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The Influence of Birch (*Betula pendula*) False Heartwood on the Mechanical Properties of Wood-Plastic Composites

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Heikko Kallakas

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Kase (*Betula pendula*) väärlülipuidu mõju puitplastkomposiitide mehaanilistele omadustele

HEIKKO KALLAKAS

TALTECH
KIRJASTUS

Contents

List of Publications

The list of author’s publications, on the basis of which the thesis has been prepared:

I Kallakas, H.; Poltimäe, T.; Süld, T.-M.; Kers, J.; Krumme, A. (2015). The influence of accelerated weathering on the mechanical and physical properties of wood-plastic composites. Proceedings of the Estonian Academy of Sciences, 64, 94−104.

II Kallakas, H.; Shamim, M.A.; Olutubo, T.; Poltimäe, T.; Süld, T.M.; Krumme, A.; Kers, J. (2015). Effect of chemical modification of wood flour on the mechanical properties of wood-plastic composites. Agronomy Research, 13 (3), 639−653.

III Kallakas, Heikko; Ayansola, Solomon, Gbenga; Tumanov, Tanel; Goljandin, Dmitri; Poltimäe, Triinu; Krumme, Andres, Kers, Jaan. (2019). Influence of Birch False Heartwood on the Physical and Mechanical Properties of Wood-plastic Composites. BioResources, 14 (2), 3554−3566.

Author’s Contribution to the Publications

Contribution to the papers in this thesis are:

I The author prepared the composite samples, carried out the mechanical tests, analysed the results and wrote the paper.

II The author participated in the composite samples preparation and chemical modification of wood flour. The author carried out the flexural tests, data analysis and writing the paper.

III The author participated in the composite samples preparation and chemical modification of wood particles. The author carried out the flexural test, tensile test, FTIR analysis, analysing the experimental results and writing the paper.

Introduction

Forest is one of the most important natural resources in Estonia where over the half (51.4%) of the country's landscape is covered with forests. Birch (*Betula pendula* and *Betula pubescens*) is the third most common tree species in the Estonia that covers 30.1% of the total area of stands (*Quarterly Bulletin of Statistics Estonia*, 2018). Estonia has several veneer and plywood manufacturing companies that use the birch wood as raw material. Birch wood is also utilized in the furniture and glued laminated timber industries. However, birch often develops a brownish-reddish discoloration in its sapwood which is referred to as red heartwood or false heartwood. In the woodworking, the utilization of this birch false heartwood has been problematic, because this discoloration is a wood defect that leads to the price reduction of the material. For example, in plywood industry, false heartwood does not produce quality veneer and plywood due to the lower properties (e.g. higher moisture content, lower bonding quality, more fragile) than normal birch sapwood. In addition, the visual appearance of false heartwood and mechanical properties of plywood containing false heartwood are not suitable for everyone. Thus, false heartwood either is used in the middle layers of lower quality plywood or burned in factory as source of energy. Therefore, there is the need to investigate more ways to use birch false heartwood by giving it more value and maximizing the outcome of quality birch wood.

One option could be utilizing the birch false heartwood as wood filler material in the wood plastic composites (WPC). WPCs are materials that are manufactured typically from thermoplastic polymers as matrix material and wood in form of particles, fibres or flour as filler material. The procedure for the manufacturing of WPCs is relatively simple and typical plastic industry processes can be used. Generally, wood filler is blended with thermoplastic polymer in a compounder. Then the mixture can be pelletized and used for later processing for example in injection moulding, compression moulding, or extrusion. This commonly results into a material which has enhanced mechanical properties and durability as well as keeping visual appearance for a long time without any maintenance. These composites can be used as interior and exterior building materials and applications. Various researches have been carried out on investigating the wood filler sizes, loading levels and wood species used in WPCs and material properties (Bledzki and Faruk, 2004), (Taib *et al.*, 2006), (Gwon *et al.*, 2010), (Gallagher and McDonald, 2013), (Fabiyi and McDonald, 2014), (Peng *et al.*, 2014), (Mijiyawa *et al.*, 2015)

There have been some studies about false heartwood properties and adding it more value by providing some means for using it wood material applications (Hörnfeldt, Drouin and Woxblom, 2010), (Johansson and Hjelm, 2013), (Baettig *et al.*, 2017). However, there are no studies published on the birch false heartwood usage as filler material in wood-plastic composites. Therefore, this research seeks to fill this gap and investigate the utilization of birch false heartwood as filler material in WPCs. The aim of this research was to investigate the use of birch false heartwood on the mechanical properties of the WPCs.

For this purpose, different wood filler fraction sizes were investigated in the WPCs. Different wood filler modification methods were evaluated on the birch wood to enhance the compatibility between the wood filler and polypropylene (PP) matrix. Birch false heartwood filler based WPCs were compared with pure birch sapwood WPCs to evaluate the material properties. Different mechanical tests were carried out to characterise the obtained WPCs performance under loading. This research would bring new knowledge of using the wood industry low quality by-product, birch false heartwood, in the production of WPCs and thereby increasing the value of birch false heartwood and maximizing the outcome of quality birch wood.

In addition to the publications, which this thesis has been prepared, this research has also been presented in two related articles to this thesis:

- Kängsepp, K.; Poltimäe, T.; Liimand, K.; Kallakas, H.; Süld, T.-M.; Repeshova, I.; Goljandin, D.; Kers, J. (2014). The effect of wood flour fraction size on the properties of wood-plastic composites. *Proceedings of the 9th International Conference of DAAAM Baltic Industrial Engineering : 24-26st April 2014, Tallinn, Estonia: 9th international conference of DAAAM Baltic industrial engineering; April 24 -26, 2014; Tallinn, Estonia.* Ed. T. Otto. Tallinn: TTÜ kirjastus, 366−371.
- Kallakas, H.; Martin, M.; Goljandin, D.; Poltimäe, T.; Krumme, A.; Kers, J. (2016). Mechanical and physical properties of thermally modified wood flour reinforced polypropylene composites. Agronomy Research, 14 (S1), 994−1003.

The results of this research have also been presented in several scientific conferences:

- Kallakas, H.; Poltimäe, T.; Süld, T.-M.; Kers, J. (2014). Durability of wood plastic composites: influence of weathering on the mechanical properties. *Proceedings of The Northern European Network for Wood Science and Engineering: The Northern European Network for Wood Science and Engineering, Edinburgh, Scotland, 13-14 October 2014.* 229.
- Kallakas, H.; Martin, M.; Goljandin, D.; Poltimäe, T.; Krumme, A.; Kers, J. (2016). Mechanical and physical properties of thermally modified wood flour reinforced polypropylene composites. 6th International Conference on Biosystems Engineering 2015 : Book of Abstracts : Tartu, Estonia 7-8 May 2015, 94.
- Kallakas, H.; Shamim, A. M.; Poltimäe, T.; Süld, M. T.; Krumme, A.; Kers, J. (2015). Mechanical and Physical Properties of Silane Crosslinked Wood Flour Reinforced Composites. *Proceedings of the 11th Meeting of the Northern European Network for Wood Sciences and Engineering: The Northern European Network for Wood Science and Engineering, Poznan, Poland, 14-15 September 2015.* Piotr Gomułka, 278.
- Kallakas, H.; Martin, M.; Ayansola, G.; Poltimäe, T.; Krumme, A.; Kers, J. (2017). Effect of Birch False Heartwood on the Physical and Mechanical Properties of Wood-plastic Composites. *Proceedings of the 13th annual meeting of the Northern European Network for Wood Science and Engineering: Northern European Network for Wood Science and Engineering, Copenhagen, Denmark, 28-29 September 2017.* University of Copenhagen, 127−132.
- Kallakas, H.; Ayansola, G.; Goljandin, D; Poltimäe, T.; Krumme, A.; Kers, J. (2017). Wood plastic composites made of false heartwood residues. International Panel Products Symposium 2017. Llandudno, Wales, UK, 4-5 October 2017.
- Kallakas, H.; Martin, M.; Poltimäe, T.; Krumme, A.; Kers, J. (2018). Effect of birch false heartwood flour on the properties of wood-plastic composites. Guelph, Canada, 24-27 July 2018.

Abbreviations

AA	Acetic anhydride
APTES	(3-Aminopropyl)triethoxysilane
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
FHW	Birch false heartwood
FTIR	Fourier-transform infrared spectroscopy
LLDPE-g-MAH	maleic-anhydride-grafted linear low-density polyethylene
MFHW	Modified birch false heartwood
MOE	Modulus of Elasticity
MSW	Modified birch sapwood
PP	Polypropylene
PVA	Polyvinyl alcohol
SW	Birch sapwood
TEVS	Triethoxyvinylsilane
T_m	Melting temperature
UV	Ultra violet
VA	Vinyl acetate
WF	Wood flour
WPC	Wood-plastic composites
wt%	Weight percent

1 Literature review

1.1 Properties of birch wood

Birch is the hardwood of the species *Betula*. Different types of the Birches grow in a wide range of geographic area (Lundqvist, Grahn and Olsson, 2013). In Northern Europe, the most common Birch species are Silver birch (*Betula pendula*) and Downy birch (*Betula pubescens*) (Michalec and Strnad, 2008). In Estonia, Birch is the third most common wood species representing 25.6% of Estonian forests with 181 m^3/ha (Raudsaar *et al.*, 2018). Birch typically grows up to 30 m high and 100 – 150 years old (*kask - Eesti Entsüklopeedia*, 2019). Birch is a diffuse porous hardwood, which has nice yellowish white glossy texture, it is relatively tough, hard and elastic, and resistant to impact forces. The properties of Silver birch (*Betula pendula*) are presented in Table 1. Birch is sapwood species and do not produce the heartwood. The growth rings are unclear or barely noticeable. However, birch has a low weather resistance and is susceptible to fungi and insects. According to Rendle (1969), birch wood is easy to bend when it is straight grained. It is easy to be used in common wood industry operations (saw, veneering, carving, plane, screw, and nail). Birch is susceptible for impregnation and therefore it is easy to paint, varnish and glue it. (Heräjärvi, 2005) According to research by Strnad and Johansson (2008) birch is comparatively cheap compared to other hardwood species and it is useful to use it as general inexpensive wood material in general common wood products. Birch wood main usage is for veneer and plywood products, furniture, glued laminated timber, parquet, bended details, toothpicks, tool handles, packaging, door and window frames. It is also used as a raw material for the pulp and paper industry.

The main factor that determines the quality of birch wood is the uniform colour and how much stem has heartwood staining which is called as false heartwood. Other important factors that affect birch wood quality are presence of knots and cracks, defects in stem shape, wood structure defects, fungal damage and mechanical damage. Based on these properties the quality requirements are defined for the birch wood where the highest quality is free of any false heartwood and has the highest price. Highest grades are used in furniture and decorative panels. Lower quality birch exhibit the substantial amount of false heartwood and is used in lower quality and price products or inner layers of the lower quality plywood (Reimann *et al.*, 2008), (*Birch veneer*, 2019).

