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Nutmeg filler as a natural compound for the production of polyurethane composite foams with antibacterial and anti-aging properties

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ABSTRACT

Polyurethane (PU) composite foams were successfully reinforced with different concentrations (1 *wt%*, 2 *wt%*, 5 *wt%*) of nutmeg filler. The effect of nutmeg filler concentration on mechanical, thermal, antimicrobial and anti-aging properties of PU composite foams was investigated. PU foams were examined by rheological behavior, processing parameters, cellular structure (Scanning Electron Microscopy analysis), mechanical properties (compression test, impact test, three-point bending test, impact strength), thermal properties (Thermogravimetric Analysis), viscoelastic behavior (Dynamic Mechanical Analysis) as well as selected application properties (thermal conductivity, flammability, apparent density, dimensional stability, surface hydrophobicity, water absorption, color characteristic). In order to Disc Diffusion Method, all PU composites were tested against selected bacteria (*Escherichia coli* and *Staphylococcus aureus*). Based on the results, it can be concluded that the addition of 1 *wt%* of nutmeg filler leads to PU composite foams with improved compression strength (*e.g.* improvement by ~19%), higher flexural strength (*e.g.* increase of ~11%), improved impact strength (*e.g.* increase of ~32%) and comparable thermal conductivity (0.023–0.034 W m^{-1} K^{-1}). Moreover, the incorporation of nutmeg filler has a positive effect on the fire resistance of PU materials. For example, the results from the cone calorimeter test showed that the incorporation of 5 *wt%* of nutmeg filler significantly reduced the peak of heat release rate (pHRR) by *ca.* 60% compared with that of unmodified PU foam. It has been also proved that nutmeg filler may act as a natural anti-aging compound of PU foams. The incorporation of nutmeg filler in each amount successfully improved the stabilization of PU composite foams. Based on the antibacterial results, it has been shown that the addition of nutmeg filler significantly improved the antibacterial properties of PU composite foams against both Gram-positive and Gram-negative bacteria.

1. Introduction

Polyurethanes (PUs) constitute one of the most important groups of polymeric materials [1]. In 2017, the worldwide consumption of PU was established at 60.5 billion USD and it is forecasted to reach 79 billion USD by 2021 [1]. Their consumption is 67% of the total use of PU materials. Among commercially available insulating materials, such as mineral wool or expanded polystyrene, rigid PU foams exhibit better insulation properties. The thermal conductivity coefficient (λ) of PU foams varies between 0.018 and 0.025 W $m^{-1}K^{-1}$. Because of this, rigid PU foams are commonly used in varied applications, such as construction or building, industrial insulation or household appliances [2].

The main problem associated with the PU industry is the dependence of isocyanates and polyols on petrochemical products. Economic and legal requirements related to environmental protection are leading the chemical industry towards the development of new green composite materials, thus reducing the demand for polyols and additives made from non-renewable fossil fuels [3]. One of the solutions that meet these regulations is the introduction of polyols derived from natural sources, such as vegetable oils. Several studies have reported bio-polyols based on different vegetable oils, such as castor [4,5], soybean [6,7], palm [8,9], rapeseed [10,11], tung [12,13], sunflower [14] or canola [15] to develop a new kind of environmentally-friendly bio-based PU foams [16,17].

The main disadvantage of PU foams based on bio-polyols is relatively low mechanical strength. It has been stated that the addition of different kinds of organic and inorganic fillers may enhance the mechanical properties of PU composite foams. In the literature, many different inorganic fillers, such as nanoclay [18], expandable graphite [19], silica [20], talc [21] or polyhedral oligosilsesquioxanes (POSS) [22,23] has been used as a reinforcement in the production of PU foams. Incorporating bio-fillers into PU foams improves the environmentally friendly character and the mechanical properties of PU foams. Until now, many different natural fillers have been investigated. For example, Zhou et al. [24] produced rigid PU foams modified with cellulose nanocrystals. PU composite foams with enhanced mechanical properties, reduced water uptake, and greater dimensional stability were obtained. Paberza et al. [25] synthesized PU composite foams reinforced with wheat straw

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lignin at different concentrations (0–6.3 *wt%*). Improved thermal insulation properties were obtained for PU composites containing 3 *wt%* of the filler. Zieleniewska et al. [26] synthesized PU composite foams strengthen with eggshell. The incorporation of eggshells into the PU matrix improved the mechanical properties, reduced water uptake, and increased dimensional stability in selected aqueous media. The influence of potato protein, buffing dust and keratin feathers in a certain amount on the morphology as well as physical and mechanical properties of the obtained porous materials were tested in our previous study [27–29]. It has been shown that a small addition of the fillers (such as 1–2 *wt%*) improved the compressive strength of material by about 20%, due to the strengthening effect of the fillers.

Among different types of fillers used as a reinforcing filler for PU foams, up to date there are no publications that were carried out to examine the enhancement of mechanical, thermal and antibacterial properties of PU composite foams modified with the addition of nutmeg filler. Nutmeg (*Myristica fragrans Houtt.)* belongs to the family of *Myristicaceae*. It is a spice seed obtained from the fruit of a tropical tree. Nutmeg seeds are one of the richest sources of the phenolic extract. The chemical composition of nutmeg includes mainly limonene, sabinene, α-pinene, β-pinene, myristicin, and safrole. It is a well-known aromatic perennial plant with a characteristic scent that possesses multiple medicinal applications. The extracts from nutmeg seeds have been widely used as a natural flavoring agent [30,31].

To the best of our knowledge, nutmeg seeds as a filler in the PU foams have not been used to date. Keeping in view the outstanding properties of the nutmeg, it seems logical to use nutmeg seeds as a reinforcing filler for the new bio-based polyurethane composite foams. The use of nutmeg as a reinforcing filler may improve the mechanical and physical properties of PU composite foams. It is expected that the incorporation of the nutmeg filler may improve the anti-aging and antibacterial properties of the obtained materials. Due to these positive and beneficial effects, it can be stated that the use of grounded nutmeg seeds as a natural filler in PU composite foams will promote a new application path in converting nutmeg into valuable resources for producing a new class of green materials.

Therefore, this study examines the influence of nutmeg as a new reinforcing filler for PU composite foams that could be suitable for production according to the requirements of European standards. The current study focuses on the application of nutmeg filler as a natural bio-filler to obtain PU composite foams with enhanced mechanical, thermal as well as antibacterial and anti-aging properties. PU composite foams enhanced with different concentrations (1–5 *wt%*) of nutmeg filler were examined by means of antibacterial test against selected bacteria (Disc Diffusion Method). The influence of the filler addition on mechanical properties (*e.g.* compression test, bending test, impact test, dynamic-mechanical behavior), thermal properties (*e.g.* thermogravimetric analysis), application properties (thermal conductivity, flammability, apparent density, water absorption, dimensional stability) and morphology (porosity, cell size distribution, cell size diameter) of PU composite foams was examined. Based on the results, it may be concluded that the incorporation of nutmeg filler in the concentration of 1–5 *wt%* influences the rheological behavior of polyol premixes, leading to improvement or deterioration of the aforementioned properties of nutmeg-based PU composite foams.

2. Materials and methods

2.1. Materials and manufacturing

IZOPIANOL 30/10/C and PUROCYN B were provided by Purinova Sp. z o. o. IZOPIANOL 30/10/C is a commercial mixture of polyester polyol (functionality of 2, hydroxyl number of 230–250 mgKOH/g), flame retardant (Tris (2-chloro-1-methylethyl)phosphate), catalyst and chain extender (1,2-propanediol) [32]. PUROCYN B is a polymeric diphenylmethane 4, 4'-diisocyanate (pMDI) (31 *wt%* of isocyanate groups) [32]. Nutmeg filler was purchased from Green Essence Sp. z o. o.

In the first step, a mixture of IZOPIANOL 30/10/C and grounded nutmeg filler in an amount of 1, 2 or 5 *wt%* were stirred for 60 s at a speed rate of 5000 RPM. Then, the isocyanate component (PUROCYN B) was added to the mixture in a selected amount. The mixture was homogenized at 5000 RPM for approximately 60 s and poured into the open mold. During the synthesis, the start, growth, and gelation times were defined as: *start time* - time measured from the moment the components A and B are mixed until the foam starts to grow, *growth time* - the time measured from the beginning of foam growth until its greatest volume is reached, *gel time* - the time after which it is impossible to pull the synthesized PU foams from the surface in the form of threads. PU composites were conditioned for 24 h at room temperature. The schematic representation of the synthesis of PU composite foams is presented in Fig. 1.

