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Towards sustainable catalyst-free biomass-based polyurethane-wood composites (PU-WC): From valorization and liquefaction to future generation of biocomposites

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ABSTRACT

A substantial aspect of materials engineering lies in the responsible process of designing polymer-based materials. Due to environmental pollution, excessive consumption of natural resources, and increasing environmental awareness of society, there is a massive need for polyurethane (PU) materials with reduced environmental impact. To date, research on catalyst-free polyurethane-wood composites (PU-WC) has demonstrated a huge potential for commercialization in industrial production and can be used as a replacement for commonly used wood-plastic composites and wood-based panels. Based on this research, the introduction of new greener alternatives for petrochemical polyols to develop PU-WCs with a high biomass share could be interesting. In this study, up to 80% of bio-based polyol (BP) synthesized via biomass liquefaction was introduced to the polymer matrix. The effect of petrochemical polyol substitution was examined by mechanical testing, scanning electron microscopy (SEM), water absorption tests, and thermal analysis. The conducted research revealed that the structure and properties of PU-WCs strongly depend on the share of BP. The most promising composites were manufactured with up to 40% BP. The flexural strength of the PU-WC decreases from 25 to 9 MPa, and the flexural modulus varies from 1780 to 800 MPa. This may be caused by deteriorated adhesion between composite phases and a reduction in the stiffness of the materials due to the decrease in crosslinking density, which was confirmed by the decrease in glass transition temperature from 96 to 26 °C. In summary, this work shows the next step towards cleaner production of PU-WCs by substituting petrochemical polyols for alternatives synthesized using renewable resources.

1. Introduction

The responsible design of new polymer-based materials has recently been a critical aspect of materials engineering. The observed phenomenon of environmental degradation drives the emerging need for materials with reduced environmental impact, the increasing environmental awareness of society and the excessive depletion of natural resources (Arevalo-Gallegos et al., 2017). For this reason, scientists are looking to shift from petroleum-based materials to green and sustainable alternatives, which will have a significantly lower impact on the environment. This will contribute to the development of a green industry and environmentally conscious society. Moreover, the process of designing materials should focus not only on their impact during manufacturing but also on their long-term use and further disposal. This approach is becoming increasingly popular in commonly used polymeric materials, including polyurethanes (Rosenboom et al., 2022).

Polyurethanes, which are mainly used in the construction and building industry, furniture manufacturing, automotive engineering, and apparel production, are very versatile materials whose properties could be easily adapted to a particular application (Das and Mahanwar, 2020). This specific property of PU originates from the possibility of chemical and physical structure modification by changing substrates and process conditions. Selecting the appropriate components and manufacturing parameters allows to obtain polyurethane materials in the form of polyurethane foams (Polaczek et al., 2022), adhesives (Ruan et al., 2019), resins (Echeverria-Altuna et al., 2022), coatings, and thin layers (Noreen et al., 2016). The production process of polyurethane materials is primarily based on a polyaddition reaction where

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isocyanates react with compounds featuring a minimum of two hydrogen-donating hydroxyl groups, which are named polyols. This reaction leads to the generation of urethane groups, contributing to the polymer chain's growth (De Souza et al., 2021). Beyond these components, polyurethane materials may also contain chain extenders, catalysts, surfactants, fillers, blowing agents, and numerous other additives that collectively influence the material properties (Sharmin et al., 2012).

Unfortunately, all the aforementioned substances used in PU manufacturing primarily originate from petrochemical sources. To reduce the use of petrochemical feedstock, scientists are looking for less harmful and renewable alternatives to these raw materials that will enable the production of functional and environmentally sustainable materials. Currently, there are many trends in research aimed at implementing more environmentally friendly compounds, including the synthesis of non-isocyanate polyurethanes (NIPU) (Khatoon et al., 2021), the incorporation of ecological fillers (Kuranchie et al., 2021) and the development of BP and bio-isocyanates (Niesiobędzka and Datta, 2023).

The most developed and commonly used method involves incorporating ecological fillers into the polymer matrix. This not only reduces the amount of polymer used but also significantly influences the material properties because of the interactions between the filler and the polymer matrix. Moreover, the process of the filler generation may be beneficial for the environment. Fredlich (Friedrich, 2018) suggests that wood plastic composites (WPCs) have an approximately balanced cradle-to-gate carbon dioxide (CO_2) balance due to the high filler addition. This is caused by the fact that wood fibers absorb a certain amount of greenhouse gases during their growth. This quantity is comparable to emissions during energy production, fuel consumption, and material manufacturing. Therefore, wood is a very interesting filler for polyurethane composite manufacturing, and its waste management become an important issue due to the extensive process of deforestation.

Fornasieri et al. (2011) synthesized polyurethane/wood composites by incorporating chemically modified wood waste and polyols. These polyols were synthesized through poly (ethylene terephthalate) glycolysis process using ethylene glycol. The results indicated that samples with 10% wood addition have good mechanical properties, which may be caused by the presence of covalent bonding between the isocyanate-modified wood and the polyols. This results in improved interactions and adhesion between both substances and possibly contributed to an increase in Young's modulus and tensile strength. Wang et al. (B. Wang et al., 2023) evaluated the effect of flame retardants on the properties of foamed polyurethane/wood-flour composites with 40% wood addition. The authors comprehensively analyzed the thermal decomposition, flame retardancy and water absorption properties of manufactured materials. Furthermore, the flame-retardancy mechanism of ammonium polyphosphate (APP) in the composites was examined by SEM, energy dispersive spectroscopy (EDS), Fourier-transform infrared spectroscopy and 2D-IR spectra analysis. The tests demonstrated a reduction in fire risk, indicating APP efficiently enhanced composites' fire safety. Moreover, the authors claimed that APP has a significant influence on gas-phase and solid-phase flame retardance mechanisms.

Another method for the reduction of PUs environmental impact is the synthesis of BP from renewable raw materials and their subsequent use as a substitute for petrochemical polyols. Renewable resources for BP synthesis may include cellulose (Kosmela et al., 2016), lignin (Hu et al., 2014), castor oil, rapeseed oil, soybean oil (Ni et al., 2010), mustard seed oil (Borowicz et al., 2020), algae (Kim et al., 2015), wood bark and wood processing wastes (D'Souza and Yan, 2013). This substitution process increases the sustainability of materials but also may enhance the quality of PUs, reduce material costs, and improve biodegradability. In the scientific literature, various processes for the synthesis of BP are available. One such method is solvothermal liquefaction, which is based on the solvolysis reaction of bio-based substances in the presence of low-molecular-weight solvents containing a certain amount of hydroxyl groups (glycerol, poly (ethylene glycol) (PEG), etc.). This reaction results in the cleavage of biomass long chains resulting in the generation of lower molecular weight compounds. This procedure occurs within a temperature range of 120–250 °C under standard pressure conditions and with up to 3% of a homogeneous catalyst, which are mainly strong acids and strong bases. The resulting BP is a mixture of compounds rich in hydroxyl groups, including glycols and glycerol derivatives, ethers, esters, carboxylic acids, and carbohydrates. These polyols are successfully employed as substitutes for petrochemical polyols in manufacturing polyurethane materials such as PU foams, adhesives, thin layers, resins, and composites.