Table 1. Properties of Silver Birch (Betula pendula). (Saarman and Veibri, 2006), (Silver Birch | The Wood Database - Lumber Identification (Hardwood), 2019)

Properties	Silver Birch (*Betula pendula*)
Tree Sizes, m	20-30
Shrinkage, %	14.2
Average Dried Weight, kg/m^3	630-670
Janka Hardness, N	5360
Flexural Strength, MPa	107-123
Elastic Modulus, MPa	13000-15000
Tensile Strength along the grain, MPa	137
Compressive Strength along the grain, MPa	54-60

1.1.1 False heartwood formation

Naturally, some wood species (e.g. Scotch Pine, Douglas Fir, Spanish Cedar, Oak) have harder and darker colour wood at the centre of a trunk or stem than the wood nearer the bark which is known as heartwood. The surrounding layers of the heartwood are called sapwood. Normal heartwood is physiologically inactive, and its cells are dead, it is difficult to dry and more difficult to penetrate with preservatives than sapwood. (Rowell, 2005) Formation of the heartwood is normal process with the growth of the trunk or branch that occurs with the aging of the tree and it continues to grow along the width and height of the tree (Pallardy, 2008). It is said, that the heartwood is formed when the general moisture content of wood is decreased, and the phenolic compounds are stored in the wood cells (Rowell, 2005).

However, some hardwood species which naturally do not possess heartwood (e.g. poplar, beech, ash and birch), have a discoloration from the pith to the cambium (see Figure 1). This discoloration has been described with different terms such as core wood, wounded wood, black heart, wet wood, false heartwood, red heartwood, discoloured wood, pathological heartwood etc. (Shigo and Hillis, 1973), (Basham, 1991), (Hörnfeldt, Drouin and Woxblom, 2010) There is no agreement on the official terminology to be used in order to describe this discoloration of wood. In scientific papers, it is commonly referred to as false heartwood while the industry calls this phenomenon as red heartwood.

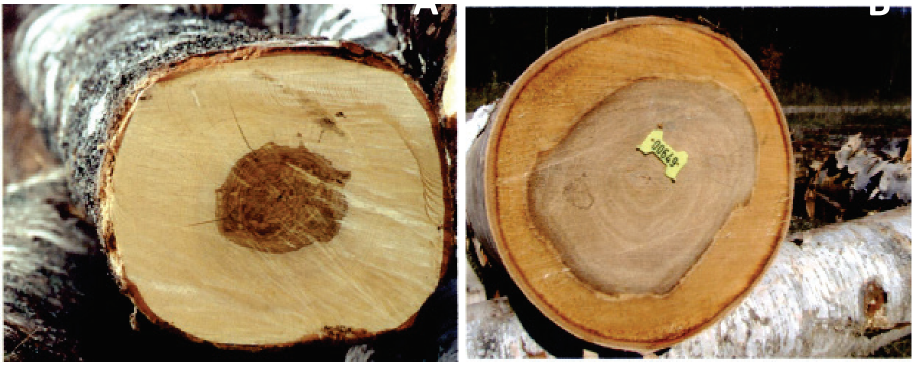


Figure 1. Birch false heartwood in silver birch (a) and paper birch (b) (Hörnfeldt, Drouin and Woxblom, 2010).

The formation of the false heartwood is generally the four-stage process. At stage one, the main triggering factor for the development of the false heartwood is the mechanical wounding such as the injuries to branches or bark, broken or decayed branches, stem wounds or development of cracks due to the very low temperatures (Shigo and Hillis, 1973). After mechanical wounding, stage two corresponds to the different stresses in the wood and drying of the tissues and cells, which are then penetrated by the oxygen. The brownish-reddish colouration may appear which is found to be the result of the polymerization and oxidation of the phenolic substances due to the air penetration in the tree (Petercord, 2006), (Hörnfeldt, Drouin and Woxblom, 2010). At the stage three, after the oxygen is penetrated into the wood through the broken branches, the fungus and bacteria starts to develop. Fungus causes the aging of the parenchyma cells and formation of the tyloses, which in turn forms the barrier with healthy wood and prevents further oxygen penetration. This damaged area of the wood has higher mineral content, higher moisture content, and higher pH. When there is no more oxygen, the fungus dies, and result is only discoloration (see Figure 2), but if the oxygen supply is high enough it may result in development of a rot and degraded wood structure which is the fourth and final stage. (Runkel, 1940), (Panshin, 1964), (Shigo and Hillis, 1973), (Hörnfeldt, Drouin and Woxblom, 2010)

Figure 2. False heartwood development from and injury (Hörnfeldt, Drouin and Woxblom, 2010).

The stem discoloration of the birch has been investigated by Hallaksela and Niemistö, (1998). They found colour changes in the pith of the birches due to dead and broken branches. However, they also noted that there had been no quality or veneer yield reduction over 30 years. It was also found that the entry of the microorganisms through the broken branches was the main reason for development of birch false heartwood. Nevalainen, (2015) investigated the discoloration of birch after sapping and found the conical-shaped, flattened discoloration developed from the hole in the down and upward direction. After five years, the discoloured area had increased already four times. The discolorations by sapping hole are more intense when discolorations caused by the broken branches and butt also appear. In other study of discoloration associated with fungi in stems after logging damage of silver birch, the authors found that wound area and length greatly influenced the length of the discoloration (Vasaitis, Bakys and Vasiliauskas, 2012). However, no correspondence of age of wound and discoloration spread in radial nor vertical direction was found. The graphical explanation of the birch false heartwood occurrence in the tree is explained in the Figure 3.

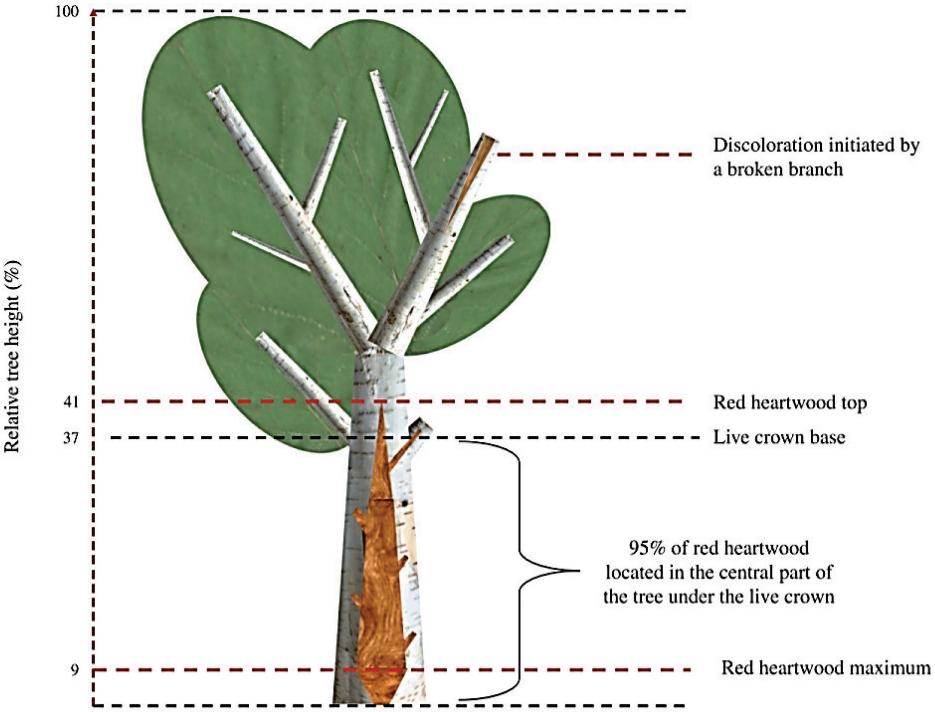


Figure 3. Formation of birch false heartwood (red heartwood) in the birch tree (Giroud, Cloutier and Alteyrac, 2008).

Giroud, Cloutier and Alteyrac, (2008) investigations showed that the amount of birch false heartwood was in correlation with tree age. It was found that on average, the false heartwood starts to appear in 40-year-old trees and then grows in diameter around the pith with the tree age (see Figure 4). The false heartwood is mainly located in the central part of the tree under the live crown (see Figure 3 and Figure 5).

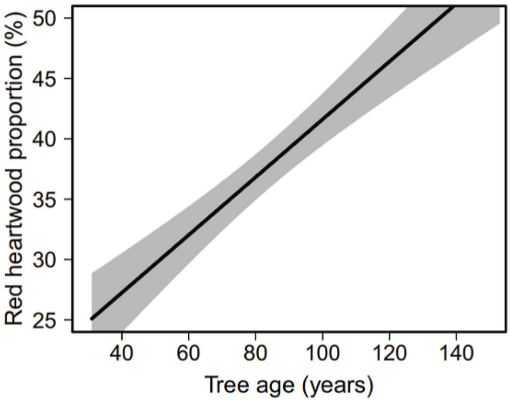


Figure 4. Birch false heartwood (red heartwood) proportion growth in years. (Havreljuk, Achim and Pothier, 2013)

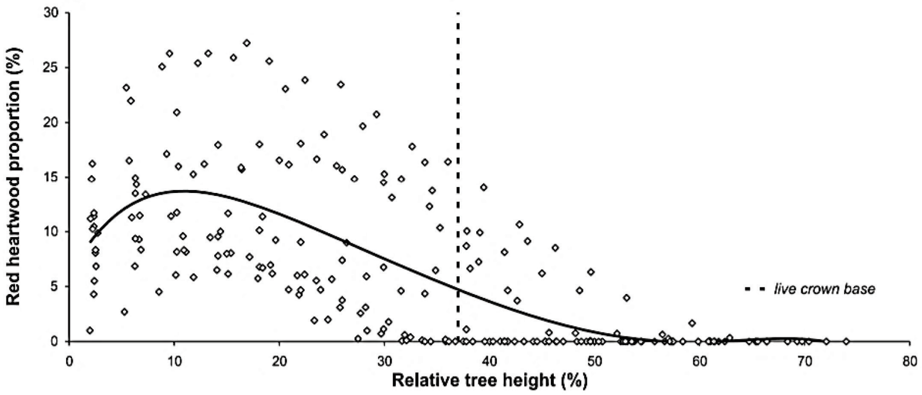


Figure 5. Proportion of birch false heartwood (red heartwood) in the stems as a function of relative tree height (Giroud, Cloutier and Alteyrac, 2008).

1.1.2 Properties of birch false heartwood

Previous researches have shown that there are no major differences in birch sapwood and false heartwood properties. It has been reported that the birch false heartwood has higher moisture content than sapwood (Sepp, 2015), (Hörnfeldt, Drouin and Woxblom, 2010). Higher moisture content affects the interfacial adhesion with hydrophobic polymer matrix and makes it more difficult to bond wood particles into polymer matrix. Johansson, (2008) investigated the modulus of elasticity and compression strength of the birch false heartwood and found no significant differences between sapwood and false heartwood in birch. According to previous study carried out by Sepp (2015), the surface roughness of birch false heartwood veneer is 150% higher and not stable compared to birch sapwood veneers. High surface roughness makes it difficult to glue different veneers together evenly and this is also the problem in WPCs, where surface roughness influences interfacial adhesion between the wood and polymer matrix. In the same study, the average tensile strength of false heartwood veneer and sapwood veneer was similar. However, the highest and lowest tensile strength values were very different in false heartwood veneers showing that false heartwood mechanical properties are not uniform and therefore affect the properties of WPCs. The density of birch false heartwood veneers was found to be 17% lower than sapwood veneers (Sepp, 2015). Density also affects the adhesion with polymer matrix, where lower density false heartwood has higher number of open pores where the adhesive can penetrate through instead of surface of the wood.

The variation of false heartwood properties compared to sapwood properties is creating the problems for manufacturers who are trying to make homogeneous products. Therefore, there the birch logs for veneer making are graded based on the allowable amount of false heartwood and different price levels are set for the graded logs.

