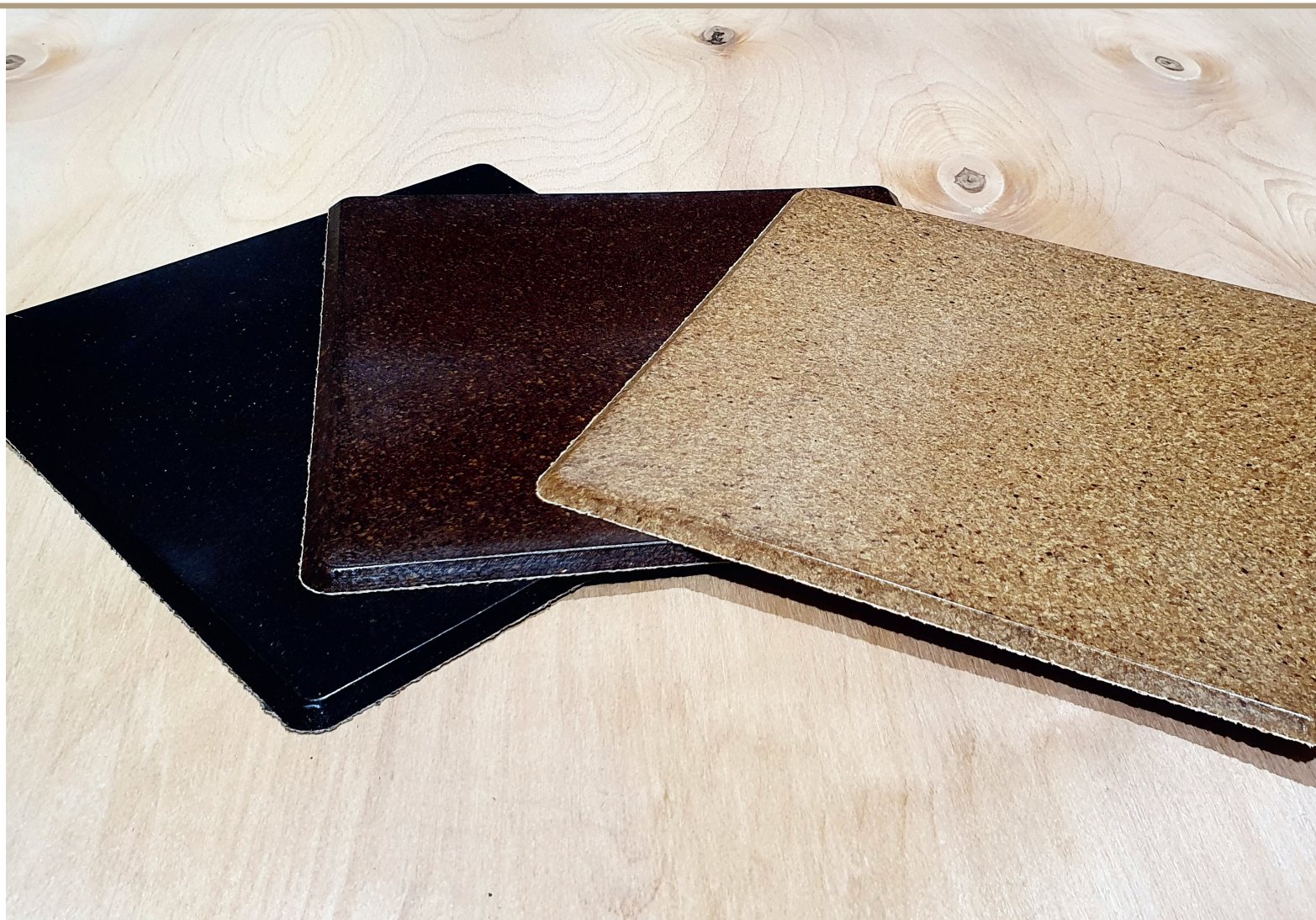
RIGA TECHNICAL UNIVERSITY

Edgars Kuka

USE OF INDUSTRIALLY PRODUCED THERMALLY MODIFIED WOOD RESIDUES FOR PRODUCTION OF WOOD PLASTIC COMPOSITES

Summary of the Doctoral Thesis



RTU Press
Riga 2022

RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry
Institute of Polymer Materials

Edgars KUKA
Doctoral Student of the Study Programme "Materials Science"

USE OF INDUSTRIALLY PRODUCED THERMALLY MODIFIED WOOD RESIDUES FOR PRODUCTION OF WOOD PLASTIC COMPOSITES

Summary of the Doctoral Thesis

Scientific supervisors
Assoc. Professor Dr. sc. ing.
JĀNIS KAJAKS
Lead Researcher Dr. sc. ing.
DACE CĪRULE

RTU Press
Riga 2022

Kuka, E. Use of Industrially Produced Thermally Modified Wood Residues for Production of Wood Plastic Composites. Summary of the Doctoral Thesis. – Riga: RTU Press, 2022. – 45 p.

Published in accordance with the decision of the Promotion Council "RTU P-02" of 10 May 2022, Minutes No. 04030-9.2.1/6.

The Doctoral Thesis has been developed in the Latvian State Institute of Wood Chemistry and Riga Technical University initially with the support of the following research program:
National Research Programme "Exploration, Sustainable Use of Forest and Subsoil Resources – New Products and Technologies"(ResProd) (2014-2018).

https://doi.org/10.7250/9789934228025
ISBN 978-9934-22-802-5 (pdf)

DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE

To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on September 9, 2022 at 10:30 a.m. in the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 3 Paula Valdena Street, Room 272.

OFFICIAL REVIEWERS

Lead Researcher Dr. chem. Ingars Reinholds
University of Latvia, Latvia

Lead Researcher Dr. sc. ing. Jānis Rižikovs
Latvian State Institute of Wood Chemistry, Latvia

Lead Researcher Dr. Ulrich Hundhausen
Norwegian Institute of Wood Technology, Norway

DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Science (Ph. D) is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Name Surname ……. (signature)
Date: ……

The Doctoral Thesis has been written in Latvian It consists of an Introduction, 3 chapters, Conclusions, 89 figures, 16 tables; the total number of pages is 177. The Bibliography contains 319 titles.

TABLE OF CONTENTS

ABBREVATIONS

ΔEab	total colour change (CIELab colour system)
ε_F	elongation at maximum strength in bending
σ_F	flexural strength
σ_T	tensile strength
ΔV	volume change
A	impact strength
*a**	parameter of red-green coordinate axes (CIELab colour system)
*b**	parameter of yellow-blue coordinate axes (CIELab colour system)
D	true diffusion coefficient
E_F	flexural modulus of elasticity
Fs	fine sized wood particles with the smallest dimension <0.2 mm
*L**	parameter of white-black coordinate axes (CIELab colour system)
L/*D*	length/diameter ratio
LSM	laser scanning microscope
MAPP	maleated polypropylene
MFI	melt flow index
MH	microhardness (the Vickers method)
ML	mass loss
Ns	normal sized wood particles with the smallest dimension 0.2–0.4 mm
Os	oversized wood particles with the smallest dimension 0.4–1.0 mm
PP	polypropylene
RH	air relative humidity
SD	sawdust
SEM	scanning electron microscope
SH	shavings
Thermo	*Thermowood®* (thermal modification process in an open reactor system)
Thermo-D	regime 212 °C / 3 h of the *Thermowood®* process
Thermo-S	regime 190 °C / 3 h of the *Thermowood®* process
TM	thermally modified
UM	unmodified
UV	ultraviolet radiation
Vis	visible light
Wabs	absolute moisture content
WF	wood flour obtained after milling
WPC	wood plastic composite
WTT 160/1	regime 160 °C/1 h of the *Wood Treatment Technology* process
WTT 170/1	regime 170 °C/1 h of the *Wood Treatment Technology* process
WTT 170/3	regime 170 °C/3 h of the *Wood Treatment Technology* process
WTT	*Wood Treatment Technology* (producer of the closed reactor system process)

INTRODUCTION

In recent years, great attention has been attributed to various composite materials, in the production of which different natural fibres (wood, hemp, flax, etc.) are used. Already in 2012, their total production in the European Union represented 15 % of all composite materials and their market share has only continued to increase [1]. The rapid development of biocomposites is facilitated by various requirements and objectives related to the protection of the environment and sustainable development, such as the European Green Deal, Directive 2000/53/EC of the European Parliament, environmental declarations, as well as the positive public attitude towards environmentally friendly products [2]. Thermoplastic polymers filled with wood particles or wood plastic composites (WPCs) are among the main of the group, which account for 38 % of all biocomposites [1]. Part of the resources used in the manufacture of WPCs are not only renewable, but they are also by-products of various woodworking processes. Another important factor that favours the development of WPCs is closely related to such environmental problem as plastic waste accumulation in the nature. Since recycled plastics can be used in the manufacture of WPCs, these materials contribute towards mitigation of this problem by increasing the demand for recycled plastics and thus positively influencing both the sorting of plastics and the development of the plastic recycling process itself.

In recent years, the share of the WPCs in the market of building materials and automotive industry has increased significantly due to their relatively good characteristics: low cost, environmentally friendly raw materials, high stiffness, good moisture resistance, recyclability, good bio-resistance, etc. These composites are mostly used in the manufacture of terrace boards, window frames, fences, railings, car interior panels, and outdoor furniture. Although WPCs have relatively good performance characteristics, over time, a number of problems have been identified. Most often they are associated with the weak compatibility between the polymer matrix and the wood particles as well as the irreversible degradation caused by water absorption. Moreover, WPCs are not fully resistant to microorganisms, as initially thought. Partially, these deficiencies can be reduced by incorporation of different additives (coupling agents, compatibilizers, biocides, etc.) into the composite, as well as by chemical or heat treatment of wood particles. Considering that any additional treatment or additive significantly increase the cost of the final product, it can higly affect the competitiveness of these materials. Since the production of thermally modified (TM) wood has been rapidly increasing (comparing the year 2011 with 2020, the volume of products manufactured by the *ThermoWood*® method has doubled), the amount of TM wood residues has enlarged as well, which could be used for production of high-value products [3]. The use of TM wood residues for WPC production could be a possible way to improve their characteristics, at the same time not significantly affecting the cost price. There is relatively little information in the scientific literature on this type of approach and the performance of these WPC materials. Consequently, the information obtained in the work will be useful for TM wood producers, for whom TM wood residues are formed. In addition, the information will be beneficial to WPC producers who, in cooperation with TM wood manufacturers, could offer a product with improved characteristics at a competitive price.

Aim of the Doctoral Thesis

The aim of the Thesis is to characterise TM wood residues and obtain WPC with improved water resistance, as well as to clarify the advantages and disadvantages of these composites, in-depth studying and explaining the causes of the changes in the properties.

Tasks of the Doctoral Thesis

The main tasks of the Thesis are covered in five points:

1. To describe TM wood residues (particle size distribution, chemical composition, length/diameter ratio, etc.) depending on the wood species, thermal modification method and intensity.
2. To study the impact of TM wood residues on the physical and mechanical properties of WPC (density, impact strength, bending properties, surface microhardness, water absorption, etc.).
3. To study the impact of TM wood residues on the performance of WPC (resistance to weathering processes, biological resistance, water resistance, etc.).
4. To analyse and try to explain the results obtained by conducting in-depth research by various methods appropriate for these purposes (SEM, LSM, UV-Vis, etc.).
5. To investigate the possibility of improving the WPC properties by changing the composition.

Scientific Significance and Novelty

The properties of TM wood residues have been studied and their suitability for WPC production has been demonstrated. The influence of the main factors of TM wood particles (particle size, thermal modification intensity, type of residues, thermal modification method) on the properties of WPC has been established. The physical, mechanical and performance characteristics of WPC have been studied in detail, explaining the obtained results and verifying them by various instrumental methods (UV-Vis spectroscopy, scanning electron microscopy, laser scanning microscopy, etc.). The mechanism of colour change (fading) of the WPC under the influence of UV radiation is explained, as well as discolouration depending on the type of radiation (full spectrum of the solar radiation, UV part of the solar radiation, and visible light of the solar radiation) is determined. The possibilities of improving the properties of WPC with TM wood particles by changing their composition have been studied. The importance of TM wood particles for the production of water resistant WPC, providing high resistance against rot fungi, as well as against long-term soaking and soaking/drying cycle conditions, has been tested and proven. The drawbacks of the obtained WPC are also elucidated, giving a clear direction for further research.

Practical Significance

In the work, the advantages of using TM wood residues for WPC production have been demonstrated, giving confidence in the competitiveness of the material in the market. The influence of different wood particles characteristics on the WPC properties has been presented, providing the necessary knowledge to control the most important parameters in the production process, as well as to obtain quality products with the desired characteristics. The methods of processing these materials into products, as well as advantages and disadvantages, have been clarified. The mechanism of the colour change of WPC under the influence of UV radiation has been explained, which makes it possible to purposefully adjust the additives for strengthening the protection of the polymer matrix. The optimal WPC composition has been obtained providing significantly improved water resistance, which cannot be achieved using unmodified wood particles. The superiority of the newly developed material has been also proven during different performance tests. The expediency of adding various additives to improve the properties has also been clarified. For WPC with TM wood particles, general characteristics conforming to material testing standards have been obtained and summarized, which, based on them, gives confidence in the fulfilment of the requirements of various existing applications, as well as gives the opportunity to find new applications for these materials.

Main Theses to be Defended

1. TM wood residues are suitable raw materials for the production of competitive WPC with good service properties.
2. Residue type, modification method, modification intensity, particle size and wood species of TM wood can significantly influence WPC properties.
3. Additives can ensure significant improvement of mechanical, physical and service properties of WPC with TM wood particles.
4. Fading of WPC under the exposure to UV radiation is caused by the changes in the polymer matrix.

Approbation of the Research Results

The results published in scientific journals that are indexed in Scopus databases:

1. Cirule, D., Sansonetti, E., Andersone, I., **Kuka, E.**, Andersons, B. 2021. Enhancing Thermally Modified Wood Stability against Discoloration. Coatings, 11(1), 81.
2. **Kuka, E.**, Andersons, B., Cirule, D., Andersone, I., Kajaks, J., Militz, H., Bicke, S. 2020. Weathering properties of wood-plastic composites based on heat-treated wood and polypropylene. Composites Part A: Applied Science and Manufacturing, 139, 106102.
3. Cirule, D., Verovkins, A., Andersone, I., **Kuka, E.**, Andersons, B. 2020. Thermally modified birch wood interaction with liquids. Eur. J. Wood Wood Prod. 78, 849–857.

4. Andersone, I., Dobele, G., Andersons, B., Kurnosova, N., **Kuka, E.**, Volperts, A., Grinins, J. 2019. A study of thermo-hydro-treated (THT) birch wood by chemical analysis and Py-GC/MS. Holzforschung, 73(7), 653–661.
5. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. 2018. Wood particle size influence on water resistance and mechanical properties of thermally modified wood-polypropylene composites. International Wood Products Journal, 9(2), 90–95.
6. **Kuka, E.**, Cirule, D., Kajaks, J., Janberga, A., Andersone, I., Andersons, B. 2017. Fungal Degradation of Wood Plastic Composites Made with Thermally Modified Wood Residues. Key Engineering Materials, 721, 8–12.
7. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. 2016. Wood plastic composites made with thermally modified birch wood residues. International Wood Products Journal, 7(4), 210–215.
8. Cirule, D., Meija-Feldmane, A., **Kuka, E.**, Andersons, B., Kurnosova, N., Antons, A., and Tuherm, H. 2016. Spectral sensitivity of thermally modified and unmodified wood. BioResources, 11(1), 324–335.

The results published in the scientific conference proceedings:

1. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. The potential of wood ash as an additive for heat-treated wood plastic composites. Proceedings of the 16th annual meeting of the Northern European Network for Wood Science and Engineering (WSE2020), December 1–2, 2020, Helsinki, Finland, 23–25.
2. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Bikovens, O., Andersons, B. Comparison of thermally modified wood residues for production of wood plastic composites. Proceedings of the 15th annual meeting of the Northern European Network for Wood Science and Engineering (WSE2019), October 9–10, 2019, Lund, Sweden, 107–109.
3. **Kuka, E.**, Cirule, D., Kajaks, J., Andersons, B. The effect of coupling agent on the properties of heat treated wood plastic composites. Proceedings of the 14th Annual Meeting of the Northern European Network for Wood Science and Engineering (WSE2018), October 2–3, 2018, Tallinn, Estonia, 103–105.
4. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. Wood particle size influence on water resistance and mechanical properties of thermally modified wood-polypropylene composites. Proceedings of the 13th Annual Meeting of the Northern European Network for Wood Science and Engineering (WSE2017), September 28–29, 2017, Copenhagen, Denmark, 133–138.
5. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. Surface changes of artificially weathered polypropylene-thermally modified wood flour composites. Proceedings of the 12th Annual Meeting of the Northern European Network for Wood Science and Engineering (WSE2016), September 12–13, 2016, Riga, Latvia, 233–239.
6. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. Wood Plastic Composites Made with Thermally Modified Birch Wood Residues. Proceedings of the International Panel Products Symposium 2015, October 7–8, 2015, Llandudno, UK, 241–251.

