



A novel approach in wood waste utilization for manufacturing of catalyst-free polyurethane-wood composites (PU-WC)

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ABSTRACT

In recent decades, due to the increase in environmental awareness and noticeable environmental degradation, the area of wood waste management has attracted increasing attention. The purpose of this study is to develop a new type of highly filled polyurethane wood-composite (PU-WC) by the utilization of large amount of wood wastes without addition of a catalyst. Although wood-plastic composites (WPCs) are widely known, there is still a lack of knowledge about WPCs with a polyurethane matrix. Obtained results showed that composites with a wood content of up to 80% show mechanical properties to commonly used MDF boards. This may be caused proper adhesion between polyurethane matrix and the wooden filler which was confirmed by scanning electron microscopy. The flexural strength of the manufactured composites varied between 19.25 and 25.11 MPa, while the flexural modulus varied between 966 and 1255 MPa. Dynamic mechanical analysis (DMA) of the composites showed a shift of T_{gp} (from -70.3 to -52.3 °C) and $T_{g\alpha}$ (from 94.9 to 117.8 °C) to higher temperatures with increasing filler amount. The observed shift could be interpreted as a reduction of polymer chain mobility and an increase in cross-linking density of composites with a higher amount of wood. This is caused by chemical reactions between isocyanates and reactive hydroxyl groups on the wood surface. Thermogravimetric analysis has shown that PU-WC degrades in one step with T_{max} at around 360 °C and $T_{2\%}$ significantly reduce with greater addition of wood. Water absorption tests that water absorption strongly depends on wood content and varies between 13 and 80%. Moreover, cyclic water absorption tests showed no considerable difference between the water adsorption of samples after each cycle. Our work suggests that PU-WC can be used successfully as a potential substitute for wood or different types of wood-plastic composites (WPC).

1. Introduction

The area of wood waste management in the recent decades has become an important issue due to the increase of the global environmental awareness. Noticeable environmental degradation, deforestation, and global warming had led to the search for sustainable methods of reducing wood waste. For this reason, there is huge need for new types of materials with limited environmental impact and manufactured in accordance with the principle of a circular economy.

In legal acts, the European Union emphasizes that there is a huge need for implementation of more sustainable solutions in wood waste management. However, a large amount of wood waste is still incinerated for the production of electricity and heat [1]. Although incineration allows for partial use of the potential of wood, it is associated with the generation of a certain amount of greenhouse gases. Moreover, a raw material with a high production potential is irretrievably lost. To

optimize the use of valuable waste, the European Union has announced Directive 2018/851 [2] that specifies how solid waste should be managed. Provided instructions in the directive refer to the pyramid of waste management. Recently, in the literature more and more often the scientists present a modified version of this pyramid called the “inverted pyramid for solid waste management” [3]. According to this hierarchy, methods such as recycling and reuse of wastes are more preferred than energy recovery. Sustainable wood waste management can reduce the consumption of raw wood raw materials, limit the deforestation process, and preserve the area of old-growth forests. Analyzing the Statistical Yearbook of Forestry [4] it can be observed that the forest area covers 9459 thousand ha. of Poland. The share of forest land in the total land arena is approximately 30.9%. To maintain biodiversity in forests, it is necessary to limit their exploit. This may be due to optimizing the management of wood waste by the implementation of new production methods.

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Wood resources can be processed into products with different properties, shapes, and sizes. The application of these products can be found in the production of paper, household products, construction, furniture, and automotive industry [5]. Saw dust, wood flour, shavings, and bark are among others the most important by-products generated during wood processing [6]. All above-mentioned by-products generated during wood processing are mainly used for manufacturing of plywood, particleboard, fiberboard and wood-plastic composite materials, but part of this by-product is still commonly incinerated and landfilled.

In the industry, one of the most innovative methods for utilization of wood flour is the manufacturing of wood-polymer composites (WPC). Despite the fact that WPCs have been known since the 1970s and were popularized in the 1990s, this type of materials still attracts wide interest from industry and scientists [7]. Wood plastic composite is a composite material formed by wood powder or wood fiber as the reinforcement phase and thermoplastic polymer matrix. Due to the high addition of biomass filler, wood plastic composite can be described as biomaterials [8,9]. The properties of the composite are strongly dependent on the type of matrix, filler, additives, as well as the parameters and type of processing. Thermoplastic polymers are mainly used for the manufacture of WPCs, [10]. Most research on this material has focused on matrices composed of polyethylene (PE) [11], polypropylene (PP) [12], polyvinyl chloride (PVC) [13], and polystyrene (PS) [14]. The interest in these matrices is due to the high availability of these polymers, low cost, and proper processing conditions. It is crucial to select such matrices with a processing temperature below the wood degradation (approximately 220 °C). Improper selection of the processing temperature may cause partial decomposition of the wood structure. Partial disintegration of the wood structure, and generation of by-products have a huge impact on the properties of the composite. Recent developments regarding WPCs showed possibility of implementation of new matrices types. Chen and Gardner [15] have studied Nylon 66 as a matrix in WPCs. This research showed that the addition of wood to the polyamide matrix caused an improvement in thermal stability, storage modulus, and reduced glass transition temperature compared to the unfilled material. Diestel and Krause [16] in their extensive research manufactured wood plastic composites from thermoplastic polymer (Desmopan 9370 AU) and polyester (Desmopan 3070 AU) thermoplastic polymer (TPU). The authors investigated the influence of filler content, TPU type, and amount of moisture during processing on properties of composites. The authors successfully obtained materials with up to 70% wood flour. Incorporation of wood fiber into the TPU matrix caused an increase of the mechanical properties and density of composites. On the other hand, deterioration of the impact strength and the abrasion resistance of the composite was noticed. Moreover, the authors prove that moisture does not have significant impact on mechanical properties and water absorption of manufactured materials. This result is somewhat surprising because TPUs have severe moisture sensitivity. Recent developments in WPCs have led to the preparation of novel matrices composed of biodegradable polymers. Qiang et al. [17] manufactured polylactide-pine wood flour wood composites by extrusion blending followed by injection molding. In addition, the obtained composite was toughened with a Styrene-butadiene-styrene (SBS) block copolymer. Biodegradable WPC was composed of PLA (45–90 wt%), pine wood flour (5–50 wt%) and SBS (5 wt%). The addition in SBS caused an improvement of impact strength and elongation at the break. On the other hand, the addition of SBS decreased the tensile strength of the composites. Singh and Mohanty [18] in their work fabricated a biodegradable composite from polyhydroxybutyrate-co-hydroxyvalerate (PHBV) and wood fiber. Composites with a wood fiber content up to 40% were prepared using extrusion followed by injection molding. The authors showed an improvement in the tensile and flexural modulus. Moreover, scanning electron microscopy has shown the presence of interfacial interaction between wood fiber and PHBV, which may be evidence of good compatibility between

the filler and the matrix. The same material for WPC matrix was used by Chan et al. [19]. In their study, authors investigated the effect of weathering on the properties of WPC manufactured using PHBV and up to 50% addition of wood flour. The authors have proved that neat PHBV and composite with 20% addition of WF maintains its mechanical properties over the year period. On the other hand, the Young's modulus and tensile strength of PHBV/WF composites with 50% addition of WF decreased after 12 months of weathering. Moreover, the tests revealed bleaching of all prepared samples during real-time sunlight exposure.

An equally important parameter which affects the properties of these types of composites is the type, amount, and properties of the filler. Wood components can be divided into softwood and hardwood. The most important types of hardwood are maple and poplar and types of softwood are spruce and pine [8]. Softwood species have lower strength than hardwood but have a higher content of cellulose per unit of hemicellulose. This feature of softwood leads to higher interfacial adhesion between the wood particles and the polymer matrix. Proper adhesion allows for better load transfer between two phases of the composite, which may increase the impact strength of the composite.