2.2. Characterization techniques

The average size of the nutmeg filler (in a polyol dispersion) was determined by the Dynamic Light Scattering (DLS) method using a Zetasizer NanoS90 instrument (Malvern Instruments Ltd, UK). The measurement was evaluated at 5 min intervals.

The dynamic viscosity of the polyol premixes was determined according to ISO 2555 using a Viscometer DVII+ (Brookfield, Germany). The measurement was performed in the function of a shear rate (0.5–100 s^{-1}) at a temperature of 25 °C.

The chemical structure of nutmeg was evaluated by Fourier-transform infrared spectroscopy (FTIR) using Nicolet iS50 FTIR Spectrometer with DGTS/KBr detector (Thermo Fisher Scientific, USA). The measurement was performed in the range of 3500 to 400 cm^{-1} with a maximum resolution of 4 cm^{-1}. FTIR was performed with a DGTS/KBr detector.

The morphology of PU foams was determined by JEOL JSM-5500 L V scanning electron microscopy (JEOL Ltd., USA). The samples were scanned in the free-rise direction at the accelerating voltage of 10 kV and with 50x and 150x magnification. Statistical analysis of the size distribution of the PU foam cells was calculated on the basis of 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 in accordance with ISO 845 standard.

The content of closed-cells of PU composite foams was determined according to ISO 4590 standard.

Compression 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.

Flexural strength (ε_f) of PU composite 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}.

The brittleness of PU composite foams was evaluated according to ASTM C421. Brittleness was calculated as a percentage of total weight loss. The result was the average obtained for 12 cubic samples.

Surface hydrophobicity of PU composite 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 surface energy of PU foam composites was calculated on the basis of measured contact angles.

The thermal properties of PU foam composites 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 $T_{10\%}$, $T_{50\%}$ and $T_{80\%}$ of mass loss were determined.

Water absorption of PU foam composites was performed according to

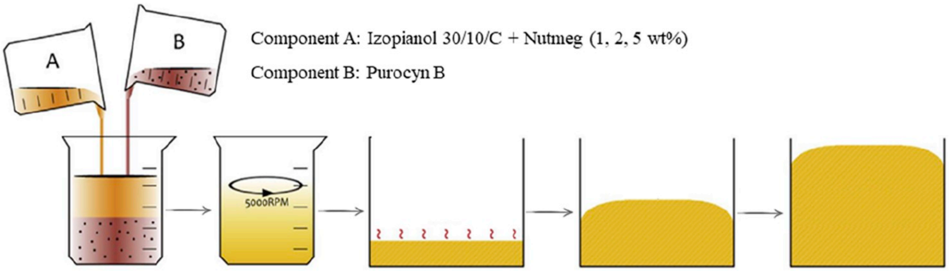

Fig. 1. Schematic procedure of the synthesis of PU composite foams.

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).

$$WA = m\text{-}m_0/m_0 \tag{1}$$

Color measurement was evaluated to determine the color change of PU composite foams before and after aging. The color change was performed using a CM-3600 d spectrophotometer (Konica Minolta Sensing, Japan) in the wavelength range of 360–740 nm. The value of total color change *(ΔE*)* was calculated in accordance with equation (2), where *(L*)* is brightness, *(a*)* is a red-green component and *(b*) is* a blue-yellow component.

$$\Delta E = \sqrt{(a^*)^2 + (b^*)^2 + (L^*)^2} \tag{2}$$

Aging in a climate chamber was performed using a UV 2000 apparatus (Atlas Material Testing Solution, USA). The destructive parameters, such as humidity, temperature, and UV radiation were examined. PU samples were conditioned in a climate chamber with the following parameters: temperature of 70 °C, the relative humidity of 70% and radiation intensity of 0.7 W m^{-2}. Samples were conditioned in a climate chamber for 7 days. After this time, an effect of combined, destructive parameters (temperature, humidity, and UV radiation) on selected properties of PU foam composites (*e.g.* color change, cellular structure, thermal properties) was evaluated.

Antibacterial properties of PU foams against *Escherichia coli (G-)* and *Staphylococcus aureus (G +)* were examined according to the National Committee for Clinical Laboratory Standards [33] by Disc Diffusion method. Selected bacteria were mixed with the growth medium (agar) at a temperature of 40 °C, poured on Petri dishes and solidified. After 30 min PU sample with a diameter of 8 mm was placed on the solidified agar. Such prepared foams were incubated in a hermetic thermostat at 37 °C for 24 h. After this time, optical images of the bacterial growth zone around the PU were made and the results were measured.

The thermal conductivity of PU composite foams was measured using the heat flow meter apparatus (LaserComp 50 (HFMA, LaserComp Inc., USA) with a 2.5 cm × 2.5 cm size heat flow transducer. The upper and lower plates of the HFMA instrument were set at 12.5 °C and 37.5 °C, respectively, with a mean temperature of 25 °C. Prior to testing the sample specimens, the instrument was calibrated using a similar thermal conductivity reference sample to improve the accuracy of the measurement.

The fire behavior was analyzed using a cone calorimeter apparatus according to ISO 5660 in S.Z.T.K. 'TAPS' - Maciej Kowalski Company (Poland). Each specimen with dimensions of 100 × 100 × 25 mm^3 was wrapped with aluminum foil and burned at an external heat flux of 35 kW m^{-2}. The parameters were recorded during the time.

3. Results and discussion

3.1. Characterization of nutmeg filler

The viscosity of the PU system is an important parameter affecting the proper foaming process and the formation of a stable structure of PU foams [34]. The results presented in Table 1 indicate that the addition of nutmeg filler affects the dynamic viscosity of PU premixes. The incorporation of nutmeg filler results in increased viscosity due to the fact that nutmeg particles may interact with polyether polyol through hydrogen bonding and Van der Waal's interaction [35]. The greatest dynamic viscosity possesses a PU system containing the highest concentration of nutmeg filler – 5 *wt %.*

All PU systems are classified as non-Newtonian fluids - at an increased shear rate, the viscosity of PU systems decreases. Such dependence is characteristic for pseudoplastic fluids and is typical for PU systems modified with different types of organic/inorganic fillers [36,37].

Particle size is another parameter influences the further mechanical and thermal properties of PU systems. It has been well described in previous studies, that small particles tend to agglomerate leading to the formation of the large clusters in the PU matrix [38]. On the other hand, too large particles may affect the viscosity of PU systems and disturb the foaming process leading to the deterioration of further properties of PU foams. Due to this, the particle size of nutmeg filler was measured in a polyol dispersion. The results presented in Fig. 2 indicate that the size of nutmeg particles ranges from 60 to 120 nm with the highest percentage of particles at ~80 nm.

Chemical analysis of nutmeg was evaluated by FTIR spectroscopy (Fig. 3). The characteristic bands located at 3290 cm^{-1} (-OH vibration) and 290 cm^{-1} (-CH_2 vibration) correspond to the presence of cellulose, hemicellulose, and lignin. The band located at 1700 cm^{-1} corresponds to the vibration of (C=O) and (C=C) [39]. The shoulder peak localized at 1620 cm^{-1} indicates the presence of symmetric aromatic ring (C=C) [39]. Functional groups of flavonoids (which correspond to the aromatic ring vibration) are located in the range of 1610–1600 cm^{-1} and 1480-1450 cm^{-1} [40,41]. Other characteristic bands of the phenol groups could be found at 1170-1110 cm^{-1} (C-OH stretching vibration) [30].

3.2. Foaming kinetic and apparent density of PU composite foams

It is well known that the reaction of the synthesis of the PU materials

Table 1
Dynamic viscosity of PU systems.

	Dynamic viscosity η [mPa·s]			
	0.5 RPM	5 RPM	10 RPM	100 RPM
PU_N_0	630	420	380	190
PU_N_1	1100	800	700	320
PU_N_2	1300	1100	950	480
PU_N_5	2100	1300	1100	540

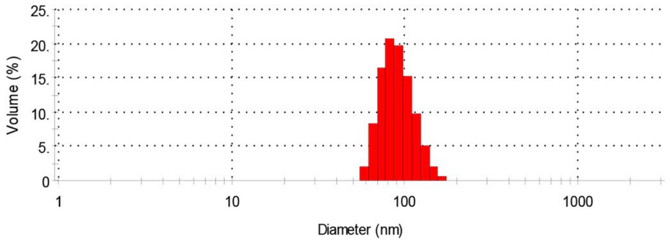

Fig. 2. Nutmeg particle size distribution.

is highly exothermic [42,43]. The rate of temperature increase determines the reactivity of the reaction mixture, which is associated with the individual components of the mixture. The results of the growth kinetics and foam heights are the average of the results obtained for the four foams prepared from each series. Compared to the controlled PU_N_0 foams, PU composite foams modified with the addition of nutmeg filler are characterized by reduced values of the maximum temperature during the PU composite foams synthesis (T_{max}). With the addition of 1–5 *wt%* of nutmeg filler, the value of T_{max} decreases from 128 to 120 °C. This result indicates the incorporation of nutmeg filler decreases the activity of PU mixtures which is manifested by the extension of cremation, expansion and stabilization times, lowering T_{max} and lower height of obtained foams. Previous studies have shown that the addition of organic fillers reduces the value of T_{max}, which may be related to the fact that fillers can absorb some of the heat generated during the synthesis of PU materials [27,29,44,45]. An analog tendency is observed in our study as well.

