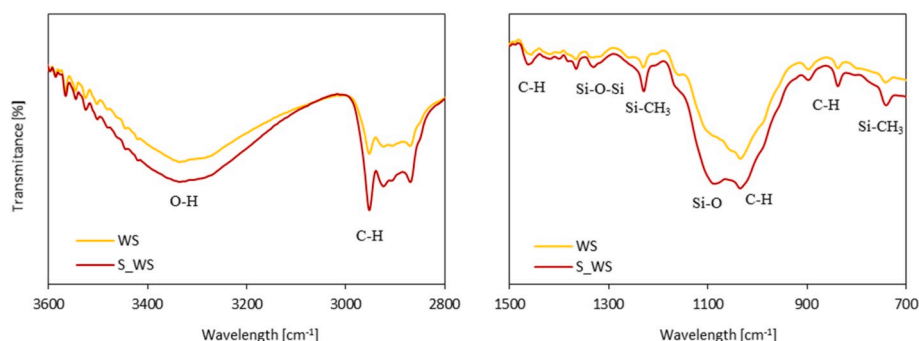


Fig. 5. FTIR spectra of a) WS and b) S_WS.

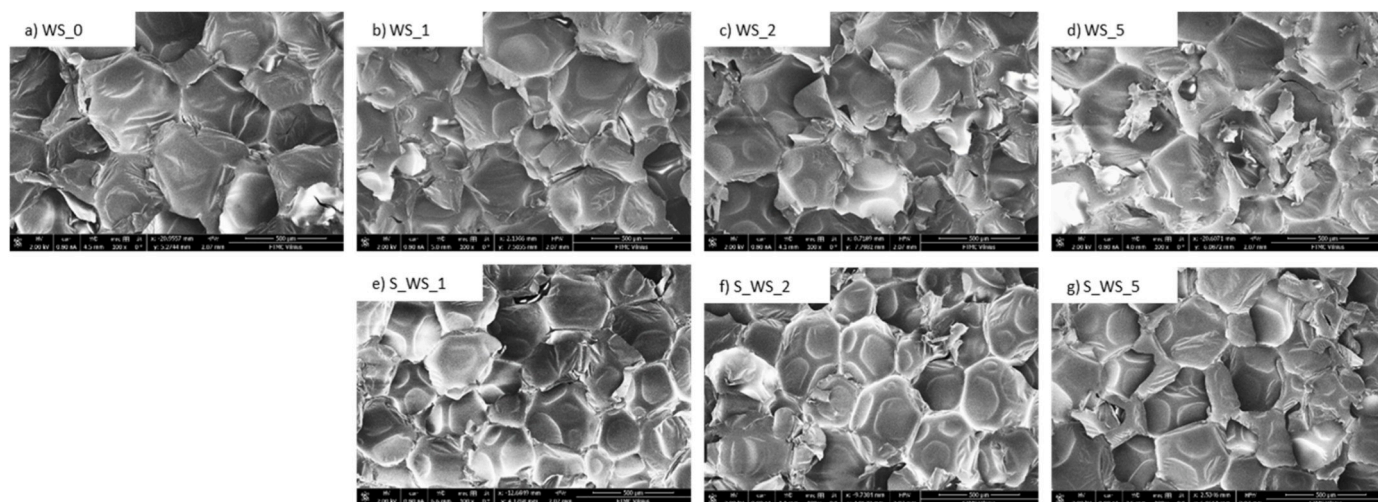


Fig. 6. The microstructure of PU foams modified with WS and S_WS (x 100).

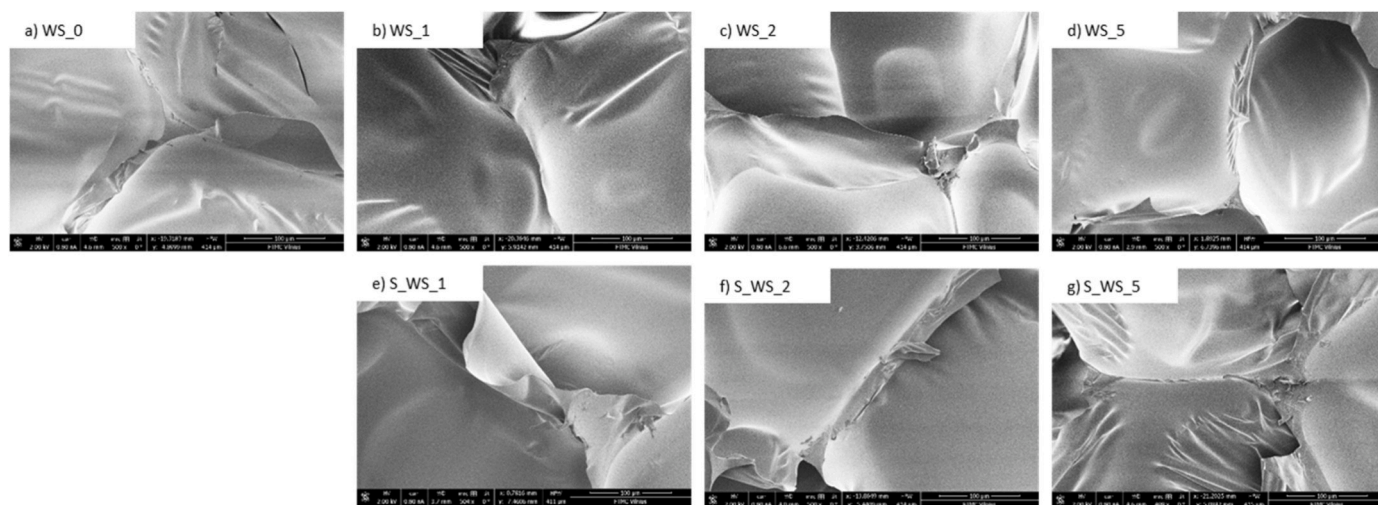


Fig. 7. The microstructure of PU foams modified with WS and S_WS (x 500).