On the other hand, the hardwood structure is characterized by a lower cellulose-to-hemicellulose ratio compared to softwood. For this reason, interfacial adhesion between both phases of the composite may be limited. Despite the fact that hardwood has high mechanical properties, limited adhesion may lead to deterioration of mechanical parameters [7,20]. Fabiyi et al. [21] investigated the resistance to decay and moisture sorption of HDPE-based (high-density polyethylene) WPC. In their study, the authors incorporated poplar wood, Douglas fir, black locust, white oak, and ponderosa pine as fillers into the polymer matrix. This study showed that black locust and white oak provide longer durability for WPC. This effect may be caused by the lower water absorption of these wood species. Samples with the addition of ponderosa pine and hybrid poplar exhibited poorer moisture sorption and limited decay resistance. Siwek et al. [22] in their study examined the influence of different fractions of commercially available wood flour on the mechanical and physical properties of wood-polymer composites. The authors divided wood flour by weight into five sizes 80, 130, 255, 405 and 485 µm. As a matrix 70 wt% cellulose propionate (CP) was used. The results showed that mechanical properties and stiffness of the composites in comparison to the polymer matrix was increased regardless of the size of the filler fraction. The authors claim that the composites with particle size 255 µm are characterized by optimal combination of particle size, particle-matrix interaction, matrix/filler ratios. The authors support this conclusion by modification of impact, tensile and flexural strength and MFR (mass-flow rate).

Recently, scientists are trying to reduce the environmental impact of WCP and introduce waste materials into composites. Zhou et al. [23] proposed the manufacture of WPCs with the addition of reprocessed WPC wastes. The authors manufactured composites with addition of up to 85% wood content where up to 75% of wood flour was replaced by waste WPCs. All materials were manufactured using HDPE as a matrix and MAPE (maleic anhydride-grafted polyethylene) as a compatibilizer. This research shows that incorporation of WPC waste and proper selection of compatibilizer allows for manufacturing of useful and sustainable products that are in line with green chemistry and the theory of circular economy. Tang et al. [24] fabricated ultra-high-filled wood-plastic composites (UH-WPC) using recycled polypropylene (r-PP) as the matrix and 60–85 wt% recycled wood fiber (r-WF). Recycled wood fibers were retrieved from sawdust generated during processing of phenolic resin wood products. The authors investigated rheological behavior creep resistance, and mechanical properties of manufactured materials. The authors suggested that the proposed method may be beneficial for the integration of industrial waste into polymeric materials and may allow for the cyclic utilization of waste. Furthermore, the implementation of this solution will improve production efficiency, reduce the amount of waste, and is in line with the theory of the circular economy.

Despite huge interest in WPC, only a few studies have considered an exchange of the traditional polymer matrix with a polyurethane one. Furthermore, the area of polyurethane wood composites has not been explored in depth, and it has not yet been established whether these materials have promising properties, which will allow them to be used as construction and building materials which can be used as a substitute for terrace boards, wooden panels, and table tops. Furthermore, the potential advantage of these materials can be the reduction in the use of catalysts, urea-formaldehyde, phenol-formaldehyde, and melamine-urea-formaldehyde resins in the production of wood composite materials. The application of previously mentioned resins to wood-based panels can cause the release of formaldehyde. The World Health Organization and the US Environmental Protection Agency announced that formaldehyde, which can be an important source of indoor air pollution, has been classified as a potentially hazardous substance. This view is also supported by other scientific studies that confirmed that exposure to formaldehyde is harmful to the nervous system, immune system, and liver [25]. Furthermore, formaldehyde has been confirmed to be a human carcinogen [26,27].

Our recent studies proved that bio-polyols synthesized by biomass liquefaction can be used during manufacturing of polyurethane wood composites [28]. This study focuses on development of the PU-WC manufacturing method, determination of additional properties of this type of composite, and indicating its potential application. The main aim of this work was to develop a new type of highly filled polyurethane wood composite (PU-WC) by utilization of large amount of wood wastes. For this reason, six sets of composites were manufactured using up to 80% pine wood shavings. Furthermore, no additional catalysts were used during the synthesis of the materials, which is related to the principle of green chemistry. PU-WCs were manufactured using the two-step compression molding method. The mechanical properties of PU-WC were characterized by flexural tests, Charpy impact strength test, and Shore D hardness. To determine the thermal properties, dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) were conducted. As water resistance is a crucial parameter for these types of materials, the water absorption test, cyclic water absorption, dimension stability were determined. The structure of PU-WC before and after cyclic water adsorption tests was characterized by scanning electron microscopy (SEM).

2. Materials and methods

Full characterization of materials used for manufacturing of polyurethane-wood composites and their sources are presented in section S1 of Supplementary Data file (SD). Moreover, detailed description of methods used for composites characterization are described in section S2 of Supplementary Data file (SD). In brief, polyurethane-wood composites were characterized by three-point bending test, impact tests, hardness, water absorption tests, thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), thermal conductivity test, and scanning electron microscopy (SEM). All tests were performed in accordance to the appropriate standard. A description of the apparatus used and test parameters were also included in the SD.

2.1. Preparation of polyurethane materials and polyurethane wood composites (PU-WC)

To separate impurities and wood shavings particles larger than 2 mm, pine wood shavings were segregated by sieving and dried at 100 °C for 24 h. All PU-WCs were manufactured in one step method using a two-component system. The mixture of petrochemical polyols (Rokopol® RF551, Rokopol® M6000, and surfactant) was mixed with polymeric methylene diphenyl diisocyanate (pMDI). No catalyst was used during the production of the composites. The calculated isocyanate index was equal to 1. The dried pine wood shavings were mixed for 10 min with the previously prepared substance using planetary mixer. The reaction of

polyurethane synthesis [29] and an example of the reactions between wood components (lignin and cellulose) and isocyanates [30,31] are shown in Fig. 1. After proper homogenization, the material was placed in a steel mould (205 × 100 × 10 mm) and hot pressed at 100 °C for 15 min. The samples in the moulds were transferred to a cold press and then pressed for 5 min to maintain shape and to cool down the samples. Six PU-WCs with up to 80% pine wood shavings were manufactured. Density of the samples was $\rho = 0.78 \pm 0.02 \text{ g/cm}^3$. The manufactured samples are shown in Fig. 2. Percentage composition of obtained samples are presented in Table 1. Samples were coded C XX, where XX indicates the amount of wood filler.

3. Results and discussion

3.1. Wooden filler characterization

Wood particles size distribution is an essential parameter which highly affects wood polymer composites properties. The effect of the size distribution of wood particles on composite properties has been widely discussed in the literature [32,33]. Although this paper does not investigate the effect of wood shavings size and its properties on PU-WC, the characteristic of pine wood shavings is presented in Table 2 to allow comparison of this parameter with other scientific papers. Furthermore, pine shavings have not been divided into different fractions, because such a procedure causes additional costs during processing and complicates the production process [34].

3.2. Mechanical properties of composites

Fig. 3. and Fig. 4. demonstrates the effect of wood content on the selected mechanical properties of wood-polyurethane composites. All composites were designed to have a density of $0.78 \pm 0.02 \text{ g/cm}^3$, which allowed their comparison. Analyzing presented results, an increase in mechanical properties up to 60% filler addition can be observed. This effect may be due to the proper adhesion between the filler and the PU matrix, which allows good stress transfer between the matrix and the filler. These tests revealed that samples with higher filler addition shows deterioration of mechanical properties. The flexural strength for the C 80 sample was 19.25 MPa, which indicates a decrease of 5.86 MPa (23%) compared to the C 60. This can be attributed to deteriorated stress transfer caused by too high filler content, stress concentration on material defects, and incomplete covering of the filler by the PU material. Unbonded filler acts as a material discontinuity because these fragments do not transmit stresses. Moreover, wood can be considered as an active filler because of the presence of active hydroxyl groups on its surface. As it was shown in Fig. 1. these active groups may react with isocyanates during PU synthesis, changing isocyanate index. A decrease in this index may result in a decrease in flexural strength, flexural modulus, and hardness of samples with a higher filler addition.