1.2 Components of composites

1.2.1 Matrix polymer

Polymers that are most widely used in the production of WPCs can be divided into two major groups based on their origin (Faruk *et al.*, 2012):

1. Synthetic polymers such as polyethylene, polypropylene, polyvinyl chloride, polystyrene as thermoplastic matrices and epoxy resin, phenol formaldehyde, polyester and vinyl esters are used as thermoset matrices.
2. Bio based polymers such as polylactide acid, polyhydroxybutyrate, starch, soy based biodegradable resin.

Thermoplastic polymers are primarily used, because they are easy to process. Nevertheless, not all of the thermoplastic polymers can be used for WPCs production. The main criteria for polymers in WPCs is the melting temperature which has to be less than the degradation temperature of wood (≈210˚C). Common thermoplastic polymers that have the suitable melting temperature for production of WPCs are shown on Figure 6.

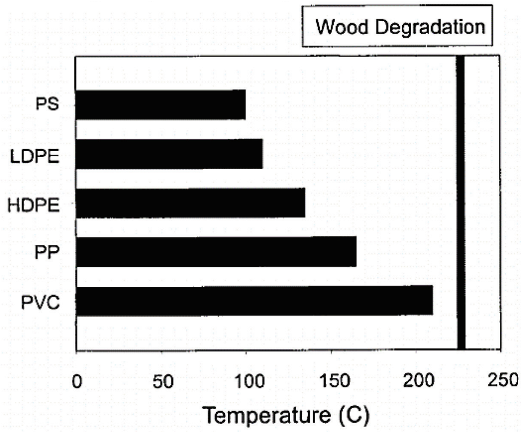


Figure 6. Processing temperatures for the suitable thermoplastics in WPCs (Shen, Haufe and Patel, 2009).

PP is one of the most common polymer matrices used in the production WPCs production. PP is a thermoplastic, semi-crystalline propylene polymer. PP has a methyl (CH_3) group at each link in the chain, so there are several possible side chain arrangements available (see Figure 7). In case of isotactic polymer structure, all the methyl groups are located on one side of the backbone whereas in case of syndiotactic structure, the location is alternating regularly on both sides. Depending on the molecular weight and the content of the isotactic or syndiotactic structure, the properties of the PP may fluctuate within wide limits. Most commonly used are PPs with a molecular weight of 80000 to 200000 g/mol and an isotactic content of 80 to 95% (Christjanson, 2007). PP is subdivided into homopolymer and copolymer. Homopolymers have a higher crystallinity and a melting point of T_m = 161 to 165°C, already softening at 155°C. In the case of homopolymers, crystallinity and melting point depend on tactility. Copolymers typically contain some amount of ethylene comonomers. The melting point of the copolymers ranges from T_m = 140 to 155°C. In the case of copolymers, the crystallinity and melting point depend on the tactility and the comonomer and its content. PP density ranges from 0.90 to 0.91 g/cm^3. PP homopolymers are more rigid than copolymers, because the homopolymer flexural modulus is 1.14 to 1.65 GPa, and copolymers have flexural modulus of 0.90 to 1.20 GPa. PP flexural strength is 41.37 to 48.26 MPa. Generally, WPCs made of PP have good strength properties, are rigid, relatively good resistant to creep, and wear resistant (Klyosov, 2007).

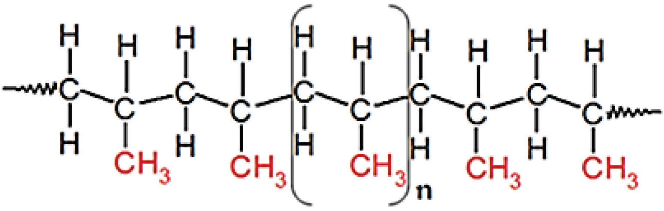


Figure 7. Polypropylene structure (Maddah, 2016).

PP has been widely used in the production of different natural fibre composites. For example, Park *et al.* (2006) and Placet (2009) investigated the hemp fibre reinforce PP composites. Jayaraman (2003) and Mukhopadhyay and Srikanta (2008) investigated the sisal fibre reinforced PP composites. Rana, Mandal and Bandyopadhyay (2003) and Park *et al.* (2006) investigated the jute fibre reinforced PP composites.

1.2.2 Wood filler

Different wood industry by products can be utilised as filler material in the wood plastic composites such as wood chips, shavings, fibres, mechanical pulp and cellulose. These types of fillers are easy and inexpensive way to reinforce the polymer matrix. Wood filler geometry and size as well as distribution and content are important for WPCs production of (Andrzej K. Bledzki and Faruk, 2004), (Migneault *et al.*, 2009), (Ayrilmis, Kaymakci and Ozdemir, 2013). In WPC industry, wood filler is divided into two groups: fibrous and particles. Particles have almost even dimensions in all directions and can have different shapes. Wood fibres can withstand most of the load applied, because they have high aspect ratio (5 to 8 times higher than wood flour), (Stark and Rowlands, 2003). Therefore, wood fibres are considered reinforcing in the composites (Wolcott and Englund, 1999).

The idea to use wood filler in the polymer matrix is to reduce the usage of synthetic polymer and increase the mechanical properties of the material. For WPCs manufacturing, wood can be used in the form of short fibre, particle or flour. When decreasing the wood filler particle size, the modulus and yield strength will increase. With the wood flour (WF), the greatest modulus increase is observed. When using the fibres, both strength and stiffness are increased with increasing the fibre length. For the processing techniques of WPCs and for better adhesion between the filler and polymer matrix, the smaller sizes are better (Wolcott and Englund, 1999). Previous studies have shown that composites with smaller particle size (under 4 mm) and about 30 wt% of wood have good mechanical properties due to the better interfacial adhesion between polymer matrix and wood particles (Lomelí-Ramírez *et al.*, 2014). Increasing the wood filler content increases the tensile and flexural modulus by making the material stiffer. At the same time tensile and impact strength are decreased when wood filler content increases from 0 to 60 wt%. (Takase and Shiraishi, 1989) (Yam *et al.*, 1990)

Generally, there is no limit of using different wood species in the WPC production and many wood species are used in the WPCs. Softwood is more used in the WPCs than hardwoods, because softwood fibres have higher aspect ratio (form 80% to 130% higher than hardwood), (Hodzic and Shanks, 2013). Hardwood, however, has more cellulose (28%) in its structure than softwood (20%) and therefore hardwood increases the strength and stiffness of the composites (Oksman and Sain, 2008). Hardwood fibres have better impact strength than softwood fibres (Bledzki and Faruk, 2003). The higher number of extractives in some wood species, decreases water absorption of the wood fibres due to the extractives interacting with celluloses and lignin hydroxyl groups. (Ashori and Nourbakhsh, 2010)

However, when using the wood filler, it is important to note that WF starts to degrade on temperatures over 210°C. At this temperature, the lignin and hemicellulose start to degrade whereas cellulose starts to degrade at temperatures over 240°C (Oksman and Sain, 2008).

1.2.3 Additives

WPCs are mainly made of hydrophobic polymer matrix and hydrophilic wood filler. Wood is hydrophilic due to the hydroxyl groups found in the cellulose and hemicellulose molecular chains. As WPCs properties depend on the interfacial adhesion of the components, then the hydrophilic nature of wood results in poor compatibility between filler and matrix that in turn results in poor strength and composites durability (Faruk *et al.*, 2012), (Gardner, Han and Wang, 2015).

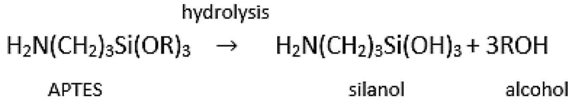
In order to overcome this problem and improve the compatibility between wood filler and polymer matrix, different wood filler modifications are considered for modifying the wood surface properties. These modification chemicals are called coupling agents and their main function is to improve the adhesion of cellulose filler and plastics by creating covalent bonds between them. The purpose of the chemical modification of the wood is to reduce number of available wood hydroxyl groups and to increase the cross-linking with polymer matrix. Coupling agents mainly improve the adhesion between the polymer and wood by covalent bonding and in addition the coupling mechanism can also be the entanglement of the polymer chains or generating strong secondary bonds (hydrogen bonds) (Klyosov, 2007). These coupling agents also act as dispersing reagents by neutralizing the wood filler and the polarity of polymer surface (Lu and Mcnabb, 2000).

For wood fillers, various chemical methods are used to improve the adhesion of wood and the polymer. There are mainly three chemical methods that can be applied for wood fillers: silane modification, esterification, and graft copolymerization (Pickering, 2008). Silanes are one of the main coupling agents that are used in WPCs and other natural fibre composites. There are several studies showing how silanes improve the mechanical properties and durability of WPCs (Farsi and Ghasemi, 2010), (Gwon *et al.*, 2010), (Nakatani *et al.*, 2011), (Lv *et al.*, 2015). Silanes are such coupling agents, which have hydroxyl group at one end, which is an intermediate unit in the formulation of silanol groups upon the formation of a stable covalent bond with the filler surface. A general structure of silane is the following (Klyosov, 2007):

$$R - (CH_2)n - SiX_3 ,$$

where R is the functional group that triggers affinity and reactivity with the polymer matrix (amino, epoxy, vinyl, alkyl) and X is reactive (hydrolysable) chemical group that provides a covalent bond with the wood filler (OCH_3, $–OC2H_5$, $CH_3COO–$). Silanes reduce the number of wood hydroxyl groups by making the wood more hydrophobic. This provides a better connection to the polymer. In the WPCs most commonly used silanes are aminosilanes, long alkyl chains, alkoxysilanes, vinyl alkoxysilanes and their oligomers. Aminosilanes such as γ-aminopropyltriethoxysilane are most widely used as coupling agent for natural fibres, where the amino group also possesses the strong affinity to the hydroxyl groups of wood filler. Silane interaction with natural wood fibres is typically the following process (Xie *et al.*, 2010):

- Hydrolysis (in water and alcohol);
- Self-condensation (pH of the solutions should be adjusted to acidic environment around 4).
- Adsorption (silanol groups adsorption with hydroxyl groups of natural fibres by hydrogen bonds, formation of –Si-O-Si- bond). APTES silane hydrolyses process:



$$\underset{\text{APTES}}{H_2N(CH_2)_3Si(OR)_3} \xrightarrow{\text{hydrolysis}} \underset{\text{silanol}}{H_2N(CH_2)_3Si(OH)_3} + \underset{\text{alcohol}}{3ROH}$$

- Grafting (formation of –Si-O-C- bonds during heating and liberating the water).

It is important to select a silane with the correct functional group, which reacts with the corresponding polymer matrix. 3-aminopropyltriethoxysilane (APTES) and triethoxyvinylsilane (TEVS) silanes coupling reaction between wood fibres is presented in the scheme on Figure 8. Silane is usually added at 3 to 10% by weight of wood filler. Using coupling agents can result with strong interface, which in turn result in higher strength and stiffness of the composite due to the efficient stress transfer from matrix to the filler. (Faruk *et al.*, 2012) It has been shown that the silanes decrease the water absorption of the WPCs (Jia, Zhao and Cai, 2015). Mechanicals properties also increase with the using of silane coupling agents with PP and cellulose composites (Gwon *et al.*, 2010) (Nakatani *et al.*, 2011). However, one must consider that the prices of coupling agents are relatively high and therefore they are mainly used only in special applications and high demanding products.