A recent analysis by Guo et al. (2023) reveals the mechanism and kinetics of wheat straw liquefaction in three different solvents: ethylene glycol, glycerol and a mixture of PEG400 (poly (ethylene glycol) with $M_w = 400$ g/mol) and glycerol. The authors revealed that the choice of liquefaction solvents had a significant impact on the composition of liquefied products and the efficiency of the liquefaction process. They proposed that the liquefaction process can be divided into two processes. Firstly, there is a rapid liquefaction of hemicellulose due to chemical structure degradation, followed by slower liquefaction attributed to the decomposition of the crystalline phase in cellulose and acid-soluble lignin. Prolonged liquefaction time may result in a recondensation process that increases the solid residue. Moreover, the authors suggested that the proposed process is an endothermic process with a second-order kinetics reaction and an activation energy of 9.31 kJ mol^{-1}.

Arman et al. (Amran et al., 2019) presented the optimization of the oil palm empty fruit bunch fibre (EFB) and EFB-based cellulose (EFBC) liquefaction process by determining the appropriate temperature and reaction time. The authors proposed the most suitable process parameters through a comparison of biomass conversion ratio, hydroxyl value, molecular weight and viscosity of the synthesized polyols. The selected BP were used for manufacturing polyurethane materials. The results obtained indicated that BP had a significant effect on the cellular structure of the materials, which influenced Young's modulus (MPa), compressive strength and thermal properties of PUFs.

In previous research (Olszewski et al., 2023a), a polyurethane catalyst-free highly-loaded wood (up to 80 wt%) composites was developed through a two-step compression molding process. The pine wood shavings were mixed applying optimized processing with commercially available polyols and isocyanate resulting in high-performance composites. Of note, the developed material enjoyed a precise density, promising mechanical properties ($\sigma_{max} = 25.11$ MPa and $E = 1255$ MPa), and superior water absorption characteristics of particleboards and medium-density fiberboards (MDF). Based on these achievements, the development of a more sustainable catalyst-free with a high biomass share could be interesting. Greener products rather than fossil-based PU are a necessity for the further development of future generations of biocomposites. For this reason, introducing biomass liquefaction products, which are potential substitutes for petrochemical polyols, may be beneficial for the environment. This will allow for an enlarged environmental safety window as well as less use of hazardous substances for the sake of taking the next step towards the commercialization of green PU materials.

This study aims to determine the influence of petrochemical polyol substitution with previously synthesized BP on the structure and properties of PU-WC. The polyol addition aims to reduce the environmental impact of the PU-WCs. To achieve this goal, we manufactured five sets of catalyst-free PU-WC composites with petrochemical polyol substitution of up to 80% by BP synthesized via biomass liquefaction. The mechanical properties of bio-based PU-WCs were evaluated by a three-point bending test, Shore D hardness and Charpy impact tests. The structure of composites was analyzed using SEM. Furthermore, thermal properties were examined by dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and heat flow meter. Additionally, water absorption, cyclic water absorption, and dimension stability were determined to assess the impact of aqueous environments on the composite properties. The present work has huge potential to contribute to the development of new eco-friendly wood materials, which will be primarily sourced from renewable raw materials and could be easily implemented in industrial production to increase the availability of next-generation green materials.

2. Materials and methods

Comprehensive information regarding the substances used in the production of PU-WCs can be found in section SD1 of the Supplementary Data file (SD). Additionally, all the methods used for the characterization of PU-WCs are described in section SD2. PU-WCs were subjected to various mechanical tests, including three-point bending tests, Charpy impact strength test, and hardness evaluations. The thermal and thermomechanical properties of composites were tested using thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and thermal conductivity measurement. SEM was used to evaluate the structure of PU-WCs. Finally, the impact of aqueous environments on the composite properties was evaluated by water absorption, cyclic water absorption, and dimension stability tests. All tests were conducted according to relevant standards. SD file contains information about all test equipment and applied test parameters.

2.1. Manufacturing of PU-WCs

Before manufacturing PU-WCs, pine wood shavings were initially sieved to separate too large wood particles. After this, the filler was dried at 100 °C for 24 h. The manufacturing of PU-WCs was carried out using a one-step method involving a two-component system (Component A and Component B). As a component A, a mixture of Rokopol® RF551, Rokopol® M6000, and surfactant was used. Component A was premixed using a mechanical mixer. Then, Component B (Ongronat 2100 - polymeric methylene diphenyl diisocyanate – pMDI) was added to Component A and homogenized using a mechanical mixer. The calculated ratio of NCO/OH groups (I_{NCO} - isocyanate index) was equal to 1. Notably, all materials were manufactured without the use of any chemical catalyst. The prepared mixture was mixed with pine wood shavings using a planetary mixer for 10 min.

Possible reactions which may occur during material synthesis are shown in Fig. 1. These reactions involve the interaction between bio-/petrochemical polyols and isocyanates, leading to polyurethane synthesis. Additionally, reactions between wood components (hemicellulose, cellulose, and lignin) and isocyanates may occur. After mixing, the material was transferred into a steel mold (205 × 100 × 10 mm) and then subjected to hot pressing using an industrial hot press ($T = 100$ °C; $t = 15$ min, $p = 5$ MPa). To cool down the samples and maintain their shape, the samples were cold pressed ($T = 20$ °C; $t = 5$ min; $p = 2.5$ MPa). Five sets of PU-WCs with varying amounts of BP were manufactured, with BP content ranging from 0% (0 g/php – grams per 100 g of polyol) to 80% (80 g/php). For this purpose, the amount of petrochemical polyol Rokopol RF 551 was consecutively reduced from 80% (80 g/php) by 20% (20 g/php) and replaced by BP. The amount of M6000 polyol (20 g/php = 20%) has not been changed, as the addition of this polyol reduces the brittleness of the composites. To minimize the influence of density on the composite's properties, the density was set to $\rho = 0.78 \pm 0.02$ g/cm^3. Samples after the manufacturing process and after cutting out are shown in Fig. 2 and the percentage composition of the obtained samples is presented in Table 1. The samples were labeled as PU-WC *XX*% Bio, where '*XX*' represent the percentage of use BP.