Table 4

Structural parameters and thermal conductivity results of PU foams modified with WS and S_WS.

| Sample | Cell size [μm] | Apparent density [kg m^{-3}] | Porosity [%] | Thermal conductivity (after 1 day) [$\text{W m}^{-1} \text{K}^{-1}$] | Thermal conductivity (after 7 days) [$\text{W m}^{-1} \text{K}^{-1}$] |
|--------|-----------------------------|---|--------------|--|---|
| WS_0 | 474 \pm 9 | 39 \pm 1 | 92.1 | 0.025 | 0.035 |
| WS_1 | 392 \pm 8 | 40 \pm 2 | 90.8 | 0.025 | 0.034 |
| WS_2 | 374 \pm 7 | 42 \pm 1 | 90.2 | 0.027 | 0.034 |
| WS_5 | 335 \pm 8 | 46 \pm 1 | 87.5 | 0.028 | 0.036 |
| S_WS_1 | 457 \pm 9 | 39 \pm 2 | 92.3 | 0.023 | 0.03 |
| S_WS_2 | 450 \pm 8 | 40 \pm 2 | 93.1 | 0.024 | 0.031 |
| S_WS_5 | 417 \pm 8 | 42 \pm 3 | 93.4 | 0.026 | 0.030 |

affecting the rheological surrounding and changing the nucleation mode from homo- to heterogeneous [8]. The reduced energy of nucleation promotes the formation of smaller cells. This effect is more prominent in the case of PU foams modified with S_WS. It can be also concluded that the silanization of WS leads to the more hydrophobic character of WS particles, leading to a more intense nucleation process and reducing the average size of the cells [19,67,68]. As presented in Fig. 8, the incorporation of S_WS results in a more uniform structure and smaller cells as compared to PU foams modified with un-treated WS. In the case of PU foams modified with WS most of the pores are in the range of 300–350 nm, while for WS the pore diameters are between 300 and 800 nm.

The cellular structure of porous materials affects the apparent density. It can be seen that with increasing WS and S_WS amount, the apparent density varies considerably (Fig. 9). Compared to WS, the apparent density increases by ~ 15 and $\sim 8\%$, for samples WS_5 and S_WS, respectively. An increased apparent density of PU foams modified with WS and S_WS is mostly connected with the role of solid filler particles during the foaming process. As mentioned previously, the incorporation of WS and S_WS results in greater viscosity of the PU systems and limited expansion of bubble cells, increasing the apparent density of PU foams. On the other hand, the apparent density is additionally enhanced by the density of the fillers (the density of WS is ca. 1.2 g cm^{-3}). Based on the results of apparent density, it can be concluded that

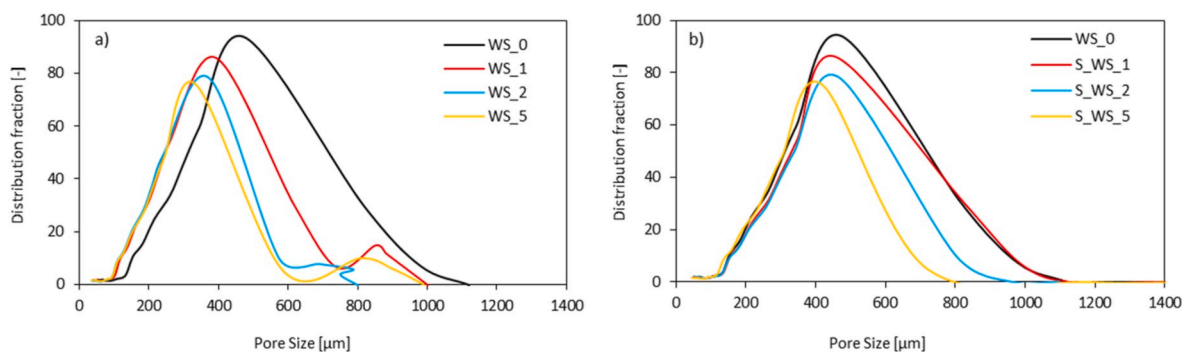


Fig. 8. The cell size distribution of PU foams modified with a) WS and b) S_WS.

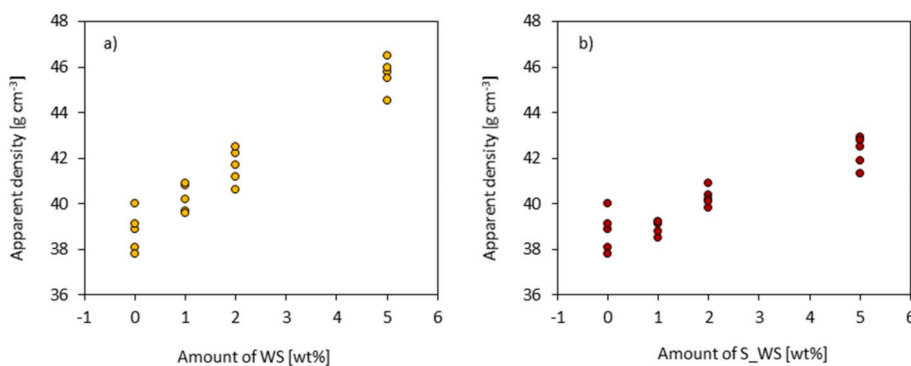


Fig. 9. The impact of a) WS and b) S_WS on the apparent density of PU foams.

the silanization of WS improves the compatibility between WS particles and the PU matrix. A high number of functional groups attached to WS particles enable an efficient interfacial adhesion leading to chemical interaction and increased cross-link density of the resulted foams (Fig. 10). Therefore, the value of apparent density is reduced, as compared to PU foams modified with untreated WS.