The addition of nutmeg filler influences the foaming process, which was evaluated by measuring the processing times – cream time, expansion time and the tack-free time (Table 2). All PU composites are characterized by extended start, expansion and tack-free times. For example, compared to controlled PU_N_0 foam, the incorporation of 5 *wt%* of nutmeg increases the cream time from 40 to 61 s and expansion time from 230 to 249 s. During the foaming process, solid particles of nutmeg act as nucleating centers and a greater bubble formation is observed. The higher viscosity of PU systems containing nutmeg filler (see Table 1) limits the expansion of PU systems and reduces the mobility of the molecules. This affects the foaming kinetics disruption and slows down the rate of PU polymerization. This effect was also noticed by other researchers when introducing organic fillers into the PU mixture [46]. The results of expansion time are in agreement with the results of the final height of PU composites. The results presented in Table 2 and Fig. 4 indicate that the final height of PU composite foams is reduced by ~2, ~4 and ~7% at 1, 2 and 5 *wt%* of nutmeg filler, respectively. It was also found that PU compositions exhibit a shorter tack-free time, indicating that solid particles of nutmeg may act as a curing accelerator. Compared to controlled PU_N_0, total processing times of PU composite foams are higher, however, the results are still in agreement with operation conditions required for PU foams synthesis. Contrary results have been found by Liu et al. [19] in the case of PU foams containing waste ash. It has been concluded that the fillers show different reaction manner depending on chemical composition as well as the particle size distribution of the fillers.

Apparent density results are presented in Table 2. The apparent density varies considerably with an increase of nutmeg concentration from 1 to 5 *wt%*. Compared to PU_N_0, the apparent density increases by 6, 9 and 14% for samples containing 1, 2 and 5 *wt%* of nutmeg, respectively. This may be connected with the role of solid filler particles during the foaming process. As mentioned previously, the higher concentration of nutmeg filler results in greater viscosity of the PU system and limited expansion of bubble cells. On the other hand, the incorporation of nutmeg filler with specified density (*ca.* 1.3 g cm^{-3}) affects the apparent density of PU composites as well. Similar dependency has been found in the literature [47,48].

3.3. *The cellular structure of PU composite foams*

Cellular structure influences thermal, mechanical and physical properties of porous materials [37,49]. Appropriate correlation between filler concentration, the viscosity of the PU system and distribution of the filler particles in the PU matrix seems to be a crucial factor to obtain PU materials with well-developed morphology [50]. The morphologies of PU composites are shown in Fig. 5. As observed in Fig. 5a, the structure of controlled PU_N_0 foam is nearly uniform and high content of closed-cells is observed. The incorporation of nutmeg filler leads to the formation of a more inhomogeneous structure with a greater number of open-cells. As presented in Fig. 5b and c the incorporation of 1 and 2 *wt%* of nutmeg do not affect the structure of PU composites. The closed-cell structure of PU_N_1 and PU_N_2 is still well preserved, however, with the addition of 5 *wt%* of nutmeg the structure becomes less uniform and the number of defective cells is increased. Compared to the controlled PU_N_0 foam, the porosity of PU composites is slightly

Table 2
Selected properties of PU composite foams.

	PU_N_0	PU_N_1	PU_N_2	PU_N_5
Temperature [°C]	132	128	124	120
Cream time [s]	40 ± 2	51 ± 2	56 ± 1	61 ± 2
Expansion time [s]	230 ± 9	235 ± 6	242 ± 7	249 ± 5
Tack-free time [s]	338 ± 9	342 ± 8	351 ± 9	372 ± 8
Apparent density [kg m^{-3}]	35 ± 5	37 ± 4	38 ± 4	40 ± 5
Cell size [μm]	345 ± 9	322 ± 7	318 ± 6	305 ± 6
Closed-cell content [%]	87	88	87	79
Height [mm]	230	225	220	215

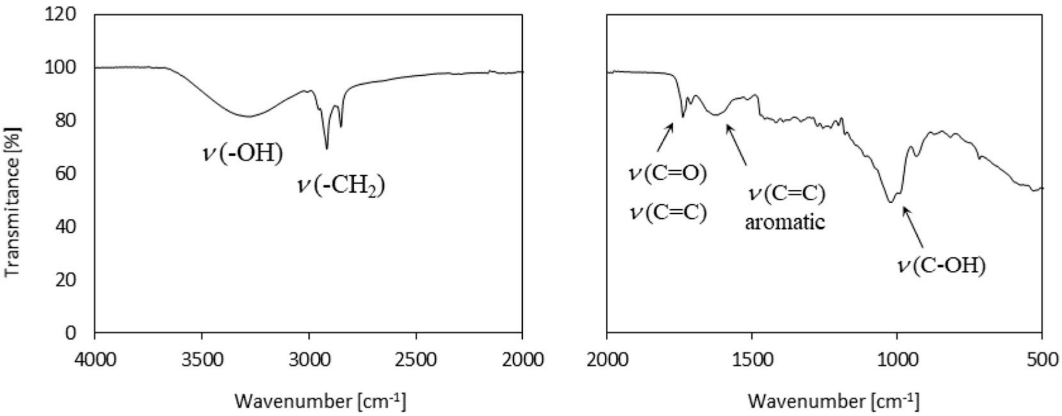

Fig. 3. FTIR spectra of nutmeg.

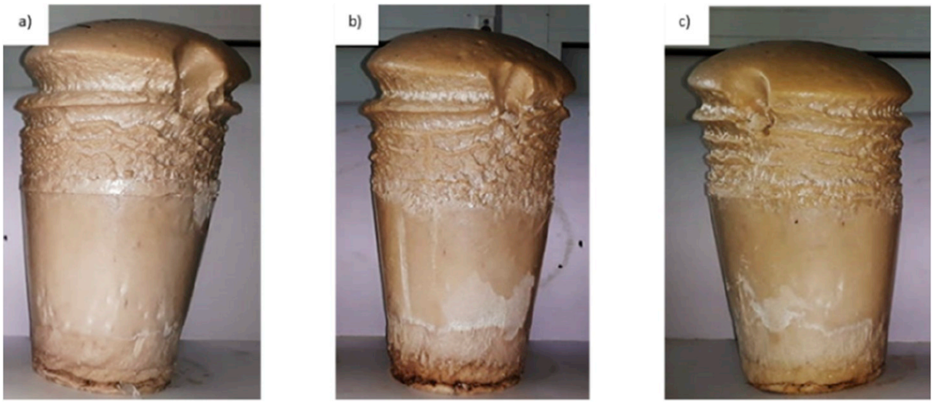

Fig. 4. PU composite foams modified with a) 1 *wt%*, b) 2 *wt%* and c) 5 *wt%* of nutmeg filler.

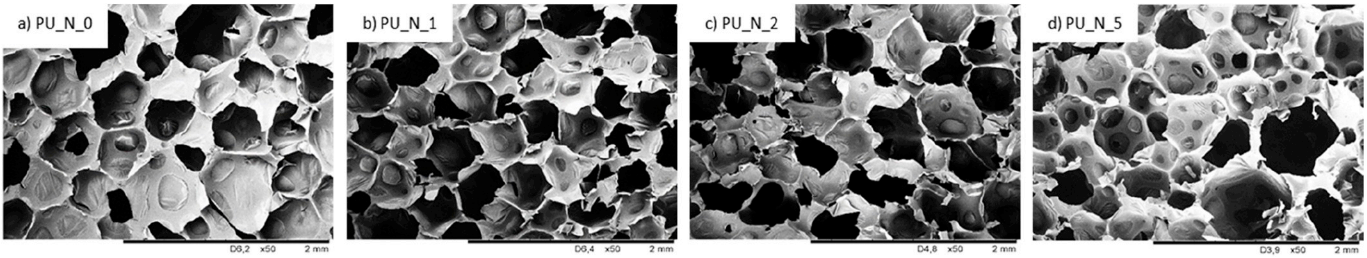

Fig. 5. The cellular structure of a) PU_N_0, b) PU_N_1, c) PU_N_2 and d) PU_N_5 observed at a magnification of ×50.

reduced (Table 2). For example, for sample PU_N_5, the porosity decreases from 87% to 79%. The possible explanation of structure disintegration may be found in interphase interaction between filler surface and PU matrix which disrupts the foaming process and results in the formation of more defective structure [51]. Moreover, as presented in Fig. 6, the nutmeg 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 nutmeg surface and the PU matrix, which in turn leads to cell collapse and the formation of open pores in the foam structure [21].