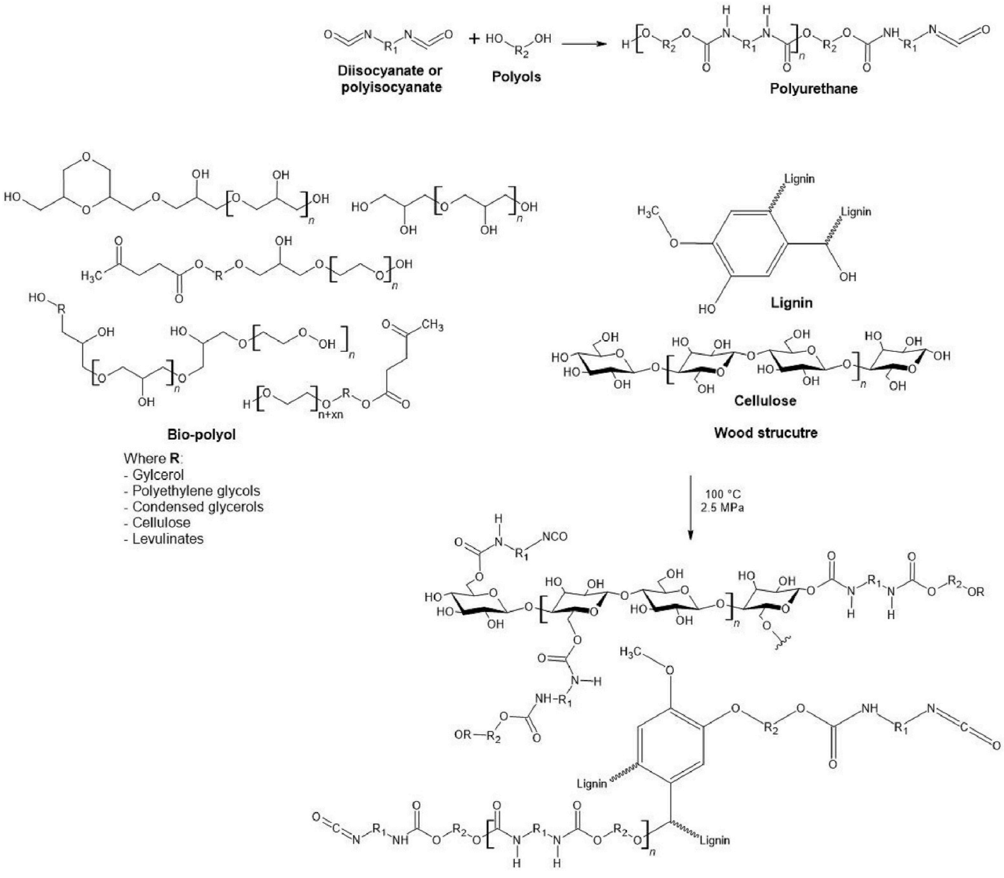


Fig. 1. Possible reactions occurring during PU-WC synthesis.

Fig. 2. Manufactured polyurethane-wood composites (from left PU-WC 0% Bio; PU-WC 20% Bio, PU-WC 40% Bio, PU-WC 60% Bio, and PU-WC 80% Bio).

Table 1
PU-WCs percentage composition.

Sample	Percentage composition of sample [%]					
	Rokopol RF551	Rokopol M6000	Bio-based polyol (BP)	pMDI	Pine sawdust	Tegostab B8465
PU-WC 0% Bio	16.16	4.17	0	18.01	60	1.17
PU-WC 20% Bio	11.77	3.92	3.92	19.21		
PU-WC 40% Bio	7.42	3.71	7.42	20.28		
PU-WC 60% Bio	3.52	3.52	10.55	21.24		
PU-WC 80% Bio	0	3.35	13.38	22.11		

3. Results and discussion

3.1. *Characterization of wood shavings*

The filler's characteristics are among the most crucial factors that significantly affect the properties of WPCs. Due to the fact that the impact of wood particle size distribution on the properties of various wood composites has been extensively explored in other scientific studies (Delviawan et al., 2019; Siddikur Rahman et al., 2018), in this research, the influence of filler size is not the scope of this research. This data is presented to allow comparisons presented research with other papers. The most essential properties of filler are summarized in Table 2. One of the reasons that wood shavings were not separated into fractions was a reduction of additional processes, which may increase further costs of materials production in industrial processes.

Table 2
Characteristic of wood shavings.

Particle size [mm]	Percentage content [%]	Water content before drying [%]	Water content after drying [%]
<0.1	0.02	5.59 ± 0.16	1.15 ± 0.06
>0.1	1.85		
>0.2	2.74		
>0.4	12.23		
>0.6	25.10		
>1	52.78		
>2	5.28		

3.2. *Mechanical properties of composites*

The selected mechanical properties of PU-WCs are presented in Figs. 3–5. To decrease the influence of material density on the properties, the density of all samples was 0.78 ± 0.02 g/cm^3. As can be seen in Fig. 3 the three-point flexural tests show a significant relationship between the addition of BPs and mechanical properties of composites. The flexural modulus for the PU-WC 0% Bio was 1750 MPa and decreased to 1000 and 780 MPa for PU-WC 40% Bio and PU-WC 80% Bio, respectively. The flexural strength decreased from around 25 MPa for PU-WC 0% Bio to 12.5 and 9.8 MPa for PU-WC 40% Bio and PU-WC 80% Bio, respectively. The observed decrease in flexural modulus and flexural strength could be interpreted as a decrease in crosslinking density caused by the addition of BPs and the potential change in glass transition temperature (T_g). The decrease in T_g was confirmed by DMA analysis and was further discussed in subsection *3.5.2. Dynamic mechanical analysis (DMA)*. This is a somewhat surprising result since the addition of BPs in other types of materials (especially PU foams) was responsible for the increase in crosslinking density and mechanical properties (Kosmela et al., 2017). In the case of PU-WCs, this effect may be caused by reduced reactivity of BPs, which mainly contain secondary hydroxyl groups. The reactivity of these groups is not boosted by the addition of an appropriate catalyst. In the case of PU foams, the most commonly used catalysts are organotin (dibutyltin dilaurate tin-2-ethylhexanoate) and amine catalysts (DABCO - 1,4-diazabicyclo [2.2.2]octane) (Jiang et al., 2022; Li et al., 2017; Zhang et al., 2020). Moreover, the introduction of BP with a more complex structure may cause the presence of steric hindrances, which may reduce the reactivity of the polyurethane matrix and weaken the interactions between the phases of composites, which leads to the reduction of adhesion. For this reason, the stress transfer between wood particles and the PU matrix deteriorates. This may cause accelerated cracking of the material in the most stressed areas. On the other hand, the addition of the BPs caused a slight increase in the maximal deformation of PU-WCs. This effect may be interpreted as the increase of the composite's elasticity due to the decrease of crosslinking density and interaction between both phases.

Analyzing the results of compression tests presented in Fig. 4 a significant reduction of compressive strength with the addition of BPs may be noticed. This effect may be caused by the reduction of the composite's stiffness by the reduction of the crosslinking density. Moreover, due to the limited adhesion in samples with the addition of BP, the stress transfer between phases deteriorates. The maximal compressive strength of composites decreased from 39.94 MPa for PU-WC 0% Bio to 21.74 and 11.33 for PU-WC 40% Bio and PU-WC 80% Bio, respectively. The same effect is observed for strain at different compression levels. Moreover, the maximum compressive strength of samples with BP occurs at lower elongations. This may be evidence of conciseness reduction, which leads to the accelerated failure of material. This effect is especially noticeable on strain/stress curves for these materials, which are presented in Fig. 4b. From Fig. 5, it can be noted that impact strength

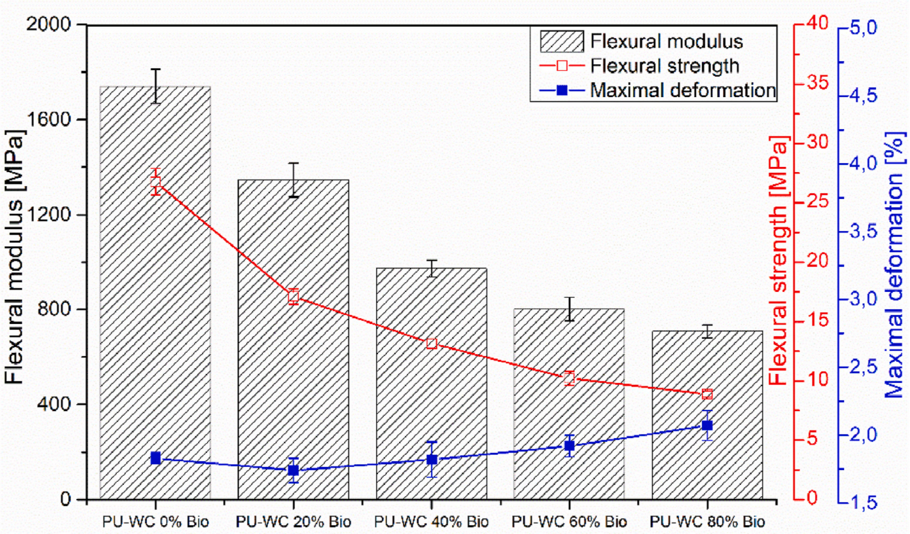


Fig. 3. PU-WCs three-point flexural test results.