3.3. Water adsorption tests

3.3.1. Water adsorption and dimensional stability tests

The water adsorption test was carried out to determine the equilibrium moisture content in the samples. Fig. 5a. reveals a relationship between filler content and water adsorption of the composites. Analyzing the curves, all samples reach equilibrium state after around 360 h (15 days). The water adsorption increases with the amount of wooden filler which can be explained by the higher water adsorption of wood fiber in comparison to polyurethane matrix. This is caused by specific structure of wood filler which contains free hydroxyl groups of celluloses, lignin, and hemicelluloses. These groups can form additional hydrogen bonding which increase water absorption [35,36]. Moreover, increased water absorption may be caused by partial foaming of material, and the presence of material defects. These defects allow water to

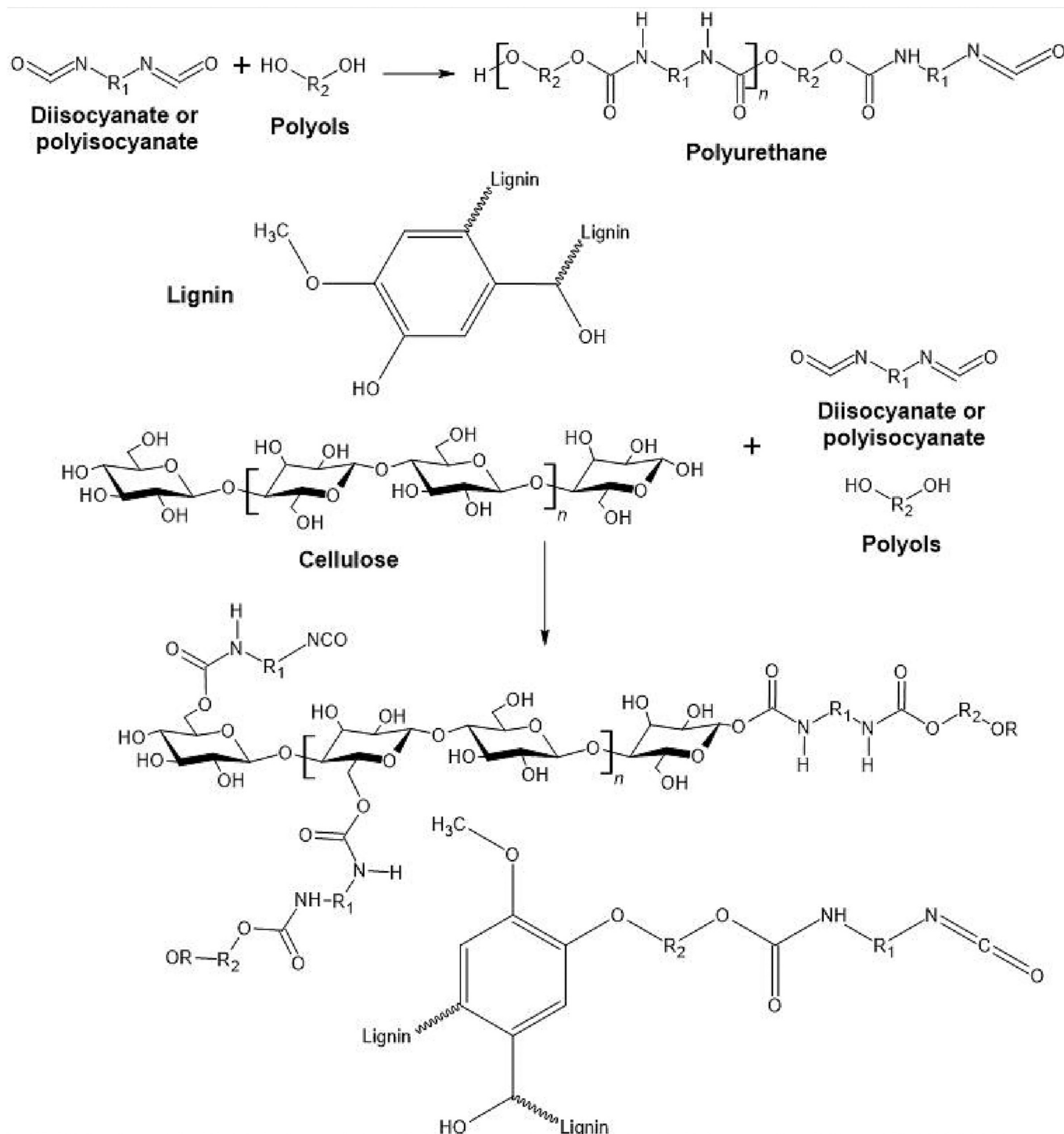


Fig. 1. Proposed course of reactions occurring during polyurethane-wood composites manufacturing.

penetrate the free spaces inside the composites. It can be noticed that water absorption at equilibrium state increased from 13% for C 30 sample, increased up to 80% for C 80. This huge difference may be caused by differences in the water absorption of both composite phases, an increasing number of defects in the materials with filler content, and incomplete coverage of the filler by the polymer matrix in samples with a higher filler content. A slight decrease in water absorption at the end of the measurement may be due to the presence of low-molecular products in the material and extractives in the wood, which can dissolve in water. Moreover, this decrease may be related to the detachment of small, poorly bonded pieces of material/wood from the sample.

Fig. 5b. shows an increase in the volume of cubic samples during water absorption. Analyzing the curves, it was observed that the percentage increase of volume significantly depends on the amount of filler. A higher value of this parameter can affect the accelerated wear of the material due to the formation of micro-cracks in the material structure, which may cause material fracture.

3.3.2. Cyclic water absorption tests

The cyclic water adsorption test was performed to determine the resistance of the composites to repetitive swelling and drying. A test cycle lasted 120 h, which is around three times shorter than the time