The addition of nutmeg filler leads to a significant decrease in cell size. Compared to the controlled PU_N_0 foam, the cell size of PU composites decreases from 345 to 322, 318 and 305 μm with the incorporation of 1, 2 and 5 *wt%* of nutmeg filler, respectively. It has been stated in previous works, that the solid particles may affect the rheology around the growing air bubbles and reduce the nucleation energy changing the nucleation character from homogenous to heterogeneous. Lower barrier of nucleation supports the formation of a great number of smaller cells, which in turn tend to coalescence into larger. This phenomenon is the most prominent in the case of PU composites containing 5 *wt%* of nutmeg. As presented in Fig. 7, most pores are located in the range of 200–300 μm, however, an additional population of bigger pores with an average diameter of ~800 μm is observed as well. Similar results have been also observed in previous studies in the case of PU foams modified with other organic and inorganic fillers [21,52–55].

3.4. *Mechanical properties of PU composite foams*

The mechanical properties of PU composite foams were determined for PU samples before and after the UV-aging.

The compression strength ($\sigma_{10\%}$) of PU composite foams was measured in two directions - perpendicular and parallel to the foam growth direction. According to the results presented in Table 3, the incorporation of nutmeg filler strongly affects the compression strength in both cases. Compared to controlled PU_N_0 foam, the value of $\sigma_{10\%}$ (measured parallel to the foam rise direction) increases by ~19 and ~15% for samples modified with 1 and 2 *wt%* of nutmeg filler. In the case of foams with the addition of nutmeg in an amount of 5% by weight, a slight decrease in compressive strength by ~10% was observed. Similar dependence is observed in the case of flexural strength and impact strength. With increasing the concentration of nutmeg filler the values of flexural and impact strength slightly decrease.

The results presented in Fig. 8 clearly indicate that no correlation between the $\sigma_{10\%}$ and the density of the PU composite foams is observed. Samples with a higher density are characterized by lower values of $\sigma_{10\%}$. The analog tendency is observed in the case of flexural and impact

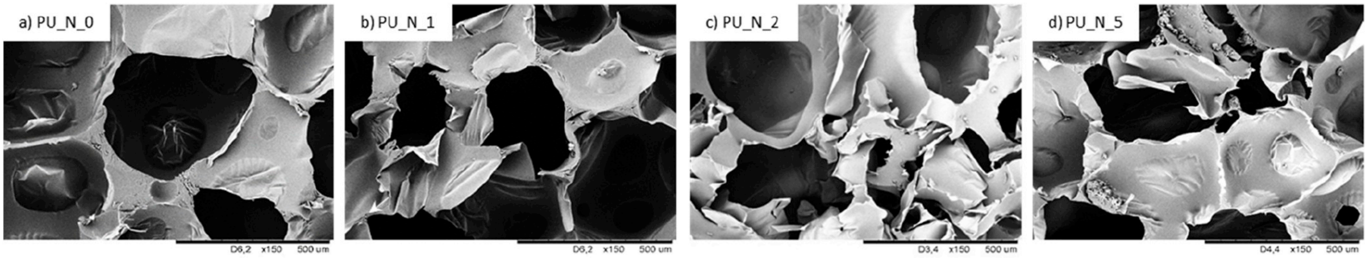

Fig. 6. The cellular structure of a) PU_N_0, b) PU_N_1, c) PU_N_2 and d) PU_N_5 observed at a magnification of ×150.

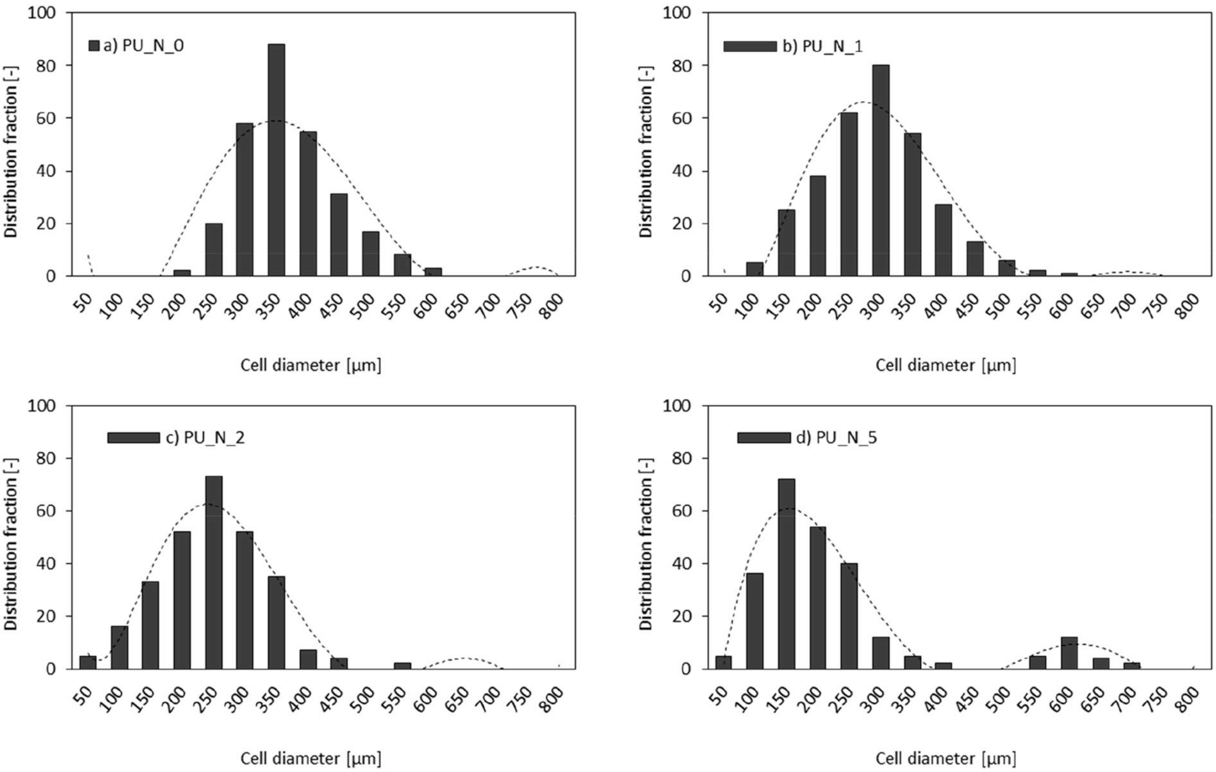

Fig. 7. Distribution of cell size of a) PU_N_0, b) PU_N_1, c) PU_N_2 and d) PU_N_5.

Table 3
Selected mechanical properties of PU composite foams (compressive strength, flexural strength, elongation and impact strength) measured before and after the UV-aging.