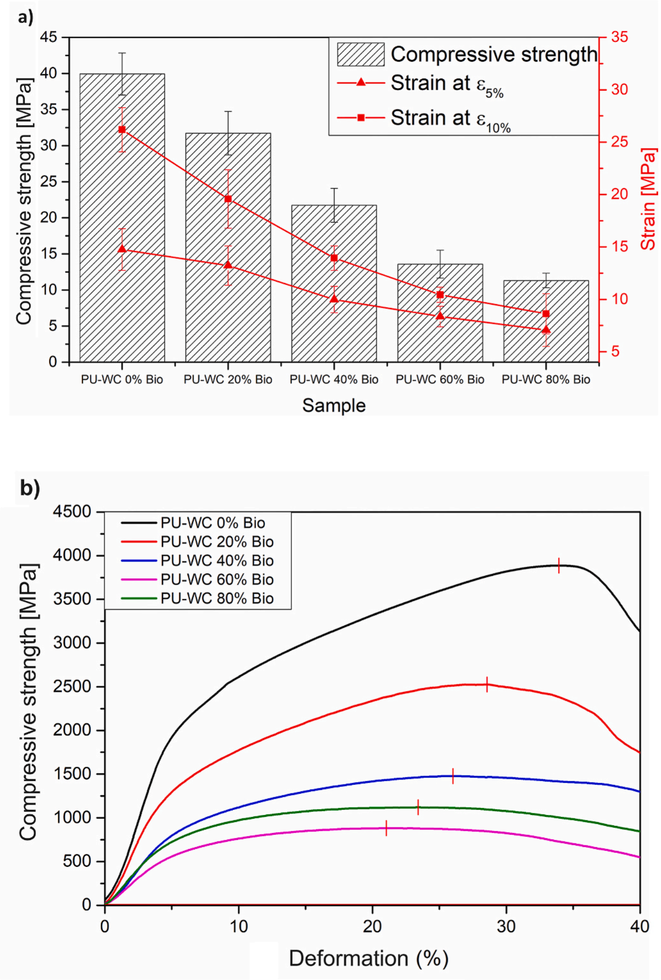


Fig. 4. (a) Compressive strength and strain at 5% and 10% deformation and (b) selected compression curves.

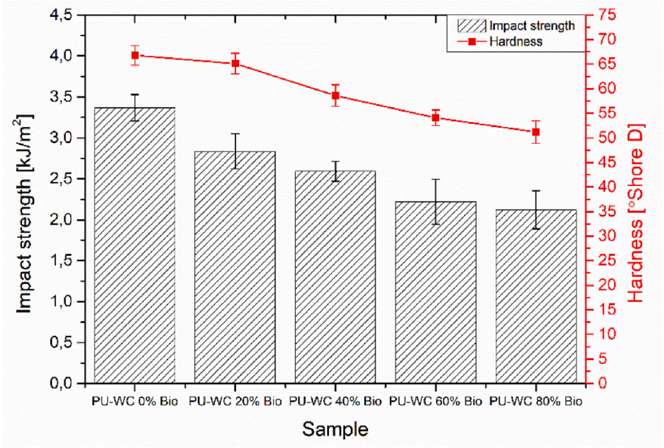


Fig. 5. PU-WCs impact strength and hardness results.

and hardness also decrease with the addition of BPs. This can also be attributed to deteriorated stress transfer caused by limited adhesion. On the other hand, the influence on the impact strength of composites is lower than for other mechanical parameters. This may be due to the increased ductility of PU-WC with higher biopolyol addition, which was confirmed by increased maximal elongation in flexural tests. Improved ductility may reduce vulnerability to cracking at stress concentration points. The most important stress concentration points are filler agglomerates, unbonded filler fragments, and pores caused by local foaming. Additionally, the properties of manufactured composites were compared to the currently available materials on the market to confirm their usefulness (SD 4. *Comparison to the wood-based materials available on the market)*.

3.3. Influence of aqueous environments on PU-WCs

As the wood-like materials are vulnerable to moisture, water adsorption and dimensional stability tests were conducted to study the influence of the aquatic environment on the behaviour of PU-WCs with BP addition. The results of these tests are presented in Fig. 6. The tests revealed a significant influence of BPs on water absorption. Water molecules may be transferred into four possible locations, i.e. a) interfacial voids between polyurethane matrix and wood, b) wood via specific structure and presence of functional groups, c) voids generated during local foaming of material and d) polyurethane matrix water absorption (Petchwattana et al., 2017).

Results indicate an increase in time to reach an equilibrium state for samples with higher BP addition. Samples with up to 60% BP addition

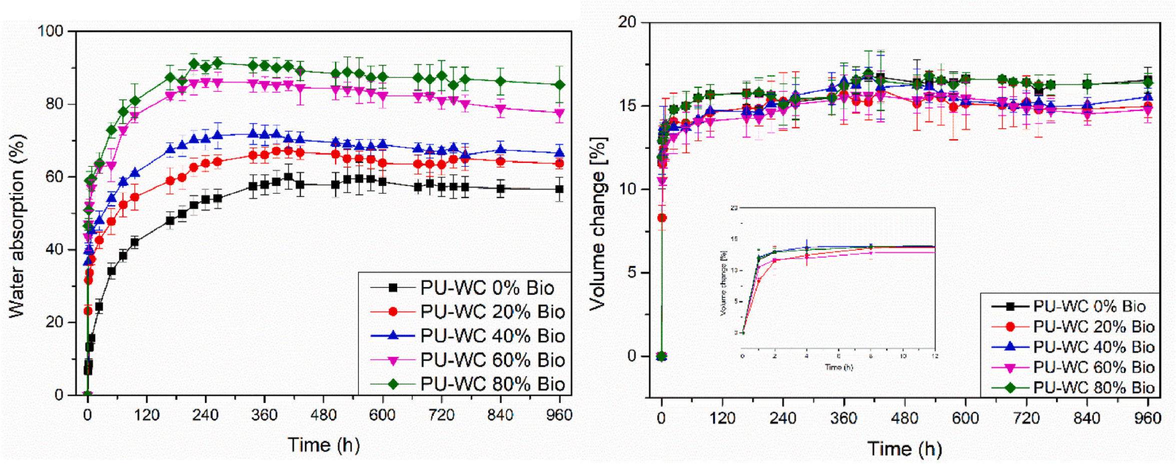


Fig. 6. **a)** Water absorption and **b)** dimensional stability of PU-WCs

reached the equilibrium state after around 360 h. For samples with higher BP addition, the equilibrium state was reached after 240 h (5 days earlier). Analyzing water uptake of PU-WCs, a significant increase in water absorption with the addition of BPs can be noticed. A possible explanation for this effect may be a limited coating of filler by the polyurethane. Exposed free hydroxyl of wood on the material external and internal surfaces may cause accelerated water intake (Al-Maharma and Al-Huniti, 2019; Q. Q. Wang et al., 2023). Moreover, these effects could be intensified by a potential increase in the hydrophilicity of the material with the addition of BP. The water absorption at the equilibrium state increased from 58 % for PU-WC 0% Bio to 71 % and 82 % for PU-WC 40% Bio and PU-WC 60% Bio, respectively. Analyzing the influence of BP on the dimensional stability of PU-WCs, only minor differences comparable to measurement error can be noticed. This is due to increased water uptake of partially exposed wood in samples with deteriorated adhesion between both phases. It can also indicate that the primary mechanism of water uptake in these materials is the diffusion of water to material voids, not the water uptake of wood-fiber and polyurethane matrix.