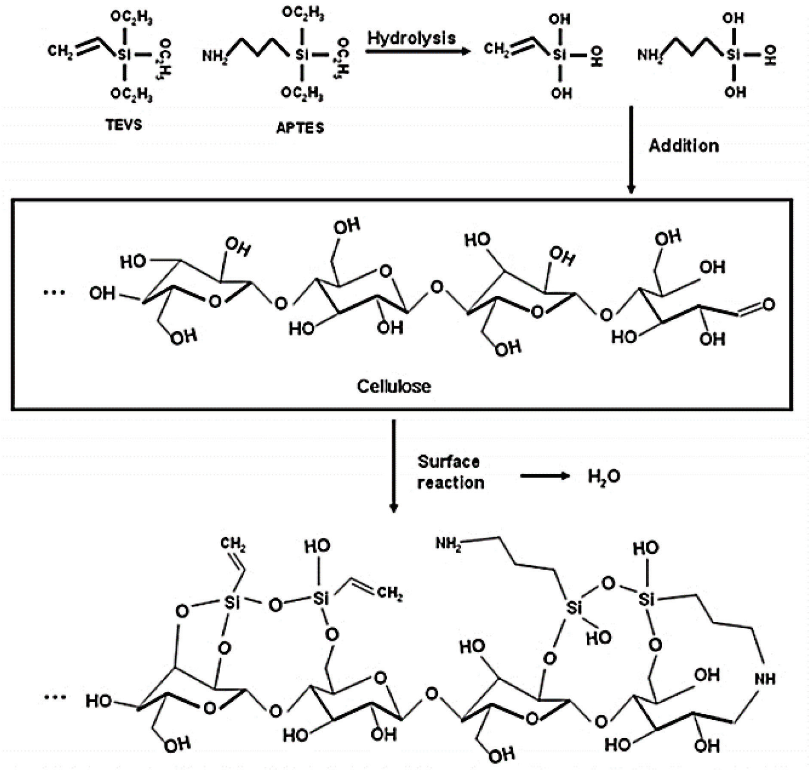


Figure 8. APTES and TEVS coupling reaction with wood fibres (Gwon et al.*, 2010).*

1.3 Mechanical properties of Wood-Plastic Composites

1.3.1 Tensile properties of composites

The tensile properties are one of the important and mainly tested properties for the natural fibre reinforced composites. Fibre strength and orientation in the composite are the most important factors for determining the suitable natural fibre for a specific application. A tensile test determines the average properties over thickness and the stresses are uniform throughout the material cross-section. The tensile properties show how the material reacts to the applied loads in tension. Tensile test is used to determine the tensile strength, yield strength, elongation, modulus of elasticity, reduction in area, yield point, and other tensile properties.

Adding different amount of WF to the PP matrix gradually decreased the tensile strength at each wood loading level from 10-50 wt%. It was explained as poor interfacial strength between the hydrophobic polymer and hydrophilic wood that causes the micro-voids between the interfaces. Therefore, these micro-voids reduce the stress transfer from PP matrix to the wood reinforcement (Kim *et al.*, 2011). However, the studies have shown that modification of the wood particles with different silane coupling agents increases the tensile strength (Kim *et al.*, 2011), (Jia, Zhao and Cai, 2015). According to Kim *et al.* (2011) the WF modification of 2.5 wt% with different silanes increased the tensile strength. At 10 wt% WF loading, the tensile strength was found to increase with APTES modification of WF, already 10.2 % compared to unmodified WF composites. At above 30 wt% WF loading, the silane modification significantly improved the tensile strengths.

Another important factor that influences the tensile strength is the wood filler type. Different wood filler types and wood species have different effect on the tensile WPCs. Huang *et al.* (2011) investigated the two different commercially available softwood particles C120 and L9. They found that there were about 13% differences in tensile strength between the two softwood particle based WPCs.

One of the main things that affects the tensile properties is the wood filler size. Tensile properties increase with increasing the wood particle size. One of the important things to consider is the fibre aspect ratio, where higher aspect ratio improves the stress transfer from polymer matrix to wood fibres and therefore enhances the mechanical properties (Kociszewski *et al.*, 2012). Various researchers have studied the effect aspect ratio on WPCS properties and how to improve the mechanical properties with higher aspect ratio (Zaini *et al.*, 1996), (Stark and Rowlands, 2003), (Migneault *et al.*, 2009), (Basiji *et al.*, 2010), (Kociszewski *et al.*, 2012).

1.3.2 Flexural properties of composites

Flexural properties are another key aspect to consider in the mechanical performance of WPCs. Flexural properties are strongly affected by the material top and bottom surface properties. In the flexural test, the stresses are the highest in the material top (compression) and bottom (tension) surfaces while in the middle the stresses are zero. The flexural strength shows how the material property resists the bending forces perpendicular to longitudinal axis before it yields (Dhir *et al.*, 2017). As for the tensile strength, the flexural strength also is affected by the wood particle loading level in the composites. However, in here the trend is different. When in tensile test, the addition of wood particles into PP matrix decreased the tensile strength, then in the flexural test, it is the opposite and the addition of the wood particles increases the flexural strength. The flexural strength is not increasing gradually with wood particle loading and starts to decrease after 30 wt% of wood loading level (Kim *et al.*, 2011). After 30 wt% of wood loading level, the interfacial strength of PP and wood particles starts to decrease causing the decrease in flexural strength. Nevertheless, the coupling agents substantially improve the flexural properties at higher wood loading levels. For example, the addition of 2.5 wt% APTES into the WPCs are showing 77 % higher flexural strength than unmodified WPCs at 50 wt% wood loading level. (Kim *et al.*, 2011)

Important factor influencing the flexural properties is also the wood particle size and distribution in the WPCs. Izekor, Amiandamhen and Agbarhoaga, (2013) focused on the geometry particle sizes of WF in the WPCs. They showed that the flexural properties increased with the increased wood particle size. The highest flexural strengths were achieved with the particle sizes over the 2.00 mm. However, as same as for the tensile test, the most important factor was found to be the aspect ratio not particle size that influences the flexural properties. With higher aspect ratio, the stress is more efficiently transferred from the matrix to the fibre/particle creating the stronger material. (Stark and Rowlands, 2003). In another study by Kajaks *et al.* (2016) it was shown that when using the very small WF size such as plywood sanding dust, then the increase in flexural strength is very small whereas the increase in flexural modulus can be 2.42 times. Therefore, it is important to choose optimal wood particle aspect ratio for the optimal composite performance based on the field of application.

1.3.3 Flexural creep properties of composites

Long-term mechanical durability is one of the most important factors that affects many materials that are intended to use in structural applications, because many of these applications are subjected to long-term flexural members. Creep shows the time dependent behaviour of the material with the increase in strain over time during long-term loading. Creep can result in creep rupture or load-duration behaviour under constant load (Li, Mattila and Vuorinen, 2015). These are the important parameters to consider for designing the structural applications from WPCs. Typically, polymers are the viscoelastic materials that exhibit both viscous and elastic behaviour under loading. For the linear viscoelastic materials, the whole strain is the sum of three individual components: immediate elastic deformation (e_1), delayed elastic deformation (e_2) and Newtonian flow (e_3). In case of linear viscoelastic materials, the rate of e_1, e_2 and e_3 are exactly proportional to the rate of the applied stress and therefore the creep compliance is defined as function of time (equation 1), (Ward and Sweeney, 2004):

$$J(t) = \frac{e(t)}{\sigma} = J_1 + J_2 + J_3\text{ , (1)}$$

where J_{1-3} correspond to e_{1-3}.

Plastic materials deform continuously under the constant load. The creep will happen in three stages as seen in Figure 9. At the initial stage when the stress is applied, the strain starts at rapid rate then slows with time. This is called primary creep and when the stress is removed, the material returns to its original shape. At the constant loading after primary creep material reaches to the steady state which is called secondary creep stage. In this region the material has relatively uniform strain rate. This is followed by the accelerated creep rate which results in creep fracture of rupture. The rapid increase is called tertiary creep and it is caused by the necking and formation of internal cracks and voids causing the increase of local's stress of the component. In tertiary creep, material structure is permanently changed and strength is lost. (McKeen, 2009) (*Long term performance of polymers*, 2019) Therefore, it is important to design the composite material in order to avoid the tertiary creep stage and estimate the material serviceable life with the end of secondary creep (steady state region).

In the graphic (see Figure 9), the curves correspond to the strain rates where the decreasing strain rate is primary creep, almost constant strain rate is secondary creep (steady state) and increasing strain rate is tertiary creep.

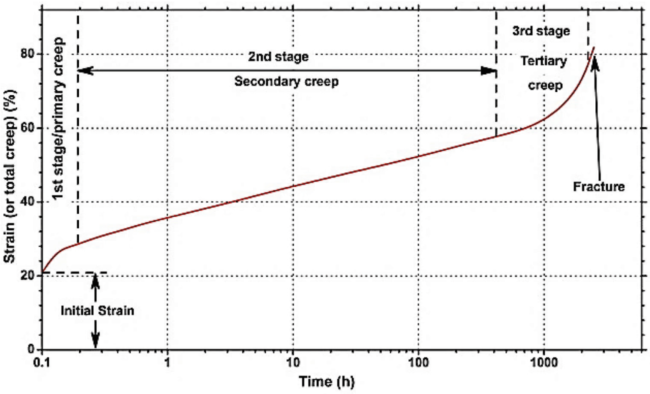


Figure 9. Strain versus time creep behaviour of plastics. (McKeen, 2015)

solid wood is relatively stiff material and has low creep properties (Park and Balatinecz, 1998) . It has been studied, that the flexural modulus of solid wood is about five times higher than neat PP (Kazemi-Najafi, Nikray and Ebrahimi, 2012). Therefore, the addition of the wood filler into the polymer matrix significantly influences creep properties of the material. The addition of wood increases the flexural modulus (about 97%) and decreases the creep strain of material (Kazemi-Najafi, Nikray and Ebrahimi, 2012). Various studies have shown that increasing filler loading increases the brittleness of the composites (Park and Balatinecz, 1998), (Premalal, Ismail and Baharin, 2002), (Park *et al.*, 2008), (Wang *et al.*, 2009). Increasing the wood filler loading level from 10 wt% to 40 wt% decreases the creep strain about 60% (Lee *et al.*, 2004). In other study, the Najafi and Najafi (2009) investigated the effect of different wood loading levels in the HDPE composites. They found that increase of creep deflection in time with higher wood filler loading levels was less than lower loading levels. It is also shown that the stress level affects the creep strain of WPCs. When the stress level is lower, the creep strain at the same wood filler loading levels is also lower (Park and Balatinecz, 1998), (Lee *et al.*, 2004). The same correlation with wood filler loadings and stress levels is also noticed after the loading where higher stresses and filler loadings have smaller instantaneous recovery and permanent recovery. In their study, Najafi and Najafi (2009) showed that HDPE based WPCs with higher loading levels over 40% start to show nonlinear creep curves. It was reported by Morlier (1994), that wood-polymer composites show nonlinear behaviour in property with high stress levels.

The effect of polymer matrix properties is also important. The recycled polymer has lower creep deflection than virgin polymer and it was found that the differences increase with increasing the creep time (Wang *et al.*, 2009), (Najafi and Najafi, 2009). Another important factor that influences the creep properties of the WPCs is the surrounding temperature because thermoplastic polymers are softening with elevated temperatures resulting the reduced creep resistance. Therefore, increasing the temperature increases the relative creep of the WPCs. For example, in case of PP based WPCs with temperature increase from room temperature (23°C) to 60°C, the relative creep increased almost twice of room temperature creep. Other study by van den Oever and Molenveld (2019), investigated the commercially available WPC decking boards for long term loading under different temperatures. They found that creep deflections at 50°C were higher than normal room temperature and were already very close to the 10 mm limit expected to be the safe level for the WPC boards according to EN 15534-4.