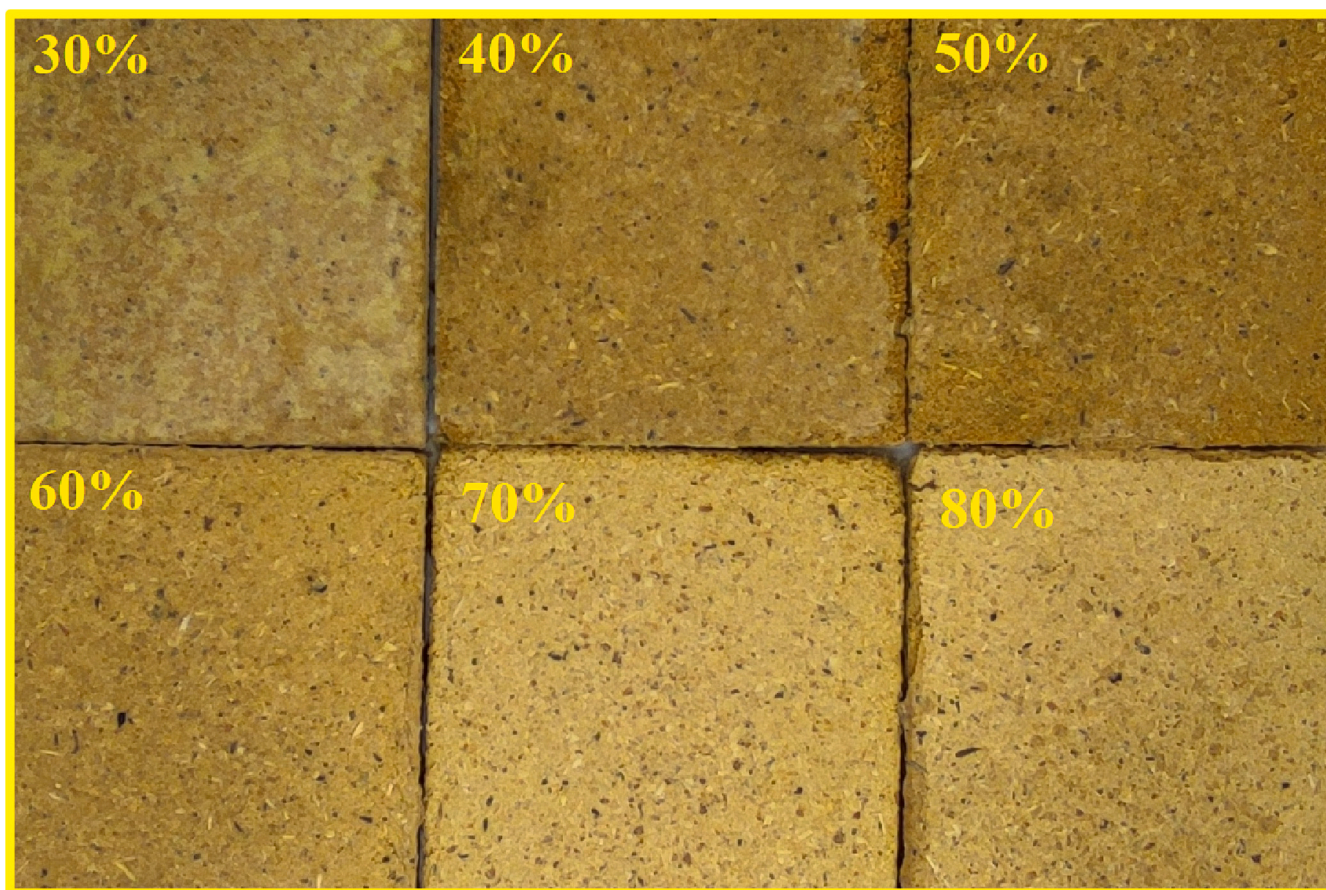


Fig. 2. Manufactured polyurethane-wood composites.

Table 1
Composition of obtained materials.

Sample	Composition of sample				
	Rokopol RF551	Rokopol M6000	pMDI	Pine sawdust	Tegostab B 8465
C 30	28.73%	7.11%	32.55%	30%	1.71%
C 40	24.54%	5.97%	27.94%	40%	1.54%
C 50	20.41%	5.06%	23.17%	50%	1.36%
C 60	16.29%	4.02%	18.49%	60%	1.19%
C 70	12.18%	3.00%	13.80%	70%	1.02%
C 80	8.05%	1.96%	9.14%	80%	0.84%

Table 2
Size distribution and water content of the wooden filler.

Mesh size [mm]	Particle 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		

required to reach the equilibrium state. In Fig. 6, it can be noted that there is no considerable difference between the water adsorption of samples after each cycle. During this test, few processes occur at the same time. These processes include the dissolution of extractives in wood, the leaching of unbound substances in composites, and the

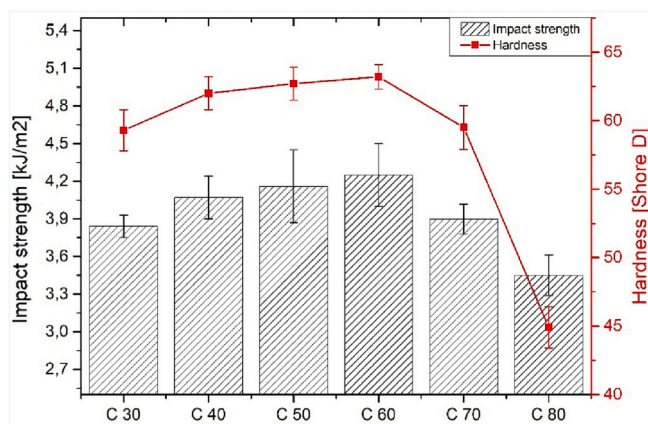


Fig. 3. Impact strength and hardness of manufactured polyurethane-wood composites.

swelling of the wood associated with the cracking of the matrix. For manufactured composites, the difference between each water absorption cycle is insignificant. These results differ from those obtained by Yeh et al. who performed similar tests but for composites composed of 50% wood and polypropylene [37]. This may be due to proper coverage of the wood fibers by the PU matrix and better water resistance of matrix. For a better evaluation of cyclic water absorption, future studies should focus on an increase in the number of water absorption cycles.

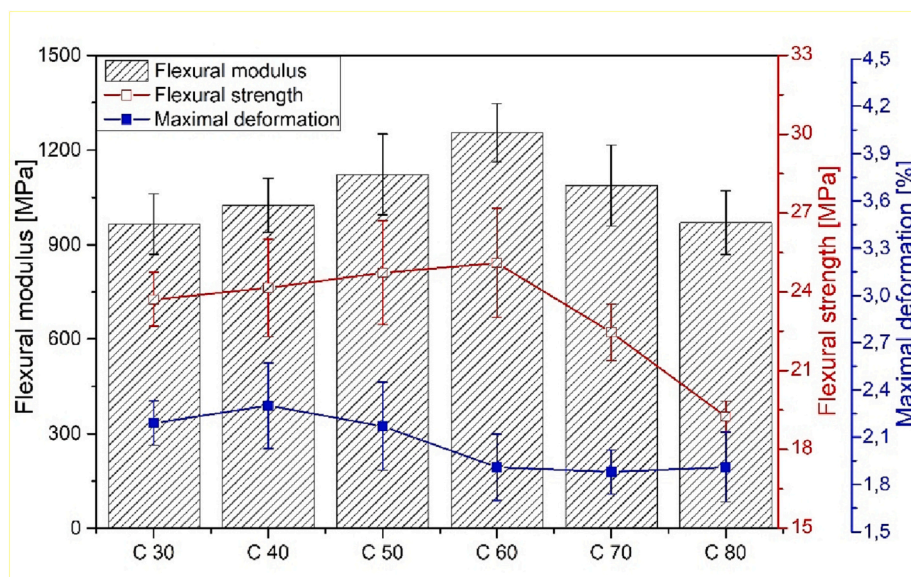


Fig. 4. Results of three-point flexural tests for polyurethane-wood composites.