The vulnerability of PU-WCs to the cyclic swelling and drying cycles was tested by cyclic water absorption tests. All samples were subjected to five swelling-drying cycles. Each cycle lasted one week (120 h of swelling – 48 h of drying). Analyzing Fig. 7, it is clear that the addition of BP has a significant influence on the cyclic water absorption tests. What is interesting here is the noticeable reduction of PU-WC mass after the first cycle. This effect is visible for samples with at least 40% BP addition. This effect may be attributed to the leaching of unbound compounds and the dissolution of extractives. After the second cycle, a slight increase in water absorption can be noticed. This may be caused by the penetration of water into the spaces with previously leached substances. For the next cycles, a consecutive decrease of maximal water absorption occurred. This may be caused by further release of substances into the water or their dissolution, which results in a mass loss of samples.

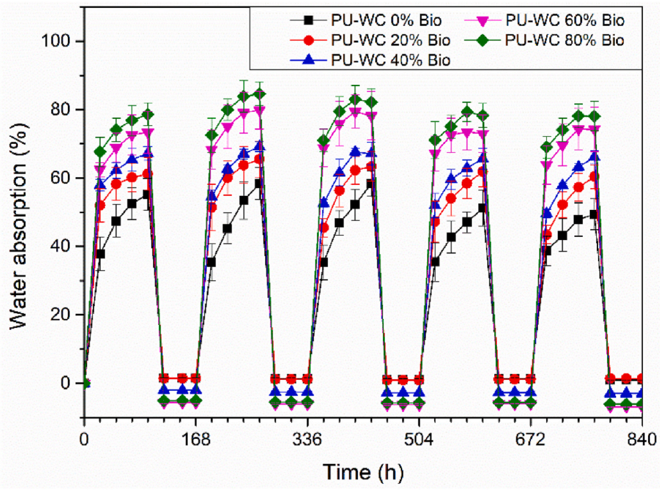


Fig. 7. Cyclic water absorption of composites.

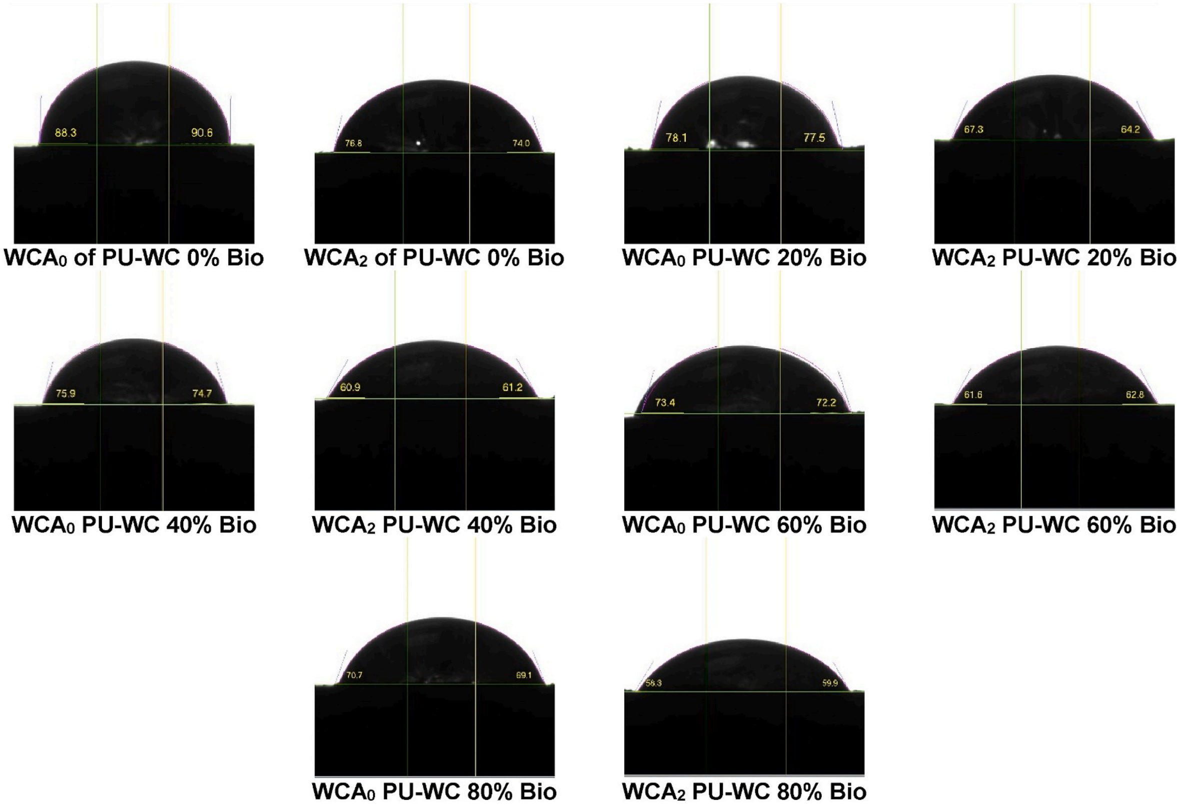
3.4. *Contact angle measurement (CAM)*

CAM was carried out to determine the influence of BP addition on the hydrophobicity/hydrophilicity and surface properties of PU-WCs. Due to the porosity of the composites and the intense absorption of liquids, the test was conducted using glycerol. The results of this test are presented in Fig. 8 and Table 3. As shown in Table 3, all materials have WCA_0 lower than 90°, therefore, they can be considered hydrophilic. The WCA_0 decreases with addition from 89.0° to 75.0 and 71.2° for PU-WC 40% Bio and PU-WC 80% Bio, respectively. At the same time, adhesion work and surface energy significantly increased. This indicates a greater wettability of the liquid to the material, which may be related to the simultaneous increase in water absorption of the composites. The observed change may be due to the introduction of more polar segments made of BP into the structure of the composite. For this reason, water molecules are more easily absorbed into the surface of the material and are more quickly absorbed into the deeper layers of the material. This result is in line with the results of water absorption tests, where water absorption increases with BP content. Moreover, the abovementioned porosity and significant surface roughness had a noticeable impact on the measurement error. For this reason, the measurement deviation may be higher than standard measurements.

3.5. *Thermal properties*

3.5.1. *Thermogravimetric analysis (TGA)*

The influence of BPs on the process of thermal decomposition of PU-WCs was validated by the thermogravimetric analysis. The results of these tests are presented in Fig. 9 and Table 4. Moreover, TG and DTG curves of pine wood shaving and unmodified matrix are presented in the SD file. Our previous studies (Olszewski et al., 2024) have shown that the addition of synthesized BP to the polyurethane-isocyanurate foams (PU-PIR foams) slightly increases thermal stability. This is a somewhat surprising result, as in the case of PU-WCs, obtained data shows a minor decrease in thermal stability due to the BP addition. This is the most visible during comparison of temperature at 5% mass degradation ($T_{5\%}$). $T_{5\%}$ decreased from 270 °C for PU-WC 0% Bio to 254 °C and 243 °C for



WCA_0 of PU-WC 0% Bio
WCA_2 of PU-WC 0% Bio
WCA_0 PU-WC 20% Bio
WCA_2 PU-WC 20% Bio
WCA_0 PU-WC 40% Bio
WCA_2 PU-WC 40% Bio
WCA_0 PU-WC 60% Bio
WCA_2 PU-WC 60% Bio
WCA_0 PU-WC 80% Bio
WCA_2 PU-WC 80% Bio

Fig. 8. Glycerol contact angles of composites at $t = 0$ min (WCA_0) and $t = 2$ min (WCA_2).