1.4 Summary of the literature review and aim of the study

Birch is the third most commonly available wood species in Estonia which is mainly used for the veneer, plywood, glued laminated timber and furniture products as well as pulp and paper industry. The birch wood quality is mainly determined by the uniform colour which depends on the sapwood staining that is called false heartwood. Other defects such as knots, cracks, defects in stem shape, wood structure defects, fungal and mechanical defects also determine the birch quality. In addition, lower quality birch wood exhibits the substantial amount of false heartwood and is therefore used in the inferiority products.

False heartwood is the wood defect that develops in the combination different factors such as injuries of the branches, stem wounds, crack formation, penetration of oxygen in the wood cells, polymerization and oxidation of the phenolic substances, fungi and bacteria development, aging of parenchyma cells and formation of tyloses. On the average, false heartwood starts to develop in 40-year old trees and grows in diameter with the tree age. False heartwood is mainly located in the central part of the tree under the live crown.

Several thermoplastic polymers can be used for WPCs production. One of the most commonly used polymer matrix is PP because of its easy processability, good strength properties, relatively good resistance to creep and wear resistance. Different wood filler types are used to produce the WPCs. Softwood fibres have better aspect ratio while hardwood has higher cellulose content which increases the mechanical strength and stiffness of the composites. Various chemical methods are used to improve the adhesion of wood and polymer. Aminosilanes such as APTES are one of the most widely used coupling agent for natural fibres.

It is very important to understand WPCs mechanical behaviour for their application in various fields. Wood filler length and orientation in the polymer matrix is an important factor that determines WPCs mechanical properties. Mechanical properties can be evaluated through assessment of ultimate tensile and flexural strengths or load-duration behaviour under constant or cyclic loading.

The main aim of this research was to investigate the use of birch false heartwood on WPCs mechanical properties. To achieve the aim of the study, the following objectives were set:

- To develop the proper technology for producing the birch false heartwood composites.
- To find the optimum wood particle size to produce WPCs.
- To learn the effect of birch false heartwood on the mechanical properties and durability of WPCs.
- To study the influence of chemical modification with APTES of birch false heartwood on the mechanical properties of WPCs.

For these objectives, the following activities were carried out:

- Different wood particle sizes were tested in the WPCs
- Various wood particle modifications were carried out to find the optimum mechanical properties of WPCs.
- Different methods were used to evaluate the mechanical properties of WPCs.
- Wood particle chemical modification was evaluated with FTIR analysis.

2 Experimental

This chapter gives an overview of the materials used in this work, processing and analysis methods applied to investigate the properties of the wood-plastic composites. The main idea of this thesis was to develop a new type of WPCs containing a birch false heartwood component, that exhibit the good mechanical and physical properties. Various birch wood particle sizes and chemical modifications were studied before false heartwood composites were made. The overview of the materials and methods used in this thesis is shown in Table 2. The schematic diagram of the WPC processing steps used in this thesis is shown on Figure 10.

Table 2. Materials and methods.

Materials	Methods	Aim of the paper	Paper
Polymer: PP, LLDPE-g-MAH Wood filler: Birch sapwood, Modification: APTES, PVA	Wood/polymer ratio: 35 wt%/65 wt%; Flexural strength, Charpy impact strength, Water absorption and thickness swelling; UV exposure and colour analysis.	Investigate the influence of wood particle size, UV radiation, and moisture absorption to the WPC structure, mechanical and physical properties.	Paper I
Polymer: PP Wood filler: Birch sapwood Modification: NaOH, PVA, APTES, AA, AA and DMF, VA and DMF, Acrylonitrile	Wood/polymer ratio: 35 wt%/65 wt%; Flexural strength; Charpy impact strength; DSC analysis; SEM analysis	Investigate the influence of the chemical modification of WF on the interfacial strength of WPC	Paper II
Polymer: PP Wood filler: Birch sapwood and false heartwood Modification: APTES	Wood/polymer ratio: 60 wt%/40 wt%; Flexural strength; Tensile strength; Water absorption and thickness swelling; UV exposure and colour analysis. FTIR analysis	Investigate the effect of birch false heartwood on the physical and mechanical properties of WPCs	Paper III

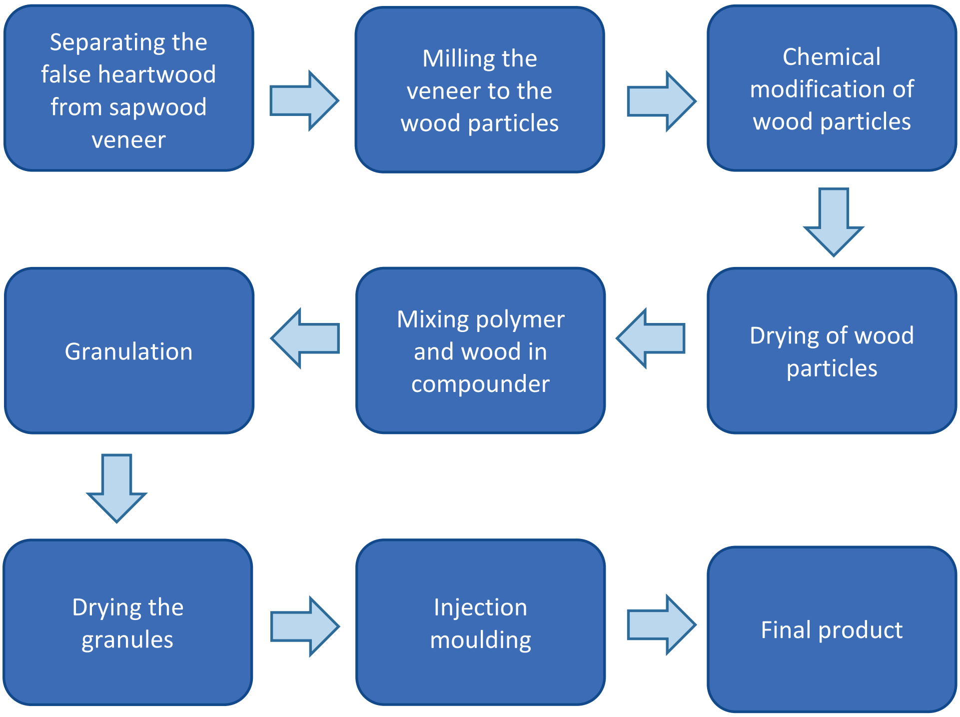


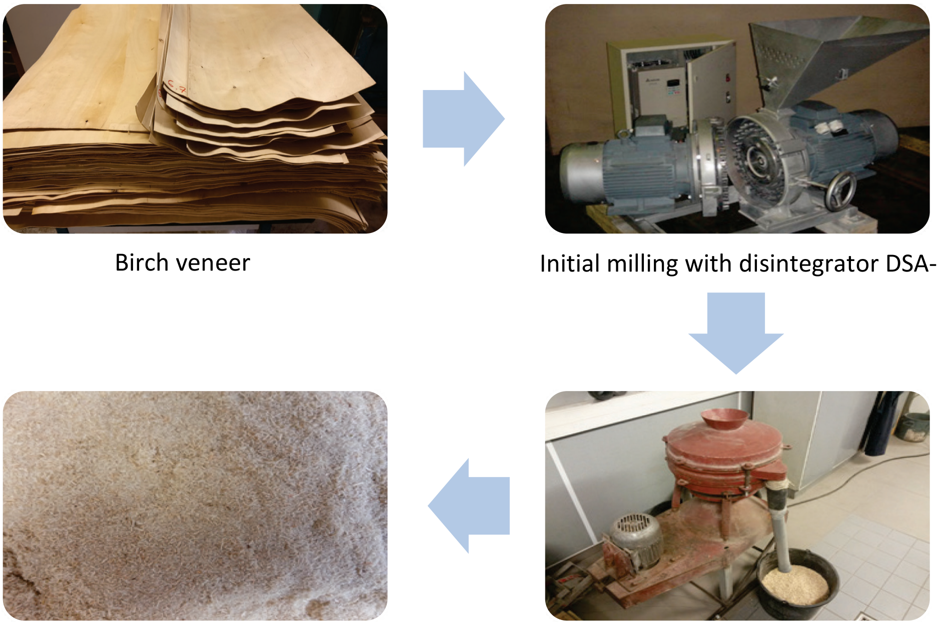
Figure 10. WPC processing diagram

2.1 Materials

2.1.1 Wood filler

Birch (*Betula pendula*) sapwood (paper I and II) and birch false heartwood (paper III) were used as filler materials in WPCs. Both, birch sapwood and birch false heartwood were obtained in the form of veneers from the Estonian plywood manufacturing company Kohila Vineer OÜ. The wood filler processing is shown on Figure 11. The experimental work started with the separation of the birch false heartwood veneer pieces from the sapwood veneer pieces by hand (paper III). Birch veneer pieces where then initially crushed mechanically using the disintegrator DSA-3 to even size chips. After that, the veneer chips were mechanically refined into the wood particle length of 1 mm using the separation milling with disintegrator DSL-115. The wood particle length and distribution was measured using the analytical sieve shaker method with Fritsch Analysette c3. The used sieve sizes were from 25 to 0.025 mm. In paper I, three different WF fraction sizes were investigated (≤ 0.63 mm, 0.63–1.25 mm and 1.25–2 mm)

During the milling process, the energy consumption of the milling process of veneer chips was measured. The energy consumption data showed (see Figure 12) that the birch false heartwood needs more energy for milling than birch sapwood, which can be explained with the extractives found in the false heartwood.



Birch veneer

Initial milling with disintegrator DSA-3

Refining with disintegrator DSL-115

Wood particle with mesh size 1mm

Figure 11. Wood particle processing

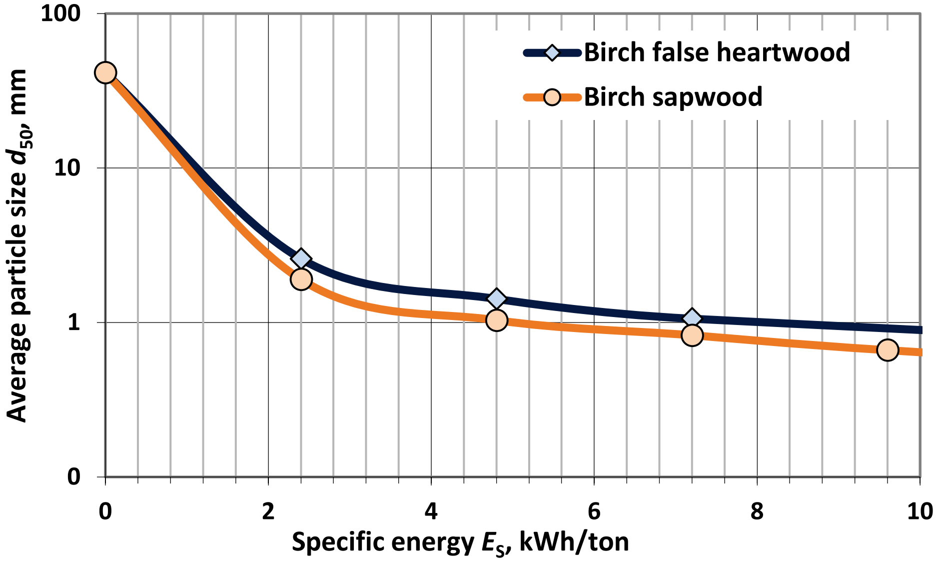


Figure 12. Relationship between average particle size of milled birch sapwood and false heartwood and specific energy of milling

2.1.2 Wood filler modification

After the wood filler material was processed, it was chemically modified to make it compatible with thermoplastic polymer matrix. Different chemical modifications were investigated in papers I and II. In paper III the most suitable method with APTES was followed and is explained in this thesis.