3.4. Mechanical performance of PU foams

The mechanical properties of PU foams are dependent on the apparent density. Previous studies have shown that the type of filler, particle's size as well as surface modification and interaction with the PU matrix have the greatest impact on the mechanical performance of the obtained materials [69]. Therefore, the impact of WS and S_WS on compressive strength, flexural strength, and impact strength was evaluated.

The results of compressive strength ($\sigma_{10\%}$) are presented in Fig. 11. Compared to WS₀, the value of $\sigma_{10\%}$ increases by $\sim 3\%$ for samples

modified with 1 wt% of WS. An insignificant deterioration in $\sigma_{10\%}$ is observed for samples filled with 2 and 5 wt% of WS – the value of $\sigma_{10\%}$ decreases by ~ 3 and $\sim 11\%$. PU foams modified with S_WS exhibit better mechanical properties as compared to their WS counterparts, which suggests that not only apparent density but also chemical structure and foam morphology affect compressive strength. For example, the incorporation of 1 wt% of S_WS results in improvement of $\sigma_{10\%}$ by $\sim 18\%$ as compared to WS₀. Such dependence may be explained in terms of characteristic features of their structure. As shown in Fig. 6, PU foams modified with WS are characterized by a more uniform structure and a higher number of closed-cells compared to PU foams modified with untreated WS. This results in the better mechanical behavior of PU foams.

The results presented in Fig. 11 indicate that samples with a higher density are characterized by lower values of $\sigma_{10\%}$. This may be explained by the morphology of PU foams. As shown in Fig. 6, samples modified with lower content of the fillers possess closed-cell structure, which provides superior support to withstand the compressive load. Reinforcing effect can be also provided by interfacial adhesion between WS

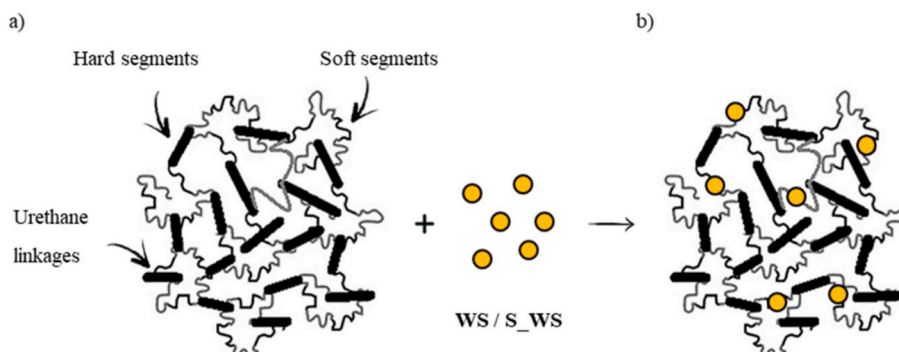


Fig. 10. The effect of WS on the cross-linking of PU foams: a) without and b) with the addition of WS.

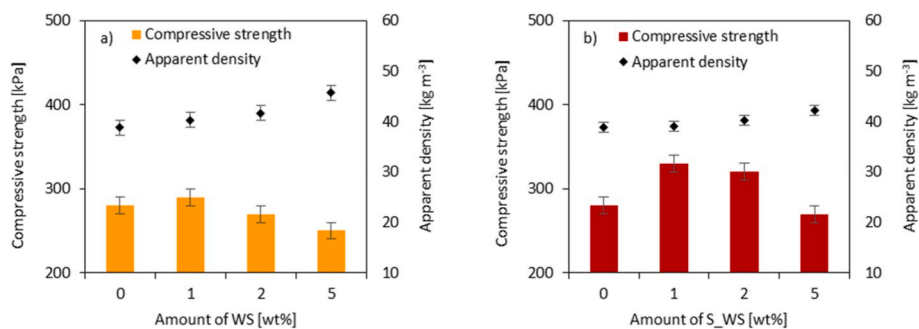


Fig. 11. The impact of a) WS and b) S_WS on the compressive strength of PU foams.

particles located in the cell struts, and PU matrix, which facilitates the stress transfer. At higher loadings of fillers, the overall structure of PU foams become less uniform, since fillers particles can go through the cells damaging their structure and reducing the crosslinking density of the PU matrix. Because of this, with increasing fillers content the structure of the modified PU foams becomes more porous with a greater content of open cells, which deteriorates the mechanical properties of the materials, even though the density increased due to the addition of the fillers. Also, it should be pointed out, that fillers used in a large amount exhibit a high tendency to agglomerate, which in turn leads to the microphase separation of the cellular structure and promotes the failure of the foams under the compressive load. Because of the many voids present in the structure of the PU foams and non-uniform distribution of the filler's particles, the mechanical properties are reduced. A similar trend has been observed in other studies as well [70–73].

The incorporation of WS influences flexural (σ_f) and impact strength of PU foams (Fig. 12 and Fig. 13). Compared to WS_0 the aforementioned properties are improved, however, with increasing filler content the mechanical properties tend to decrease. In the case of PU foams modified with un-treated WS, the greatest improvement of the mechanical properties is observed with the addition of 1 wt% of WS. Comparing to WS_0, the σ_f increases by ~5%, while the impact strength increases by ~2%, respectively. Further addition of WS decreases the tensile strength by 5% and impact strength by 17% for PU foams modified with 5 wt% of WS. Previous studies have shown that the solid particles of the embedded filler act as reinforcing centers and generate localized stresses under the action of a loading force. When the growing crack encounters filler particles located in the PU matrix, energy dissipation occurs. An excess of solid particles and aggregates acts as additional stress concentration centers that promote cracking of the sample leading to the deterioration of the mechanical properties [74,75].