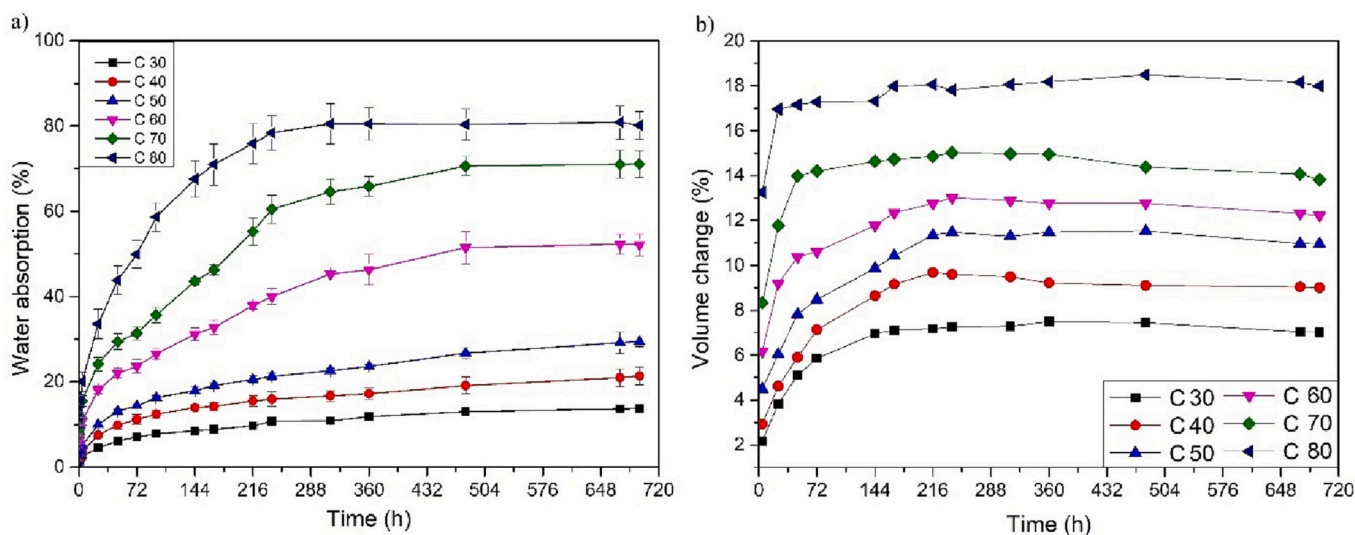


Fig. 5. a) Water absorption and b) volume change of cubic composites samples.

3.4. Thermal properties

3.4.1. Thermogravimetric analysis (TGA)

The results of the thermogravimetric analysis are presented in Fig. 7. and Table 3. Analyzing thermal decomposition of unfilled material, two-step degradation process can be noticed. The first step with $T_{max1} = 346$ °C corresponds to the degradation of the rigid segments of PU structure and the generation of lower molecular weight products, polyols, amines, and isocyanates [38]. The second step of degradation between 380 and 500 °C may be assigned to the degradation of soft segments of polyurethane which are composed of long chains of polyols – M6000 and RF 551 [39]. However, polyurethane composites degrade in one step with T_{max} around 360 °C. The decomposition at this temperature can be related to the dissociation of urethane bonds, leading to the formation of isocyanates, polyols, amines, and carbon dioxide [38,40]. Furthermore, the shape of this peak is also influenced by the decomposition of pine wood shavings with T_{max} around 360 °C. It should also be emphasized that wood degradation is not a single step process and its takes place from 200 to 350 °C. This decomposition process can

be attributed to the decomposition of hemicelluloses and cellulose. In the temperature range from 250 °C to 500 °C, degradation of lignin occurs [41]. In addition, a small peak around 70 °C can be observed for composites. This peak may be due to the presence of volatile compounds and water in the composites. This effect has a significant influence on the temperature of the 2% and 5% mass loss of samples. A significant decrease $T_{2\%}$ from 291 °C for matrix to 196 °C for C 80 can be noticed. This is due to the increase of wood filler amount, which contain certain amount of moisture which evaporates during test. Moreover, the decrease of the thermal stability of composites may be caused by the lower thermal stability of wooden shavings compared to the polyurethane matrix.

3.4.2. Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of wood and WPCs have been studied by various researchers [42,43]. They found that this technique can be used to describe viscoelastic behavior of wood, and polymeric wood components (cellulose, hemicelluloses, and lignin). The results of the dynamic mechanical analysis are presented in Fig. 8. and Table 4.

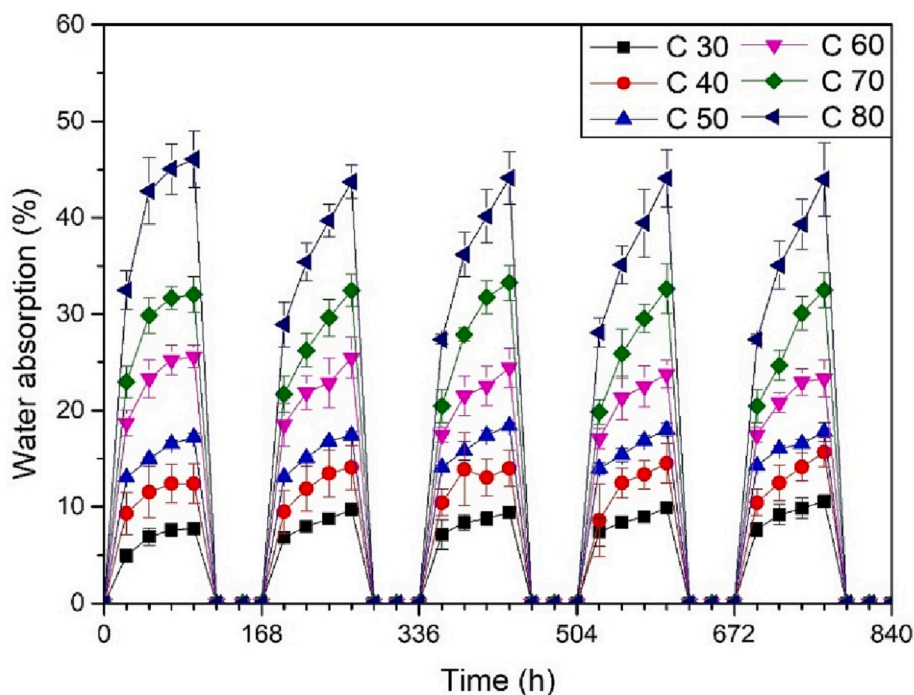


Fig. 6. Cyclic water absorption of composites.

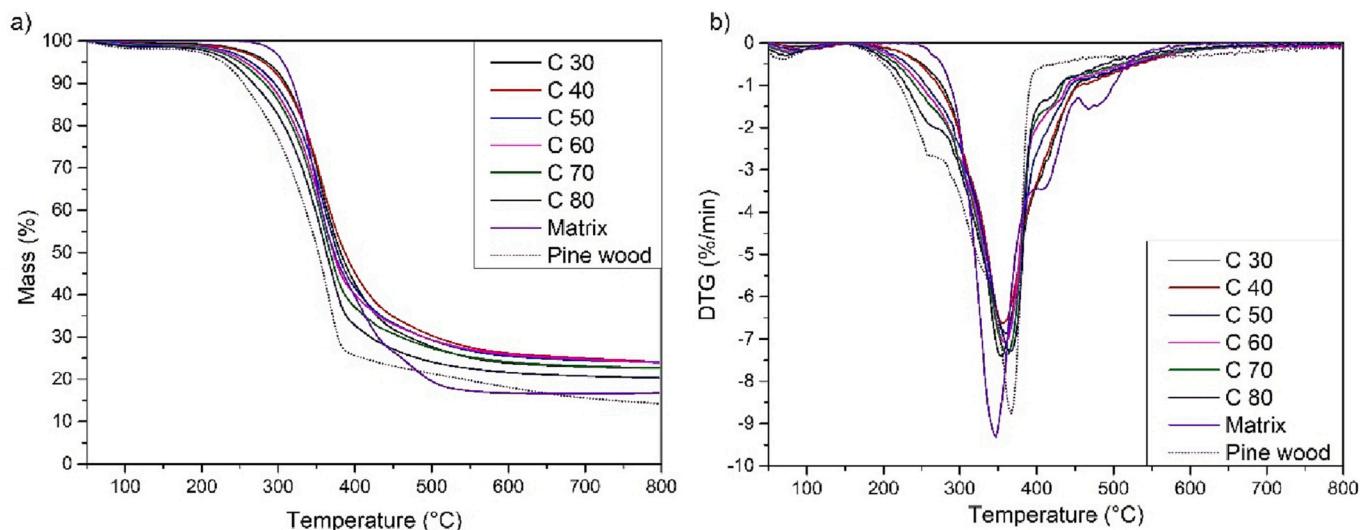


Fig. 7. a) TG and b) DTG curves of matrix and PU-WC composites.