The results published in the scientific conference books of abstracts:

1. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. Changes in mechanical properties for re-dried WPC with thermally modified wood particles after water absorption test. Proceedings of the International Panel Products Symposium 2017, October 4–5, 2017, Llandudno, UK, 167.
2. **Kuka, E.**, Cirule, D., Kajaks, J., Andersone, I., Andersons, B. Artificial weathering (QUV) of wood plastic composites made with thermally modified wood residues. Book of Abstracts of the 2nd Workshop on Application of NIR Spectroscopy for Wood Science and Technology Research, April 19–21, 2016, San Michele all' Adige, Italy, 46–47.
3. **Kuka, E.**, Cirule, D., Kajaks, J., Andersons, B. Thermally modified wood by-products as a filler for production of wood plastic composites. Book of Abstracts of the 3rd Biopolymers International Conference, December 14–16, 2015, Nantes, France, 71.

1. SUMMARY OF THE LITERATURE REVIEW

Forests and their products are of particular importance in the world and in Latvia, therefore the rational use and research in this direction is vital for further development. The preservation and sustainable use of wood resources is important also for achieving the environmental objectives set by the European Union [4], [5]. In this context, wood residues should be used for the production of various products and not for energy production resulting in CO_2 emissions [6]. Wood residues are formed in very large quantities during any woodworking process. In Latvia, the most common tree species are pine, birch, and spruce, which, in this context, require special attention, since they form the largest amount of wood residues. Wood has unique properties that allow it to be widely used for the manufacture of the most diverse products with high added value and low environmental impact. However, most often, wood residues are used to generate energy or even simply disposed in landfills [7]. Wood is a natural composite material with a porous structure in which the cell walls consist mainly of cellulose, hemicelluloses, and lignin. Hemicelluloses and amorphous cellulose are responsible for the hygroscopicity of wood. Besides, depending on the moisture content, the properties of wood change significantly. Wood is an anisotropic material that has a specific micro- and macro-structure, which varies depending on different factors, but mostly it is influenced by the peculiarities of each individual tree species. In terms of wood residues, both chemical and structural properties largely remain also at the particles' size level, which therefore are important and must be considered during composite manufacturing. Although wood is a material with a number of excellent characteristics, it has also several disadvantages that limit its application, for example, dimensional changes under the influence of moisture, weak resistance to the action of microorganisms, combustibility, and hydrophilicity [8].

Wood modification has been developing rapidly in recent years. Of all the methods, thermal modification of wood is convincingly the most common one. Using it, more than 1 million m^3 of TM wood is produced annually in the world [9]. As a result of thermal modification, the hydrophilicity of wood decreases, which is explained mainly by the decrease in the hemicelluloses amount. Changes occur also for the other components of wood: the proportion

of crystalline cellulose (phase) increases, cross-linked lignin structures are formed, and new extractives are created. As a result, wood acquires improved dimensional stability and moisture resistance, as well as increased resistance to the effects of microorganisms; however, the mechanical properties are slightly deteriorated [10]. TM wood is produced also in Latvia, and the largest producers are *Stora Enso Latvija* and *Ošukalns* Ltd. Therefore, the rational use of TM wood residues is also topical in Latvia. Since the most common TM wood products are boards, TM wood residues are formed during processing (sawing, milling, etc.) after modification. In such woodworking processes, the proportion of residues can be up to 65 %, depending on the type of the final product, but in the case of boards, it is be lower [11]. During the thermal modification process, defective products (twisted, cracked, and visually impaired boards) are often created. By grinding them, a suitable raw material for use in composites can be obtained. Considering this, the total amount of TM wood residues could be up to 50 % of the volume of the modified wood.

Recycling has a significant role in achieving the environmental goals, which allows the material to be re-used after the end of its service life. This is especially important regarding plastic waste, which has been acknowledged as one of the major problems in the world. When plastic products get into the environment, microorganisms are not able to decompose these materials so easily for several reasons: the hydrophobicity of polymers, high molecular weight, semi-crystalline structure, and the presence of additives that can be harmful to microorganisms. Consequently, the decomposition of plastics in nature takes place over several hundred years, which is forcing us to collect plastic waste with a goal of disposal or, at best, recycling by partially reducing the need to produce primary polymers [12]. In this context, WPCs can contribute in solving the global waste problems as well as are in the line with the European Commission's bio-economic strategy, since wood residues and recycled plastics are the main constituents, and the WPC themselves are also recyclable, thus ensuring a closed-loop economy. This, in turn, ensures a longer storage of carbon, reduction of waste, and, by increasing the demand for recycled plastics, contributes to the development of waste sorting and recycling processes [13].

WPCs are thermoplastic polymers filled with wood particles. In recent years, WPCs have taken a significant place in the market of building materials, automotive and furniture industries. The success partly is based on the ability of WPCs to compete with monolithic tropical hardwoods due to their excellent durability and minimal periodic maintenance. WPCs are considered environmentally friendly eco-materials, since the products can be recycled several times, and their losses in the process are minimal [14]–[16]. The properties of WPCs are influenced by various factors, such as the type of the thermoplastic polymer matrix, the characteristics of the wood filler (quantity, wood species, size, shape, chemical composition, treatment, etc.) and the presence of different additives. Extensive literature research was conducted to characterise the general properties of WPCs in order to clarify the main drawbacks, as well as to identify the currently used methods for improvement of the WPC properties. From the literature review, it can be concluded that insufficient water resistance is one of the main disadvantages of WPCs. The absorption and desorption of water results in irreversible and significant reduction of the mechanical properties, causes dimensional

fluctuations, and provides favourable conditions for the development of microorganisms, against which WPCs are not protected [16]–[18]. In addition, the discoloration of WPCs under the influence of UV radiation has also been identified as a significant drawback, for the prevention of which fundamental research in this direction is vital [17]. To eliminate some of the drawbacks, in-depth studies have been carried out concerning modification of the WPC composition, including both the use of various additives and the treatment of the wood filler. With such methods, some improvements can be achieved; however, often they are not sufficient, as they involve the use of expensive additives, have a negative effect on the other characteristics, or are not feasible on an industrial scale. A great improvement in the properties of WPCs can be obtained by the use of coupling agents, and among them the most common and effective are maleinized polyolefins. The optimal amount in WPCs is usually around 3 wt% or higher. Although the coupling agent can significantly improve several WPC properties, it still fails to provide excellent water and biological resistance that could potentially be provided by using TM wood residues [18], [19].

2. MATERIALS AND METHODS

The schematic representation of the experimental plan of the Thesis is shown in Fig. 2.1. Six different components were used in the formulations of WPC: wood particles, thermoplastic polymer, antioxidant, inorganic filler, pigment and coupling agent. In order to assess the potential of using TM wood residues in the production of WPCs, as well as to identify possible issues, which may be introduced due to the wood filler, significant focus was attributed to investigate different types of TM wood residues and their characteristics. TM wood residues vary depending on various factors that were considered in the development of this work. The main influencing factors are related to the process of wood modification (methods and intensity), the selected wood species, and the type of wood mechanical processing that is carried out on the wood after modification. Since the objective of the work is to use TM wood residues, in all cases the thermal modification was carried out for boards, using the most commonly used methods of modification, intensities, and tree species. The TM wood residues used in the Thesis and their types, depending on the above factors, are summarised in Fig. 2.1. As for the methods of thermal modification, two fundamentally different processes were used – closed (*Wood Treatment Technology* (WTT)) and open (*Thermowood®* (Thermo)) type systems. In the case of WTT, the modification process occurs in water vapour medium in elevated pressure during which the wood does not dry out and hydrolysis reactions predominate. In the case of Thermo, the wood is modified at atmospheric pressure in water vapour medium. During this modification process, wood is dried and therefore pyrolysis reactions predominate. For all TM wood particles used in the work such important properties as particle size distribution, length/diameter ratio, chemical properties, and equilibrium moisture content were characterised. Unmodified wood particles were also tested to establish the differences. Polypropylene (PP) was used as a thermoplastic polymer matrix (*Mosten MA-712* PP). It has good physico-mechanical properties, high polymer melt viscosity and it is one of the dominant type of plastics found in waste streams. In some WPC formulations, also additives were used – antioxidant (*Hostanox O3 P*),

TiO_2 (*Hombitec RM 400*), Fe_2O_3 (*Xfast Rot 2817*), and maleinised polypropylene (MAPP) (*Licocene PP MA-7452*), which were supplied by the corresponding manufacturers of these additives. Carbon black and wood ash, which were also used to improve the properties of the WPC, were derived from other by-product streams related to wood products: carbon black from the brushing process of the charred wood surface and the wood ash from the process of generating thermal energy by burning wood chips.

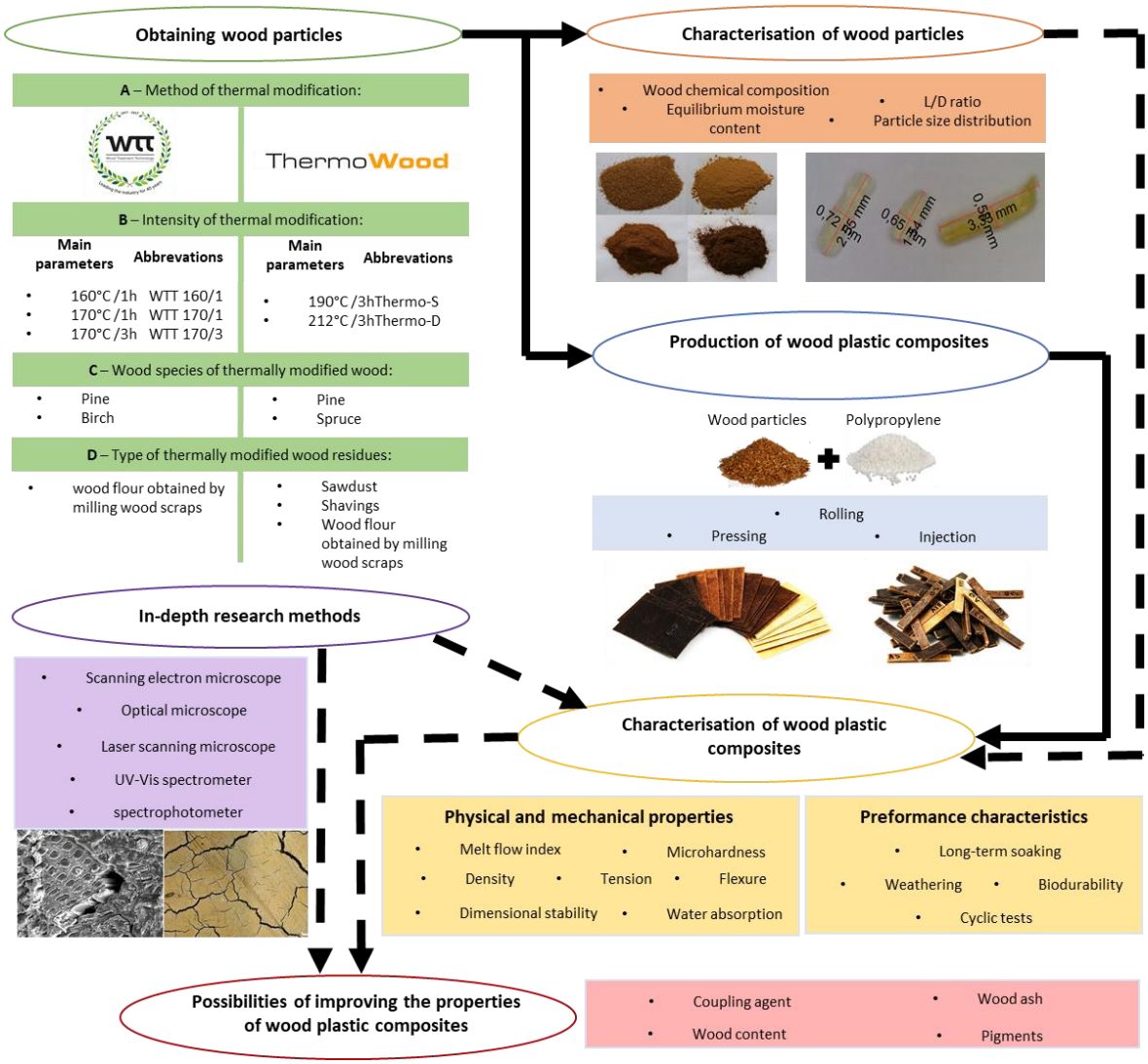


Fig. 2.1. Schematic representation of the experimental plan of the Thesis.

To assess the impact of different types of wood particles (wood species, modification method, residue type, particle sizes), WPCs were made of 50 wt% wood particles and 50 wt% PP, including in its composition also the previously mentioned antioxidant. In all the cases, the antioxidant amount was 1.5 wt% of PP. WPCs were made by two-roll mills. Bar and dog-bone shaped specimens were produced by injection moulding, and film shaped specimens by pressing. The most important characteristics for WPCs were tested: melt flow index (ISO 1133-1:2011), flexural properties (ISO 178:2019), tensile properties (ISO 527-1:2019), impact resistance (ISO 179-1:2010), microhardness (*Vickers*), density (ISO 1183-1:2019), water

absorption and dimensional stability (ISO 62:2008). WPCs' resistance to rot fungi (CEN/TS 15083-1:2005), weathering (natural and artificial weathering tests), prolonged soaking, cyclic soaking/drying and cyclic freezing (ISO 321:2002) were also evaluated. In-depth research was carried out using various instrumental methods. Changes in colour and light transmittance were studied with a spectrophotometer and an UV-Vis spectrometer. Surface characterisation after weathering processes was analysed with a laser scanning microscope (LSM) and an optical microscope. Fracture sites after mechanical tests were studied with a scanning electron microscope (SEM). All the data obtained were mathematically processed by calculating the standard deviation, as well as by performing a single-factor variance analysis to find out whether the differences between the specimen series were statistically significant. For optimal systems, in-depth studies to improve WPC properties by adjusting the composition were carried out. More specifically, the effect of wood content (40–60 wt%) and addition of different additives were analysed. The content of pigments, MAPP and wood ash in the WPC formulations were 5 wt%, 1–3 wt%, and 2–10 wt%, respectively.

3. MAIN RESULTS OF THE WORK

3.1. Characterisation of Thermally Modified Wood Residues

WPCs are significantly influenced by the type and properties of wood particles; therefore, their characterization is very important. It is also necessary in order to clarify general trends that would allow the use and adaptation of an appropriate wood filler for a particular WPC application. One of the influencing factors is the thermal modification method. In this context, the work dealt with open (Thermo) and closed (WTT) type systems. In order to ascertain the effect of modification method, regimes were initially identified, which would be comparable for both methods in terms of intensity. This was found by analysing the mass loss (ML) of wood during the modification process, as well as the TM wood's chemical changes and equilibrium moisture content. Both ML (see Fig. 3.1) and other results showed that, among the two methods, the most similar are regimes Thermo-D and WTT 160/1.

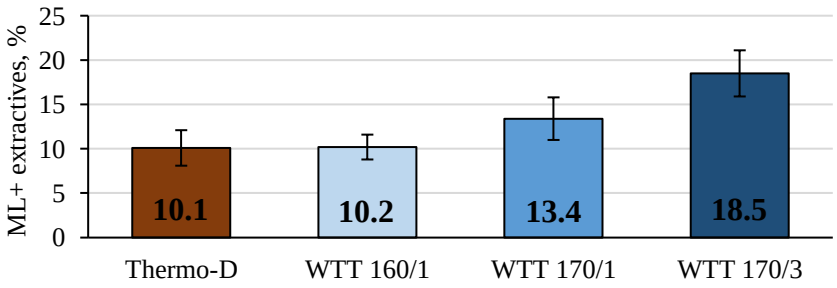


Fig. 3.1. Pine mass loss (ML) + extractives in Thermo and WTT thermal modification processes at different processing intensities.

In the course of the further work, these regimes of similar intensity were compared. Of the results obtained, the content of extractive had the most significant differences between the methods (see Table 3.1), where extractives in the WTT 160/1 wood particles were twice as

many as in Thermo-D. Slight differences were also observed in the content of α-cellulose where the amount was lower in the case of WTT 160/1 wood particles, which could indicate a more significant degradation of amorphous cellulose [20]. This means that the wood particles obtained by using the WTT method could be mechanically weaker, which is also in line with general trends, comparing the wood characteristics between the two methods [21]. The particle size distribution of the wood particles obtained under the same conditions did not significantly differ between the methods. No significant difference was observed also regarding the *L*/*D* ratio. Overall, the results suggest that wood residues from different modification methods could have a relatively similar effect on WPC. Some influence could only be caused by the differences in the content of extractives, since it is known that, in the case of unmodified (UM) wood particles, the presence of extractives can improve moisture resistance, however, impairing mechanical properties of WPC [22].