Table 3
The wetting properties of PU-WCs: WCA_0 - water contact angle at 0 min, WCA_2 - water contact angle at 2 min, ACAR - average contact angle reduction after 2 min (ACAR), $T = 22$ °C.

Sample	WCA_0 [°]	WCA_2 [°]	ACAR [%]	Adhesion work$_0$ [mJ/m^2]	Surface energy$_0$ [mN/m^2]
PU-WC 0% Bio	89.0 ± 3.2	76.3 ± 4.5	14.2	64.19 ± 3.49	23.94 ± 1.77
PU-WC 20% Bio	79.9 ± 3.3	66.7 ± 6.8	16.5	74.16 ± 3.57	29.09 ± 1.87
PU-WC 40% Bio	75.0 ± 3.4	61.4 ± 1.8	18.1	79.41 ± 2.85	31.88 ± 1.53
PU-WC 60% Bio	73.4 ± 2.3	62.4 ± 2.0	14.9	81.12 ± 2.43	32.79 ± 1.31
PU-WC 80% Bio	71.2 ± 1.9	63.6 ± 2.1	10.7	83.44 ± 1.92	34.05 ± 1.05

PU-WC 40% and PU-WC 80%, respectively. This effect may be explained by the earlier degradation of BP chains than petrochemical polyol RF551. The difference between $T_{10\%}$ of samples is smaller, and $T_{50\%}$ is almost identical for all materials. Despite the fact that curves show one visible peak of maximal degradation around $T_{max} \approx 370$ °C, the thermal decomposition process of PU-WCs is complex and should be divided into four decomposition stages.

Before the start of the degradation process, a small peak at around 100 °C is visible. It is due to the moisture content and the release of residual volatile substances (Madhav Gondaliya et al., 2023). The first degradation step occurs from 200 °C to 300 °C and may be assigned to the degradation of PU soft-segments composed of P400 BP (Jiao et al., 2013; Olszewski et al., 2023b) and the beginning of hemicelluloses and cellulose degradation. The second step, which occurs around 300–400 °C, may be attributed to the degradation of cellulose in wood structure, further degradation of soft segments compostes of BP P400 and decomposition of hard segments of PU (Fatima Ezzahrae et al., 2023; Olszewski et al., 2023b). Overlapping of these three effects results in the occurrence of the maximum degradation rate around $T_{max} \approx 360$ °C. The third degradation step may be noticed in the temperature range of 400–500 °C and may be assigned to the decomposition of lignin and the longest chains in soft segments (Jeske et al., 2012; Olszewski et al., 2023b). These segments are mainly composed of petrochemical polyols (M6000, RF551) and the longest chains of BP, which are composed of (PEG) chains and possible condensation products of PEG. The last degradation step above 500 °C arises due to the thermolysis of degradation products formed during previous degradation steps. Additionally, a minor increase in char residue can be noticed. This may be due to the addition of BP, which has a higher molecular mass and may contain solid particles which are products of recondensation during the liquefaction process.

3.5.2. *Dynamic mechanical analysis (DMA)*

Table 5 and Fig. 10 show the DMA results for PU-WCs. The curves for pine wood and polyurethane matrix are presented in the SD file. It can be noticed that composites with up to 20% BP addition show two glass transition temperatures (T_g), and composites with higher BP addition have three T_g. In the case of PU-WCs, all glass transition temperatures were determined from the maximal values of loss modulus peaks. According to the current convention, the $T_{g\alpha}$ was assigned to the glass transition of the main polymer chain, and $T_{g\beta}$ and $T_{g\gamma}$ are the secondary loss peaks. Due to the complex structure of manufactured material, observed peaks are a superposition of several effects which occur in the sample during the test. For this reason, the effect of BP should be described for each peak separately. Analyzing the secondary peak β ($T_g \approx -70$ °C), it could be noticed that the addition of BPs did not affect the temperature of this transition. The appearance of this peak can be attributed to the overlapping of glass transition temperature of long and elastic chains of petrochemical polyol M6000, secondary glass transition of Rokopol RF 551 (Olszewski et al., 2023a), and glass transition of

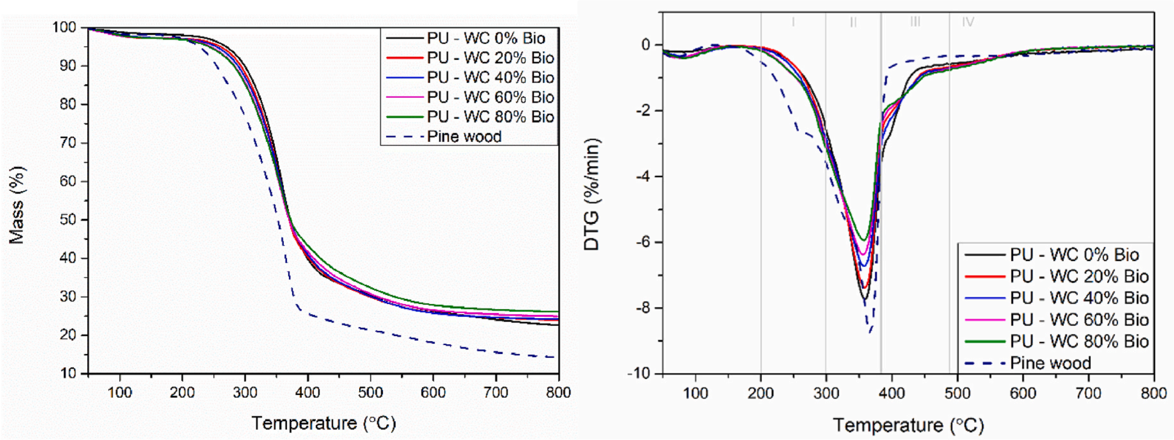


Fig. 9. **a)** TGA and **b)** DTG results of PU-WCs.

Table 4
Results of thermogravimetric analysis.

Sample	% mass loss in temperature [°C]			T_{max1} [°C]	Char residue after test [%]
	5%	10%	50%		
PU-WC 0% Bio	270	299	372	359	22.62
PU-WC 20% Bio	261	293	370	358	23.99
PU-WC 40% Bio	254	288	371	357	24.16
PU-WC 60% Bio	245	283	370	356	24.94
PU-WC 80% Bio	243	282	372	357	26.11
Pine wood	227	257	351	366	14.26

Table 5
Detailed results of DMA.

SAMPLE	$T_{g\beta}$ [°C]	$T_{g\alpha}$ [°C]	$T_{g\gamma}$ [°C]	Storage modulus at 25 °C [MPA]	Tanδ [-]
PU-WC 0% BIO	−73	96	–	1550	0.120
PU-WC 20% BIO	−70	82	–	1228	0.121
PU-WC 40% BIO	−67	33	183	953	0.132
PU-WC 60% BIO	−69	26	178	807	0.144
PU-WC 80% BIO	−71	23	172	567	0.141
PINE WOOD[a]	−69	66	–	4494	0.030

[a] A sample cut from a pine board.

noncrystalline structures of hemicelluloses and celluloses in the wood structure (Ashaduzzaman et al., 2020). Long chains of polyol M6000 with low glass transition temperature provide partial elasticity and resistance to cracking of composite.