Table 3
Results of thermogravimetric analysis.

Sample	% mass loss in temperature [°C]		T _{max1} [°C]	T _{max2} [°C]	Char residue after test [%]
	2%	5%			
Matrix	291	306	346	408	17
C 30	248	285	354	–	23
C 40	242	280	356	–	24
C 50	225	264	360	–	24
C 60	218	257	359	–	24
C 70	210	250	362	–	23
C 80	196	238	365	–	20
Wood	171	227	366	–	14

Glass transition temperatures (T_g) were determined from the peak maximum of the loss modulus. The composites are characterized by two glass transition temperatures. According to the commonly used nomenclature from the highest to the lowest transition temperature, the peaks are called the peak α and peak β . Peak α is described as the glass transition temperature ($T_{g\alpha}$) of the main polymer chain, and the peak β is responsible for the secondary loss peak. In polymer blends or composites, $T_{g\beta}$ is often derived from the second component [44]. To determine the origin of peak β , polyurethane matrix and the wood were analyzed. The peak β occurs at about -60°C . According to the results presented in Table 4, this signal can come from pine wood as well as polyurethane matrix. In the case of wood, the appearance of the peak in the -60°C range is attributed to the presence of noncrystalline areas of cellulose and hemicellulose [45]. The polyurethane matrix consists of a mixture of two polyols (Rokopol RF551 and M6000). The signal at -60°C for the

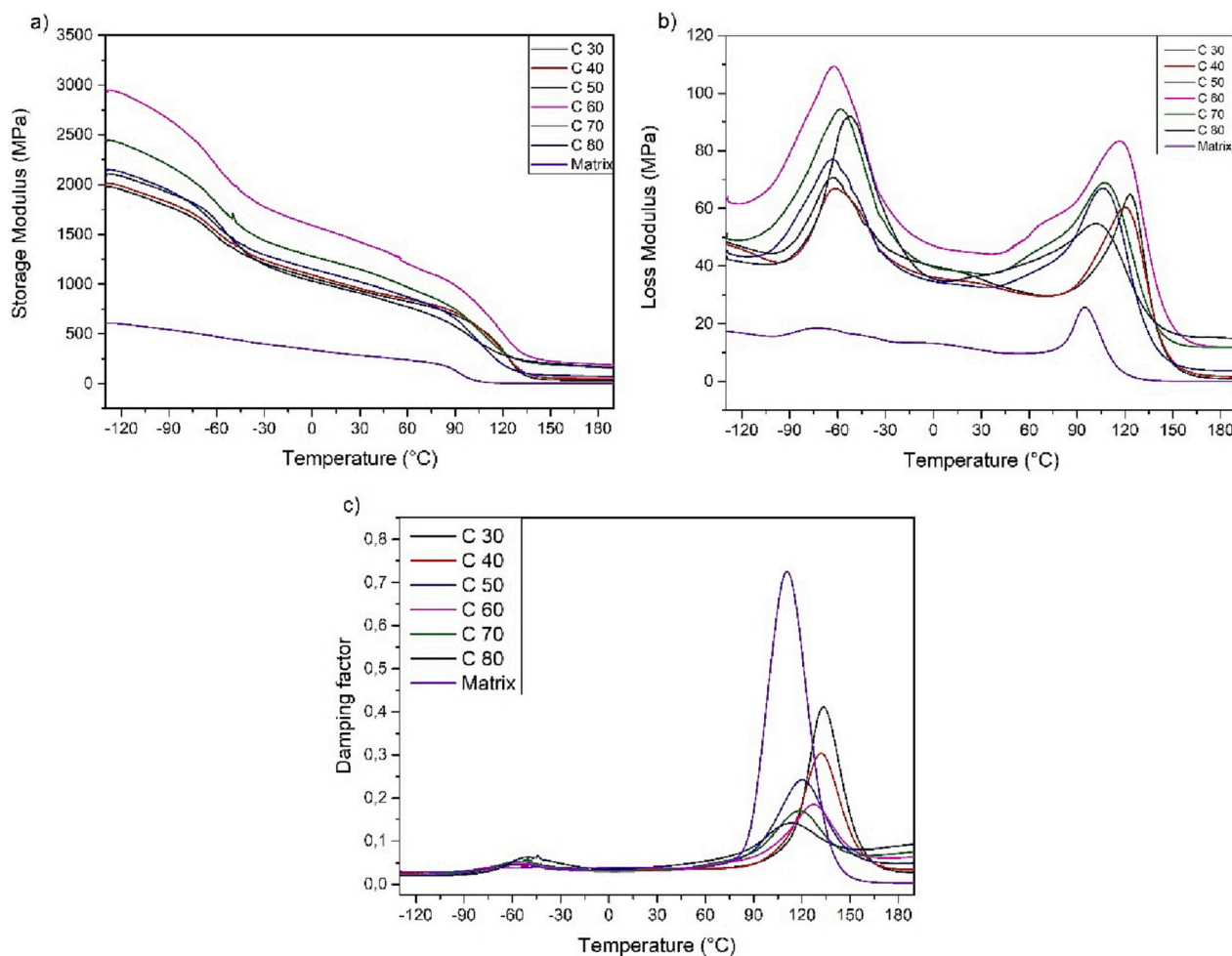


Fig. 8. a) Storage modulus, b) loss modulus, and c) damping factor of pure matrix and wood-polymer composites.

Table 4

Results of dynamic mechanical analysis of pure matrix, composites and pine wood.

Sample	$T_{g\beta}$ [°C]	$T_{g\alpha}$ [°C]	Storage Modulus at 25 °C [MPa]	Tan δ [-]
PU matrix	-70,3	94,9	290,1	0,73
C 30	-63,3	123,2	958,6	0,41
C 40	-60,9	120,4	977,5	0,31
C 50	-63,6	106,5	1038,2	0,24
C 60	-61,7	117,8	1453,6	0,18
C 70	-58,4	108,6	1168,3	0,17
C 80	-52,3	105,8	924,7	0,14
Pine wood*	-69,8	66,2	4494,1	0,03

* sample cut from a pine board.

polyurethane sample originates mainly from the higher molecular weight and linear structure polyol Rokopol M6000 and also from the secondary loss peak of the main chain of the second polyol Rokopol RF551. For composites, there is clearly a shift in the maximum peak β maximum towards higher temperatures compared to the neat material. The second peak of $T_{g\alpha}$ is observed around 100 °C for the polyurethane matrix and composites. For wood, $T_{g\alpha}$ occurs around 70 °C and indicates the presence of moisture bounded to hemicellulose [46]. For the polyurethane matrix, the maximum at 100 °C can be assigned to the glass transition of the polyurethane segments composed of Rokopol RF551 polyol. Similar to $T_{g\beta}$, the alpha transition occurs at higher temperatures for composites. This indicates in both cases a higher cross-linking density of the composite materials compared to the neat material [47].

Based on the analysis of the storage modulus, the composite containing 60% by weight of wood shavings has the highest value of E' (at 25 °C). For the samples with higher addition of filler the E' values decrease. The sample C 60 shows the highest values of E' in the whole investigated temperature range. The results obtained using DMA coincide with other results of mechanical tests. Moreover, analyzing damping factor (Tan δ) it can be noticed that the efficiency of stress transfer decreases with the increase of amount of wood filler in the composites. The composite with 30% filler (C 30) has the highest tan δ value. This is related to the highest percentage of polyurethane, which has a significantly higher damping index compared to wood.