	Compressive strength $\sigma_{10\%}$ (parallel) [kPa]	Compressive strength $\sigma_{10\%}$ (perpendicular) [kPa]	Flexural strength ε_f [kPa]	Elongation at break [%]	Impact strength [kJ m^{-2}]
Before UV-aging					
PU_N_0	230 ± 9	135 ± 4	412 ± 5	11.4	0.340
PU_N_1	273 ± 8	168 ± 5	458 ± 5	10.8	0.450
PU_N_2	265 ± 6	160 ± 4	440 ± 8	11.0	0.420
PU_N_5	207 ± 6	140 ± 6	410 ± 9	11.8	0.300
After UV-aging					
PU_N_0	140 ± 9	105 ± 4	360 ± 9	11.4	0.250
PU_N_1	160 ± 8	125 ± 5	385 ± 9	10.8	0.320
PU_N_2	158 ± 6	118 ± 4	375 ± 6	11.0	0.300
PU_N_5	145 ± 6	108 ± 6	340 ± 7	11.8	0.260

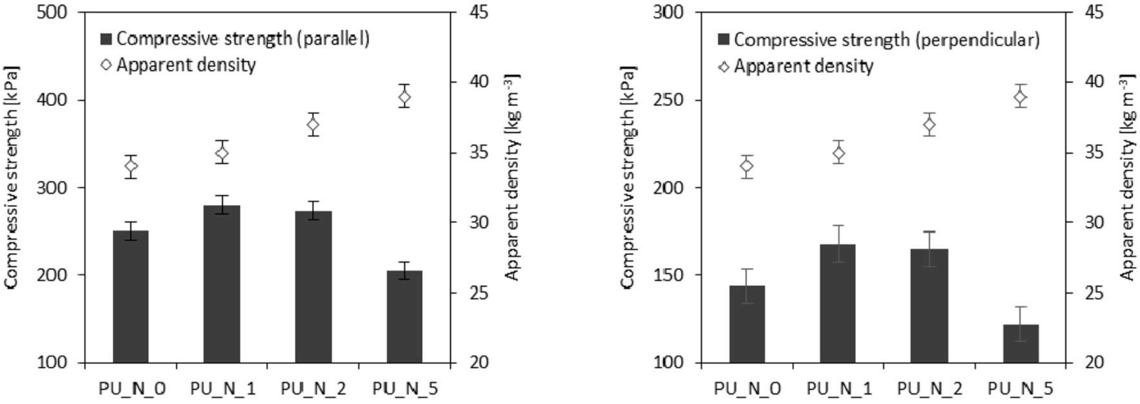

Fig. 8. Correlation between apparent density and compressive strength of PU composite foams.

strength (Fig. 9). This may be explained by the morphology features of PU foams. It has been well described in previous studies, that the mechanical properties of PU foams depend on the cellular structure of porous materials. As presented in Fig. 5 the incorporation of nutmeg filler leads to more inhomogeneous structure with a greater number of open cells. During the mechanical tests, the broken cells may generate additional micro-cracks which results in deterioration of mechanical properties. On the other hand, at a higher concentration of nutmeg filler, the particles tend to agglomerate. The poor interfacial adhesion between the polymer struts and the surface of filler agglomerates leads to phase separation of the PU matrix. Because of this, under the action of external loading, an unexpected cracking of the PU samples occurs. It should be also pointed out that the incorporation of nutmeg filler may disturb the stoichiometry of the reaction between the polyol and isocyanate leading to the limited formation of PU bonds which results in the formation of weaker cellular structure. The analog tendency has been described in other works as well [56–59].

The results of the mechanical properties of PU composite foams after the UV-aging are presented in Table 3. Compared to non-aged PU foams, significant deterioration of the mechanical properties of foams is observed after UV aging. The values of compression, flexural and impact strength are lower as compared to their non-aged counterparts, however, the difference is not as prominent as in the case of PU_N_0. A similar result was found for PU foams modified with cinnamon extract [60]. The authors stated that the addition of cinnamon extract may increase the cross-linking formation in the foam structure due to the polyphenols present in the cinnamon composition. A similar explanation may be found in the case of PU foams containing nutmeg filler.

3.5. Contact angle, water uptake, brittleness, and dimensional stability of PU composite foams

Water uptake 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 Table 4 indicate that with increasing the concentration of nutmeg filler the water uptake of PU composite foams slightly increases. This may be connected with the more inhomogeneous open-cell structure of modified foams. Based on SEM images (see Fig. 5) the addition of high loading of nutmeg filler, such as 5 *wt%* results in the opening of the foam cells. PU foams with the broken-cells structure are able to absorb more water compared to materials with closed-cell structure. The incorporation of nutmeg filler with hydrophilic nature affects the water uptake as well. Among different chemical compounds, nutmeg contains a great number of polyphenols with –OH groups. Because of this, the character of PU composite foams modified with nutmeg filler becomes more hydrophilic, which is also confirmed by the reduced value of the contact angle (Table 4).

The values of brittleness are presented in Table 4. An increase in brittleness could be observed in PU composite foams with nutmeg filler. The lowest value of brittleness exhibits controlled PU_N_0 (X%) while the highest value is observed for PU_N_5 foam. A similar result was reported in the case of rigid PU foams modified with basalt waste [61]. The authors have stated that increased values of brittleness may be attributed to the lower content of the PU matrix. Similar dependence is observed in the presented work.

The changes in linear dimensions (Δl), volume (ΔV), and mass (Δm) of PU foams after conditioning at −20 and + 70 °C for up to 14 days were examined. The results of aging measurements are presented in Table 4. Compared to controlled PU_N_0 foam, the incorporation of nutmeg filler results in insignificant changes in linear dimensions, volume, and mass. After the special treatments, the changes in Δl, ΔV, and Δm are random and no logical correlation between the results is observed. However, all PU composite foams are in great agreement with the regulations of civil engineering standards. According to this, after the conditioning in special treatment, such as high and low temperatures, PU materials should not exhibit more than 3% changes in dimensional linearity [62].

3.6. Microbial properties of PU composite foams

The results of the antibacterial activity of PU composites against *Staphylococcus aureus* and *Escherichia coli* are presented in Table 5. It can be concluded that significant inhibition of selected bacteria is presented for all samples after 24 h of exposure. Sample with 5 *wt%* of nutmeg filler exhibits the best antibicidal properties. Strong antimicrobial activity against gram-positive and gram-negative bacteria may be attributed to the various extracts and the essential oil of nutmeg seeds. Some important antimicrobial compounds reported in nutmeg are trimyristin, myristic acid, α-pinene, β-pinene, *p*-cymene, β-caryophyllene and carvacrol [30,31]. Due to antimicrobial activities, nutmeg could be considered as a significant natural source of antioxidants and antimicrobials in the development of PU composites with improved antibacterial properties.

3.7. Color analysis of PU composite foams

The optical results are presented in Table 6. The incorporation of nutmeg has an impact on the color of PU composites foams. Compared to PU_N_0, all PU composites filled with nutmeg filler have a more intense color, which is confirmed by the reduced value of lightness (L*). Moreover, the obtained PU composites are characterized by a more intense shade of yellow (increased value of a*) and red (increased value of b*). The yellowish and reddish shade may be attributed to organic

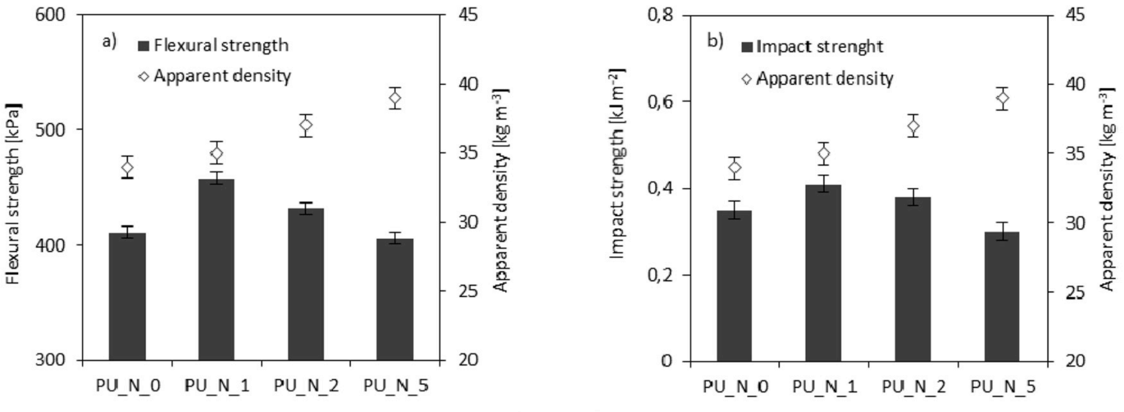

Fig. 9. Correlation between apparent density and a) flexural b) impact strength of PU composite foams.

Table 4
Contact angle, water absorption, brittleness and changes in linear dimensions (Δl), volume (ΔV) and mass (Δm) of PU foams measured before and after conditioning at +70 °C and −20 °C.