In order to find out how the modification intensity and the wood species affect the properties of the TM wood particles, boards of three wood species (birch, pine, and spruce) were modified with both modification methods by using various regimes. TM wood particles from the modified boards were obtained by grinding. The chemical composition is very important for obtaining good interaction between the components in WPC. Given that the nonpolar polymers that are used in WPCs do not have functional groups with which covalent bonds can be formed, it is very important to reduce the polarity of wood particles as much as possible, which would ensure better compatibility of the two components and the formation of larger amount of dispersive bonds. The results of the chemical analysis of wood particles, depending on the modification intensity, method, as well as the species of wood, are presented in Table 3.1.

Table 3.1

Chemical composition of unmodified (UM) and thermally modified (WTT and Thermo method) birch, pine, and spruce wood at different modification intensities

Wood species	**Modification regime**	**Wood chemical composition, %**			
		Extractives	**Lignin**	**α-cellulose**	**Hemicelluloses**
Birch	UM	1.3 ± 0.1	28.0 ± 0.5	44.0 ± 0.0	26.7 ± 0.4
	WTT 160/1	15.4 ± 0.2	24.6 ± 0.1	47.2 ± 0.1	12.8 ± 0.0
	WTT 170/1	14.6 ± 0.3	24.6 ± 0.1	49.5 ± 0.3	11.3 ± 0.2
	WTT 170/3	12.7 ± 0.3	28.9 ± 0.3	49.9 ± 0.0	8.5 ± 0.3
Pine	UM	2.6 ± 0.0	30.8 ± 0.4	44.9 ± 0.3	21.7 ± 0.4
	WTT 160/1	7.1 ± 0.0	36.8 ± 0.0	41.2 ± 0.1	14.9 ± 0.1
	WTT 170/1	6.4 ± 0.2	36.9 ± 0.3	48.7 ± 0.6	8.0 ± 0.7
	WTT 170/3	8.3 ± 0.1	37.2 ± 0.0	48.4 ± 0.8	6.1 ± 1.0
	Thermo-D	3.4 ± 0.1	37.1 ± 0.4	46.4 ± 0.1	13.1 ± 0.1
Spruce	UM	1.5 ± 0.1	34.3 ± 2.3	40.4 ± 0.1	23.8 ± 2.3
	Thermo-S	1.5 ± 0.1	37.9 ± 0.7	41.1 ± 0.4	19.5 ± 0.4
	Thermo-D	2.5 ± 0.2	38.0 ± 0.2	43.5 ± 0.1	15.9 ± 0.3

It can be seen that WTT wood have a significantly higher extractives content compared to the UM wood. In the case of birch, the extractives are as much as 10–12 times higher, depending on the modification regime. In the case of pine, the differences are smaller, but still significant (2.5–3.2 times higher, depending on the modification regime). By comparing the extractives of the Thermo wood with the UM wood, it can be observed that the differences are not so significant. In the case of the most intensive regime Thermo-D, the extractives content is only 1.5–2.0 times higher, depending on the tree species, but in the case of Thermo-S spruce, the content is similar. Nevertheless, it should be considered that, despite the similar content, the chemical composition of extractives is significantly different [20], [23], [24]. The relative content of α-cellulose in TM wood is larger. This is an important aspect also in the context of WPC, since cellulose is one of the main reinforcing components that determine the mechanical properties of wood particles [17]. However, it should be considered that cellulose is also partially altered in the thermal modification process. It has been established that the degree of crystallinity of cellulose increases and the average degree of polymerization decreases [20], [25]. When comparing the amount of α-cellulose between different wood species, it is evident that the least amount of α-cellulose is in spruce. However, even in this case, the relative content of α-cellulose is larger for the TM wood particles mainly due to the degradation of other wood components. Comparing the content of the most hydrophilic component of wood, namely, hemicellulose, it can be seen that its content in TM wood particles is significantly lower. In the case of birch for the most intensive regime WTT 170/3, the content of hemicelluloses is around 3.1 times lower than for the UM wood. In the case of pine for the regime WTT 170/3, the reduction is even more significant (3.6 times lower). In the case of the other modification method, namely Thermo, the reduction in the case of pine and spruce is similar for the most intensive regime Thermo-D (212 °C/3 h), but not even close to regime WTT 170/3. Thermo-D pine and spruce, respectively, have 1.7 and 1.5 times less hemicelluloses than in the case of UM wood. For Thermo-S spruce, the reduction is even lower, which indicates that, in the case of these TM wood particles, a significant improvement in the WPC moisture resistance cannot be expected. The content of lignin in birch particles at milder wood thermal modification regimes (WTT 160/1 and WTT 170/1) has decreased, but at stronger ones (WTT 170/3) increased, which could be explained by the initial degradation of lignin forming low molecular phenol-type compounds, followed by cross-linking reactions of lignin, predominantly occurring with hemicellulose degradation products as well as with the previously formed phenol-type compounds [21]. This could also explain the decrease in the extractives content at the strongest WTT regimes. Certainly, the reduction of hemicelluloses also has a great influence, at the expense of which the content of other wood components increases [21], [26]. In the case of pine and spruce, with increasing modification intensity, the lignin content increases evenly. In addition, the extractives content also increases evenly. A similar tendency is observed for both thermal modification methods. It is known that the lignin of coniferous trees is more thermally stable than the lignin of deciduous trees, which can also explain such a steady increase. Thermal stability is connected with more thermally stable guaiacyl groups in coniferous lignin [27].

One of the most important characteristics of wood particles is size, which mainly affects the mechanical properties of WPC, but can also have a significant impact on other properties [28]–

[30]. By analysing the distribution of the wood particle size after grinding under the same conditions through a 1-mm sieve (see Fig. 3.2), it can be seen that due to thermal modification, the size of the wood particles is significantly affected. In the case of both birch and pine, a similar tendency has been observed that, by increasing the intensity of the thermal modification of wood, the average size of wood particles decreases. This is explained by the fact that in the thermal modification process, a partial thermal degradation of wood occurs, which causes both changes in microstructure and chemical composition in the wood, with a decrease in the degree of polymerization of cellulose and an increase in the proportion of lignin, which in general leads to a deterioration in the mechanical properties and fragility of wood [20]. Similar trends were observed for spruce and pine in the case of the Thermo method.

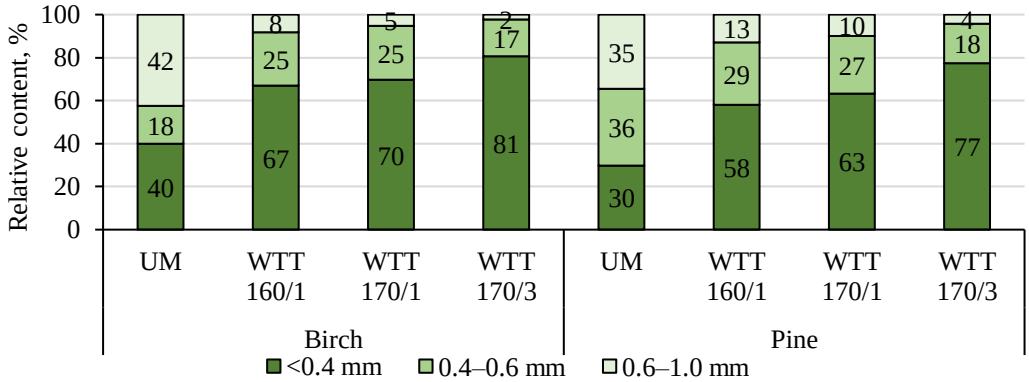


Fig. 3.2. Particle size distribution (%) of unmodified (UM) and WTT (at 3 different modification intensities) birch and pine wood particles.

Another important parameter is the *L*/*D* ratio, which characterizes the reinforcing ability of the particles. According to Klyosov (2007), in the case of WPC, wood particles are divided into: 'oversized' (0.4–1.0 mm), 'normal sized' (0.2–0.4 mm) and 'fine sized' (<0.2 mm) particles [17]. In the course of the further work, when preparing particles for experiments that determined the *L*/*D* ratio and the effect of wood particle size on the WPC properties, this classification was used. Correspondingly, sieves of the appropriate size (0.4 mm and 0.2 mm) were used for the fractionation process. The *L*/*D* ratio was determined for each particle size fraction (<0.2 mm, 0.2–0.4 mm, 0.4–1.0 mm) for four particle types (UM birch, UM pine, WTT 170/1 birch, WTT 170/3 pine). The summary of these results is reflected in Fig. 3.3.

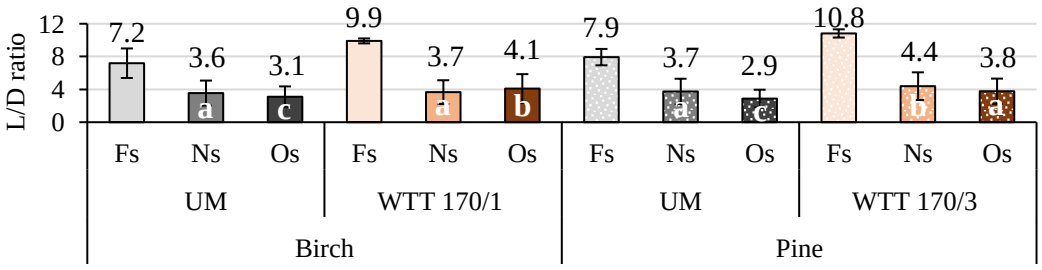


Fig. 3.3. *L*/*D* ratio for different particle fractions depending on the wood species and modification regime; fine sized (Fs): <0.2 mm; normal sized (Ns): 0.2–0.4 mm; oversized (Os): 0.4–1.0 mm; values with the same letter are not significantly different ($p > 0.05$).

The results show that the *L*/*D* ratio depends on the particles' size fraction, wood species and wood modification. The largest *L*/*D* ratio in all cases is for the smallest wood particles size fraction, and as the particle size increases, the *L*/*D* ratio decreases. Since the smallest wood particles both have smaller size and larger *L*/*D* ratio (the particles are more elongated), they also have a larger specific surface. Both the *L*/*D* ratio and the specific surface have a significant effect on the properties of the WPC, and the higher these values, the better is the interaction between the matrix and the wood particles, which facilitates the transfer of stresses from the matrix to the reinforcing component [31]. From the results obtained, it can be also seen that the *L*/*D* ratio is higher in the case of WTT wood particles compared to the corresponding fraction of UM wood particles, suggesting that in the case of TM wood particles a better reinforcing function will be ensured. This could result in enhanced flexural strength and modulus of elacticity for WPC with TM wood particles compared to UM wood particles, since these properties are known to improve as the *L*/*D* ratio increases [32].

In the work, the effect of different types of wood residues on the WPC properties was analysed, thus initial characterisation of these residues was important. The TM wood residues, which were sawdust and shavings from the wood processing activities of pine wood modified according to the Thermo-D regime, were obtained from the by-product streams of *Stora Enso Latvija*. The chemical composition of these residues is the same as described above (see Table 3.1), but the most significant differences could only be related to the particle sizes and the *L*/*D* ratio, which were studied in more detail. The particle size distribution for sawdust and shavings was determined without any additional treatment. The results show that the wood residues formed at the TM wood production site are predominantly <1.0 mm in size. In addition, about 60 % of the particles have a size of <0.4 mm. This means that such residues could already be fully compliant with the further WPC production without additional pre-processing. These values may vary slightly depending on the equipment used, technological parameters, as well as on the characteristics of the wood (moisture content, density, etc.) [33], but the general situation is clear that during these processes TM wood residues of sufficiently small size are formed.

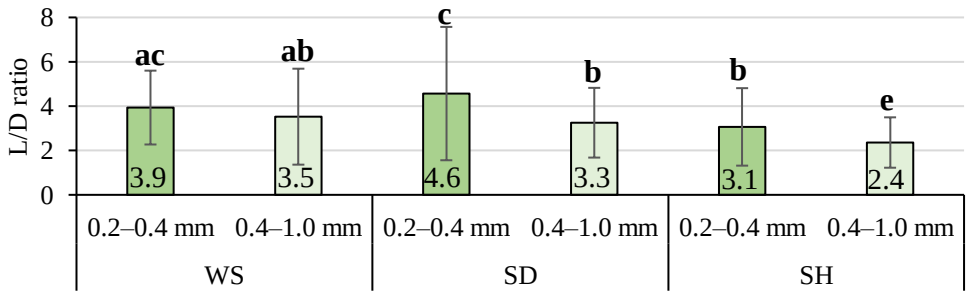


Fig. 3.4. *L*/*D* ratio for 0.2–0.4 mm and 0.4–1.0 mm particle size fractions of Thermo-D pine depending on the wood residue type (WF – wood flour obtained after grinding Thermo-D pine wood scraps; SD – sawdust; and SH – shavings); values with the same letter are not significantly different ($p > 0.05$).

By comparing shavings and sawdust, the particle size distribution is very similar, but the *L*/*D* ratio differs (see Fig. 3.4). Shavings, regardless of the particle size fraction, have the smallest *L*/*D* ratio in comparison with the other types of wood residues. These results indicate that, in the case of shavings, the WPC will have inferior mechanical properties comparing to the other WPC. For the particle fraction with a size of 0.4–1.0 mm, no statistically significant difference between the sawdust and particles obtained by grinding wood scraps is observed. However, for the particle fraction with a size of 0.2–0.4 mm, the *L*/*D* ratio for sawdust is higher by 16 %. The average *L*/*D* ratio of the latter is around 4.6, which is significantly higher than for typical UM wood sawdust according to the literature data (3–4) [17].

3.2. Effect of Thermally Modified Wood Particles on the Properties of Wood Plastic Composites

In the previous subsection, wood particles were described; now, it is necessary to find out how these particles affect the properties of WPC. It should be noted that in a number of parameters TM wood particles were more appropriate for the production of WPC comparing to UM wood particles. Initially the general impact of TM wood particles on the WPC properties was examined and compared with the reference, which in this case is WPC with UM wood particles. One of the most important technological parameters is the melt flow index (MFI), which characterizes the rheological properties of WPC. The MFI allows to understand what methods of industrial processing are applicable for the manufacture of products in the case of a particular material. If MFI is more than 2.3 g / 10 min, then this material can be used in the manufacture of moulded products using injection moulding equipment. If MFI is more than 0.1 g / 10 min, then extruders can be used in the manufacture of various profiles, pipes, boards, and other similar products. In turn, if MFI is less than 0.1 g / 10 min, then the only method of processing such a material is pressing [34]. MFI results for WPC are reflected in Fig. 3.5.

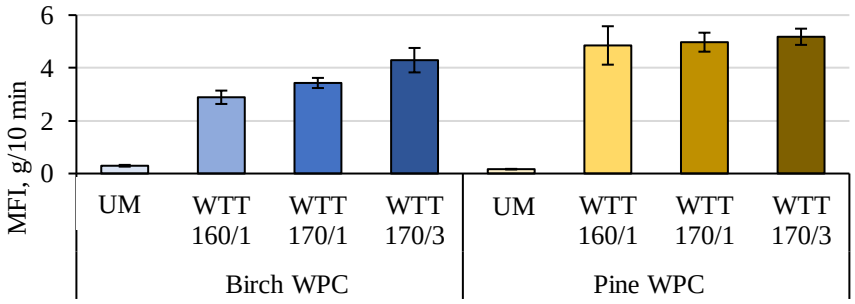


Fig. 3.5. Melt flow index (MFI) for WPC with UM and WTT unfractionated wood particles.

For WPC with UM wood particles, MFI is relatively small. In the case of birch and pine, it is around 0.3 g / 10 min and 0.2 g / 10 min, respectively, indicating that the processing possibilities for these composites are limited without the addition of lubricants. The MFI of WPC with WTT wood particles is significantly (more than 10 times) higher, therefore, the processing possibilities are broader, which allows to significantly increase the range of products. The obtained results can be explained by the fact that WTT wood particles have a

better compatibility with the PP matrix leading to an improved wood particles dispersion in the polymer melt, which reduces wood particle agglomeration. Larger content of wood extractives in the TM wood particles (see Table 3.1) could also play a very important role. The presence of low molecular components on the boundary surface between the particles and the polymer matrix can increase WPC melt flowability [35]. Judging by the literature data, by increasing the content of particles in WPC by 10 wt%, MFI is rapidly declining (by about 25 %), but since WPC with TM wood particles have a sufficiently high MFI, it is likely that a higher content of wood particles can be used without sacrificing the recyclability of the material [36].

In the work, the density of WPC was also determined, but no significant differences were found between UM and TM wood residues, except for regime WTT 170/3 in the case of birch, where slight decrease in the density was observed. Nevertheless, the density of all WPCs obtained was within 1.06–1.07 g/cm^3, regardless of the method and intensity of the thermal modification, and also wood species despite the significant differences in the wood densities for birch (0.65 g/cm^3), pine (0.50 g/cm^3), and spruce (0.45 g/cm^3). Since the density of the PP itself is only 0.89 g/cm^3, this means that during the production of WPCs, the PP melt penetrates the cavities of the wood cells, thereby significantly increasing the density of the material approaching the density of the wood substance (1.54 g/cm^3). The penetration of PP into the wood structure has already been observed earlier in the case of UM wood [37], but in this work, it was also found in the case of TM wood (see Fig. 3.6).