On the other hand, the addition of the BP has a significant influence on the position and the shape of peak α, which may be attributed to the glass–liquid transition of PU segments composed of BP and petrochemical polyol Rokopol RF551. $T_{g\alpha}$ for the PU-WC 0% Bio sample was 96 °C and decreased to 33 °C and 23 °C for PU-WC 40% Bio and PU-WC 80% Bio, respectively. This is a rather unexpected result because, in the case of polyurethane foams, an addition of BPs increases the glass transition temperature (Chen and Lu, 2009; Yue et al., 2017). This may be caused by possible phase separation due to the differences in polarity, decreased crosslinking density, and lower glass transition of the BP chain in comparison to RF 551. Moreover, BPs contain less reactive secondary hydroxyl groups, which may not react with isocyanate and may act as a steric hindrance and plasticizer, which decreases glass transition temperature. One possible explanation for this result is the presence of different types of catalysts in PU foams, which increases the reactivity of hydroxyl groups with isocyanates. The decrease in the glass transition temperature may be connected to the observed decrease in mechanical properties. The mechanical testing was performed during the viscoelastic transition. For this reason, the mechanical properties of PU-WCs with a higher amount of BP were reduced.

What is interesting in the case of PU-WC is that the additional peak is observed ($T_{g\gamma}$) in temperatures around 175 °C for samples with a greater amount of BP. This peak may indicate the formation of highly cross-linked structures, which may be due to the structure of condensed glycerols or isocyanurates, which were generated during the trimerization of isocyanates (Hejna et al., 2017; Ivdre et al., 2020).

3.6. *Thermal conductivity of BP modified PU-WC*

As the potential application of materials is the construction and the building industry depends on the thermal conductivity, the influence of BP on insulation properties was examined. According to the theory, the thermal resistance (R) is closely related to the thermal conductivity (λ) and thickness of the sample (d), as shown in equation (1).

$$R = \frac{d}{\lambda} \tag{1}$$

All the samples tested had a comparable thickness. Therefore, when the thermal conductivity decreases, the resistance increases. In addition, heat transfer increases when thermal conductivity increases and thermal resistance decreases. The data presented in Table 6 shows a minor decrease in the thermal conductivity of PU-WCs with the addition of BP. For PU foams, heat transfer can occur through different mechanisms, which include heat transfer through the polymer, gas mixture inside pores, and radiation (radiative heat transfer) (Biedermann et al., 2001). The chemical structure of PU-WCs was changed by the addition of BP. For this reason, modified composites may contain structures which thermal conductivity is different than the reference sample. Moreover, modified adhesion may have an influence on the thermal resistance at the interface between matrix and filler. In the case of PU-WCs, where heat may be transferred between both phases with different thermal conductivities, reduced adhesion may create gaps or air pockets, which act as insulating barriers, reducing thermal conductivity. The contact arena between both phases of the composite is reduced, and heat transfer through the material is limited. Additionally, BP contains a small amount of water, which leads to the local foaming of material. For this reason, modified PU-WCs may have slightly different microstructures than reference materials. The thermal conductivity decreases from 0.1212 W/mK to 0.1161 and 0.1051 W/mK for PU-WC 40% Bio and PU-WC 80% Bio, respectively. Therefore, the addition of bio-poly slows

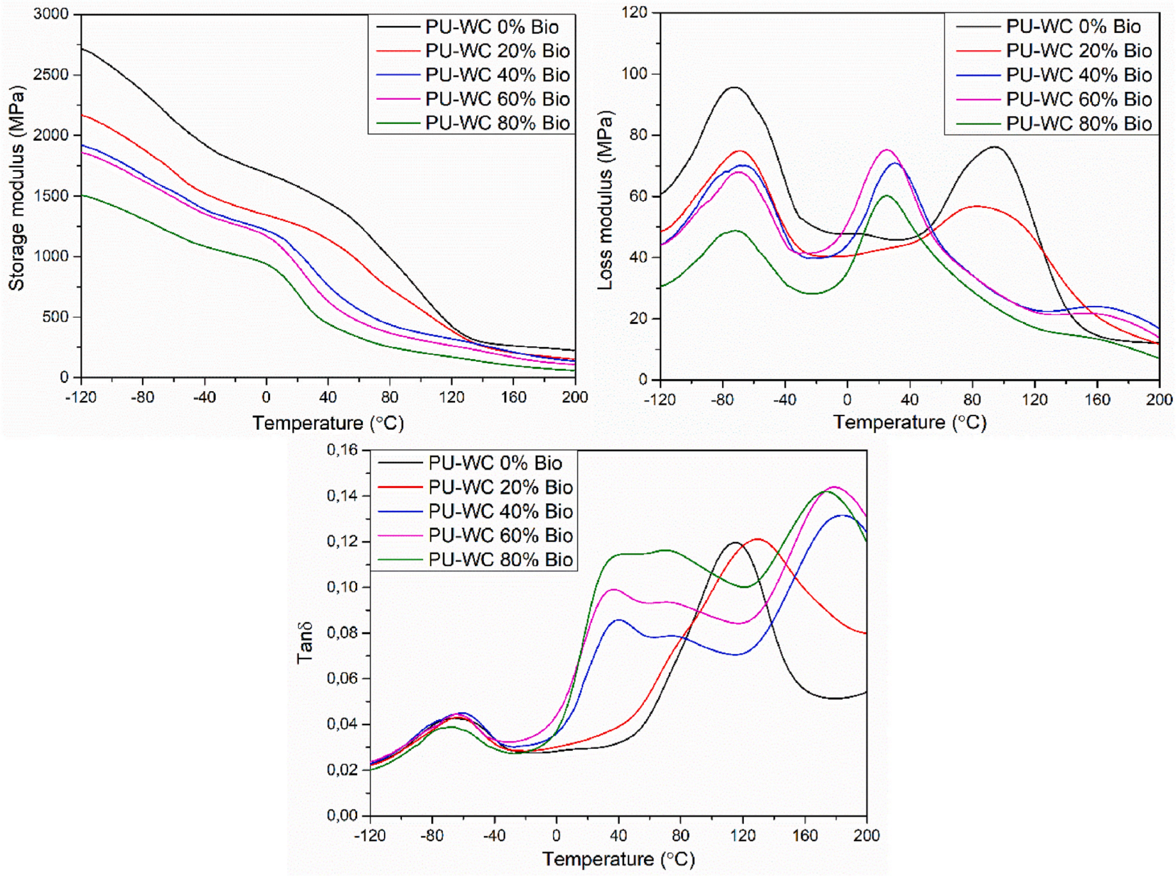


Fig. 10. Results of DMA **a)** Storage modulus, **b)** loss modulus, and **c)** damping factor.

Table 6
Thermal conductivity of PU-WCs

Sample	λ [W/mK]	R [m^{2}K/W]
0% Bio	0,1212	0,0915
20% Bio	0,1175	0,0949
40% Bio	0,1161	0,0978
60% Bio	0,1051	0,1140
80% Bio	0,1040	0,1174
Pine wood*	0.1130	x

down heat transfer. All obtained results are comparable to the thermal conductivity of pine wood. The value of thermal conductivity is satisfactory and is in the range for well-insulated buildings (between 0.1 and 0.2 W/mK (Gustavsen et al., 2011). It is significantly lower than the established thermal conductivity coefficient for floors and ceilings (0.3 W/mK). Moreover, it almost fulfils the required thermal conductivity for underfloor heating panels (0.08 W/mK). Additionally, maximal thermal resistance is lower than required (0.15 m^{2}K/W).