	Contact angle [°]	Water absorption [%]	Brittleness [%]	Temperature of +70 °C			Temperature of −20 °C		
				Δl [%]	ΔV [%]	Δm [%]	Δl [%]	ΔV [%]	Δm [%]
PU_N_0	128 ± 2	11.2 ± 0.4	4.9 ± 0.2	1.70 ± 0.01	1.20 ± 0.01	1.55 ± 0.01	1.65 ± 0.01	1.55 ± 0.01	1.54 ± 0.01
PU_N_1	122 ± 2	10.8 ± 0.3	5.5 ± 0.3	1.60 ± 0.01	1.12 ± 0.01	1.70 ± 0.01	1.84 ± 0.01	1.77 ± 0.01	1.58 ± 0.01
PU_N_2	119 ± 1	12.4 ± 0.1	6.5 ± 0.3	1.45 ± 0.01	1.21 ± 0.01	1.80 ± 0.01	1.66 ± 0.01	1.99 ± 0.01	1.68 ± 0.01
PU_N_5	116 ± 2	15.1 ± 0.2	10.1 ± 0.2	1.35 ± 0.01	1.80 ± 0.01	1.30 ± 0.01	1.92 ± 0.01	1.89 ± 0.01	1.59 ± 0.01

Table 5
Microbial properties of PU composite foams against *Staphylococcus aureus* and *Escherichia coli.*

	Suspension of Staphylococcus aureus (CFU/ml)		*Suspension of Escherichia coli* (CFU/ml)	
	Initial	After 24 h of exposure	Initial	After 24 h of exposure
PU_N_0	76×10^6	76×10^6	76×10^6	74×10^6
PU_N_1	76×10^6	38×10^6	76×10^6	40×10^6
PU_N_2	76×10^6	30×10^6	76×10^6	35×10^6
PU_N_5	76×10^6	15×10^6	76×10^6	9×10^6

Table 6
Color analysis of PU foams before UV aging, where ΔE^* - total color change, L^* - degree of lightness, a^* - red/green parameter, b^* - yellow/blue parameter.

	Colorimetric Parameters			
	L*	a*	b*	ΔE*
PU_N_0	10.4	22.4	−4.8	7.1
PU_N_1	23.2	42.5	−4.1	17.2
PU_N_2	38.5	45.4	−2.8	24.0
PU_N_5	42.5	43.5	−1.0	30.2

extractives, such as polyphenols, quinones or flavonoids of nutmeg seeds.

It is well known that nutmeg exhibits strong antioxidant properties [31]. It has been reported that nutmeg lignans may produce an active substance containing catechol structure, which may be responsible for the high antioxidant potential of nutmeg. Because of this, PU composites were tested after the UV aging. One of the main parameters which provide knowledge about the degradation process is the color change. An organoleptic analysis indicates that after the UV exposure, the color of PU foams changed from yellow to orange (Fig. 10). In general, the color change of PU foams after the UV exposure is connected with the oxidation of aromatic amines, which are synthesized in the reaction of isocyanate and water. This, in turn, leads to the formation of chromophores which promotes the color change of PU foams. It should be also pointed out that the color change of PU foams is enhanced by the presence of the chemical compounds which are sensitive to the oxidation process, such as aliphatic polyesters or polyethers. As compared to controlled PU_N_0 foam, the surface of PU composites containing nutmeg filler is characterized by a lower number of holes and cracks (Fig. 11). This indicates that the addition of nutmeg filler can increase the bond strength between molecules and improve the stability of PU foams.

The results of the color analysis of PU foams after UV aging are presented in Table 7. After the UV exposure, the most visible color change (determined by ΔE^*) is observed for controlled PU_N_0 foam. For PU composites the difference in ΔE^* before and after the UV exposure is reduced. This indicates that the incorporation of nutmeg filler may successfully enhance the anti-aging properties of PU composites. As mentioned previously, the resistance of nutmeg against UV radiation (and high temperature) is attributed to the chemical structure of nutmeg seeds which involves organic extractives, such as polyphenols, quinones or flavonoids. Based on this result, it can be concluded that the incorporation of nutmeg filler may significantly improve the stabilization of the PU composites and may be used as an anti-aging compound in the production of PU foams.

3.8. Dynamic mechanical analysis (DMA) of PU composite foams

The results of the dynamic mechanical analysis of PU composite foams are presented in Table 8 and Fig. 12. Based on the results, it may be concluded that the addition of nutmeg filler affects the value of glass transition temperature (T_g) which is determined as a maximum value of the curve loss tangent (tanδ). The lowest value of T_g is observed for samples filled with 5 *wt%* of nutmeg filler. It has been described previously that the value of T_g is connected with the aromaticity and cross-linking density of PU materials [58]. Based on this, it should be concluded that the incorporation of a high concentration of nutmeg filler (such as 5 *wt%*), leads to limited interaction between PU chains. Due to this, the mobility of PU chains is increased while the cross-linking density decreases. This results in a reduced value of T_g. Moreover, the isocyanate groups can react with nutmeg groups (such as hydroxyl groups) and disturb the formation of stable polyurethane bonds between polyol and isocyanate. The increased viscosity of PU systems filled with solid particles of nutmeg filler may also disturb the foaming process and reduce the reactivity of PU systems. It can also be seen that, compared to controlled PU_N_0 foam, as the concentration of nutmeg filler increases, the width of the T_g peak becomes wider as a result of various relaxation mechanisms. This may be connected with more pronounced heterogeneities of PU network structure due to the broader distribution of molecular weight between crosslinking centers.

As presented in Fig. 12b the incorporation of 1 and 2 *wt%* of nutmeg filler results in improved storage modulus value (*E*'). This may be connected with the well-developed closed-cell structure of PU foams. With

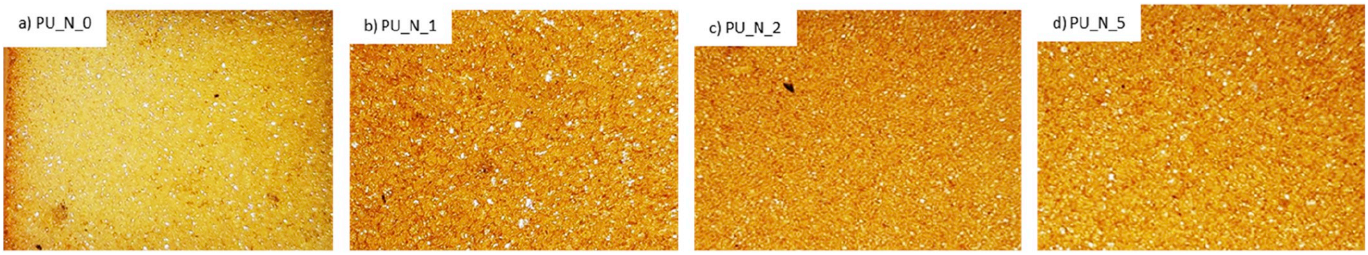

Fig. 10. PU composite foams after the 7 days of UV-aging.

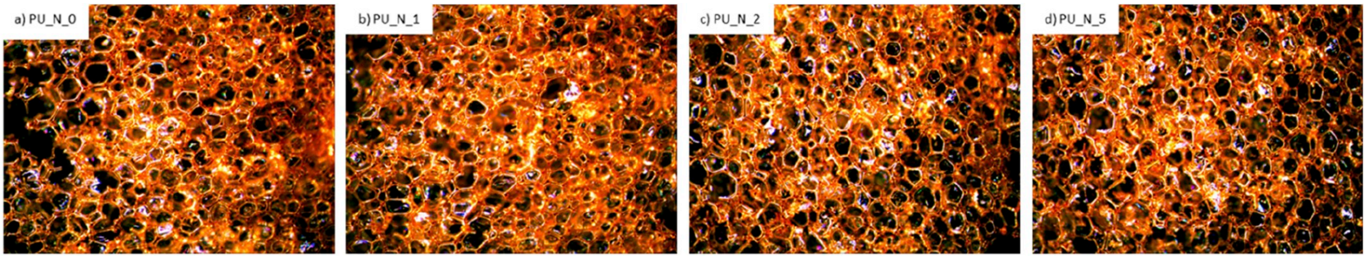

Fig. 11. Morphology of PU composite foams after 7 days of UV aging.

Table 7
Color analysis of PU foams after UV aging, where *ΔE** - total color change, *L** - degree of lightness, *a** - red/green parameter, *b** - yellow/blue parameter.

	Colorimetric Parameters			
	L*	a*	b*	ΔE*
PU_N_0	19.5	23.4	−4.1	23.2
PU_N_1	29.2	78.1	−3.0	24.1
PU_N_2	49.9	78.3	−2.9	27.5
PU_N_5	58.5	79.3	0.5	29.5

Table 8
TGA results of PU composite foams investigated under the nitrogen atmosphere.