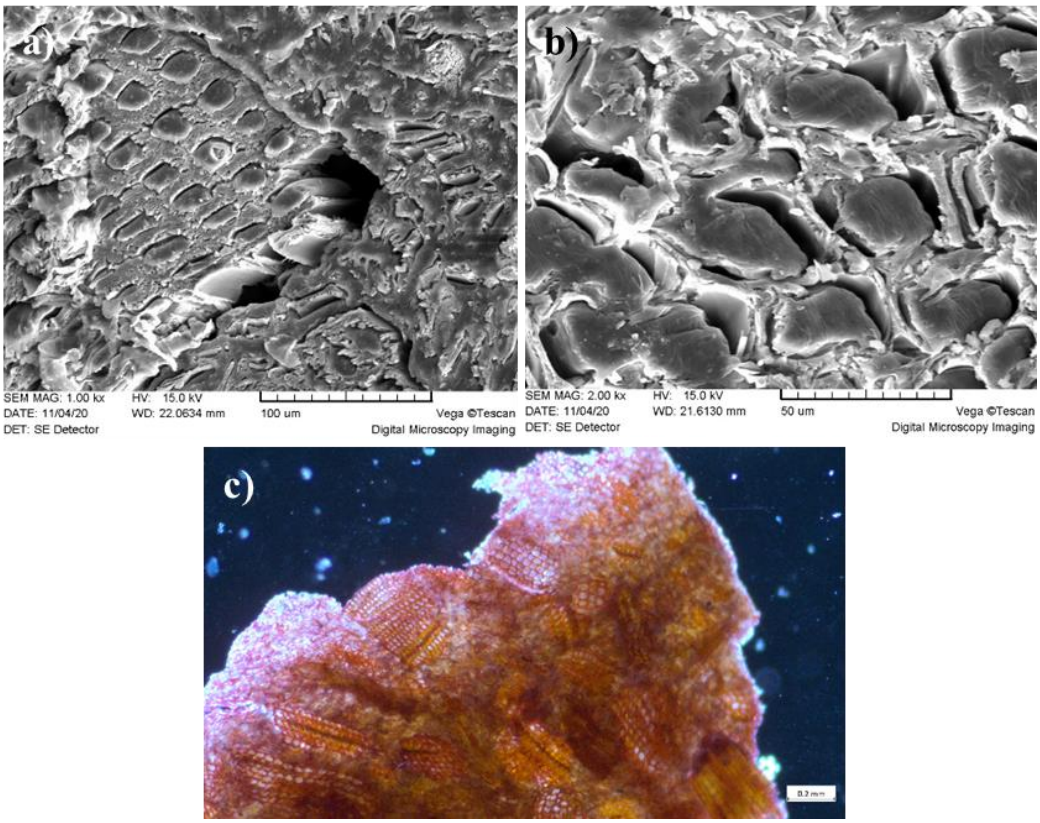


Fig. 3.6. WPC structure in a scanning electron microscope: (a) taken at 1000× and (b) 2000× magnification, and in a reflected light microscope; (c) taken at 50× magnification.

The mechanical properties of WPCs were also determined; the results are summarized in Table 3.2. The results show that WPCs with WTT wood particles have greater flexural strength (σ_F), flexural modulus of elasticity (E_F), and microhardness than the corresponding WPCs with UM wood particles. This is explained by the fact that there is an improved compatibility between the WTT wood particles and the PP matrix, resulting in better contact and, consequently, more physical bonds, which makes it more difficult for the particles to be pulled out from the PP matrix (more energy is required). Improved dispersibility of the wood particles is also likely to have its effect, which results in more even particle dispersion and, as a result, a more efficient stress transfer. Some effect could also be due to the physical properties of the particles (particle size and *L*/*D* ratio). A more detailed study regarding these aspects was carried out in the continuation of the work. Impact strength is the only property that is reduced for the WPC with WTT wood particles, but this is a reasonable outcome, which can be justified by the reduced deformation ability of the material causing it to become more rigid.

Table 3.2

Flexural strength (σ_F), flexural modulus of elasticity (E_F), impact strength (A), microhardness (MH) for PP and WPC with UM and WTT wood particles; (wood particles: PP);
(+ increase / – decrease against WPC with UM wood chips)
* no statistically significant difference ($p > 0.05$) compared to UM

	Modification regime	**σ_F, MPa**	**E_F, GPa**	**A, kJ/m^2**	**MH, MPa**
PP (0:100)	-	45 ± 1	1.5 ± 0.1	Did not break	110 ± 9
Birch WPC (50:50)	UM	37 ± 1	3.5 ± 0.1	5.5 ± 0.4	108 ± 16
	WTT 160/1	38 ± 1 (+3 %)	3.9 ± 0.1 (+11 %)	4.9 ± 0.7 (–11 %)	130 ± 9 (+20 %)
	WTT 170/1	40 ± 2 (+9 %)	4.3 ± 0.2 (+24 %)	4.6 ± 0.4 (–16 %)	129 ± 12 (+19 %)
	WTT 170/3	39 ± 2 (+5 %*)	4.2 ± 0.2 (+21 %)	3.8 ± 0.6 (–30 %)	130 ± 12 (+20 %)
Pine WPC (50:50)	UM	36 ± 1	3.3 ± 0.1	4.6 ± 0.5	109 ± 11
	WTT 160/1	37 ± 1 (+5 %)	3.7 ± 0.1 (+11 %)	4.2 ± 0.4 (–7 %*)	117 ± 14 (+8 %*)
	WTT 170/1	39 ± 1 (+9 %)	4.1 ± 0.2 (+22 %)	4.2 ± 0.5 (–9 %*)	130 ± 13 (+20 %)
	WTT 170/3	43 ± 2 (+22 %)	4.6 ± 0.2 (+38 %)	3.5 ± 0.3 (–23 %)	139 ± 14 (+28 %)

By using SEM, images were taken for the impact strength specimens at their fracture sites with the aim of elucidating the WPC rupture mechanism. All the locations presented with the arrows in Fig. 3.7, in the case of both UM and TM wood particles, indicate a damaged interface between the particle and PP matrix. In general, from the results it can be concluded that the WPC rupture mechanism is connected with the weak adhesion between the wood particles and the PP matrix, as a result of which the particles are pulled out of the polymer matrix, which causes the material to break. It should be noted that breakage of wood particles was not observed.

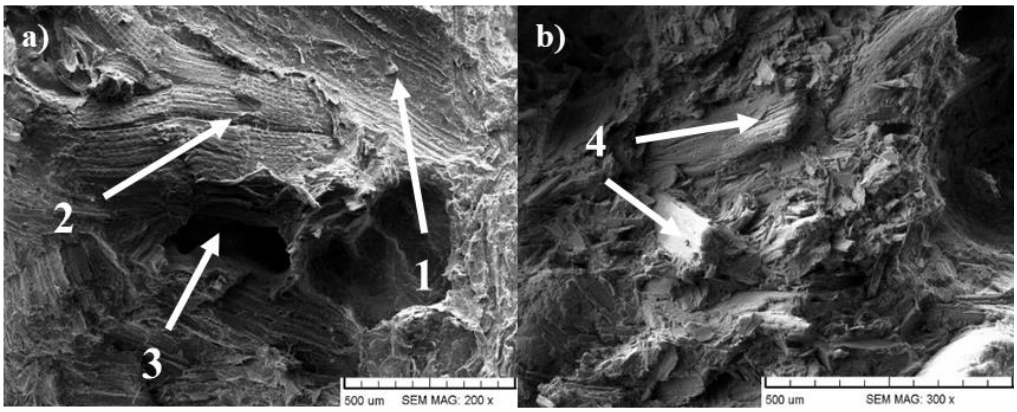


Fig. 3.7. SEM images of the fracture sites of impact strength specimens:
a) WPC with UM pine wood particles (taken at 200× magnification),
b) WPC with WTT 170/3 pine wood particles (taken at 300× magnification).

Water absorption results (see Fig. 3.8) indicate a significantly improved water resistance of WPCs with TM wood particles, which increases with increasing the modification intensity. After 280 days in water, the WPCs with WTT wood particles, depending on the wood species and the modification intensity, have about 2–3 times lower W_{abs} than the WPC with UM wood particles. Similar improvements were found also for the results concerning dimensional stability. The significant improvement can be explained by the lower water absorption capacity of WTT particles (due to the reduction in the proportion of hemicelluloses), as well as by the improved interaction between the particles and the PP matrix, which contributes to a more efficient dispersion and encapsulation of wood particles in the polymer matrix.

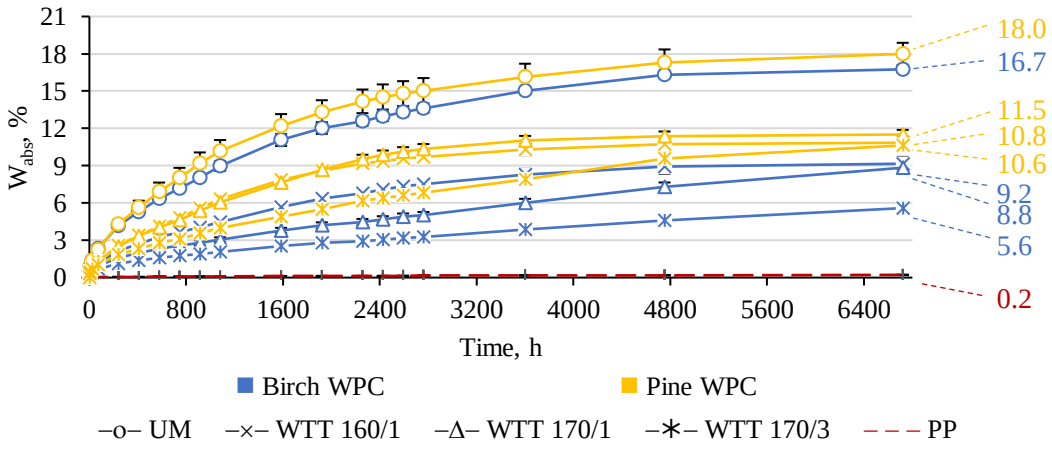


Fig. 3.8. Water absorption dynamics for PP and WPC with UM and WTT unfractionated wood particles.

3.3. Effect of the Wood Particle Size, Thermal Modification Method, and Residue Type on the Properties of Wood Plastic Composites

In the work, significant focus was attributed to evaluation of the effect of **wood particle size** (fine sized: <0.2 mm; normal sized: 0.2–0.4 mm; oversized: 0.4–1.0 mm) on the characteristics of WPC. The results showed that there are significant differences between UM and TM wood particles. In the case of TM wood particles, the size fraction, has no or only minor effect on the WPC properties. For the following properties differences were statistically insignificant ($p > 0.05$): density, dimensional stability, dynamics of water absorption (see Fig. 3.9), the maximum water uptake, as well as the changes in bending properties, caused by prolonged soaking. The most significant effect of different wood particle size fractions had only on the mechanical properties, where in the case of fine sized fraction, the impact strength was lower by 13–15 %, and the flexural strength and flexural modulus higher by 3 % and 9 %, respectively, than in the case of normal sized or oversized fraction. Besides, the differences regarding the bending properties were statistically significant only in the case of pine for regime WTT 170/3. By summarising the obtained results, it can be concluded that wood particle size in the case of TM wood particles has a relatively minor effect on the overall WPC properties, and the only detectable influence is on the mechanical properties. The results of the experiments suggest that both birch and pine TM wood particles with dimensions up to 1.0 mm do not need to be sieved, dividing them into several fractions, since this activity will not be beneficial for achieving a significant improvement in WPC properties. On the contrary, wood particles size has a high importance in the case of UM wood particles showing significant influence in all of the tested WPC properties.

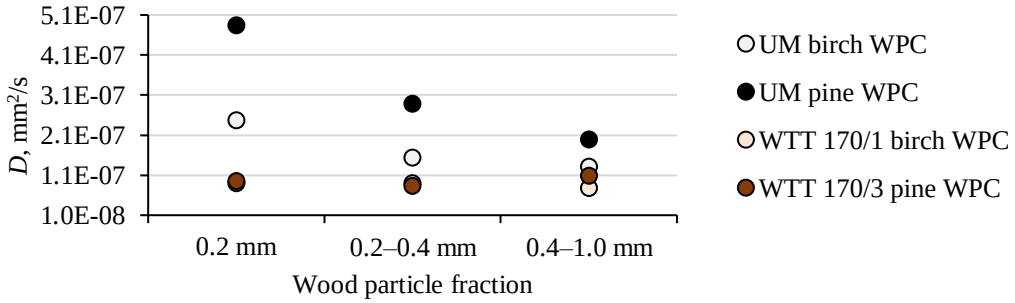


Fig. 3.9. True diffusion coefficient (D) for WPC with UM and WTT wood particles depending on the wood particle size.

The influence of the **thermal modification method** on the WPC properties was also studied. The results presented previously regarding the wood particle comparison between the modification methods suggested that a potential effect on the mechanical properties and water resistance is possible due to significantly different content of wood extractives. The results concerning WPC properties show that similar intensity regimes (WTT 160/1 and Thermo-D) have no significant effect on the dimensional stability, but there are differences regarding water absorption and mechanical properties. WPC with Thermo-D wood particles have higher water

absorption (W_{abs} higher by 9 %), which could be due to lower content of extractives resulting in more accessible OH groups for the water molecules. In addition, the lower content of extractives in Thermo-D particles can explain the higher flexural modulus of elasticity and flexural strength, as well as lower impact strength, compared to the WPC with WTT 160/1 particles (see Fig. 3.10). Overall, the results indicate that TM wood residues from any modification process can be used to produce WPC, but it must be taken into account that the obtained WPC may have slight differences in mechanical properties and water absorption.

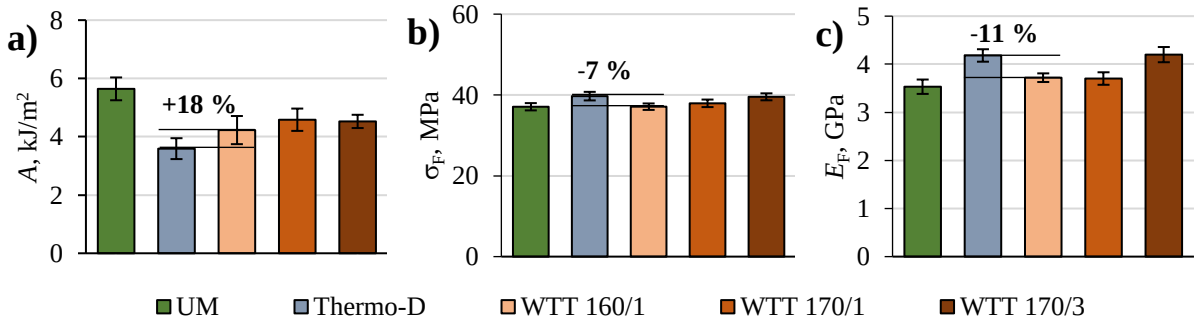


Fig. 3.10. Effect of the pine modification method on WPC a) impact strength (A), b) flexural strength (σ_F), and c) flexural modulus of elasticity (E_F).

The effect of different **types of TM wood residues** on the WPC properties was studied. As previously determined, the largest difference between different types of wood residues was in the L/D ratio, suggesting some influence on the mechanical properties. The results of the mechanical tests showed that the use of shavings instead of sawdust does not significantly affect the impact strength, however, it does reduce the flexural strength and modulus of elasticity by 12 % and 15 %, respectively. As the deterioration in mechanical properties is relatively small, TM wood shavings have also a potential to be used in production of WPCs. Concerning water absorption and dimensional stability (see Fig. 3.11), the impact on these properties was relatively small. This can be explained by the negligible influence of the L/D ratio on the water resistance of WPCs, which is found in the case of UM wood particles [38]. In general, the results obtained indicate that the wood residue type has a relatively small impact on the WPC properties. The only exception is 10–15 % smaller bending properties in the case of shavings.

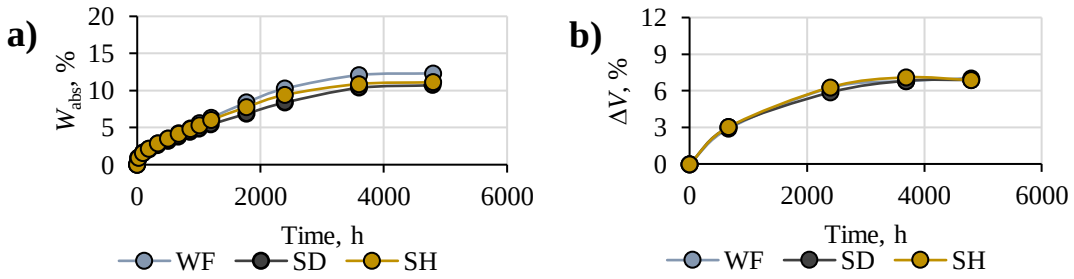


Fig. 3.11. Effect of Thermo-D pine residues (WF – wood flour obtained after grinding Thermo-D pine wood scraps, SD – sawdust, and SH – shavings) on the WPC a) water absorption and b) dimensional stability.