The results of the flexural strength of PU foams modified with silane treated WS are presented in Fig. 12. From the obtained results, the flexural strength of the PU foams is changed dramatically after the silane treatments. The flexural strength of PU foams modified with 1–5 wt% of silane treated WS increased by 10, 30 and 35%, respectively, with respect to controlled WS_0, which has a flexural strength of 400 kPa. It

indicates that the flexural strength of PU foams modified with the silane treated WS is significantly improved compared with that of the controlled WS_0. A similar trend is observed in the case of impact strength (Fig. 13). After the silane treatment, the impact strength of PU foams modified with 1–5 wt% of silanized WS is increased by 5, 12 and 19% when compared with controlled WS_0. The above findings indicate that the silanization treatment of WS could improve the tensile and impact strength properties of the PU foams. It is primarily due to that the silane coupling agents can act as a bridge and then emphasize the adherence of the filler and PU matrix through chemical bonds, which considerably improve the interfacial interaction and thus enhance the flexural and impact strength [76]. Moreover, the additional –OH groups present on the surface of the WS particles may promote the formation of better mechanical interlocking between the filler and PU matrix, and loose structure of WS can absorb more impact energy, which also results in enhancing the mechanical properties of the PU foams.

3.5. Thermal conductivity of PU foams

Thermal conductivity is the most important property of PU foams [62]. The total value of thermal conductivity coefficient (k) consists of λ_{gas} , λ_{solid} , $\lambda_{\text{radiation}}$ and $\lambda_{\text{convection}}$ [77]. Thermal conductivity of PU foams modified with WS and S_WS was measured after 1 day and 7 days after the foams synthesis. The results presented in Table 4 indicate that the addition of 1 wt% of WS increases the value of thermal conductivity by ~4%. Further addition of WS increases thermal conductivity by ~13 and 17% for PU foams modified with 2 and 5 wt% of WS. Contrary results are observed for PU foams modified with S_WS. It is observed that S_WS has almost no effect on the thermal insulating properties of PU foams. The thermal conductivity does not change for PU foams modified with 1 and 2 wt% of S_WS and increases slightly with the further addition of S_WS. Such changes in thermal conductivity are mostly related to changes in porosity and the size of cells. Another possible mechanism is related to the different polarities of filler and polymer, which leads to a weak interface permeated by micro-pores capable of encapsulating blowing gas, especially for fillers with poor compatibility. This dependence is more prominent for PU foams modified with un-treated WS. As

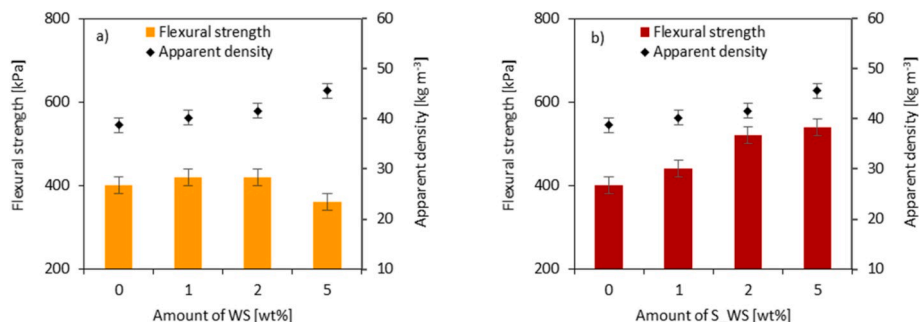


Fig. 12. The impact of a) WS and b) S_WS on the flexural strength of PU foams.

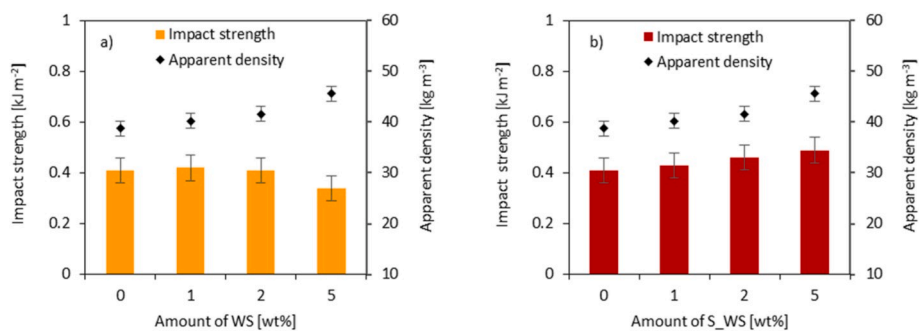


Fig. 13. The impact of a) WS and b) S_WS on the impact strength of PU foams.

mentioned earlier, WS particles tend to agglomerate, leading to some destruction of the cell structure and higher content of open cells. More broken cell walls in the structure of PU foams modified with WS leads to an increase of $\lambda_{\text{convection}}$. The silanization of WS leads to better adhesion between the filler surface and PU matrix, which results in a more uniform structure and a greater porosity when compared with PU foams modified with WS. The well-dispersed S_WS particles located in the cell struts prevent heat transfer by block radiation, acting as diffusion barriers. This, in turn, suppresses thermal radiation through processes of scattering or absorption improving the insulating properties of resulting PU foams [78]. After 7 days, the thermal conductivity of PU foams modified with WS ranged from 0.034 to 0.036 $\text{W m}^{-1} \text{K}^{-1}$, while for PU foams with S_WS the values ranged from 0.030 to 0.031 $\text{W m}^{-1} \text{K}^{-1}$. The obtained results are comparable to the thermal conductivity of commercial insulation materials, such as polystyrenes or mineral wool. Also, according to ASTM E170, all modified PU foams exhibit lower thermal conductivity than the maximum thermal conductivity required for commercial thermal insulation boards. Similar results have been obtained in previous works [4,63]. For example, Kairyte et al. have shown that the addition of paper waste filler decreases the value of thermal conductivity since the filler's particles work as a gas barrier that decreases the CO_2 diffusion rate through polyurethane matrix [79]. Kurańska et al. [80] have shown that despite the high content of the closed cells the coefficient of thermal conductivity increased for samples modified with basalt waste in the amount of 3–40 wt%, however, the value of the thermal conductivity (ca. 0.025 $\text{W m}^{-1} \text{K}^{-1}$) was still considered at an acceptable level from an industrial point of view. An analog trend has been observed in the case of our study as well.