3.7. *Scanning electron microscopy (SEM)*

The influence of BP on the microstructure of PU-WCs was analyzed using SEM. Fig. 11 presents the SEM images of the frozen-fractured surfaces of the PU-WCs. Analyzing the microstructure, the chaotic but repetitive and uniform structure of both phases can be noticed. At the microscopic scale, the structure of manufactured composites is not oriented in any direction, which may indicate that materials may be isotropic in this scale. No significant differences between manufactured PU-WCs were noticed. In the case of all materials, the polyurethane matrix is directly connected with wood fibres, which indicates strong adhesion between both phases (Gadhave et al., 2019). Good adhesion is mainly due to the possible reactions between hydroxyl groups on the wood-fiber surface and isocyanates. The reactions presented in Fig. 1 provide chemical bonding between the polymer chain and the filler. Moreover, the presence of polar groups in the polymer chain and on the filler surface may lead to the formation of hydrogen bonds, which also increase adhesion (Ferdosian et al., 2017). This effect is boosted by the highly developed wood fibre surface. The wood fibre is strongly embedded in the matrix. Therefore, no wood fibre pullouts can be noticed. An important issue for the mechanics of composites is the fracture mechanism of the material. In this case, the cracking of the material proceeds simultaneously through the polymer matrix and the filler. Furthermore, failure of fibres which are parallel and perpendicular to the fracture axis can be observed. A very interesting phenomenon is the internal tear of wood fibre, which occurs in samples with high adhesion between filler and matrix.

Additionally, material defects have an almost equally important influence on the parameter in the case of fracture mechanism. Presence of defects introduces stress concentration points and reduces the cross-section of the specimen (Mehdikhani et al., 2019a, 2019b). In all analyzed specimens, voids between wood filler and matrix were noticed. This is caused by the intentional reduction of sample density and the introduction of gas during material manufacturing. In the case of PU-WCs, a specific type of void is the local foaming caused by the release of CO_2 during the reaction of moisture from wood and BP with isocyanates. This reduces the density of samples. On the other hand, PU in the process of expansion may better fill the spaces between the filler, which leads to improved adhesion and limited water absorption. In specific areas of the composite microstructure, polyurethane matrix passing through wood channels can be observed. On the other hand, density reduction and materials defects lead to a decrease in the

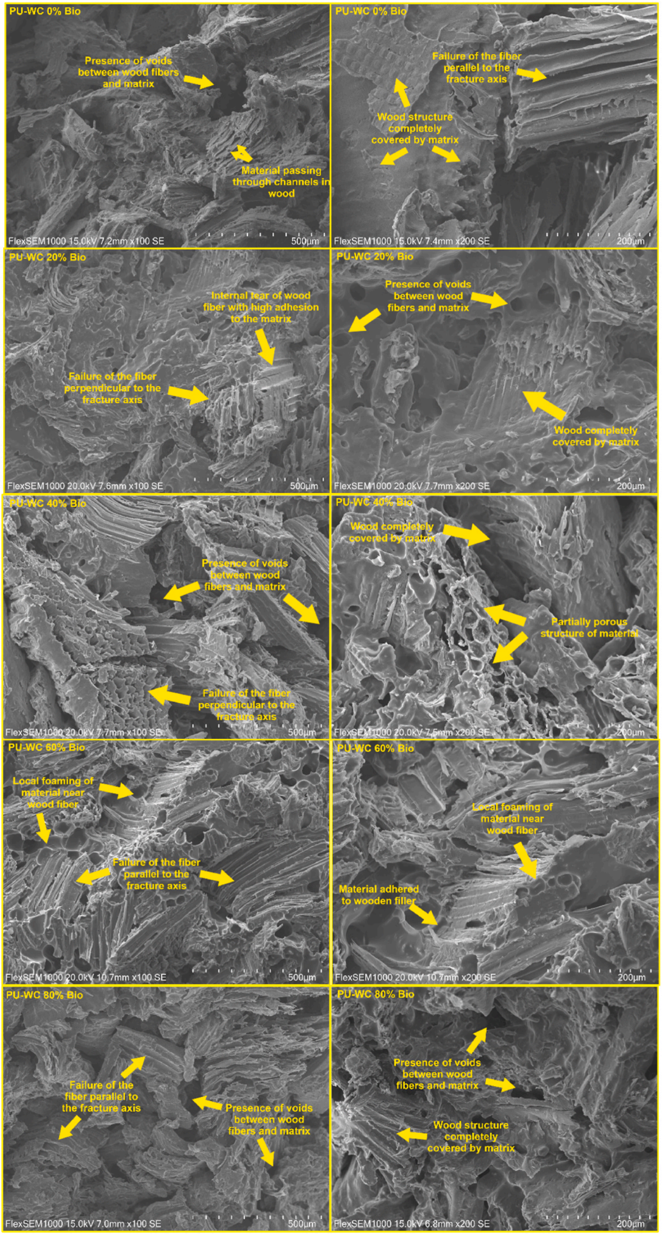


Fig. 11. Microstructure of PU-WCs

mechanical properties. For this reason, a very important variable which may condition the application of materials is material density. The proper value of this parameter is necessary to find a balance between the cost of the material, the mechanical properties and the thermal conductivity.

4. Conclusions

In this study, new types of sustainable catalyst-free PU-WCs were manufactured to achieve greener substitutes for commonly used materials. The main aim of the BP addition was a reduction of petrochemical resource consumption during PU-WC manufacturing. For this reason, PU-WC with up to 80% addition of BP were manufactured using a one-step method involving a two-component system and hot-pressing. It was concluded that the most promising composites were manufactured with up to 40% BPs. The properties of PU-WC 40% Bio are comparable to commercially available wood-like materials, and they contain a significant addition of substances obtained from renewable substances. It should be emphasized that PU-WCs were manufactured without the addition of formaldehyde, which is considered potentially harmful to human health.

This study has shown a significant influence of biopolyols on the structure and properties of PU-WCs. This may be caused by a reduction in the stiffness of the materials due to the decrease in crosslinking density. Furthermore, the presence of less responsive secondary hydroxyl groups in the BPs' structure may limit their reactivity with isocyanates. For this reason, it may act as a steric hindrance or plasticizer and reduce glass transition temperature. The most significant influence of BPs was noticed for mechanical properties. The flexural strength of the PU-WC varies in a range of 15–35 MPa, and the flexural modulus varies from 800 to 1780 MPa. On the other hand, due to the slight improvement of elasticity and reduction of T_g, the influence of BP addition on impact strength was lower. This parameter varies between 2.4 and 3.4 kJ/m^2. The water absorption tests indicate a significant increase in time to reach an equilibrium state for samples with higher BP addition. Additionally, BP addition increased the water absorption of composites. These effects may be due to the limited coverage of the wood fibre by the matrix and the increase in hydrophilicity of the material with the addition of BP. Analyzing the dimensional stability of PU-WCs, no considerable difference between samples can be noticed. This may indicate that the major mechanism of water uptake in these materials may be water diffusion to material voids, not water uptake of wood-fibre and polyurethane matrix. The thermal conductivity test proved that modified PU-WCs have thermal properties comparable to wood-based panels and can be successfully used in the furniture and construction industry.

Taken together, these findings suggest that manufactured PU-WCs demonstrate huge industrial potential, which could be further improved by simple changes in chemical or physical structure. The present findings might reduce the impact of the polyurethane industry on the environment and allow for the manufacturing of sustainable and useful materials. This is the next step towards limiting the environmental impact of PU and clean production of the new generation of green composites. Future studies on these materials should focus on the development of composites with different densities, the safe use of PU-WCs and the potential emissions to the air and in the aquatic environment.

Ethical approval

Not applicable.

CRediT authorship contribution statement

Adam Olszewski: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Paulina Kosmela:** Validation, Methodology, Investigation, Formal analysis. **Łukasz Piszczyk:** Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2024.143046.

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