3.4. Performance Characteristics of Wood Plastic Composites Made with Thermally Modified Wood Particles

In addition to the already discussed characteristics, there are other very important ones, which are specific and related to the definite application of the WPC. Since WPCs are used mostly outdoors, they must be able to withstand sufficiently adverse conditions, which include the interaction with water, temperature fluctuations, biological attacks, as well as UV radiation. A significant deterioration in the WPC properties is caused by the **interaction with water**. During the use phase, WPCs are subjected to periodic water exposure, which can lead to a gradual degradation of the material. Cyclic soaking/drying tests on WPCs with UM and WTT 170/3 wood particles were performed to determine how significantly such condition can affect the WPC properties.

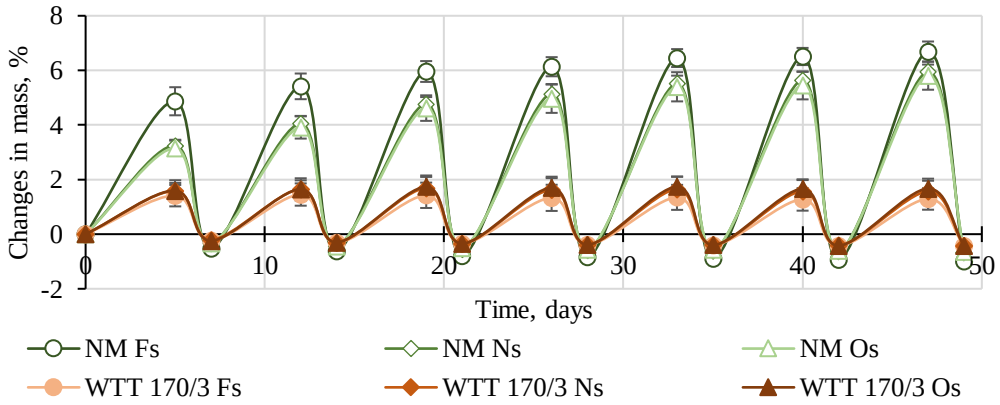


Fig. 3.12. Mass changes during the cyclic soaking/drying test for WPC with UM and WTT 170/3 pine particles of different sizes (fine sized (Fs): <0.2 mm; normal sized (Ns): 0.2–0.4 mm; oversized (Os): 0.4–1.0 mm).

The results of the mass change during the cyclic soaking/drying test (see Fig. 3.12) indicate that the situation in the case of TM wood particles is significantly better than in the case of UM wood particles. In each subsequent cycle, which involves drying of WPC specimens to an absolutely dry state and subsequent soaking for 5 days, the absorbed amount of water in the case of WPC with TM wood particles is constant in contrast to the WPC with UM wood particles, for which the amount of the absorbed water increases with each cycle. This tendency continues throughout the soaking/drying test, which includes a total of 7 cycles. The results suggests that the cyclic soaking and drying conditions for WPC with UM wood particles causes cracks or other defects in the material, which facilitates deeper penetration of water into the WPC after each subsequent soaking cycle. In order to determine whether it can cause some effect on the mechanical properties, a bending test was performed for WPC after exposure to 7 soaking/drying cycles. For comparison purposes, the results are also given on the possible maximum deterioration caused by exposure to water, which could be represented by a set of specimens exposed to a long-term soaking until equilibrium (200 days). The bending test was performed for re-dried specimens, and the results are presented in Fig. 3.13.

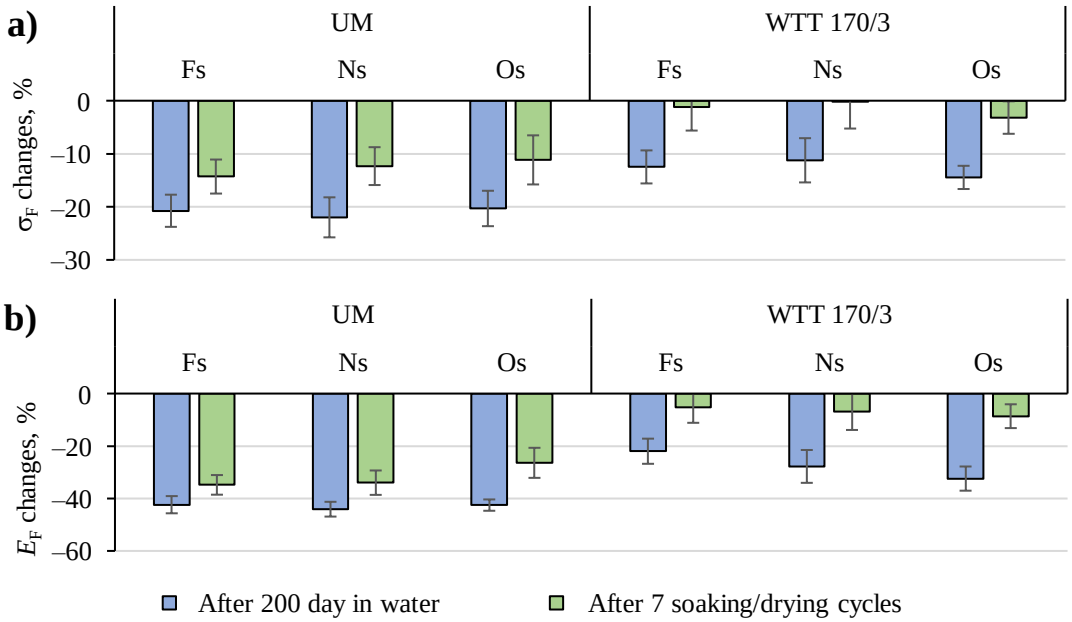


Fig. 3.13. Changes in a) flexural strength (σ_F) and b) flexural modulus of elasticity (E_F) after long-term (200 day) soaking and 7 soaking/drying cycles for dry WPC with UM and WTT 170/3 pine particles of different size fractions (fine sized (Fs): <0.2 mm; normal sized (Ns): 0.2–0.4 mm; oversized (Os): 0.4–1.0 mm)).

Also, the results of the bending properties, both after cyclic soaking/drying and after long-term soaking, indicate that WPCs with TM wood particles are much more resistant to water than WPC with UM wood particles. After soaking/drying tests, the flexural strength and the flexural modulus of elasticity in the case of UM wood particles deteriorated by 11–14 % and 26–35 %, respectively, depending on the particle size. In turn, for WPC with TM wood particles, the deterioration in flexural strength was not statistically significant, but the flexural modulus of elasticity decreased by 5–9 %. In the case of long-term soaking, the deterioration for both WPCs is significantly greater, but still, it is about two times less in the case of TM wood particles. The deterioration of the mechanical properties can be explained by the weakening of the interaction and the formation of cracks between the wood particles and PP matrix, which are caused by the swelling and shrinkage of the wood due to moisture fluctuations. This causes deformation in the PP matrix, which is unable to return to its original state due to irreversible creep deformation. The formation of cracks between the components after long-term soaking is demonstrated in the SEM images (see Fig. 3.14). The improvement in the case of TM wood particles is explained both by better encapsulation of the wood particles in the polymer matrix, which significantly impairs the water absorption process, and by greater dimensional stability of the TM wood particles themselves, which reduces the damage in the interface between the wood particles and PP matrix due to smaller swelling and shrinkage [21]. Although the improvement for the WPC with TM wood particles in comparison to WPC with UM particles is significant, it is still necessary to take into consideration the fact that the properties will deteriorate at prolonged soaking conditions, which may restrict the application of these WPCs in particularly wet areas that are exposed to regular and prolonged water contact.

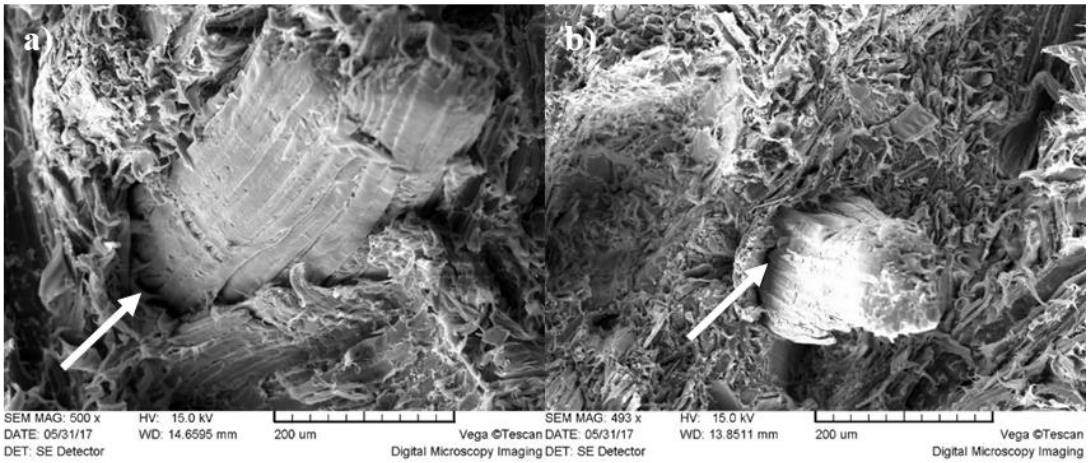


Fig. 3.14. SEM images of fracture sites of dried bending test WPC samples after long-term soaking (200 days): a) WPC with UM pine particles; b) WPC with WTT 170/3 pine particles.

The **biological durability** of WPC is highly dependent on the absorbed water content. Since these materials absorb relatively little water, it was initially assumed that WPCs are resistant against microorganisms, however, during long-term use it was revealed that it is not completely true [39]. In this work, the biological durability was evaluated by exposing the WPCs to brown rot fungi (*Coniophora puteana*). Since the presence of moisture is vital for microorganisms, before the test two water pre-treatment methods were used: short-term (2 weeks) and long-term (52 weeks). After the long-term water pre-treatment, the absorbed water amount depending on the wood particles type was 2.4–3.9 times larger than after the short-term pre-treatment. The results of the mass loss (ML) after the exposure to the brown rot fungus (see Fig. 3.15) show that the long-term pre-treatment, as expected, provided a more favourable medium for the development of fungi indicated by the increase in ML. The situation was similar for all the WPCs. Nevertheless, the results show that, in the case of WPC with WTT wood particles, the bio-durability is significantly higher than that of the WPC with UM wood particles. The improvement is especially significant in the case of films (see Fig. 3.15 b)), in which the ML for the WPC with WTT wood particles is at least 4 times smaller than that for the WPC with UM wood particles. In addition, by comparing the ML in the case of bar shaped specimens and films, the results suggest that the biodegradation occurs predominantly in the surface layers. The changes in mechanical properties after the fungi test were also analysed by preforming bending tests for the bar shaped specimens. The results indicated of a significant deterioration in the bending properties, however the decrease was very similar to the decrease reported above concerning the damage caused by the water exposure of the same duration (see Fig. 3.13). This allowed to verify the statement made in the literature that the action of fungi has a relatively negligible effect on the deterioration of WPC mechanical properties, and the main damage is caused by the action of water. The results also show that the WTT regime has a significant effect on the bio-durability, showing higher resistance in the case of the most intensive regimes. The improvement in the case of TM wood particles can be explained by the enhanced bio-durability of the particles themselves, as well as by the improved interaction between the particles and the polymer matrix, which contributes to their encapsulation.

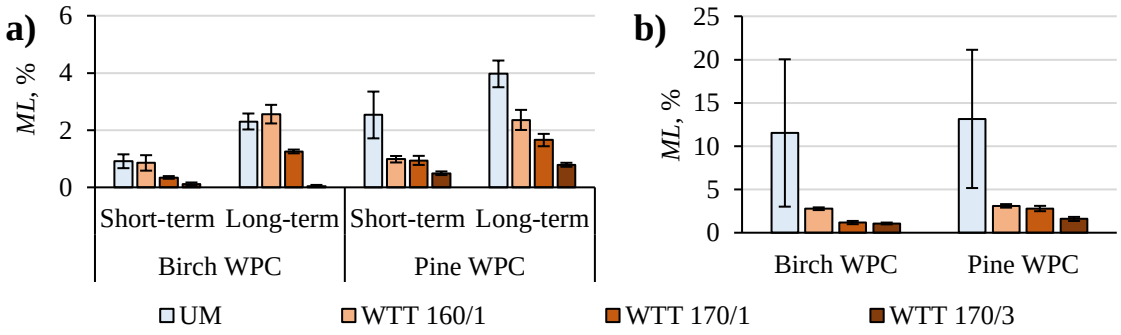


Fig. 3.15. WPC mass loss (ML) after the fungi test with *Coniophora puteana*: a) for bar shaped specimens with short-term (2 weeks) and long-term (52 weeks) water pre-treatment; b) for films with short-term (2 weeks) water pre-treatment.

Decorative properties are among the main ones that attract the customer and create the value for the WPC product. In the work, both artificial and natural weathering tests were carried out in order to investigate the stability of these properties during **weathering tests and exposure to various types of radiation**. Although it is known that mainly UV radiation is responsible for the discolouration of WPC, there are still contradictions in the literature regarding the mechanism of the colour change. By exposing WPCs with UM wood particles to UV radiation for 500 h, their colour significantly changed (see Fig. 3.16), reaching 9.5 ΔE units, which, considering the exposure dose, is similar to the result reported by others [40]–[42]. The situation of WPC with TM wood particles (Thermo-D, WTT 160/1 and WTT 170/3) is significantly different, since already after 120 h UV irradiation the total colour change exceeded 9.5 ΔE units and continued to increase reaching 25–32 ΔE units after 500 h. By analysing the changes for each individual colour parameters, it was found that the greatest impact on the total colour change in the case of WPCs with TM wood particles is due to the increase in the L^* parameter (lightness). In the case of WPCs with UM wood particles, the L^* parameter has a significantly smaller effect on the total colour change. In this case the largest contribution is from the b^* parameter. Concerning the colour change of the polymer matrix, generally in the literature it has been concluded that the colour of the polymer matrix does not change under the influence of UV irradiation and therefore cannot be responsible for the WPC colour change [42]–[46]. However, as can be seen from the presented results, the colour change of the PP film is quite significant, which is comparable to the colour changes of WPCs with TM wood particles. The contradictions between the presented results and the literature data are because the experiment was conducted in such a way that alongside the colour change also the changes in light transmittance for the PP film were measured. This was achieved by placing a black plate under the translucent PP film at the time of spectrophotometrical measurment.

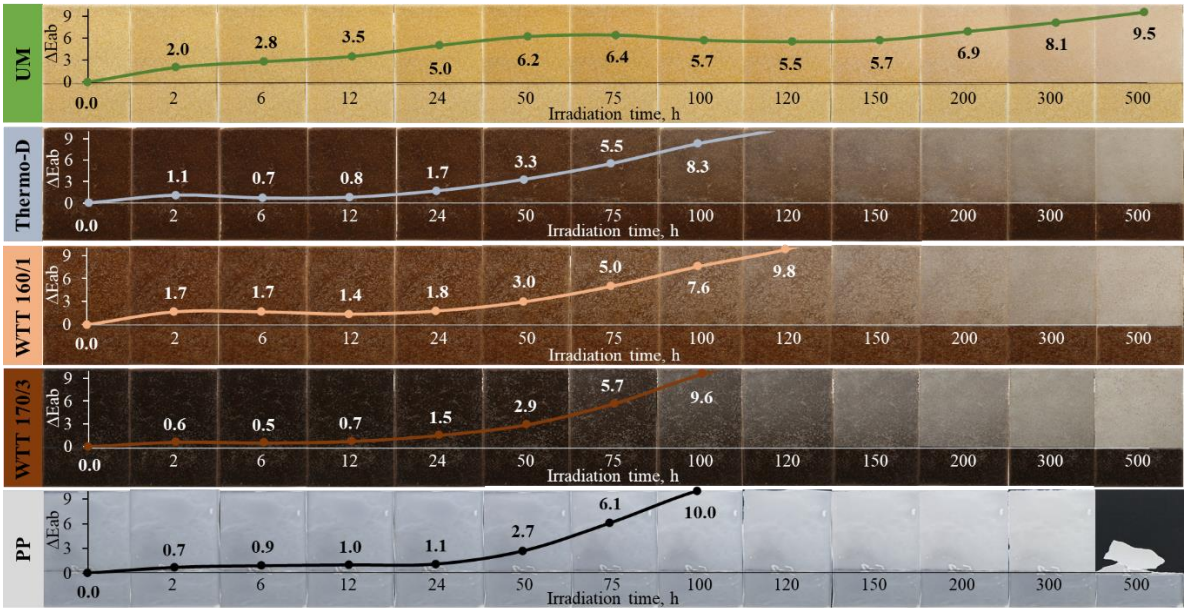


Fig. 3.16. Colour change dynamics of WPC and PP films under the influence of UV radiation.