3.5. Thermal conductivity coefficient of PU-WC

Thermal conductivity is an important parameter that enables the characterization of the insulation properties of materials designed for the construction industry [48]. The results of the thermal conductivity

Table 5

Results of thermal conductivity tests of polyurethane-wood composites.

Sample	Thermal conductivity [W/m ² K]	Thermal resistance [m ² K/W]
C 30	0,11461	0,09211
C 40	0,11438	0,09224
C 50	0,11354	0,09195
C 60	0,11191	0,09728
C 70	0,11123	0,09547
C 80	0,11003	0,10776

tests of polyurethane wood composites are presented in Table 5. The thermal conductivity and thermal resistance slightly depend on amount of wooden filler. It can be noticed that thermal conductivity slightly decreases with increasing amount of filler. This is due to the low thermal conductivity of the wood shavings. Defined parameters for all composites are comparable to pine wood [49], commercially available medium-density fiberboard [50], and materials described in other scientific reports [51,52]. Analyzing obtained results all manufactured composites can be potentially used as building insulation because their thermal conductivity satisfies the standard ranges of thermal insulators for buildings.

3.6. Scanning electron microscopy (SEM)

3.6.1. Microstructure of brittle cracking surface

The morphology of manufactured composites was defined using scanning electron microscopy (SEM). Microstructures of samples with different filler addition subjected to brittle cracking are presented in Fig. 9. Analyzing the microstructure of composites good adhesion between polyurethane matrix and wood fibers can be noticed. Material of matrix is strongly bonded to the filler. This can be interpreted as strong bonding between polyurethane and matrix which may be caused by the presence of functional groups (mainly hydroxyl groups) on the filler surface. This functional groups may react with isocyanates or generate short and long-distance interactions between polymer chains and filler. This effect may be strengthened by the developed surface area of the filler. Moreover, strong adhesion between filler and matrix may be explained by the fracture course through matrix and wooden filler. This is confirmed presence of parallel and perpendicular wood fiber fracture and by the absence of fiber pull-outs. Proper adhesion leading to the enchanted stress transfer led to improvement to mechanical properties of composites with up to 60% of wooden filler.

However, a higher amount of filler had led to the formation of agglomerates and the presence of voids between wooden filler. These effects caused stress concentration and reduction of the cross-sectional area of the samples which resulted in deterioration of the mechanical properties of composites. Decrease in mechanical properties can also be explained by the presence of partial foaming of the material. Partial foaming provides a weight reduction of the composite, but the presence of additional voids creates additional stress concentration points and further reduces the cross-sectional area of sample.

Analyzing the general appearance of the fractures, it can be observed that the C 60 composite has a structure that provides the best mechanical parameters. Relatively homogeneous distribution of the filler in the matrix, the presence of a small number of material defects and the regular course of the fracture can be noticed.

3.6.2. Microstructure of samples surface after cyclic water absorption tests

The morphology of samples after cyclic water absorption was investigated to define influence of water absorption on development of cracks and microcracks during cyclic swelling of wood inside composites. After last stage of drying all composites had no visible macroscopic cracks. Microstructures of samples with different filler addition subjected to cyclic water absorption tests (CWA) are presented in Fig. 10. Analyzing the microstructures of samples detachment of fiber fragments due to cyclic swelling of wood can be noticed. Wood fiber during water adsorption increases its volume. This results in development of stress state in the material and further deformation of matrix. After drying wood returns to previous volume but matrix remains deformed. This effect leads to limited interactions between wood and fiber and reduction of stress transfer.

In addition, cyclic swelling of the wood causes matrix deformation and the development of microcracks inside the material. These microcracks may connect, which leads to formation of macrocracks and further accelerated wear of the material. The presence of cracks causes local stress concentrations in the material which can result in a decrease

in impact strength and mechanical properties of the composite. Analyzing the microstructure of all materials, composite coded C 40 has the lowest number of cracks and microcracks. In addition, these cracks are smaller than in other composites. Cracks and micro-cracks detected on samples coded C 60 and C 80 are wider and longer. These cracks are mainly present at the interface surface between the filler and the matrix. The formation of these cracks may suggest that samples with a higher filler content are more susceptible to this type of wear.

4. Conclusions

In this study, we manufactured high-performance catalyst-free polyurethane wood composites with up to 80% of the wood by a simple process. Composites were obtained using pine wood shavings generated during wood processing in a sawmill. The proposed method allows for easy modification of the process parameters to obtain a material with a specific density and mechanical parameters. The manufactured composites have properties comparable to commercially available wood-like materials, such as medium-density fiberboards.

Mechanical tests showed that the addition of up to 60% wood shavings increases the flexural strength, impact strength and hardness of the materials. The flexural strength of the C 60 composites is 25.11 MPa and flexural modulus is 1255 MPa. The impact strength of PU-WCs varies from 3.45 to 4.25 kJ/m² and hardness from 44.9 to 62.7° Shore D. Water adsorption tests were conducted to determine resistance of composites to water. The results of these tests confirmed that water absorption increases with amount of wooden filler and is 18, 50, and 80% for sample C 30, C60 and C80, respectively. All composites reached equilibrium state after around 360 h (15 days). Cyclic water adsorption tests showed that the difference between each water absorption cycle is very insignificant. This may be due to proper coverage of the wood fibers by the PU matrix. Dynamic mechanical analysis (DMA) of the composites showed a shift of $T_{\text{g}\beta}$ (from -70.3 to -52.3 °C) and $T_{\text{g}\alpha}$ (from 94.9 to 117.8 °C) to higher temperatures with increasing filler amount. The observed shift could be interpreted as a reduction in the mobility of the polymer chain and an increase in the crosslinking density of composites with a higher amount of wood. This is caused by chemical reactions between isocyanates and reactive hydroxyl groups on the wood surface. Moreover, increase of mechanical properties of samples with wood shavings addition is connected with increase of storage modulus from 290.1 MPa for matrix to 1453.6 MPa for C 60. TGA analysis has shown that PU-WC degrade in one step with T_{max} at around 360 °C and $T_{2\%}$ decreases from 248 to 196 °C for C 30 and C 80 samples, respectively. This may be caused by a higher moisture content in samples with a higher wood content and a lower thermal stability of the wood in comparison to PU matrix. The thermal conductivity tests of PU-WC indicated that thermal conductivity slightly decreases from 0,11461 (C 30) to 0,11003 W/m²K (C 80) with increasing amount of filler, due to the low thermal conductivity of the wood shavings.

The analysis of the SEM images showed good adhesion between the wood and the polyurethane matrix, which is consistent with the other tests results. Analysis of samples subjected to brittle cracking confirmed the partially foamed structure of the composites and the presence of gaps between filler fibers. The analysis of samples subjected to cyclic water absorption tests showed detachment of fiber fragments due to cyclic swelling of the wood and possible crack propagation sites in the material due to the generation of stresses in the matrix.