3.6. Contact angle and water absorption of PU foams

Water absorption of porous materials depends mostly on the cellular structure of PU foams (the content of open and closed cells) and the hydrophobic/hydrophilic character of the additives [66–68]. The results presented in Fig. 14 indicate that with increasing the concentration of WS the water uptake of PU slightly increases. This may be connected with the more inhomogeneous open-cell structure of modified foams.

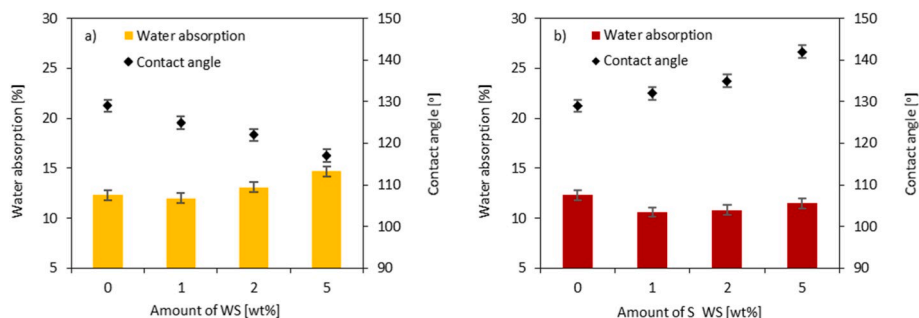


Fig. 14. The impact of a) WS and b) S_WS on contact angle and water absorption of PU foams.

Based on SEM images (see Fig. 6) the addition of WS results in the opening of the foam cells. Also, WS particles tend to agglomerate, which results in the creation of paths available to the water molecules to penetrate the foam structure. The incorporation of WS with hydrophilic nature affects the water uptake as well. Because of this, the character of PU foams modified with WS becomes more hydrophilic, which is also confirmed by the reduced value of the contact angle. Water absorption of PU foams modified with S_WS is decreased what can be connected with the hydrophobic character of S_WS. The reduced water absorption of PU foams modified with S_WS may also be associated with a more homogeneous structure of PU foams and a greater number of smaller cells that are not able to store water [62].

3.7. Dynamic mechanical analysis of PU foams

The dynamic mechanical results of PU foams are presented in Fig. 15 and Fig. 16. The addition of WS and S_WS affects the value of the glass transition temperature (T_g). Compared to WS_0, PU foams modified with WS and S_WS are characterized by a higher value of T_g , however with increasing the concentration of WS and S_WS the values of T_g slightly decrease. Comparing both series of modified PU foams, the addition of S_WS results in higher values of T_g . Based on this, it can be concluded that PU foams modified with S_WS are characterized by higher cross-linking density as compared to PU foams modified with WS. Moreover, as shown in the SEM (Fig. 6), well-dispersed particles of S_WS can generate some interlocks between the cells. The more complex PU foam structure limits the mobility of PU chains and requires more energy to reach the glass transition temperature.

According to the results presented in Fig. 16, it is seen that PU foams modified with S_WS are characterized by higher storage modulus (E') as compared to PU foams modified with un-treated WS. It can be concluded that the addition of S_WS significantly increases the cross-linking density of PU foams. The stiffness of the PU matrix is also enhanced due to the presence of the solid particles of the fillers. Moreover, the viscosity of the modified PU systems is also enhanced (see Table 2), which reduced the mobility of the polymer chains, leading to the higher stiffness of the polymer structure. In the case of PU foams modified with WS, the value

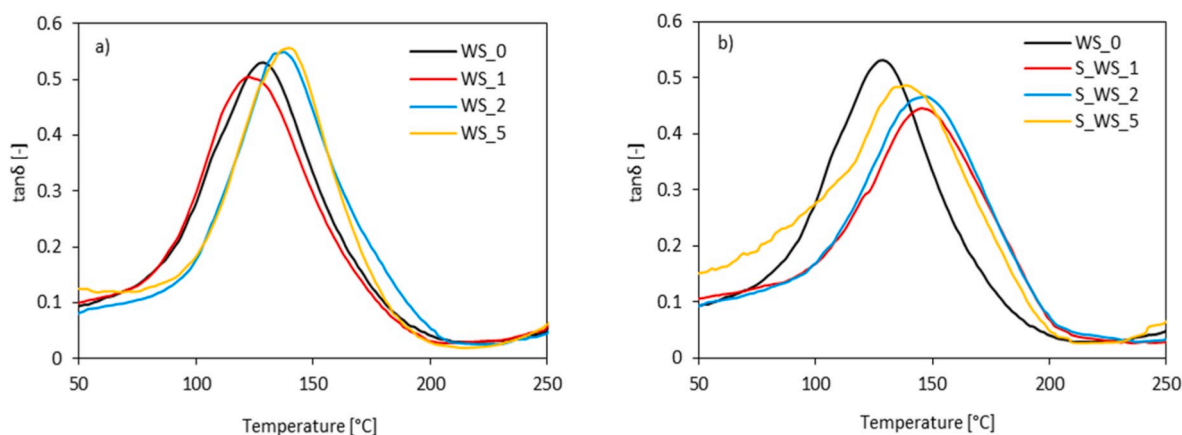


Fig. 15. Thermomechanical properties of PU foams obtained by DMTA: the effect of a) WS and b) S_WS on $\tan\delta$.