As can be seen in Fig. 3.16, the colour did not significantly change during the first 50 h for the WPC with TM wood particles, which was followed by a very rapid discolouration right after the period. Moreover, the rapid colour change occurred simultaneously for all three WPCs, regardless of the thermal modification method or regime. If we look at the colour changes or, in this case, the change in the light transmittance of the PP film, it can be seen that the changes occur at the same moment and with similar rate as the colour change of the WPC with TM wood particles. These results suggest that the decrease in the light transmittance of PP could be closely connected with the discolouration of the WPC. In addition, it should be noted that the colour of TM wood is relatively stable against UV irradiation, hence, the unexpected and rapid increase in colour changes after 50 h for WPC with TM wood particles significantly exceeding the colour changes of WPC with UM wood particles are not typical for TM and UM wood [47]–[49]. Although UV irradiation causes TM wood to become lighter, the extent is not as significant, not to mention that UM pine wood during UV irradiation darkens [50], [51].

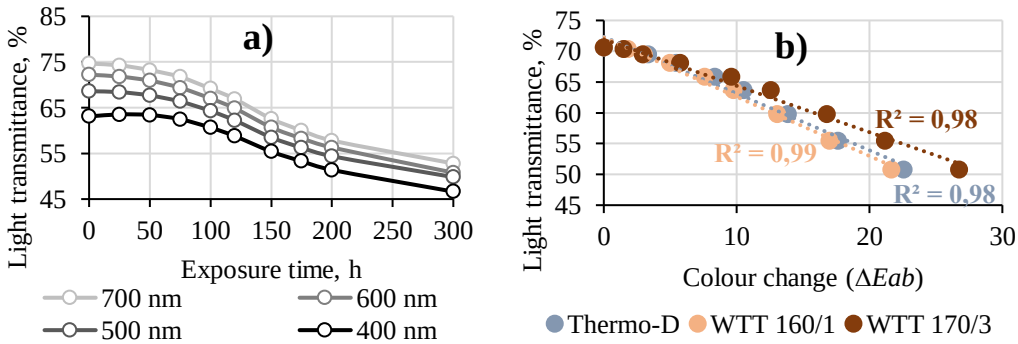


Fig. 3.17. Effect of UV radiation on: a) changes in light transmittance at 400 nm, 500 nm, 600 nm, and 700 nm for a 0.85 mm thick PP film depending on the UV exposure; b) correlation between the changes in light transmittance of the PP film (at 550 nm) and WPC discoloration.

In order to directly test how the PP matrix changes its light transmittance under the influence of UV radiation, the PP films were UV irradiated and analysed using an UV-Vis spectrometer. The obtained results (see Fig. 3.17 a)), reflecting the changes in the light transmittance of the PP film under the effect of UV irradiation, show that a significant decrease in the light transmittance throughout the visible light spectrum occurs. The most rapid changes begin after 50 h of UV irradiation, which agrees well with the previously presented colour changes of the WPC. By analysing the relationship between the changes in PP light transmittance and the WPC colour changes throughout the experiment (see Fig. 3.17 b)), a very close negative correlation was found. The set of these experiments already provides sufficiently convincing evidence to argue that the WPC colour change after longer UV irradiation periods is associated with a decrease in the light transmittance of the PP matrix, which leads to the effect of whitening. Hence, in order to prevent the characteristic discoloration of WPCs during outdoor use, it is necessary to protect the polymer matrix.

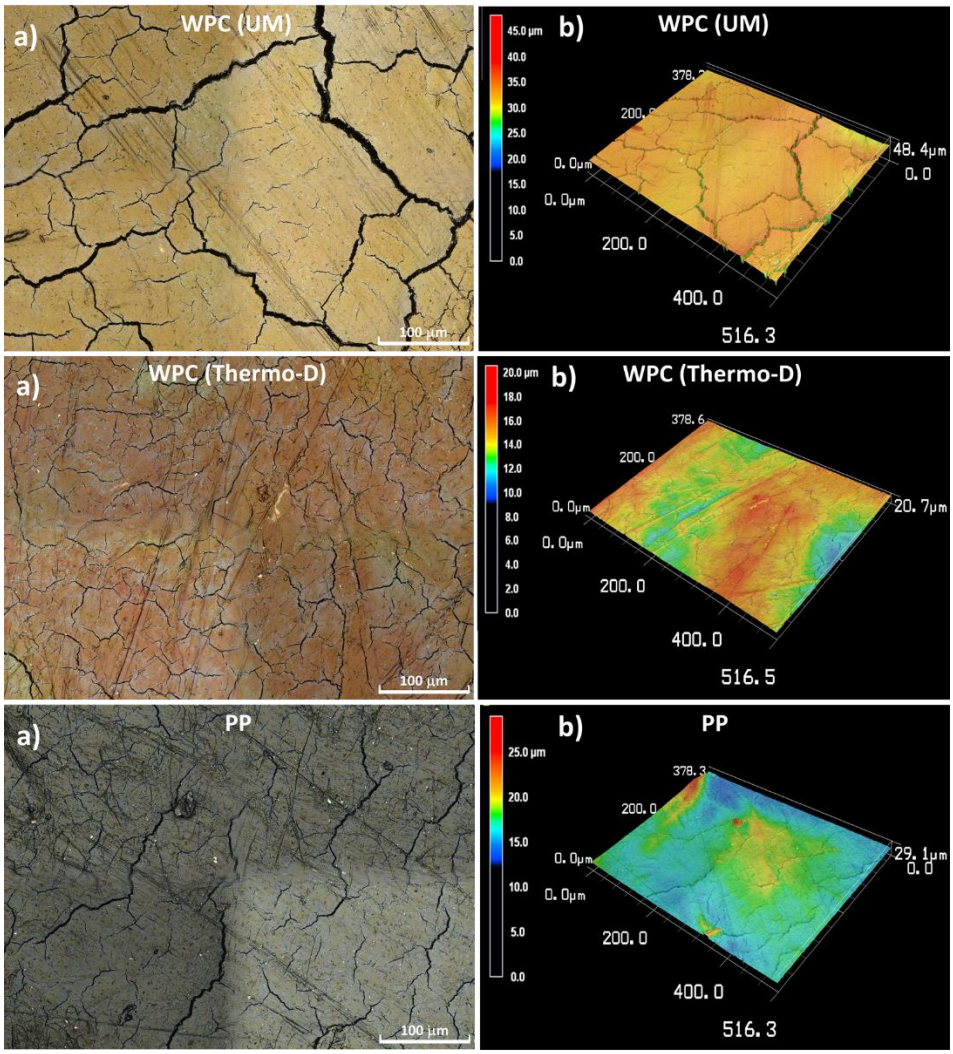


Fig. 3.18. Laser scanning microscope surface images taken at 50× magnification of WPC with UM wood particles, WPC with Thermo-D wood particles and PP after 120 h UV irradiation: a) laser + optical images; b) surface topography images.

In the PP matrix, the decrease in light transmittance can be caused by various factors, the most likely of which are associated with the formation of free radicals. These radicals are further involved in chemical reactions forming cross-links that reduce the mobility of polymer macromolecules, which in turn leads to the formation of microcracks [52], [53]. In order to investigate this aspect in more detail, an in-depth study of the UV irradiated surfaces with a LSM was performed on both PP and WPC specimens shortly after the onset of the rapid changes in light transmittance, i.e., after 120 h. In the LSM images (see Fig. 3.18), it can be observed that microcracks are present on the surface of all the specimens after 120 h of UV exposure. The cracking is more pronounced on the surface of the WPC with Thermo-D wood particles; however, the cracks are significantly narrower and shallower, which can be seen in the topography images (see Fig. 3.18 b)). In order to characterize the cracks by numerical values, the average depth was determined by line profile measurements. For the WPC with Thermo-D wood particles, 2.6 μm deep cracks were found on the surface, which is approximately twice as shallow as for the WPC with UM wood particles (average depth of cracks 6.1 μm). The results obtained suggest that UV radiation will have less influence on the mechanical properties of the WPC with Thermo-D wood particles, since it is known that the combination of the depth and length of the cracks are the main factors directly contributing to the rupture of the material [54]. The reduced crack propagation in deeper layer of the WPC with Thermo-D wood particles could be explained by a more pronounced radiation shielding, which was shown by the results of the light transmittance spectra. In the work, also the mechanical properties were analysed. The tensile test was performed for 2 mm thick WPC and PP films before and after of UV irradiation (120 h and 500 h). The results indicated that UV radiation affects only the surface, since no changes in tensile strength were observed for WPC. In turn, the strength of PP decreased by more than half (by 53 %) after 500 h of UV irradiation.

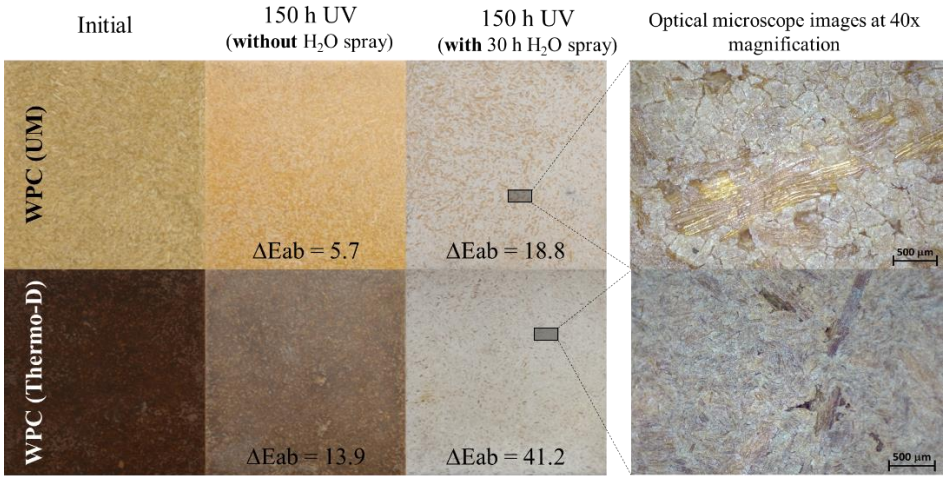


Fig. 3.19. The effect of UV irradiation and UV irradiation + water spray on colour changes and surface properties of WPC.

UV radiation, together with rainwater, are the main contributors to surface erosion for a majority of materials [54]. To find out how these factors affect WPC, weathering tests were conducted that included exposure to UV radiation with and without water spraying. The results

showed (see Fig. 3.19) that for WPC with UM wood particles the colour change caused by UV irradiation increased more than three times in the presence of water spray, which well corresponds to the data published in the literature [55]. A similar increase was observed also for the WPC with TM wood particles. The only difference between both WPCs was in the absolute values, where for the WPC with TM wood particles, the colour change after UV irradiation in the presence of water was twice as large as for the WPC with UM wood particles, reaching 41.2 units. The discoloration similar as in the case of UV irradiation without water spraying is associated with the formation of microcracks in the polymer matrix, which can be seen in the optical microscopy images (see Fig. 3.19). The images also show signs of surface erosion evident by the uncovered wood particles. The extent of the uncovered particles differs between the WPCs, where for WPC with TM wood particles it is lower than for the WPC with UM wood particles, indicating of less pronounced surface erosion. By conducting additional experiments in this direction, the process of surface erosion was also observed by determining the changes in mass. In the experiment, UV degraded WPC films (exposed for 500 h) were exposed for additional 150 h involving UV radiation and water spray cycles. The mass loss after the test was 6.3 $\mu g/cm^2$ for the WPC with UM wood particles and 3.4 $\mu g/cm^2$ for the WPC with TM wood particles. Overall, it can be concluded that the WPCs with TM wood particles are more weather resistant than the WPCs with UM wood particles despite the significant discolouration. The enhanced properties could be explained by the improved interaction between the PP matrix and TM wood particles as well as by increased UV radiation shielding. Nevertheless, the significant colour change is a major drawback, which should be eliminated.

Natural weathering was carried out in the direct solar radiation, the solar radiation behind the window glass and the solar radiation behind the windshield of a car. In each case, the spectral composition significantly differs with a decrease in the proportion of UV radiation in the above sequence. The results showed (see Fig. 3.20 a)) that the solar radiation was capable of significantly changing the colour of the WPC, but it did not cause changes in the light transmittance of the PP film. WPCs with UM wood particles became lighter after a very short exposure period (5 h) and then gradually darkened, achieving visually noticeable discolouration, corresponding to 6 ΔE units. Such discolouration tendency is characteristic of UM wood [56], [57]. On the other hand, WPCs with TM wood particles under the influence of the solar radiation became lighter, which, actually is characteristic for TM wood [58]. Considering that the use of WPCs is expanding indoors, the colour stability was evaluated also in the relevant conditions, which has not been previously done in the context of WPCs. The results showed that the colour change in the case of solar radiation behind the window glass was similar to the discolouration caused by the direct solar radiation. The situation differed in the case of windshield of a car. The windshield is capable of shielding the entire UV portion of the solar radiation, thus the radiation that passes through contains only visible light. Nevertheless, also in this case still a significant colour change was observed for all WPCs (see Fig. 3.20 b)). For the WPCs with UM wood particles, the the colour initally became lighter and comparing to the case of the other types of radiation it was more distingushed, which suggests that longer wavelength has a significant contribution in this process. It has been previously

reported that longer wavelengths induce lightening and shorter wavelengths darkening for UM wood [56]. The situation in the case of WPC with TM wood is similar as it is for solar radiation.

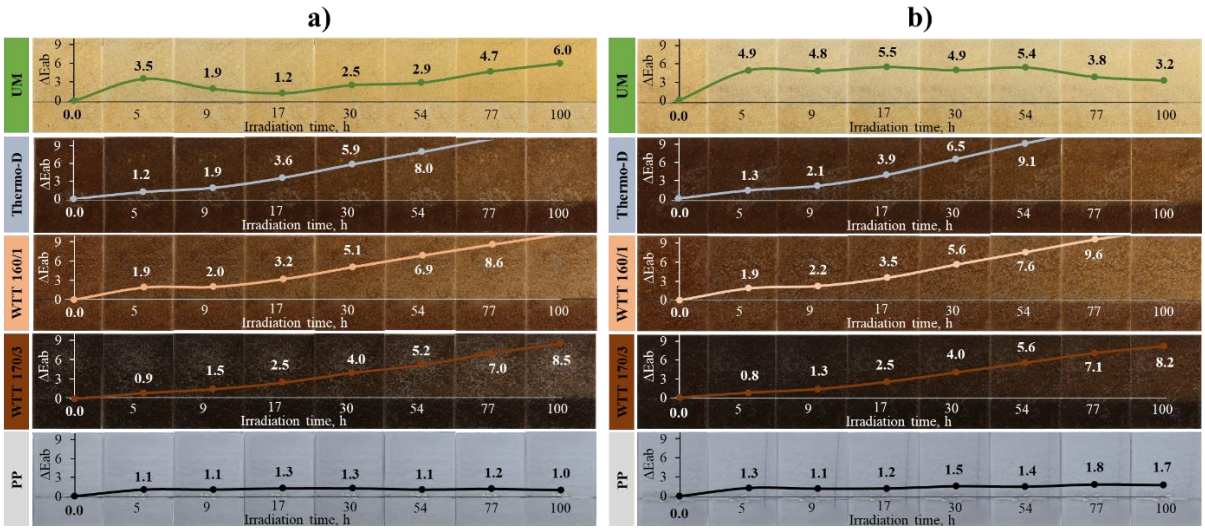


Fig. 3.20. Colour change dynamics for WPCs and PP films under the influence of a) solar radiation and b) solar radiation behind windshield.

Overall, the results indicate that the WPCs with TM wood particles have relatively poor colour stability under the influence of both UV and visible light. Consequently, if a good colour stability has to be ensured, the use of suitable additives is mandatory both indoors and outdoors. UV stabilisers should be used to protect WPCs against the effect of UV irradiation, which reduces the risk of photodegradation of the polymer matrix, while pigments or dyes capable of protecting against visible light should be used to reduce the dicolouration of wood particles.

3.5. Effect of the Material Composition on the Properties of Wood Plastic Composites

In order to explore the possibilities of improving and adapting the WPC properties to a specific purpose, the influence of WPC composition was analysed by investigating the effect of different additives and formulations. One of the factors that can be changed is the **content of wood**, which in the case of TM wood particles has had a minor attention. The obtained results showed that by increasing the content of wood from 40 wt% to 60 wt%, density and flexural modulus of elasticity increased by 38 % and 11 %, respectively, while impact strength and flexural strength, decreased by 39 % and 6 %, respectively. The water resistance, which is recognised as one of the major problems in the long-term use of these materials, significantly decreased with the increase of the wood content. The water absorption results also showed that at different wood contents WPCs with TM wood particles had significantly lower water absorption comparing to the case of WPCs with UM wood particles. Moreover, the differences were so significant that the WPCs with 60 wt% TM wood particles had lower water absorption by 40 % comparing to the WPCs with 50 wt% UM wood particles. Similar tendencies were also observed in relation to dimensional stability.

The role of the **coupling agent** is to improve the adhesion between the nonpolar polymer matrix and the polar wood particles, creating stronger bonds and promoting better particle dispersion. In the work, the effect of maleated polypropylene (MAPP) on the WPC properties was examined by changing its content as well by testing its efficiency depending on the content of wood in the composite.