Wood filler modification (paper III)

For the purification of the wood particles an alkaline solution was used with NaOH (min. 98%, p.a. 1 kg, CAS 1310-73-2) from Sigma-Aldrich Chemical Co. Alkaline modification was used for removing impurities and increasing the number of hydroxyl groups on wood particle surface. The alkaline modification of the wood particles was done according to the common procedure based on previous researches by (Doczekalska and Zborowska, 2010), (Gwon *et al.*, 2010), (Doczekalska, Bartkowiak and Zakrzewski, 2014). The wood particles were treated with 5.0 wt% (by wood content) NaOH solution at room temperature (23°C) and left for about 90 min. Then the wood particles were thoroughly washed with distilled water using the handsheet former LA-1 vacuum machine to remove the excess NaOH and then oven dried at 60°C for 24 h.

Wood particles alkaline modification was followed by silane modification. The effect of silane modification is to create the chemical bonds with wood particle surface and polymer matrix. For the silane modification, the 3-aminopropyl-triethoxysilane (APTES) was obtained from by Sigma-Aldrich Chemical Co. (assay: 98%, density 0.946 g/mL) and acetic acid was obtained from Lach-Ner (99.8%, M: 60.05 g/mol). Silane modification was done according to the common procedure by Kim *et al.* (2011): 5 wt% (by wood content) of APTES was taken and immersed in a solution of ethanol:distilled water (6:4 v/v ratio) for silane hydrolysis while continuously stirring the solution. While silane hydrolysis, the pH of the solution was adjusted to the 4-5 with acetic acid. After the silane hydrolysis, the APTES solutions was poured on the wood particles and left for 2 h. Then, the wood particles were oven dried at 60°C for 24 h.

2.1.3 Polymer matrix

Thermoplastic polymers are usually used in WPCs. It is important that thermoplastic matrix has the processing temperatures below 200°C to avoid the wood filler thermal degradation. In papers I-III, the PP was used as matrix material. In paper I, composite making technological parameters were investigated and the coupling agent LLDPE-g-MAH (Fusabond E (MB226DE)) was also used to make PP and LLDPE-g-MAH blends and improve the compatibility with wood filler. In this thesis (paper III), it is explained the usage of the thermoplastic polymer PP (PPH 11012 homopolymer) from Total Petrochemicals USA Inc as matrix material. This PP is homopolymer which is nucleated and with controlled rheology. It has a high melt flow index of 55 g/10 min, density of 0.905 g/cm^3 and melting point of 165°C. This PP also has highly antistatic nature that allows for shorter cycle times and easy demoulding, which are important for WPCs production.

2.2 Composite processing methods

In paper I-II, different polymer and wood ratios in the composites were used to test the process technological parameters and material properties. In paper III, high wood content was chosen to continue with the investigation of false heartwood effect on the WPC properties and process parameters. Therefore, the WPCs were prepared with the 60 wt% of wood filler and 40 wt% PP matrix (paper III). The composition of the mixtures are shown on Table 3. The composite mixtures were grouped into five different sample groups: neat PP (PP), sapwood composites (SW), modified sapwood composites (MSW), false heartwood composites (FHW), modified false heartwood composites (MFHW). Then PP and wood mixtures were prepared by compounding in a twin-screw compounder (Brabender Plasti-Conder PLE 651). The compounder barrel had four heating zones and temperatures were set at from the hopper to the die zone in the following order: 180°C, 185°C, 190°C and 195°C. The compounder twin-screw rotation speed was set at 60 rpm throughout the compounding process. The extruded WPC filament was then cooled with air by ventilators and then granulated into pellets. The compounded composite pellets were then stored in minigrip polyethylene packaging bags to prevent the moisture absorption.

Prior the injection moulding process, the WPC pellets were dried in the oven at 80 °C for 24 h to remove any moisture in the material. Then the WPC dumbbell-shaped multipurpose test specimens were made from the oven dried composite pellets by the injection moulding process (Battenfeld BA 230E) according to EN ISO 527-2 (2012) type 1A. The injection moulding machine had three heating zones which were from the hopper to the die zone in the following: 170°C, 180°C and 61% (from the total heating power), and injection pressure of 7 MPa. The mould cooling temperature was set to 40°C and time 6 s.

Table 3. Composition of the Composites

Sample	PP (wt%)	Birch (wt%)	NAOH (wt%)	APTES (wt%)
PP	100	-	-	-
SW	40	60	-	-
MSW	40	60	5	5
FHW	40	60	-	-
MFHW	40	60	5	5

2.3 Analysis methods

2.3.1 Tensile test

The tensile properties of the WPC samples were determined according to the EN ISO 527-2 (2012) using the Instron 5866 universal testing system. The analysis was performed with the previously injection moulded dumbbell-shaped multipurpose test specimens (dimensions are 150x20x4 mm). The test was carried out in a temperature-controlled room with the temperature of 23 °C and relative humidity of 50%. A load cell with the maximum capacity of 10 kN was used for the tensile test and the test speed was set to constant rate of 5 mm/min. Ten specimens were tested for each WPC sample and the tensile strength and the tensile modulus was calculated. The tensile strength was calculated using the equation 2:

$$\sigma_m = \frac{F}{A}, (2)$$

where σ_m is the tensile strength, expressed in MPa, F is the measured force, in newton's, A is the initial cross-sectional area of the specimen, in square millimetres. The tensile modulus was calculated using the equation 3:

$$E_t = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}, (3)$$

where E_t tensile modulus in MPa, σ_1 is tensile stress in MPa at strain value ε_1= 0.0005 (0.05 %), and σ_2 is tensile stress in MPa at strain value ε_1= 0.0025 (0.25 %).

2.3.2 Flexural test

The flexural properties of the WPC samples were determined according to the EN ISO 178 (2010) using the Instron 5866 universal testing system. The specimens dimensions were 80x10x4 mm and the test was carried out in a temperature-controlled room with the temperature of 23 °C and relative humidity of 50%. A load cell with the maximum capacity of 500 N was used for the flexural test and the test speed was set to constant rate of 2 mm/min and span length was 64 mm. Ten specimens were tested for each WPC sample and the flexural strength and the flexural modulus was calculated. The flexural strength was calculated using the equation 4:

$$\sigma_{fM} = \frac{3FL}{2bh^2} , (4)$$

where σ_{fM} is flexural strength in MPa, F is applied force in N, L is span in mm, b is width of the specimens in mm, h is thickness of the specimens in mm. The flexural modulus was calculated using the following equations 5 and 6:

$$s_i = \frac{\varepsilon_{fi} L^2}{6h} \ (i\text{=}1 \ or \ 2), (5)$$

where s_i is deflection in mm, ε_{fi} is corresponding flexural strain ε_{f1}=0.0005 and ε_{f2} = 0.0025, L is span in mm, h is thickness of the specimens in mm.

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}}, (6)$$

where E_f is modulus of elasticity in MPa, σ_{f1} is flexural stress in MPa at deflection s_1, σ_{f2} is flexural stress in MPa at deflection s_2.

2.3.3 Long-term creep test

Flexural creep test was carried out to investigate the long-term time-dependent deformation under sustained load of the WPC samples. The long term flexural creep test of the WPC samples was conducted according to the ASTM D7031-11 (2011) using the Instron 5500R universal testing system. The specimens dimensions were 80x10x4 mm and the test was carried out in a temperature-controlled room with the temperature of 23 °C and relative humidity of 50%. The test span length was set to 64 mm. Total time of the creep-recovery test was 48h (24h creep and 24h recovery) and the load level was 50% of maximum flexural load (obtained from static flexural test), which was held constant throughout the test. During the testing, the deflection at mid-span was measured five times: before loading, at 1 min with load on, at 24h with load on, immediately after the load is removed, and after 24h recovery period. Three specimens were tested for each WPC sample and the fractional deflection, relative creep, creep rate, percent recovery and creep modulus were calculated.

Fractional deflection is the ratio of total deflection (the amount of deflection 24h with loading) and initial deflection (at 1 min with loading) which is calculated using the following equation 7:

$$F_d = d_t/d_0, \text{(7)}$$

where F_d is fractional deflection in mm, d_t is the creep deflection during the period t in mm, and the d_0 is the initial deflection in mm.

Relative creep was calculated using the following equation 8:

$$R_C = (d_t - d_0)/d_0, \text{(8)}$$

where R_C is relative creep, d_t is the creep deflection during the period t in mm, and the d_0 is the initial deflection in mm.

Creep rate is showing the material deformation during the time and is calculated using the following equation 9:

$$C_r = (d_2 - d_1)/(T_2 - T_1), \text{(9)}$$

where C_r is the the creep rate (mm/min), d_2 is the creep deflection at time period T_2, and d_1 is the creep deflection at time period T_1.

Percent recovery for each specimen was defined as recovered deflection divided by the total deflection times 100.

Creep modulus was calculated using the following equation 10:

$$E_t = (L^3\ \mathrm{F})/(4\mathrm{b}h^3 d), \text{(10)}$$

where L is the length of the span in mm, F is the applied load in N, b is the specimen width in mm, h is the thickness of the specimen in mm, and d is the deflection in time t (mm).

2.3.4 Short-term creep test

Short-term cyclic creep test was performed on the WPC samples in an Anton Paar's Modular Compact Rheometer MCR 502. The specimens dimensions were 45x4x2.3 mm and the test was carried out in a temperature-controlled room with the temperature of 23 °C and relative humidity of 50%. The test span length was set to 40 mm and the samples were tested at constant stress. The WPC samples were evaluated in a creep cycling test, where the applied load levels throughout the test were 30%, 50%, and 70% of maximum flexural load obtained from static flexural test. Samples were subjected to a load level for 60 min and then released for recovery for 60 min and the cycle was repeated for each load level. For each specimen, the creep strain was registered as a function of time.

2.3.5 Fourier transform infrared spectroscopy analysis

The performance of birch false heartwood chemical modification was investigated with Fourier Transform Infrared Spectroscopy (FTIR) using a Brucker LUMOS FTIR microscope with an integrated FTIR spectrometer (Billerica, Massachusetts, United States) using attenuated total reflectance (ATR-FTIR) method. This method provides knowledge of the surface chemistry of a WPC sample by measuring the light absorption at different wavelengths from the sample surface. This test was carried out to investigate the functional groups present at the sapwood and false heartwood particles in WPC sample surface before and after APTES modification. The spectral resolution used was 1 cm^{-1} and the spectra were recorded over the range of 3500 cm^{-1} to 500 cm^{-1}. Smaller specimens were cut from the previously produced test specimens using a scalpel. Composites specimens surface was analysed in contact with a ZnSe crystal. The measurements were performed at the room temperature of 23 °C and relative humidity of 50%. At least five replicate samples were measured with up to five scans obtained for each replicate. Spectra was normalized based on the reference plot of neat PP to analyse the WPCs wood modification effect of different WPC samples. This test was carried out at the University of Leoben, Leoben, Austria.