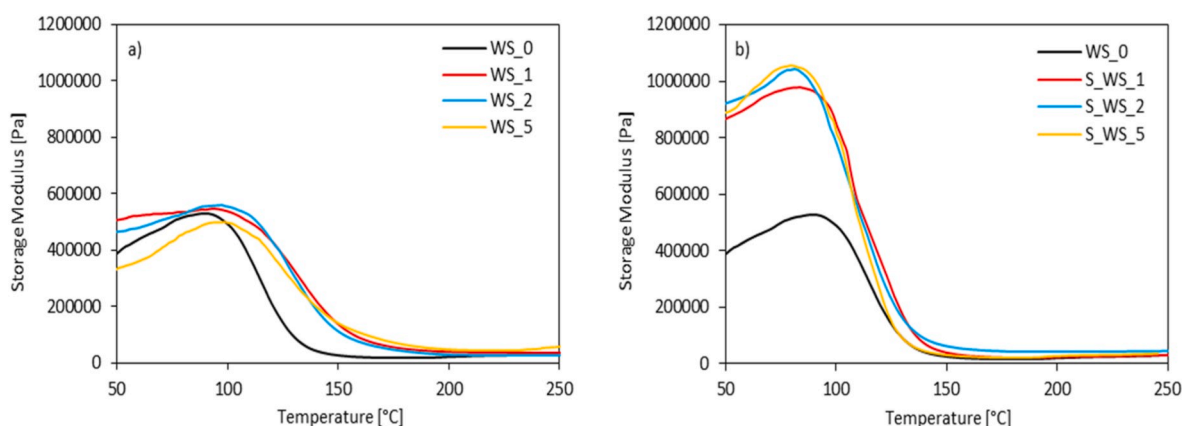


Fig. 16. Thermomechanical properties of PU foams obtained by DMTA: the effect of a) WS and b) S_WS on storage modulus.

of E' slightly decreases as the filler content increases, which indicates that the addition of WS above a certain optimal level leads to PU foams with a more flexible structure. This decrement of the E' is the most prominent in the temperature around 100 °C which is related to the hard segment domains and aromatic urethane groups of poly (ether-urethane) phase. An excess of WS particles in the PU structure may disrupt the crosslinking of the PU matrix, which is already high cross-linked, even without additional groups of the fillers. During the synthesis of PU foams, the viscosity of the polyol premixes, modified with WS is also increased and a high tendency to the agglomeration of the filler's particles is observed. Thus, the interaction between the fillers and polymer matrix can be limited. Moreover, the aggregation of WS particles may reduce the efficiency of the reaction, leading to the weakened structure and more mobile polymeric network. In the case of PU foams modified with S_WS the deterioration of E' is significantly reduced. The highest thermomechanical stability is observed for PU foams modified with the highest content of S_WS, such as 5 wt%. This confirms that the silanization of WS results in better dispersion of WS particles in the PU matrix and improved thermomechanical stability of the PU foams. A similar trend was observed in the case of PU foams modified with basalt waste filler [69]. The authors have shown that increased thermomechanical stability of PU foams filled with low amounts of filler (3–9 wt%) is a complex effect of reinforcing the efficiency of the filler. A further increase in the filler content (up to 40 wt%) causes negative changes in the cellular structure resulting in reduced thermomechanical stability of PU foams.

3.8. Thermogravimetric analysis (TGA) of PU foams

Thermogravimetric analysis (TGA) was used to evaluate the impact of WS and S_WS on the thermal properties of PU composite foams. TG profiles for all PU foams are presented in Fig. 17 and Fig. 18. Thermal degradation parameters are presented in Table 5. Characteristic temperatures were defined as $T_{2\%}$ (temperature corresponding to 2% of weight loss), $T_{10\%}$ (temperature corresponding to 10% of weight loss), $T_{50\%}$ (temperature corresponding to 50% of weight loss) and $T_{80\%}$ (temperature corresponding to 80% of weight loss). Char residues were defined at 600 °C.

Compared to the control WS_0, there are no obvious changes in TGA curves after the addition of WS and S_WS. Some differences are noticed between the characteristics temperatures. The addition of WS and S_WS results in a higher value of $T_{2\%}$. This indicates that the release of volatile products from the PU matrix increases with the addition of WS and S_WS. Taking into account that, the volatile products of biodegradable WS tend to release at lower temperatures, the higher values of $T_{2\%}$ may be connected with partial crosslinking between filler's functional groups and isocyanate groups (-NCO). This effect is more prominent for PU foams modified with S_WS and it increases with the addition of the filler. Moreover, PU foams modified with WS and S_WS exhibit slower thermal degradation in the temperature of 230–262 °C, which corresponds to the dissociation of the urethane bond. This indicates the higher crosslinking degree of PU foams modified with WS and S_WS. As presented in Table 5, compared to WS_0, the addition of 5 wt% of WS and S_WS, increased $T_{10\%}$ by 10 and 28 °C, respectively. The improvement of thermal stability of PU foams modified with WS and S_WS can be confirmed based on the results of $T_{50\%}$, which correspond to the structural decomposition