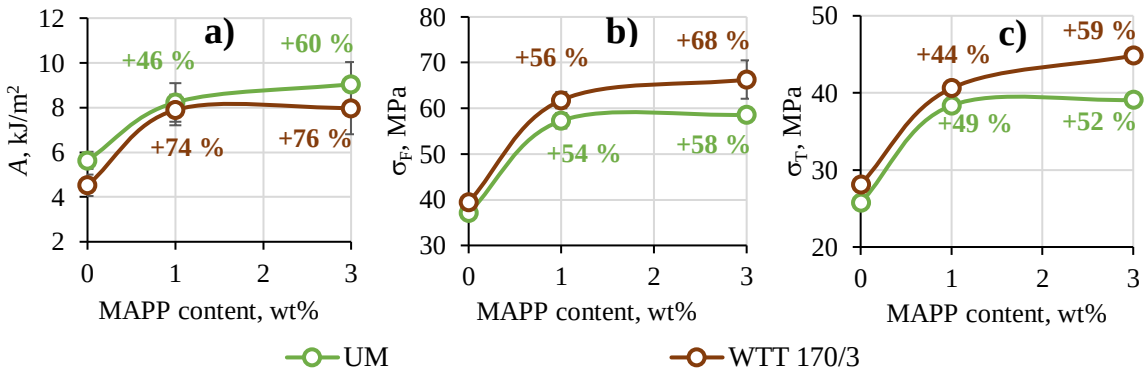


Fig. 3.21. Effect of MAPP on WPC with UM and WTT 170/3 wood particles: a) impact strength (*A*); b) flexural strength (σ_F); and c) tensile strength (σ_T).

The results showed (Fig 3.21) that by adding only 1 wt% MAPP, the impact strength increased by 74 % for WPC with WTT 170/3 wood particles, which is significantly higher than in the case of UM wood particles (46 %). Such an improvement ensures equivalent impact strength in terms of the absolute value for both WPCs, eliminating one of the largest disadvantages of WPC with TM wood particles. Similar improvements were observed in flexural and tensile strength. The flexural modulus of elasticity also increased with the addition of MAPP, but the improvement did not exceed 16 %. SEM images of the fracture sites revealed (Fig. 3.22) that by addition of MAPP the adhesion between the wood particles and the PP matrix has significantly improved. This is evident by the fact that the particles are torn, and not pulled out from the polymer matrix, which can be seen in the locations indicated by Arrows 1 and 2. However, by analysing the whole surface of the WPCs fracture site, individual cases in which particles have been pulled out were also observed. Therefore, it can be concluded that both WPCs with MAPP have a mixed rupture mechanism, which ensure high mechanical properties.

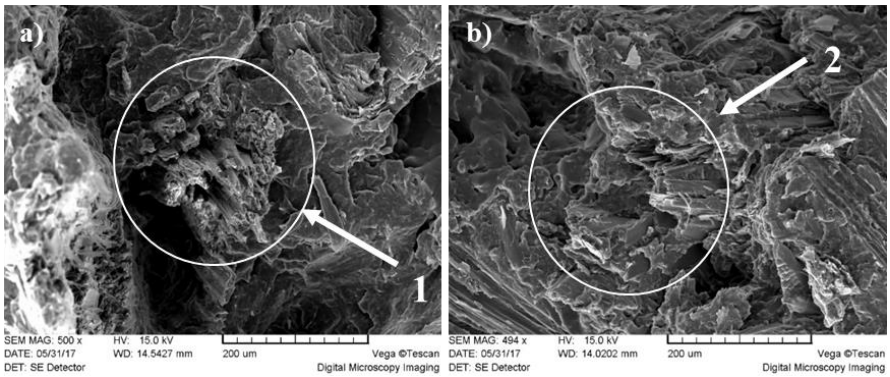


Fig. 3.22. SEM images of fracture sites of impact strength specimens: a) WPC with UM pine particles; b) WPC with WTT 170/3 pine particles.

In the work, the effect of MAPP on the microhardness, density, and water resistance were explored. The results showed that MAPP did not affect microhardness of the WPCs and had a relatively small effect on the density (not exceeding 2 %). The results concerning water resistance showed (see Fig. 3.23) that, by increasing MAPP content, the rate of the water absorption, and the maximum water uptake decreased. This can be explained by the ability of MAPP to form covalent bonds with the OH groups present in the wood. Furthermore, MAPP also positively affects wood particle encapsulation in the polymer matrix [59]. For the WPC with WTT 170/3 wood particles, by adding 1 wt% and 3 wt% of MAPP, the amount of the absorbed water after 200-day immersion decreased by 39 % and 51 %, respectively. In terms of absolute values, the moisture content in the WPCs under these conditions reached only 6 % (with 1 wt% MAPP) and 5 % (with 3 wt% MAPP), while for the WPC with UM particles with an equivalent composition, the moisture content was more than twice as high, namely, 16 % and 14 %, respectively. Similar improvements were observed also for the dimensional stability (see Fig. 3.23 b)). The results indicate that, by using TM wood particles in combination with MAPP, it is possible to obtain WPC with high water resistance, which, accordingly, can also reduce other water-related problems.

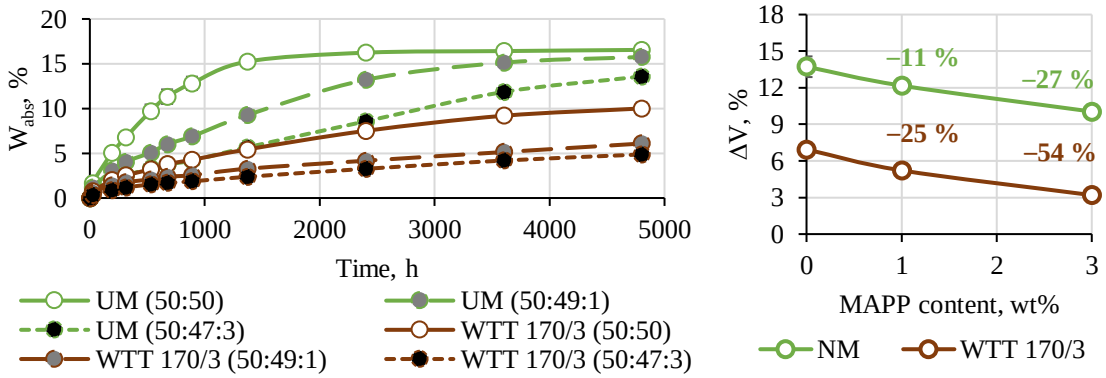


Fig. 3.23. Effect of MAPP on WPC: a) water absorption dynamics; b) volume change (Δ*V*) after 200-day immersion in water.

A 7-cycle soaking/drying test was performed to determine the effect of MAPP on WPC's resistance to periodic wetting and subsequent drying. The mass of the WPCs during the test was regularly weighed. The results showed that MAPP significantly improved the resistance to cyclic soaking/drying conditions of WPC with UM wood particles. Therefore, a significant increase in the absorbed amount after each cycle, which was observed for the WPC without MAPP, is not the case here, but the progressive degradation is not completely eliminated, since the mass still slightly increased with each cycle. For the WPC with WTT 170/3 wood particles the situation differed. In this case the amount of the absorbed water remained constant after each cycle, and the moisture content did not even exceed 1 %. These results suggest that a periodic wetting is not a significant threat to WPCs with WTT 170/3 wood particles, which is highly beneficial for ensuring long-term durability. To evaluate the impact of soaking/drying cycles on the mechanical properties, all of the WPC specimens after the water resistance test were analysed by carrying out bending tests. Changes in the flexural strength and flexural

modulus of elasticity after a 200-day immersion and after 7 soaking/drying cycles are summarized in Fig. 3.24. The results of the bending test showed that the WPCs with MAPP were more durable against water exposure than WPCs without MAPP. Unexpected were the results that showed an increase in some of the bending properties. For the WPC with UM wood particles, an improvement was observed in the flexural strength after the cyclic soaking/drying test, while for the WPC with WTT 170/3 wood particles, an improvement was observed not only in the flexural strength, but also in the flexural modulus of elasticity. Moreover, the increase was also observed after the 200-day immersion. These results additionally substantiate that the WPCs with TM wood particles are water resistant, and during prolonged exposure to water they do not lose their original properties. To elucidate the unexpected improvement in mechanical properties, additional experiment was performed. Consequently, it was found that the increase was caused by drying at elevated temperatures (103 °C), which most likely contributed to the formation of ester bonds by replacing the weaker hydrogen bonds between the carboxyl groups of coupling agent and the OH groups of wood.

The mechanical strength of WPC with 1 wt% MAPP at water saturated conditions was also tested, where it was found that, in the case of TM wood particles, the flexural strength decreased by 19 % and the flexural modulus of elasticity by 24 %. In the case of UM wood particles, the deterioration was 36 % and 45 %, respectively. The WPC resistance to soaking/freezing/drying cycles was also analysed, where it was found that, after 3 cycles, in the case of TM wood particles, the flexural strength deteriorated by 3 % and the flexural modulus of elasticity by 4 %. The reduction in the case of UM wood particles was 8 % and 10 %, respectively.

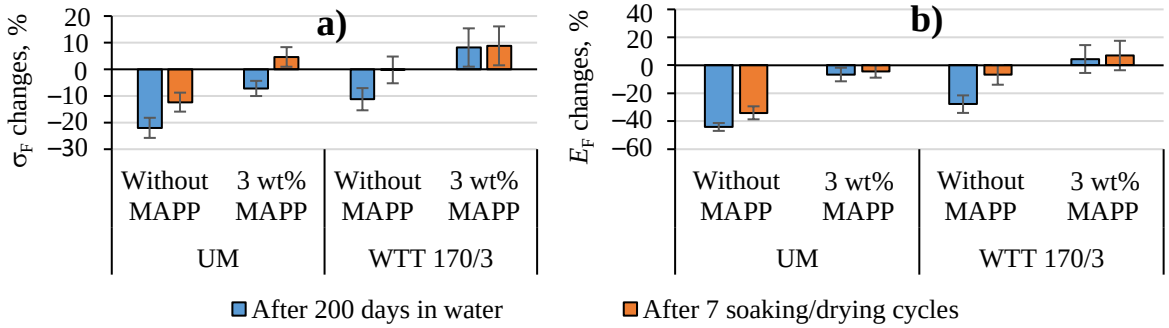


Fig. 3.24. Effect of MAPP on the changes in a) flexural strength (σ_F) and b) flexural modulus of elasticity (E_F) for dry WPC with UM and WTT 170/3 pine wood particles after a 200-day immersion and after 7 soaking/drying cycles.

The main drawback of the WPCs with TM wood particles identified in the work is the low colour stability. As previously it was concluded, photodegradation of the polymer matrix, which leads to the formation of microcracks, is the main factor causing significant colour change during UV irradiation. In the literature, it is established that one of the most effective compounds for ensuring colour stability are pigments that are usually used in WPC production [60]–[64]. However, given that pigments are not able to protect the top layers of the polymer matrix, they cannot ensure colour stability of WPC. To investigate this in more detail, the colour changes of WPC with Thermo-D wood particles were studied by using 3 types of pigments:

carbon black, TiO_2, and Fe_2O_3. The obtained results are summarized in Fig. 3.25. The colour changes in the WPC under the influence of UV radiation showed that pigments ensured significant improvement in the colour stability. However, it was still not sufficient considering that WPC colour faded causing clearly visible discolouration. By comparing the results with the previous ones (see Fig. 3.16), a similar situation can be observed – the rate of colour change is the most rapid after 50 h (point 3 in Fig. 3.25), which coincides with the decrease in the light transmittance of the PP matrix (see Fig. 3.17 a)). This also explains why the pigments did not ensure suitable colour stability. These tests once again allowed to verify that the colour changes under the influence of UV are cause by the degradation of polymer matrix. Therefore, in future studies, greater emphasis should be placed on UV stabilisers, as well as organic dyes, which could be capable of protecting the polymer matrix.

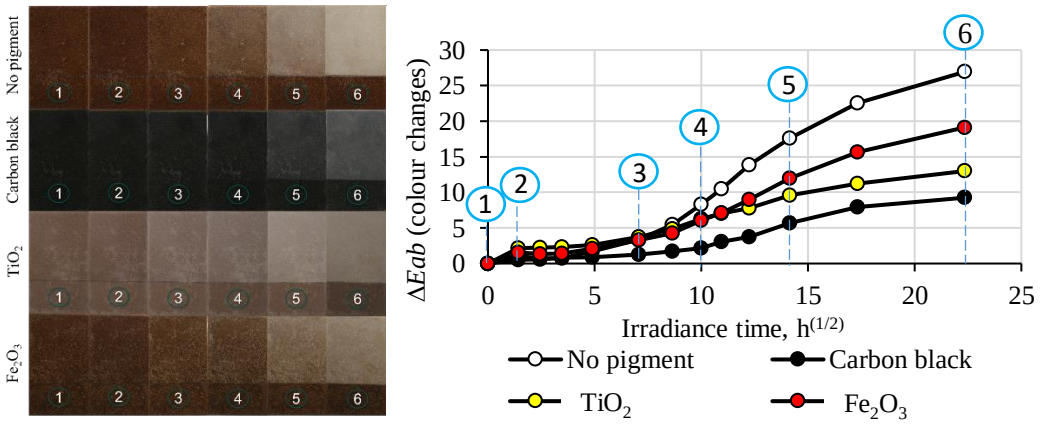


Fig. 3.25. Effect of pigments on the colour changes of WPC with Thermo-D wood particles under the influence of UV radiation (1–0 h; 2–2 h; 3–50 h; 4–100 h; 5–200 h; 6–500 h).

Inorganic additives are mainly incorporated to reduce the cost of the WPC, but they are also able to improve the mechanical properties, reduce the thermal expansion, and improve the dimensional stability [65]–[67]. One of the most widely available and relatively little used inorganic additives is wood ash, the amount of which increases significantly both in Latvia and in Europe [68]. The obtained results showed that wood ash increased the density of the WPC with TM wood particles and had relatively little effect on the mechanical properties. The density increased by 0.5 % for each 1 wt% of wood ash added. In terms of mechanical properties, the addition of wood ash up to 10 wt% (2 wt%, 6 wt%, and 10 wt%) had no statistically significant effect ($p > 0.05$) on the WPC flexural modulus of elasticity as well as impact strength, with the exception of wood ash content 2 wt% showing a statistically significant 10 % reduction of impact strength. Regarding the flexural strength, slight decrease was observed, but it did not even exceed 4 %. In general, the addition of wood ash does not exert too much influence on the impact strength and bending properties. Therefore, wood ash has a potential to be used in WPC production to reduce the cost, while at the same time, not significantly impairing the mechanical properties.

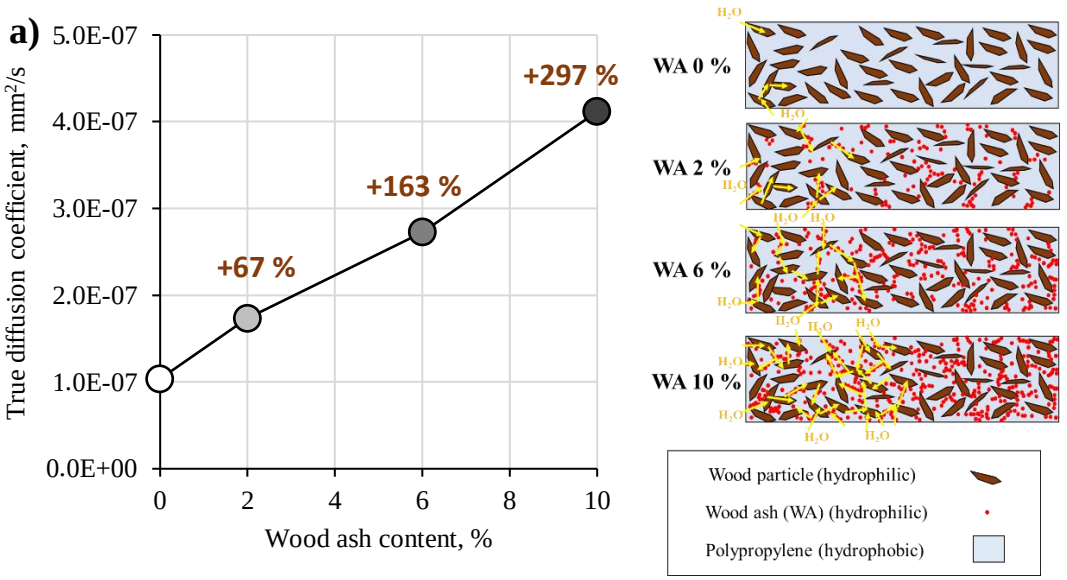


Fig. 3.26. Effect of wood ash on WPC with Thermo-D wood particles a) isotropic diffusion coefficient and b) water absorption presented as a schematic explanation of the increase.