3 Results and discussion

3.1 Tensile properties

3.1.1 Tensile strength of the WPC samples

Tensile test was carried out to analyse the property changes between birch sapwood based WPC samples and false heartwood based WPC samples. It was assumed that the higher strength and toughness could be associated to better interaction of wood filler and polymer matrix. The results of the tensile strength of the WPC samples are shown on Figure 13 (and Fig. 1a in Paper III). Adding the 60 wt% of wood filler to the PP matrix decreases the tensile strength 40% (in case of SW samples) due to the heterogeneous structure of the WPCs compared to the neat PP. Because of the high wood content and random spatial distribution of the wood particles during the injection moulding process the microscopic fractures between wood particles and PP matrix occur randomly. These microscopic cracks are leading to the main macroscopic crack formation that result to structure failure of the WPC samples under tension more rapidly than neat PP. According to Kim *et al.* (2011), increasing the wood content in WPCs decreases the interfacial bonding strength between the wood filler and PP matrix due to the hydrophilic nature of wood. Stress transfer from the PP matrix to the high contentment wood filler reinforcement is reduced because of weak incompatible interfacial regions in WPC (Kaymakci and Ayrilmis, 2014).

According Sepp (2015), the tensile strength of birch sapwood and birch false heartwood veneer are the same. In this study, also very similar tensile strength values were obtained with both, SW (21.29 ± 1.02 MPa) and FHW (21.76 ± 0.72 MPa) composites, showing that there is no effect of birch false heartwood on the tensile strength of WPCs. The modification of wood particles with 5 wt% of NaOH and 5 wt% of APTES slightly increased (6.7%) the tensile strength of the SW composites referring to the reduction of the interfacial tension and increasing the interfacial bonding between the wood filler and PP matrix. Similar increase with addition of APTES has also been reported in previous research by Kim *et al.* (2011). However, in case of birch false heartwood based WPCs samples, the modification of wood particles with 5 wt% NaOH and 5 wt% APTES did not influence the tensile strength of the WPCs. This can be attributed to the fact that false heartwood contains higher concentration of extractives, tyloses and phenolic compounds (Baum, Schwarze and Fink, 2000), (Wernsdörfer, 2005), (Hörnfeldt, Drouin and Woxblom, 2010). Moreover, previous studies have investigated that due to several low permeability compounds in the cell walls, it is very hard to impregnate the false heartwood (Hörnfeldt, Drouin and Woxblom, 2010), (Dömeny, Koiš and Paril, 2013).

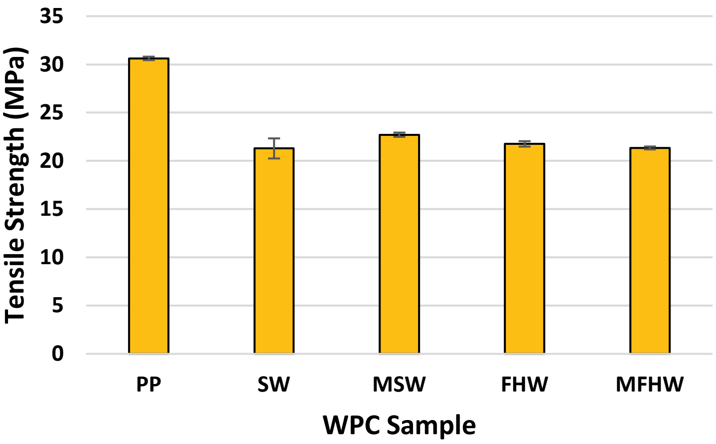


Figure 13. Influence of birch false heartwood on the WPC tensile strength.

3.1.2 Tensile modulus of elasticity of the WPC samples

Similar correlation to tensile strength results was also found with tensile MOE (see Figure 14). Tensile MOE (see Figure 14Fig 1b in Paper III) showed that adding the 60 wt% wood filler increases the material stiffness 160% in case of SW sample. The highest MOE (stiffness) of WPC samples was obtained with MSW composites (4.51 GPa ± 0.11 GPa), whereas the lowest result was obtained with MFHW composites (4.27 GPa ± 0.06 GPa). This results again shows that the modification of wood particles with APTES worked with birch sapwood increasing the tensile MOE of 5% compared to unmodified SW composites while the modification of false heartwood did not work, and MOE decreased.

From the tensile test results, it can be concluded that the birch false heartwood did not lower or increase the tensile properties. However, the small differences with false heartwood WPC samples and birch sapwood WPC samples were noted when modification of wood filler with APTES was carried out. It is seen that the modification of false heartwood is problematic.

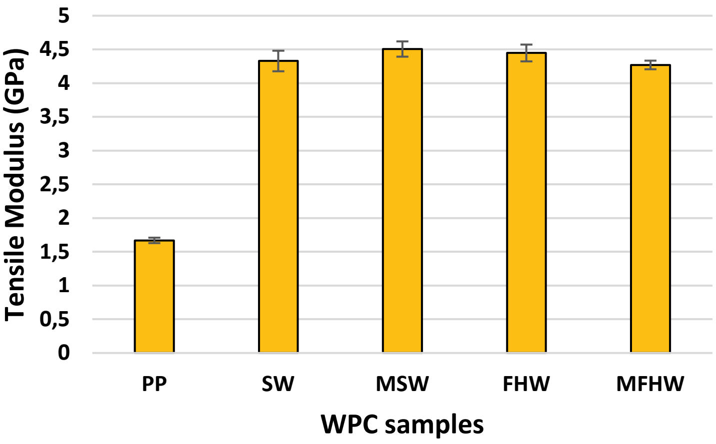


Figure 14. Influence of birch false heartwood on the WPC tensile MOE.

3.2 Flexural properties

3-point bending test was carried out to analyse the flexural property changes between birch sapwood based WPC samples and false heartwood based WPC samples. WPCs flexural strength greatly depends on the adhesion strength between polymer matrix and wood filler due to the stress which is carried over from the polymer matrix to the wood particles under loading.

3.2.1 Flexural strength of the WPC samples

In papers I-II, the influence of the chemical modification of birch wood particles on WPC interfacial strength was investigated. In these investigations (papers I-II), the 35 wt% of wood and 65 wt% PP was used. In paper II, it can be seen that the addition of 35 wt% wood filler to the PP matrix increased 10% of unmodified wood based composites flexural strength. A similar increase in flexural strength with 30–40% unmodified WF had also been noted in previous studies (Stark and Rowlands, 2003), (Karmarkar *et al.*, 2007), (Ndiaye *et al.*, 2012). The investigations also showed that increasing the wood particle fractions size decreases the flexural strength because composites with smaller wood particles are more homogenous than the ones with larger wood particles (paper I). The flexural strength results in Figure 1 in Paper II, showed that for the most cases the chemical modification enhanced the flexural strength. It was observed that the 5 wt% NaOH, PVA and AA modified wood-based WPC samples showed the lowest flexural strength and therefore indicated the poor interfacial adhesion between the PP matrix and wood filler. The best flexural strength was obtained with the esterification of the wood and APTES modification (papers I-II). Silane reactive groups provide covalent bonding with the OH-groups of wood particles and other chemical group connects with polymer by creating interfacial adhesion between the PP and wood. In Paper II and by Kim *et al.* (2011), it was noted, that NaOH modification of wood prior the silane modification significantly increases the flexural strength. Therefore, in further research in this thesis, the NaOH and APTES together was chosen as the main modification method of wood particles.

The effect of birch false heartwood on the flexural properties was investigated in Paper III. The results of the flexural strength and MOE are shown on Figure 15 and Figure 16 (Fig. 2 in Paper III), respectively. There was no significant increase in flexural strength when 60 wt% of birch sapwood or false heartwood was added to the PP matrix. The highest flexural strength was attained with the modification of birch sapwood wood particles with 5 wt.% of NaOH and 5 wt% of APTES, where the flexural strength increased 5% compared to neat PP. The low increase of flexural strength with high wood content, such as 60 wt% can be attributed to the decrease of interfacial bonding strength between the PP matrix and wood filler in the WPCs. According to Kim *et al.* (2011), increasing the wood content over 50 wt% in WPCs decreases the interfacial bonding strength between the wood filler and PP matrix due to the hydrophilic nature of wood. Same as tensile strength results in previous chapter, the SW composites flexural strength (45.70 ± 0.88 MPa) was similar to the FHW composites flexural strength (44.24 ± 1.11 MPa) showing that birch wood quality has no effect on the flexural properties of WPCs. According to Enquist and Pettersson (2000), study on the mechanical properties of false heartwood they found no significant differences in compared to sapwood which correlates with this research results. Modification effect of APTES was also same as in tensile strength results above, no differences after modification of false heartwood with APTES on the properties of WPCs was found. Therefore, it can be said again that false heartwood is hard to modify with chemicals due to the higher concentration of extractives, tyloses and phenolic compounds found in the cell walls (Hörnfeldt, Drouin and Woxblom, 2010).

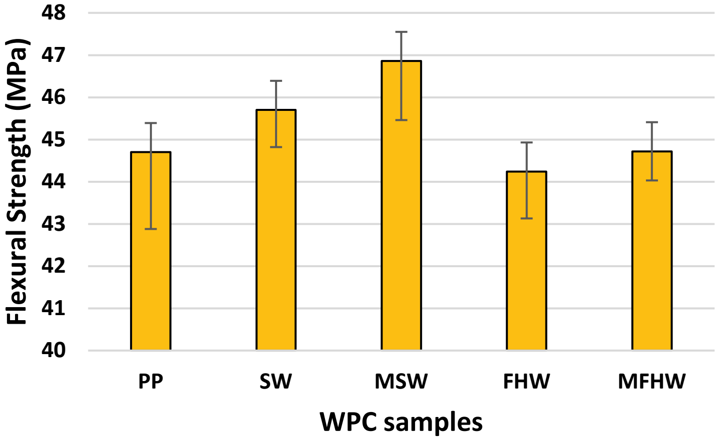


Figure 15. Influence of birch false heartwood on the WPC flexural strength.

3.2.2 Flexural modulus of elasticity of the WPC samples

In paper II, the effect of chemical modification on the flexural properties of WPCs was investigated. The MOE results of differently modified wood baes WPCs (see Figure 2 in paper II) show that the highest stiffness was achieved with four different chemical modifications: NaOH, PVA, APTES and AA. APTES. However, APTES showed the highest MOE (2.56 GPa) and therefore was chosen as the main modification method for further research (papers I and II).

From the flexural test results in Figure 15 and Figure 16 (see Fig. 2a and 2b in Paper III), one can notice that the changes in material stiffness are more substantial than flexural strength results. In Figure 16, when adding the 60 wt% of birch sapwood filler into the PP matrix, the MOE increases 219% by making the material al lot stiffer and at the same time brittle. The differences between birch false heartwood and sapwood filler are very small and in the range of experimental error (see Paper III, Fig. 2a and 2b). According to Bouafif *et al.* (2009), small differences were found on flexural strength and MOE in comparison of Cedar sapwood and heartwood based WPCs. In this research, it was seen that false heartwood had similar effect as normal heartwood in Cedar wood which proves that false heartwood can be used in the production of WPCs.

From the flexural test results, it can be concluded that the birch false heartwood did not lower or increase the flexural properties. That proves again that there is no significant difference of using the birch false heartwood or birch sapwood in the WPCs. However, the small differences with false heartwood WPC samples and birch sapwood WPC samples were noted when modification of wood filler with APTES was carried out.