Taken together, these findings suggest that polyurethane-wood composites can be successfully used as a potential substitute for wood or wood-plastic composites composed of polyolefins. These materials can be applied in the construction, furniture, automotive industries as a substitute for terrace boards, wooden panels, and table tops. The proposed method for composites manufacturing allows for the utilization of significant amounts of waste from the wood industry. This allows for introduction of more ecologically preferred waste manufacturing processes than incineration or landfilling. We recommend that further

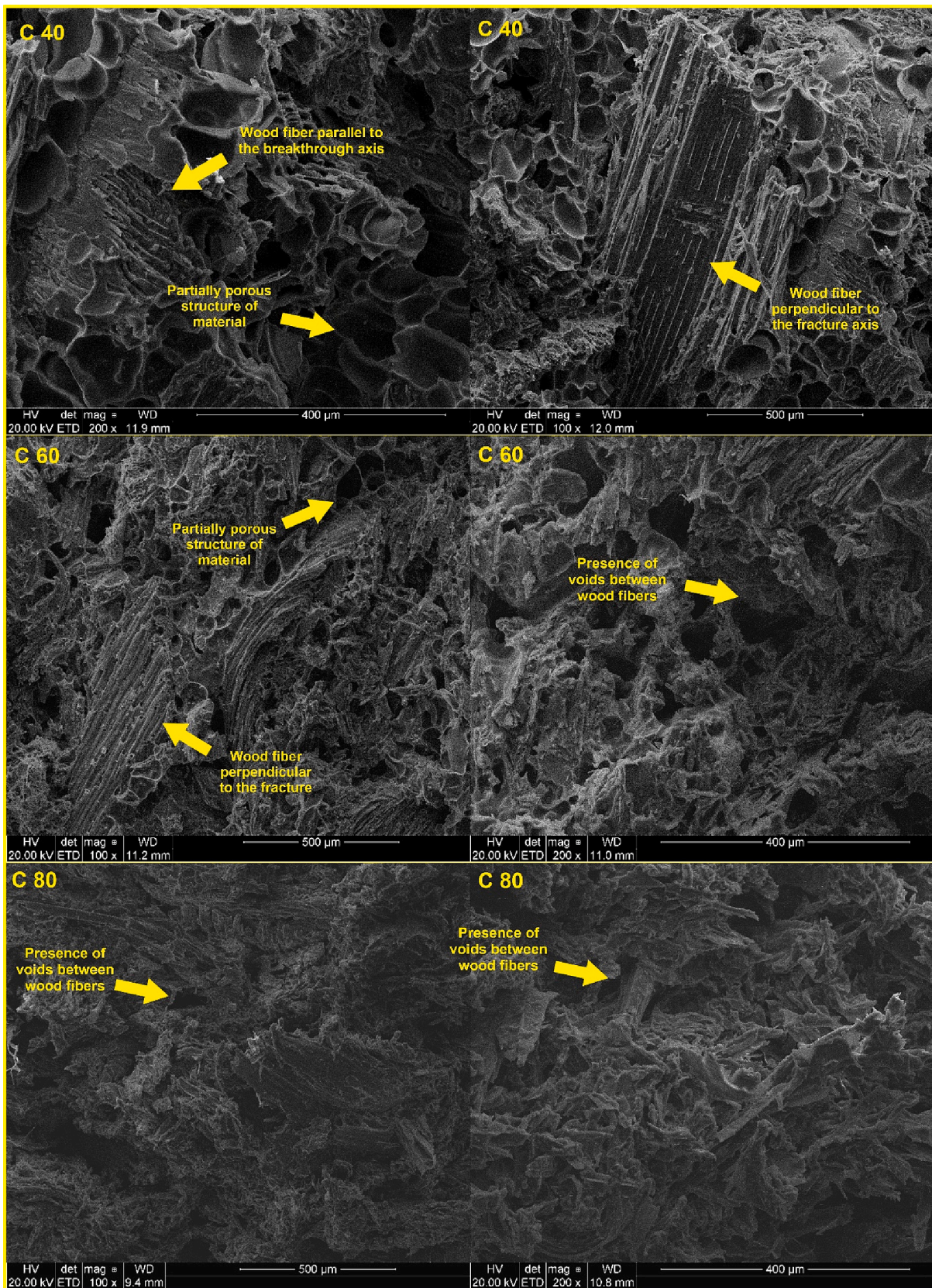


Fig. 9. SEM images of composites subjected to brittle cracking.

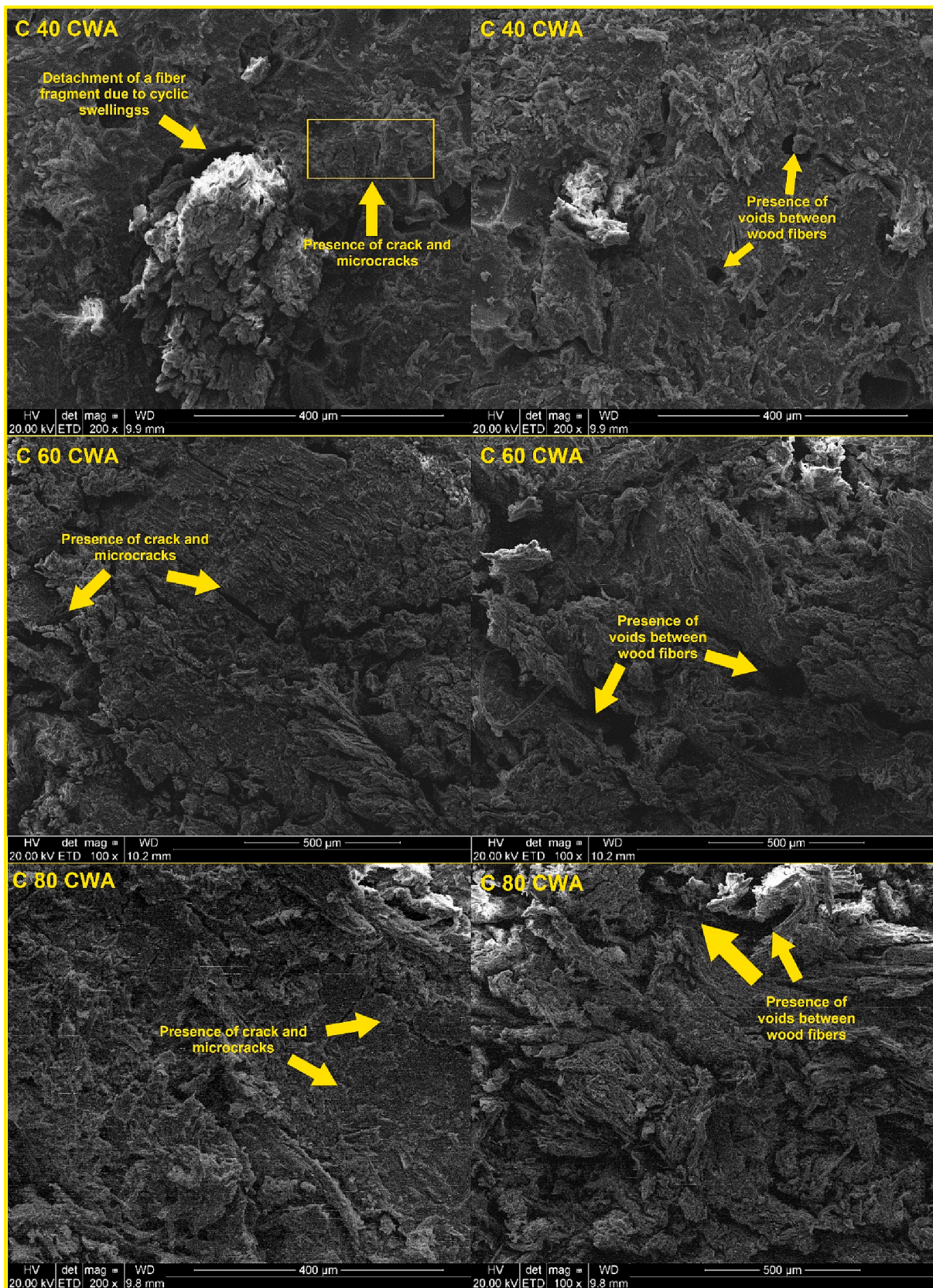


Fig. 10. Structure of sample coded C 80 after cyclic water absorption tests.

research should focus on substitution of petrochemical substances for raw materials from sustainable and renewable sources.

CRediT authorship contribution statement

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

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Declaration of Competing Interest

None.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.susmat.2023.e00619>.

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