The effect of wood ash on the WPC water resistance was studied. The results showed that by increasing the wood ash content, the rate of water absorption as well as the maximum water uptake increased. It is important to point out that by adding only 1 wt% of wood ash, the isotropic diffusion coefficient increased by an average of 30 % (see Fig. 3.26 a)). As a result, the dimensional stability of the WPC decreased as well. The obtained results indicate that wood ash can significantly facilitate the penetration of water into the WPC. This could be due to the increased contact between the hydrophilic components (wood particles and wood ash). The probability of hydrophilic agglomerate formation in the WPC is relatively high, which can create connected pathways that facilitate the water transport. A schematic representation of the potential mechanism, which causes changes in the WPC water absorption due to wood ash, is demonstrated in Fig. 3.26 b). The increase in the maximum water uptake, which was also caused by the addition of wood ash, could be explained by the hydrophilicity of the wood ash itself as well as by the development of new pathways that allow access to wood particles, which otherwise would be fully encapsulated. The results also suggest that, most likely, the wood ash is not the only hydrophilic particles that can significantly impair the moisture resistance of WPC. A similar situation could also be in the case of pigments, flame retardants, and other inorganic additives. In the future studies this aspect should be analysed in more detail, so that, if necessary, the composition of the additives could be optimised, which would not lead to the deterioration of the water resistance. In general, adding wood ash to WPCs with TM wood particles is not recommended, since their water resistance, which is the biggest advantage of these composites, is significantly impaired.

CONCLUSIONS

The most important characteristics of wood particles were studied for thermally modified (TM) wood residues depending on the thermal modification method, modification intensity, wood species, and residue type. The obtained properties of TM wood particles were compared with unmodified (UM) wood particles to evaluate the suitability for production of wood plastic composite (WPC). In the next step, WPCs were produced and physical, mechanical, and service properties were analysed depending on the abovementioned factors, as well as on the wood particle size, thus determining general trends and the most suitable wood particles for moisture resistant WPC production. To further improve WPC properties and to eliminate the identified shortcomings, investigations were carried out by changing the WPC composition. To identify and explain the different mechanisms behind the experimental outcomes, in-depth studies were performed. The following conclusions are drawn from the results of the performed experiments:

1. The use of TM wood particles instead of UM wood particles improves WPC melt flow index (more than 10 times), flexural modulus (up to 38 %) and strength (up to 22 %), microhardness (up to 28 %), dimensional stability (up to 3 times), water resitance (up to 3 times), biodurability (more than 4 times), and resistance to surface erosion (up to 2 times), but impact strength (up to 30 %) and colour stability (up to 3 times) decreases.
2. The WPC properties are significantly influenced by the thermal modification intensity and wood species of TM wood, however the method of thermal modification, particle size and residue type have little importance (effect on individual properties <15 %).
3. The addition of coupling agent up to 3 wt.% improves impact strength (up to 81 %), flexural strength (up to 68 %), flexural modulus (up to 14 %), tensile strength (up to 59 %), decreases water absorption (up to 2 times) and volume change (up to 2 times), allowing to obtain a WPC with significantly enhanced resistance to prolonged exposure to water, periodic soaking/drying cycles and periodic soaking/freezing/drying cycles, which is superior to the WPC of similar composition made with UM wood particles. The addition of pigments slightly improves the color stability of WPC (visible colour change ΔEab > 3 units), however the addition of wood ash did not justify the expectations.
4. The colour fading of WPC under the influence of UV irradiation can be explained by the decrease in visible light transmittance of the PP matrix because of the formation of microcracks, and not by the photodegradation of wood, as explained in the literature.

According to the obtained results, the theses to defend were confirmed with some exceptions:

- Not all factors influencing WPC in relation to the variations in TM wood residues were important because the thermal modification method, wood particle size, and residue type had little effect.
- Not all properties were enhanced for WPC with TM wood particles because impact strength as well as colour stability decreased.

- Not all additives improved the WPC properties because the expected improvements of wood ash were not observed. Moreover, their presence significantly reduced the water resistance of WPC.

REFERENCES

1. Carus, M., Eder, A., Dammer, L., et al. (2015) WPC/NFC Market Study 2014-10 (Update 2015-06): Wood-Plastic Composites (WPC) and Natural Fibre Composites (NFC): European and Global Markets 2012 and Future Trends in Automotive and Construction. Market study by Nova Institute GmbH, Hürth, DE.
2. The European Parliament and the Council of the European Union (2000) Directive 2000/53/EC on end-of life vehicles (OJ L 269, 21.10.2000, 34 p).
3. International ThermoWood Association (2020) ThermoWood® production statistics 2020.
4. European Commission, (2021) Wood and other products. https://ec.europa.eu/growth/sectors/raw-materials/industries/forest-based/sustainable-forest-management/wood-other-products_en. Accessed 4 December 2021.
5. European Commission, (2019) Stepping up EU Action to Protect and Restore the World's Forests. COM (2019) 352.
6. J ustin Catanoso, (2019) EU sued to stop burning trees for energy; it's not carbon neutral: plaintiffs. https://news.mongabay.com/2019/03/eu-sued-to-stop-burning-trees-for-energy-its-not-carbon-neutral-plaintiffs/. Accessed 4 December 2021.
7. Food and Agriculture Organization of the United Nations (1990) The potential use of wood residues for energy generation. In: Energy conservation in the mechanical forest industries, Food and Agriculture Organization of the United Nations, Rome.
8. Rowell, R. M. (2005) Handbook of wood chemistry and wood composites. CRC Press, Boca Ration.
9. Jones, D., Sandberg, D. (2020) A Review of Wood Modification Globally – Updated Findings from COST FP1407. Reviews 1: 1–31.
10. S andberg, D., Haller, P., Navi, P. (2013) Thermo-hydro and thermo-hydro-mechanical wood processing: An opportunity for future environmentally friendly wood products. Wood Mater Sci Eng 8: 64–88.
11. Energy Saving Group, (2009), Feasibility study on wood utilization in Serbia. United States Agency for International Development, Belgrade.
12. Arutchelvi, J., Sudhakar, M., Arkatkar, A., et al. (2008) Biodegradation of polyethylene and polypropylene. Indian J Biotechnol 7:9-22
13. Zemkopības ministrija, (2021) Ilgtspējīga aprites bioekonomika. https://www.zm.gov.lv/lauksaimnieciba/statiskas-lapas/bioekonomika/ilgtspejiga-aprites-bioekonomika?nid=2998#jump. Accessed 4 December 2021.
14. Segerholm, K. (2012) Characteristics of wood plastic composites based on modified wood: Moisture properties, biological performance and micromorphology. Dissertation, KTH Royal Institute of Technology, Stockholm.
15. El-Haggar, S. M., Kamel, M. A. (2011) Wood Plastic Composites. In: Tesinova P (ed.) Advances in composite materials – Analysis of natural and man-made materials. InTech, Cairo, pp. 325–344.

16. Nasser, R. A., Aref, I., M. (2014) The performance and properties of wood–polypropylene panels as affected by wood aqueous extraction. Forest Prod. J. 64(5–6): 192–198.
17. Klysov, A., A. (2007) Wood-plastic composites. John Wiley & Sons Inc., New Jersey.
18. Chowdhury, M. J. A., Wolcott MP (2007) Compatibilizer selection to improve mechanical and moisture properties of extruded wood-HDPE composites. For. Prod. J. 57(9): 46–53.
19. Yuan, Q., Wu, D., Gotama, J., Bateman, S. (2008) Wood fiber reinforced polyethylene and polypropylene composites with high modulus and impact strength. J. Thermoplast. Compos. Mater. 21: 195–208.
20. Esteves, B. M., Pereira, H. M. (2009) Wood modification by heat treatment: A review. BioResources 4: 370–404.
21. Hill CAS, (2006) Wood Modification: chemical, thermal and other processes. John Wiley & Sons, Ltd., Chichester.
22. Ashori, A., Nourbakhsh, A. (2010) Reinforced polypropylene composites: Effects of chemical compositions and particle size. Bioresour. Technol. 101: 2515–2519.
23. Esteves, B., Graça, J., Pereira, H. (2008) Extractive composition and summative chemical analysis of thermally treated eucalypt wood. Holzforschung 62: 344–351.
24. Esteves, B., Videira, R., Pereira, H. (2011) Chemistry and ecotoxicity of heat-treated pine wood extractives. Wood Sci. Technol. 45: 661–676.
25. Yildiz, S., Gümüşkaya, E. (2007) The effects of thermal modification on crystalline structure of cellulose in soft and hardwood. Build. Environ. 42: 62–67.
26. Boonstra, M. J., Tjeerdsma, B. (2006) Chemical analysis of heat treated softwoods. Holz als Roh – und Werkst, 64: 204–211.
27. Poletto, M. (2017) Assessment of the thermal behavior of lignins from softwood and hardwood species. Maderas Cienc y Tecnol. 19: 63–74.
28. Gozdecki, C., Wilczyński, A. (2015) Effects of wood particle size and test specimen size on mechanical and water resistance properties of injected wood-high density polyethylene composite. Wood Fiber Sci. 47: 365–374.
29. Gozdecki, C., Wilczynski, A., Kociszewski, M., et al. (2012) Mechancial properties of wood-polypropylene composites with industrial wood particles of different sizes. Wood Fiber Sci. 44: 14–21.
30. Chaudemanche, S., Perrot, A., Pimbert, S., et al. (2018) Properties of an industrial extruded HDPE-WPC: The effect of the size distribution of wood flour particles. Constr. Build. Mater. 162: 543–552.
31. Gallagher, L. W., McDonald, A. G. (2013) The effect of micron sized wood fibers in wood plastic composites. Maderas Cienc y Tecnol. 15: 357–374.
32. Stark, N. M., Rowlands, R. E. (2003) Effects of wood fiber characteristics on mechanical properties of wood/polypropylene composites. Wood Fiber Sci. 35: 167–174.

33. Füchtner, S., Brock-Nannestad, T., Smeds, A. et al. (2020) Hydrophobic and hydrophilic extractives in Norway spruce and kurile larch and their role in brown-rot degradation. Front. Plant. Sci. 11: 855.
34. Kajaks, J., Kalnins, K., Uzulis, S., Matvejs, J. (2014) Physical and mechanical properties of composites based on polypropylene and timber industry waste. Cent.Eur. J. Eng. 4: 385–390.
35. Nunes, S. G., Da Silva, L. V., Amico, S. C., et al. (2017) Study of composites produced with recovered polypropylene and piassava fiber. Mater. Res. 20: 144–150
36. Zimmerman, M. V. G., Turella, T. C., Santana, R. M., Zattera, A. J. (2014) The influence of wood flour particle size and content on the rheological, physical, mechanical and morphological properties of EVA/wood cellular composites. Materials and Design 57: 660–666.
37. Harper, D. P. A. (2003) Thermodynamic, Spectroscopic, and Mechanical Characterization of the Wood-Polypropylene Interphase. Dissertation, Washington State University.
38. Khonsari, A., Taghiyari, H. R., Karimi, A., Tajvidi, M. (2015) Study on the effects of wood flour geometry on physical and mechanical properties of wood-plastic composites. Maderas Cienc y Tecnol. 17: 545–558.
39. Wang, W., Morrell, J. J. (2004) Water sorption characteristics of two wood-plastic composites. For Prod. J. 54: 209–212.
40. Fabiyi, J. S., McDonald, A. G., Wolcott, M. P., Griffiths, P. R. (2008) Wood plastic composites weathering: Visual appearance and chemical changes. Polym. Degrad. Stab. 93: 1405–1414.
41. Lee, C. H., Hung, K. C., Chen, Y. L. et al. (2012) Effects of polymeric matrix on accelerated UV weathering properties of wood-plastic composites. Holzforschung, 66: 981–987.
42. Kallakas, H., Ayansola, G. S., Tumanov, T., et al. (2019) Influence of birch false heartwood on the physical and mechanical properties of wood-plastic composites. BioResources, 14: 3554–3566.
43. Aydemir, D., Alsan, M., Can, A., et al. (2019) Accelerated weathering and decay resistance of heat-treated wood reinforced polypropylene composites. Drv. Ind. 70: 279–285.
44. Stark, N. M. (2003) Photodegradation and photostabilization of weathered wood flour filled polyethylene composites. Dissertation, Michigan Technological University.
45. Peng, Y., Liu, R., Cao, J., Chen, Y. (2014) Effects of UV weathering on surface properties of polypropylene composites reinforced with wood flour, lignin, and cellulose. Appl. Surf. Sci. 317: 385–392.
46. Badji, C., Soccalingame, L., Garay, H., et al. (2017) Influence of weathering on visual and surface aspect of wood plastic composites: Correlation approach with mechanical properties and microstructure. Polym. Degrad. Stab. 137: 162–172.
47. Cirule, D., Meija-Feldmane, A., Kuka, E., et al. (2016) Spectral sensitivity of thermally modified and unmodified wood. BioResources 11(1): 324–335.

48. Deka, M., Humar, M., Rep, G., et al. (2008) Effect of UV light irradiation on colour stability of thermally modified, copper ethanolamine treated and non-modified: EPR and DRIFT spectroscopic studies. Wood Sci. Technol. 42: 5–20.
49. El Bakali, I., Yagi, S., Hamzah, M., et al. (2014) Influence of thermal treatment and impregnation on the durability of wood colour. J. Forest Prod. Ind. 3(1): 42–9.
50. Xing, D., Wang, S., Li, J. (2015) Effect of artificial weathering on the properties of industrial scale thermally modified wood. BioResources 10(4): 8238–8252.
51. Hon, D. N. S., Minemura, N. (2001) Colour and discolouration. In: Hon DNS, Shiraishi N (eds.) Wood and cellulosic chemistry. Marcel Dekker, New York, pp. 385–442.
52. Awaja, F., Zhang, S., Tripathi, M., et al. (2016) Cracks, microcracks and fracture in polymer structures: Formation, detection, autonomic repair. Prog. Mater. Sci. 83: 536–573.
53. Rabello, M. S., White, J. R. (1997) Crystallization and melting behaviour of photodegraded polypropylene – I. Chemi-crystallization. Polymer (Guildf), 38: 6379–6387.
54. Wypych, G. (2013) Handbook of material weathering. ChemTec Publishing, Toronto
55. Stark, N. M. (2006) Effect of weathering cycle and manufacturing method on performance of wood flour and high-density polyethylene composites. J. Appl. Polym. Sci. 100: 3131–3140.
56. Kataoka, Y., Kiguchi, M., Williams, R. S., Evans, P. D. (2007) Violet light caused photodegradation of wood beyond the zone affected by ultraviolet radiation. Holzforschung, 61: 23–27.
57. Tolvaj, L., Mitsui, K. (2005) Light source dependence of the photodegradation of wood. J. Wood Sci. 51: 468–473.
58. Cirule, D., Kuka, E., Antons, A. (2015) Disparity in discolouration of thermally modified wood exposed to solar and artificial ultraviolet irradiation. Rural Sustain. Res. 34: 12–20.
59. Rosa, S. M. L., Santos, E. F., Ferreira, C. A., Nachtigalt, S. M. B. (2009) Studies on the properties of rice-husk-filled-PP composites – Effect of maleated PP. Mater. Res. 12: 333–338.
60. Kajaks, J., Kalnins, K., Matvejs, J. (2019) Accelerated aging of WPCs based on polypropylene and plywood production residues. Open Eng. 9: 115–128.
61. Wang, W., Zhang, Z., Wang, Q., Cui, Y. (2011) Application of organic and inorganic dye to wood plastic composite. Adv. Mater. Res. 183–185: 2293–2297.
62. Stark, N. M., Matuana, L. M. (2003) Ultraviolet weathering of photostabilized wood-flour-filled high-density-polyethylene composites. J. Appl. Polym. Sci. 90(10): 2609–2617.
63. Stark, N. M., Matuana, L. M. (2006) Influence of photostabilizers on wood flour-HDPE composites exposed to xenon-arc radiation with and without water spray. Polym. Degrad. Stab. 91: 3048–3056.
64. Wang, X., Song, K., Ou, R. (2017) Effects of carbon black and titanium dioxide on ultraviolet weathering of wood flour-HDPE/lumber. BioResources, 12: 6173–6186.

65. Martikka, O. (2013) Impact of mineral fillers on the properties of extruded wood-polypropylene composites. Dissertation, Lappeenranta University of Technology, Lappeenranta.
66. Huang, R., Kim, B. J., Lee, S., et al. (2013) Co-extruded wood-plastic composites with talc-filled shells: Morphology, mechanical, and thermal expansion performance. BioResources, 8: 2283–2299.
67. Huuhilo, T., Martikka, O., Butylina, S., Kärki, T. (2010) Mineral fillers for wood-plastic composites. Wood Mater. Sci. Eng. 5: 34–40.
68. Stevens, J. (2007) Material properties of wood ash-filled and wollastonite-filled polyproplyene wood plastic composites (WPCS). Dissertation, The University of Maine.

Edgars Kuka was born in 1992 in Riga. He received his BSc in Chemistry and MSc in Materials Science from Riga Technical University in 2015 and 2017, respectively. He has been working in Latvian State Institute of Wood Chemistry (LSIWC) since 2013. He is currently a researcher with LSIWC in the Laboratory of Wood Biodegradation and Protection. His main research interests include wood modification, composite materials and material environmental performance evaluation.