	T_g [°C]	T_{10} [°C]	T_{50} [°C]	T_{80} [°C]	Char residue [%]
Before UV-aging					
PU_N_0	148	255	458	585	28
PU_N_1	152	248	435	582	27
PU_N_2	155	242	438	570	22
PU_N_5	139	213	440	569	21
After UV-aging					
PU_N_0	128	253	456	580	28
PU_N_1	135	251	503	588	26
PU_N_2	140	253	498	583	25
PU_N_5	120	246	481	577	22

increasing filler concentration the value of E′ slightly decreases, which indicates that the incorporation of the filler over a certain optimal level results in a more flexible structure of PU composite foams. This decrement of the E' is the most prominent in the temperature around 100 °C which is related to the hard segments domains and aromatic urethane groups of poly (ether-urethane) phase. An excess of solid 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 filler. Moreover, the aggregation of nutmeg particles may reduce the efficiency of the reaction, leading to the weakened structure and more mobile polymeric network. The analog trend has been observed in previous work as well [63–65].

3.9. Thermogravimetric analysis (TGA) of PU composite foams

The thermal properties of PU composite foams were determined by TGA analysis (Table 8 and Fig. 13). Characteristic temperatures were defined as $T_{10\%}$ (temperature attributed to 10% of weight loss), $T_{50\%}$ (temperature attributed to 50% of weight loss), $T_{80\%}$ (temperature attributed to 80% of weight loss) and T_{max} (temperature attributed to the highest weight loss).

Compared to PU_N_0, the composite foams modified with nutmeg filler are less thermally stable. The degradation process of controlled PU_N_0 starts at 255 °C, while the degradation of PU composites foams filled with 1–5 *wt%* of nutmeg starts at 213–248 °C, depending on the concentration of nutmeg filler. The highest loss of weight for PU_N_0 occurs in the range of 200–600 °C (the rate of weight loss ~5.5 *wt%* min^{-1}), while for PU composite foams it occurs in the range of 200–550 °C (the rate of weight loss in the range of 4.5–5.5 *wt%* min^{-1}). Reduced range of the temperature attributed to the highest weight loss is mostly related to an organic character of nutmeg filler and thermal degradation of the organic compounds such as protein, flavonoids, and oils, which decompose completely during the heating.

Some deterioration of thermal properties can be attributed to the uneven distribution of the filler in a polymer matrix which affects the crosslinking density [44]. Moreover, higher content of open voids, which are presented in the structure of modified foams (see Fig. 5) accelerates the degradation process leading to the slight deterioration of thermal properties of analyzed materials. On the other hand, the results of TGA indicates that the incorporation of nutmeg filler decreases the weight loss of PU composites during the initial step of degradation. Due to the barrier effect of incorporated filler particles, the oxygen and heat fluxes in the direction of the polymer surface are limited and the weight

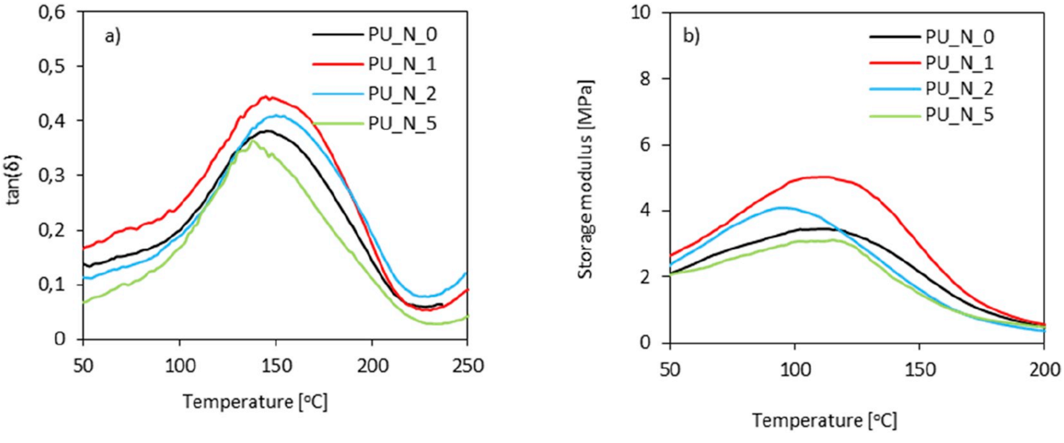

Fig. 12. Dynamic mechanical analysis of PU composite foams - a) Tan*δ* and b) storage modulus in the function of temperature.

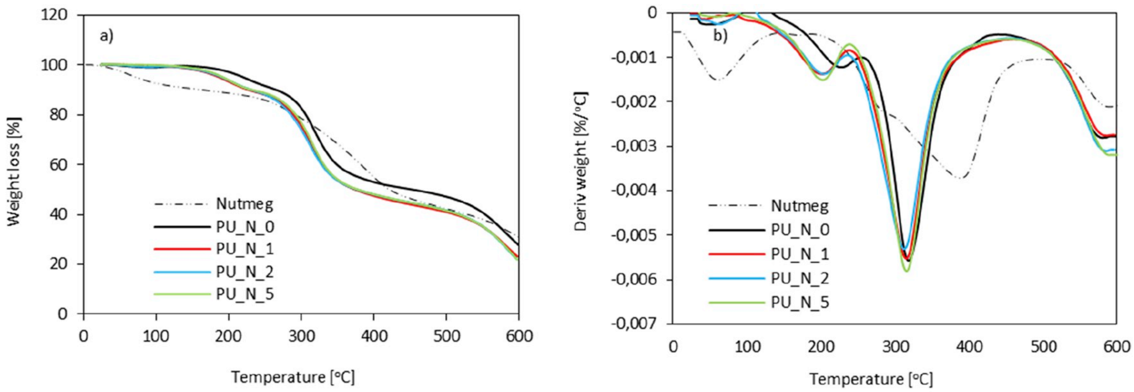

Fig. 13. a) TGA and b) DTG results of PU composite foams.

loss is reduced.

The difference between pure PU foam and PU composite foams is also confirmed by DTG analysis which is defined as the first derivative of TGA. DTG analysis provides information about the decomposition rate of PU foams during the heating process. All samples show a similar 3-steps degradation path with maximum degradation intensity in the range of 320–330 °C, which is attributed to the degradation of hard segments of PU. In the case of composite foams an additional, slight overlapped influx occurs around 325 °C. This may be connected with faster degradation of urethane bond, which is formed between urethane groups and hydroxyl groups of nutmeg filler. The introduction of organic filler, which may contain small amounts of residual water, results in the formation of more urea bonds, increasing the activation energy of thermal decomposition as compared to unmodified foam.

DSC/DTG analysis was also used to examine the degradation process of PU composites foam. The results of DSC/TGA results for samples subjected to 7 days of UV-aging are presented in Fig. 14. It can be seen, that the UV-aging affects the thermal properties of PU foams, however, the difference between non-aging and UV-aging PU composites is not significant. Comparing to PU_N_0, the more prominent difference is observed for sample modified with nutmeg filler. Comparing to their non-aging counterparts, the temperatures corresponding to 10, 50 and 80% of weight loss are shifted to higher values. This result indicates that the incorporation of nutmeg filler may stabilize the PU foams and improve the thermal properties of obtained materials.

3.10. *Thermal conductivity of PU composite foams*

Thermal conductivity (λ) is the main parameter determining the further use of PU foams as insulating materials [43,66]. The value of thermal conductivity is determined by apparent density (Fig. 15a) and morphological features of PU foams, such as the content of open and closed cells (Fig. 15b). It can be seen that the incorporation of 1 *wt%* of nutmeg filler does not influence the value of thermal conductivity as compared to the PU_N_0. With increasing the concentration of nutmeg filler the value of λ slightly increases. For example, for sample PU_N_5 the value of λ increases by 36%. Some deterioration in thermal conductivity is connected with morphological features of PU foams. As shown in Fig. 5, adding fillers in the amount of 1 and 2 *wt%* led to the more uniform structure with smaller cells, which reduces the radiant heat transfer through the cell walls. In addition, nutmeg particles, dispersed in a PU matrix, act as an effective physical barrier that limits the transfer of solid-phase heat through the conduction mechanism. Increasing the filler content to 5 *wt%* results in increased thermal conductivity of PU foams due to less uniform, open-cell structure. Taking into account, that the conductivity value of the air is higher than for the CO_2 (0.025 vs. 0.015 W $m^{-1}K^{-1}$), it is clear that due to the higher content of open cells, the thermal conductivity of PU foams is increased. The increased thermal conductivity of PU foams modified by the addition of inorganic and organic fillers is a well-known phenomenon and it was described in previous studies as well. For example, Modesti et al. [67] have shown that the thermal conductivity of PU foams modified with expandable graphite is increased due to the presence of large aggregates of the graphite flakes, which facilitates the heat transport through the solid material. Kurańska et al. [61] 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 W $m^{-1}K^{-1}$) was still considered at an acceptable level from industrial point of view. An analog trend has been observed in the case of our study as well.