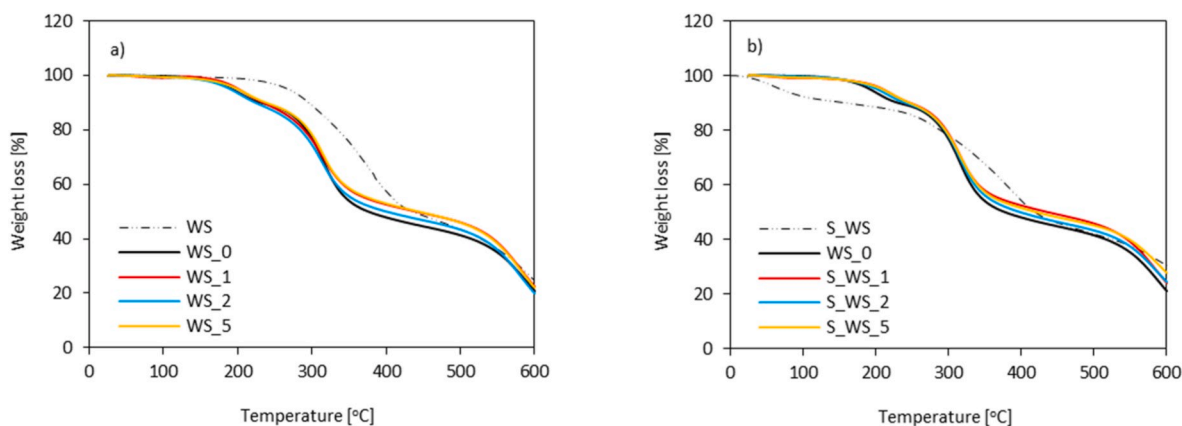


Fig. 17. TGA curves for PU foams modified with a) WS and b) S_WS.

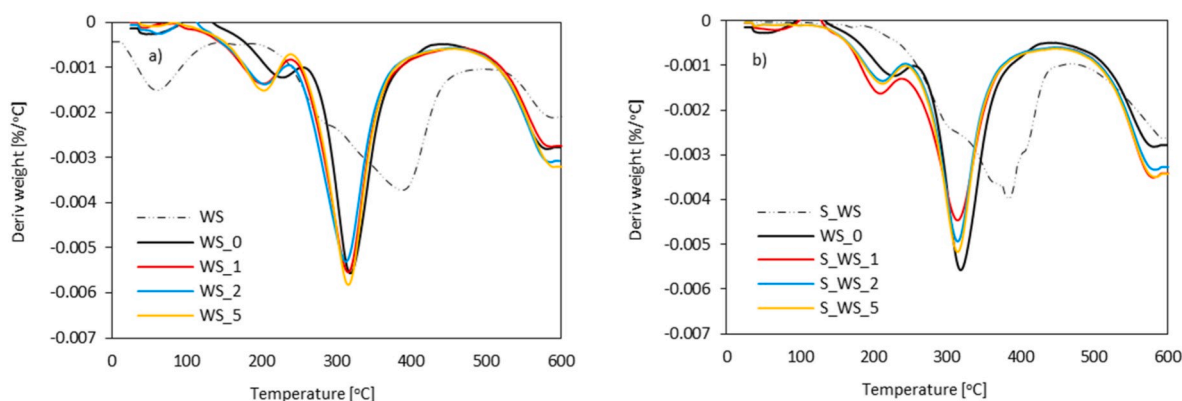


Fig. 18. DTG curves for PU foams modified with a) WS and b) S_WS.

Table 5

The results of TGA and DTGA analysis.

| Sample codes | T _{2%} [°C] | T _{10%} [°C] | T _{50%} [°C] | T _{80%} [°C] | Char residue (at 600 °C) [%] | DTG [°C] | DTG [%/min] |
|--------------|----------------------|-----------------------|-----------------------|-----------------------|------------------------------|----------|-------------|
| WS_0 | 119 | 230 | 326 | 480 | 22.1 | 320 | 0.055 |
| WS_1 | 124 | 240 | 330 | 484 | 21.8 | 321 | 0.055 |
| WS_2 | 120 | 241 | 336 | 494 | 24.5 | 319 | 0.054 |
| WS_5 | 126 | 240 | 339 | 495 | 24.8 | 318 | 0.050 |
| S_WS_1 | 135 | 255 | 340 | 498 | 27.8 | 325 | 0.044 |
| S_WS_2 | 134 | 256 | 346 | 520 | 28.1 | 320 | 0.049 |
| S_WS_5 | 140 | 258 | 361 | 509 | 29.9 | 319 | 0.051 |

of organic chains (mainly urea groups). The difference in T_{50%} between controlled WS₀ foams and PU foams modified with WS is almost constant, which confirms that the addition of even a large amount of WS does not affect the chemical structure of the resulting PU foams and indicates a high performance of WS. Compared to the PU foams modified with S_WS, the composites containing S_WS are more thermally stable. The second degradation stage of the PU modified with S_WS starts at 330–339 °C, while the PU foams modified with S_WS start to degrade in the range of 340–361 °C. This indicates that compared with PU foams modified with S_WS are characterized by higher molecular rigidity compared to controlled WS₀ and their WS-modified counterparts. The amount of char residue for the controlled PU foams is 22.1% at 600 °C. For the WS-modified PU foams, the amount of char residue increases gradually with the WS content, up to 24.8% gain for PU foams with 5 wt % of WS. Similar result is observed in the case of PU foams modified with S_WS – the char residue increases even up to 29.9% for PU sample with

the addition of 5 wt% of S_WS. It seems that S_WS may act as a radical scavenger during the thermal degradation process, leading to higher char residue as a consequence.

3.9. FTIR analysis of PU foams

The FTIR spectra of PU foams modified with WS and S_WS are shown in Fig. 19a and b, respectively. The urethane moieties of PU foams are confirmed by the presence of the main characteristic absorption bands. They are well represented by the characteristic $\nu(\text{C}=\text{O})$ vibration region (1700–1770 cm^{-1}) [81,82], $\nu(\text{N}-\text{H})$ stretching vibration region (3200–3600 cm^{-1}) [83,84] and $\delta(\text{N}-\text{H})$ bending vibration absorption band at 1590 cm^{-1} [85]. The relative position of the main characteristic bands for various functional groups in the modified foams is similar to that of the reference foams outcome. This indicates that the chemical structure of modified PU foams stayed unchanged in the presence of NS and NS suspension. By comparing the spectra, some changes are observed only in the intensity of the characteristic bands, which were appointed from the FTIR spectra of all tested materials.

In both cases, the band intensity of the carbonyl group $\nu(\text{C}=\text{O})$ from free urethane at a wavenumber of 1720 cm^{-1} is increased by increasing the content of WS and S_WS. A possible explanation may be related to the fact that the OH groups of WS and S_WS can react with the isocyanate groups, leading to urethane formation. Because of this, an increased number of urethane links in the modified PU foams can be observed. This effect is more prominent in the case of PU foams modified with S_WS.

Also, the band intensity of residual isocyanate groups $\nu(-\text{N}=\text{C}=\text{O})$ at a wavenumber of 1720 cm^{-1} is decreased by increasing the content of the filler. As shown in the FTIR spectrum, PU foams modified with S_WS

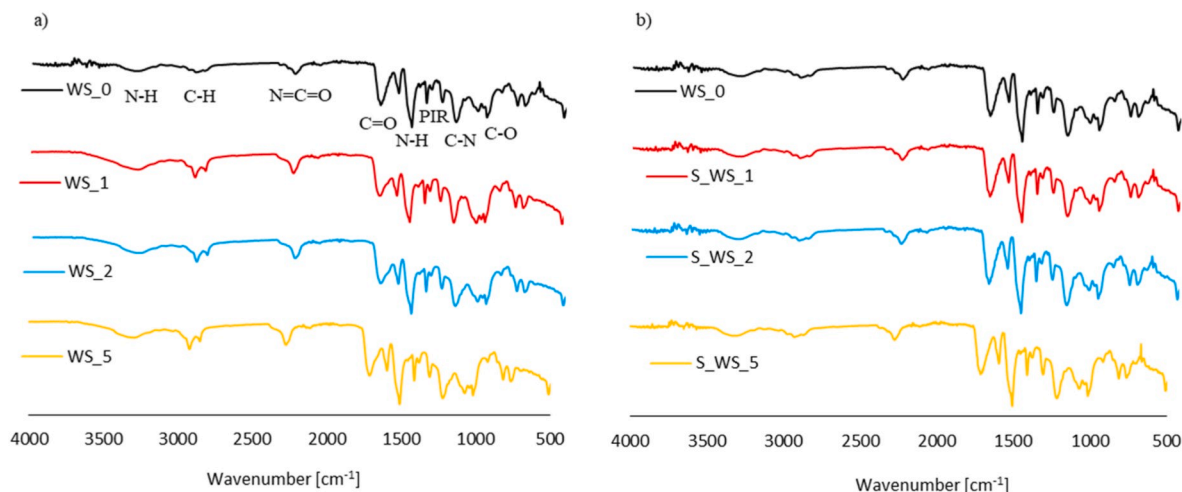


Fig. 19. FTIR of PU foams modified with a) WS and b) S_WS.

lower intensity of the band when compared with PU foams modified with WS. Therefore, the silanized WS has more available hydroxyl groups available to react with isocyanate.

4. Conclusion

PU foams were successfully reinforced using 1, 2 and 5 wt% of walnut shells (WS) and silanized walnut shells (S_WS). The addition of WS and S_WS into polyol increased its viscosity and prolonged foaming time. The study of the impact of WS and S_WS indicates that the incorporation of 1–5 wt% of both fillers influences the cellular structure of PU foams and consequently their further mechanical, thermal and insulating properties. In the SEM micrographs, reduced cell size and more homogenous structure were showed for PU foams with the loadings of 1 and 2 wt% of WS and S_WS, while the number of open cells increased with a further increase in WS and S_WS loading. Moreover, the results have shown that compared to untreated WS fillers, the application of S_WS leads to PU foams with better physico-mechanical and thermal properties of PU foams. The best results were obtained for PU foams modified with 1 wt% of S_WS. For example, the incorporation of 1 wt% of S_WS could provide PU foams with better compressive strength (improvement by ~15%), improved flexural strength (improvement by ~9%), and higher impact strength (increased by ~6%) and with the best thermal insulation properties ($\lambda = 0.023 \text{ W m}^{-1} \text{ K}^{-1}$). Furthermore, PU foams reinforced with S_WS showed improved thermal and thermo-mechanical stabilities compared to PU foams modified with WS. The introduction of S_WS into the composite resulted in an increased glass transition temperature (T_g) as well as increased storage modulus. The presented results confirm that the use of WS and S_WS as natural fillers in PU composite foams will promote a new application path in converting agricultural waste into useful resources for creating a new class of green materials. Walnut shell-derived PU composite foams may offer solutions based on the main challenges of our times – the use of renewable raw materials, the economy and the preservation of resources and minimization of the output of waste. This creates an ideal scenario for the emergence of innovative opportunities under rigid quality control procedure, that goes from the raw material to advanced polyurethane composite foams for construction and structural application.

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Declaration of competing interest

The authors declare that they have no conflict of interest.

CRediT authorship contribution statement

Sylwia Czlonka: Methodology, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Anna Strąkowska:** Methodology, Investigation. **Agnė Kairyte:** Methodology, Investigation.

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