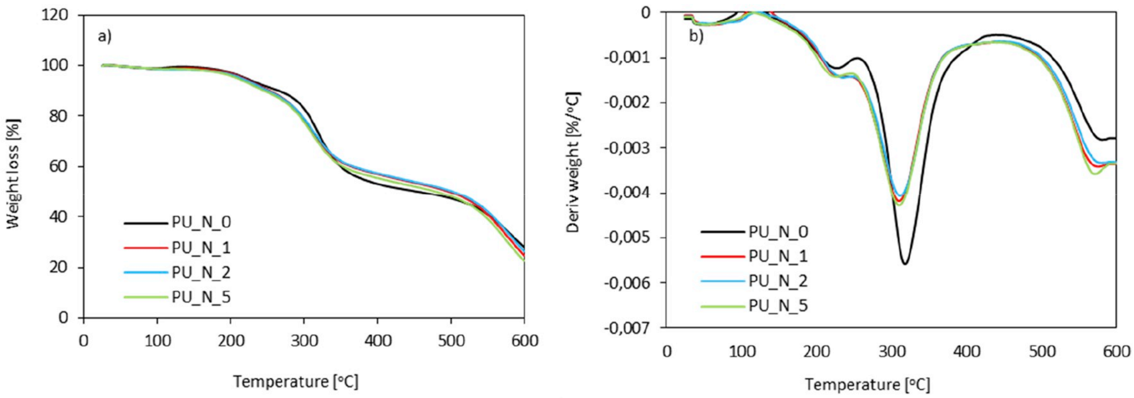

Fig. 14. a) TGA and b) DTG results of UV-aging PU composite foams.

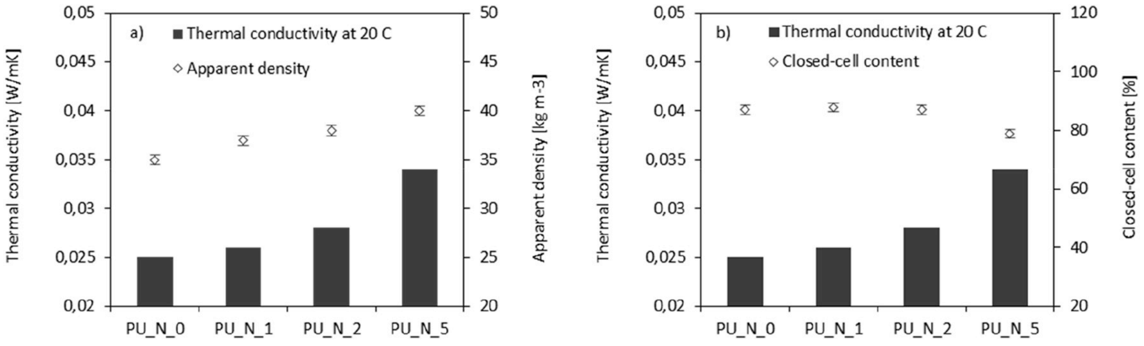

Fig. 15. Thermal conductivity of PU composite foams – dependence on a) apparent density and b) closed-cell content.

3.11. Fire behavior of PU composite foams

The flame retardant behavior of PU foams was evaluated by means of the cone calorimeter test. The results of ignition time (IT), peak heat release rate (pHRR), total heat release (THR), total smoke release (TSR) as well as an analysis of CO (COY) and CO_2 (CO_2Y) during the combustion and char residue are presented in Table 9.

One of the most important parameters is the heat release rate determined by the peak of the curve, which provides information about the flashover ignition of exposed combustible material. The results presented in Table 9 and Fig. 16, indicate that foams modified with nutmeg filler are characterized by the reduced value of pHRR, as compared to the PU_N_0. The value of pHRRs is 160, 140 and 90 kW m^{-2} for PU foams containing 1, 2 and 5 *wt%* of nutmeg filler, respectively, that is a reduction of *ca.* 30, 39 and 60%. The reduction of pHRR value may be related to the formation of a stable char layer on the polymer surface and releasing non-combustible gas. It should be pointed out that in the case of PU foams used as an insulating material, the accessible value of pHRR is 300 kW m^{-2} [68], while PU composite foams the values of pHRR do not exceed 160 kW m^{-2}. Compared to the PU_N_0, all series of the modified PU foams are characterized by a lower value of THR. In all cases, with increasing the content of the fillers, THR values decrease gradually. It has been found that the lowest value of THR is ascribed to the sample PU_N_5, which is reduced by *ca.* 18% as compared to the sample PU_N_0.

The smoke emission behaviors of PU foam were characterized by total smoke release (TSR) as well as CO and CO_2 analysis. PU composite foams modified with the addition of nutmeg filler are characterized by lower values of TSR. For PU_N_0 the value of TSR is *ca.* 1200 m^2 m^{-2} and decreases to 1050 m^2 m^{-2} for sample PU_N_5. As presented in Table 9, compared with PU_N_0, the addition of nutmeg filler decreases the COY and CO_2Y values for all modified PU foams. Additionally, PU composite foams are characterized by a lower ratio of COY/CO_2Y than the ratio obtained for PU_N_0. The ratio of CO/CO_2 gives information about the degree of complete combustion. The higher value of the ratio indicates lower completeness of the combustion process and therefore greater toxicity of the emitted smoke. This suggests, that all modified PU composite foams have greater performance in the suppression of CO comparing to controlled PU_N_0.

Table 9
Characteristic parameters describing the flammability of PU composite foams.

	TTI [s]	pHRR [kW m^{-2}]	THR [MJ m^{-2}]	TSR [m2 m^{-2}]	COY [kg kg^{-1}]	CO_2Y [kg kg^{-1}]	COY/ CO_2Y
PU_N_0	1	230	21.9	1200	0.065	1.20	0.054
PU_N_1	1	160	19.2	1150	0.050	1.40	0.036
PU_N_2	2	140	18.5	1100	0.050	1.45	0.034
PU_N_5	2	90	18.0	1050	0.045	1.55	0.029

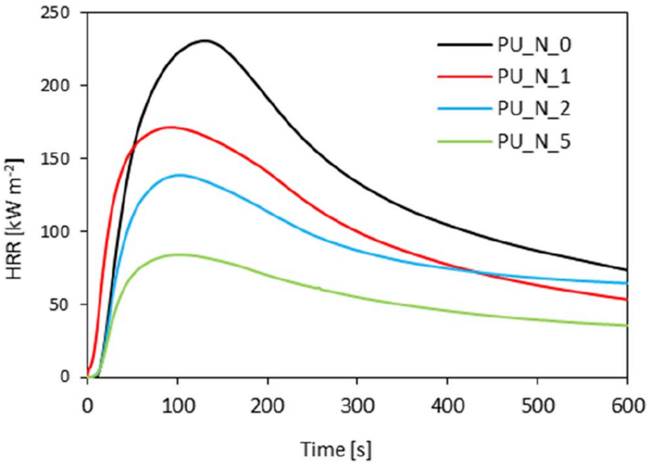

Fig. 16. Plots of HRR for PU composite foams.

4. Conclusion

PU composite foams enhanced with different concentration nutmeg filler (1–5 *wt%*) were successfully produced. The presented results confirmed that the addition of nutmeg filler influences the rheological behavior of PU systems, foaming kinetic, morphology of PU foams as well as further mechanical and thermal properties of PU composite foams. Based on the results, it may be concluded that PU composite foams filled with 1 *wt%* of nutmeg filler leads to PU composite foams with improved compression strength (*e.g.* improvement by ~19% f), higher flexural strength (e.g. increase of ~11%) and improved impact strength (e.g. increase of ~32%). Moreover, the modification of the PU foams with nutmeg filler has a positive effect on the fire resistance of PU materials. For example, the results from the cone calorimeter test showed that the incorporation of 5 *wt%* of nutmeg filler significantly reduced the peak of heat release rate (pHRR) by *ca.* 60% compared with that of unmodified PU foam. It has been also proved that nutmeg filler may act as a natural anti-aging compound of PU foams. The incorporation of nutmeg filler in each amount successfully improved the stabilization of PU composite foams. Based on the antibacterial results, it has been shown that the addition of nutmeg filler significantly improved the antibacterial properties of PU composite foams. Therefore, nutmeg can be successfully used as a cheap, environmentally friendly and easily available natural additive for the production of PU materials with antibacterial properties.

Declaration of competing interest

None.

CRediT authorship contribution statement

Sylwia Członka: Methodology, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Anna Strąkowska:** Methodology, Investigation. **Agnė Kairytė:** Methodology, Investigation. **Arūnas Kremensas:** Methodology, Investigation.

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