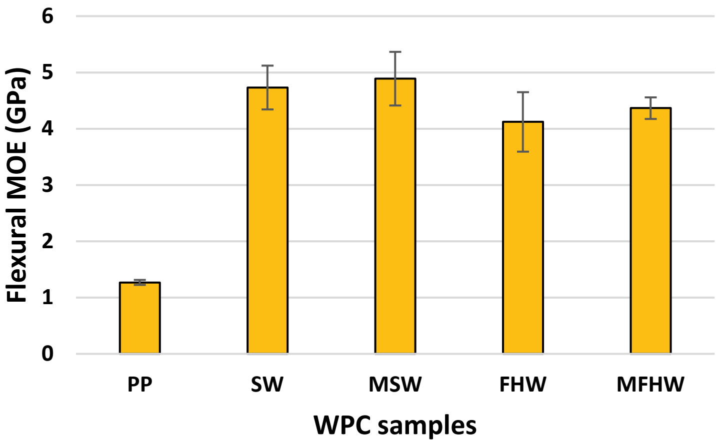


Figure 16. Influence of birch false heartwood on the WPC flexural MOE.

3.3 Long-term creep

3.3.1 Creep deflection of the WPC samples

WPCs both components (wood particles and PP) display viscoelastic behaviour. Therefore, to investigate the effect of birch false heartwood on the WPCS viscoelastic properties, the 24h creep tests were performed on both birch sapwood and birch false heartwood composites. As the fraction of the wood particles and type of PP in WPCs is constant, then time-dependent creep deflection is expected to be affected by the type of birch wood quality (sapwood or false heartwood). Figure 17 shows the time-deflection curves of the different WPC samples. The results show that false heartwood has no significant effect on WPCs creep behaviour. In general, all the WPC samples had the creep deflection differences at 1 mm range. From the previous research of Park and Balatinecz (1998), it is investigated that the creep strain in WPCs is mainly affected by the modulus of elasticity. This means that with lower modulus materials, the instantaneous creep is lower while the creep strain increase over time is mainly same in different WPCs. In this study, the MFHW composites had the lower modulus of elasticity than the other WPCs and therefore also the instantaneous creep deflection of MFHW composites is higher than other WPCs.

From the creep results (see Figure 17), the PP shows greatly higher creep deflection of all the WPC samples. With 60 wt.% wood filler content WPC samples show 285% lower creep deflection than compared to PP after 24h loading at 50% of maximum flexural load. This is due to the wood particles itself, which have high strength and stiffness and therefore cause brittleness of (in) the composites. According to Kazemi-Najafi, Nikray and Ebrahimi (2012), the highest creep deflection was observed for the PP and lowest for solid wood. Therefore, as pointed out in the other research by Wang *et al.* (2010), the creep deflections of various WPCs with different wood loading ratios decreases with increasing the wood loading while the instantaneous deflections shows no considerable differences.

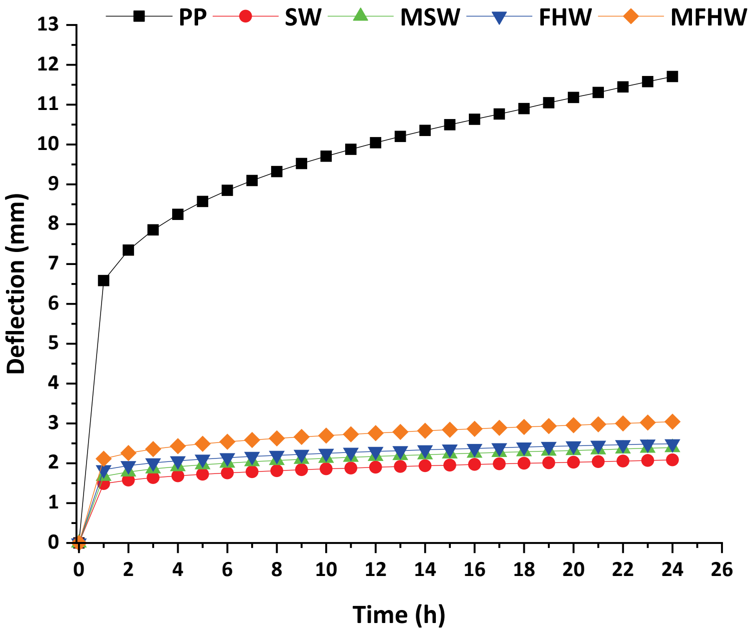


Figure 17. Influence of birch false heartwood in the WPC creep deflection.

3.3.2 Relative creep of the WPC samples

Figure 18 shows the relative creep of the studied WPC materials. For better comparison of WPC samples, the relative creep was investigated. Relative creep shows the increase in deflection compared to the initial elastic deflection. Results show that addition of the wood particles to the PP matrix has greatly decreased the relative creep. After 1 h loading, the PP produced 89% relative creep while the SW composites produced only 36% relative creep showing the improved creep resistance. Similar trend was observed by the Park and Balatinecz (1998), where they investigated that increasing the wood content steadily decreases the relative creep of the WPCs at 50% stress level.

When comparing relative creep of the SW composites to the FHW composites after 1 h of loading, then one can see that there are now significant differences. However, the relative creep difference of SW and FHW composites slightly increases during the time at every hour of 24 h loading period. This indicates that the FHW composites exhibit slightly higher resistance to creep loading compared to SW composites during the long-term creep. The addition of APTES has increased the relative creep for the both, MSW and MFHW composites due to the decreased MOE.

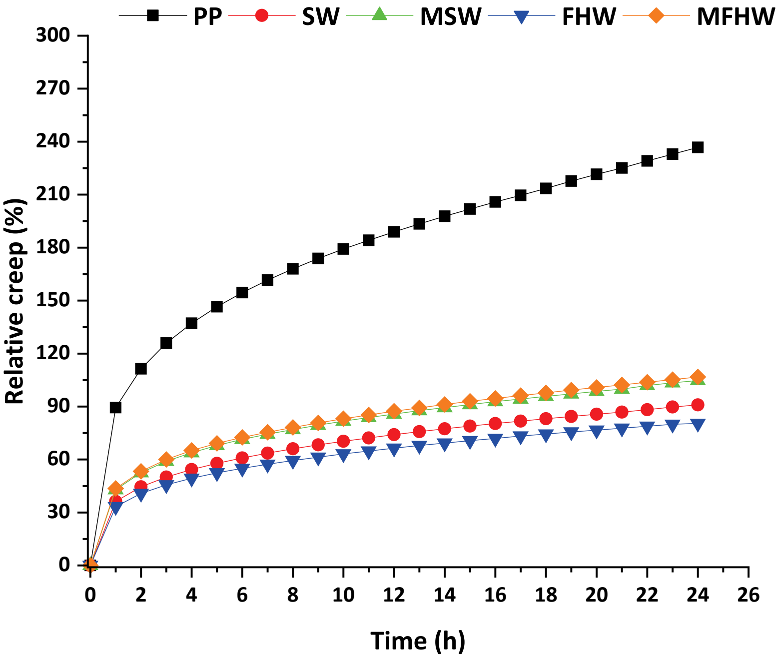


Figure 18. Influence of birch false heartwood on the WPC relative creep.

3.3.3 Creep rate of the WPC samples

Figure 19 shows the creep rate of WPSs samples studied. Results show that the creep rate is highest at the first hour in the initial stage and then decreases to the minimum on the second hour of measurement and becomes almost constant thereafter. Previous research by Kazemi-Najafi, Nikray and Ebrahimi (2012), has shown that the major creep rate changes with PP, WPC and solid wood is happening within the first 60 minutes of constant loading and then it becomes almost constant. The similar trend was also observed in this research.

In this study, the neat PP shows the highest creep rate of 10.73 mm/h at the initial stage. The addition of the wood particles to PP decreased the creep rate at the initial stage, however all the WPC samples showed similar creep rate. There were no differences between SW and FHW composites creep rates and, the addition of APTES did not affect the creep rate. According to Najafi and Najafi (2009), the lower MOE materials have higher deflections despite of the creep rate. In this study, the same trend was observed where the FHW composites have lower MOE and therefore higher creep deflection than SW composites, yet at the same time the creep rate of all the WPC samples is the same.

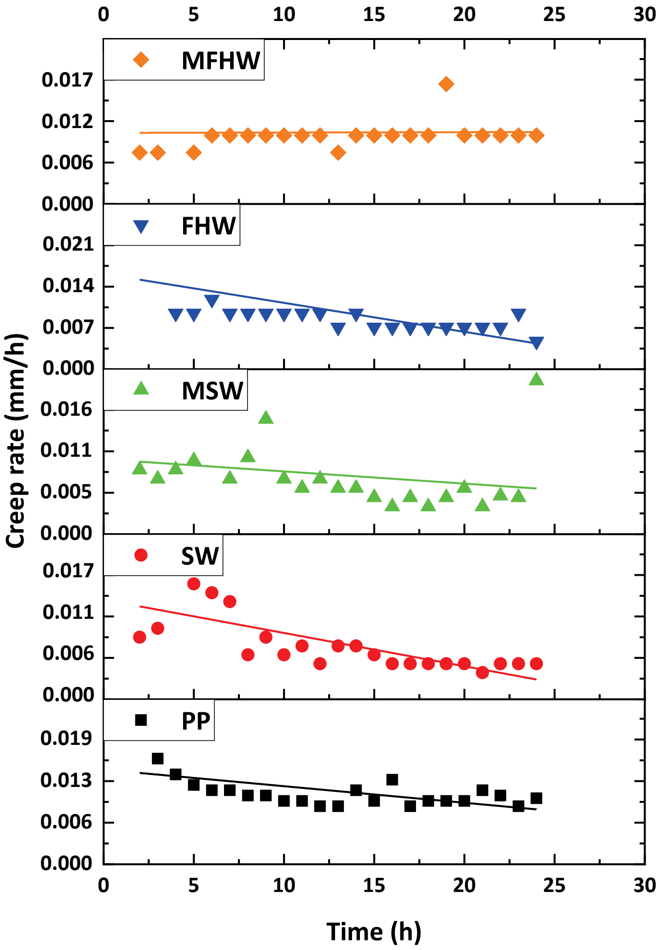


Figure 19. Influence of birch false heartwood on the WPC creep rate.

3.3.4 Creep modulus of the WPC samples

Creep modulus curves are shown on Figure 20. In general, it can be observed that the creep modulus for all the materials is highest at the initial stage and then decreases when time increases. Creep modulus differences for all the materials are highest after 1 h of loading. With the addition of wood particles to the PP matrix, the creep modulus greatly increases, indicating the reinforcing effectiveness of wood particles by making the materials stiffer. This stiffening effect is attributed to the cellulose because of its higher crystallinity (Riara, Merenga and Migwi, 2013). It was also already observed in static flexural test in this study. After 1 h of loading, the PP showed the highest (88.60%) decrease and FHW and SW composites showed the lowest (35.31% and 36.92%, respectively) decrease in creep modulus. At the end of the 1 h of loading the creep modulus in the SW and MSW composites decreased about 36.92% and 42.75%, respectively and in the FHW and MFHW composites about 35.31% and 43.53%, respectively. From these results it can be observed that the addition of APTES increased the decrease in creep modulus in both cases for MSW and MFHW composites after 1 h of loading by making the materials more elastic.

When looking at the 24 h loading period, the one can see that the creep modulus change decreases with time. The highest (235.71%) decrease in creep modulus after 24 h loading period was observed with neat PP while the lowest (83.34%) was observed with FHW composites. The addition of APTES had improved the decrease in creep modulus after 24 h of loading for both MSW and MFHW composites with 104.61% and 106.60%, respectively. This decreased stiffness can be attributed to the APTES modification of wood particles which has resulted somewhat increased elasticity of the wood during the modification process and improved wood particle dispersion in the PP matrix.

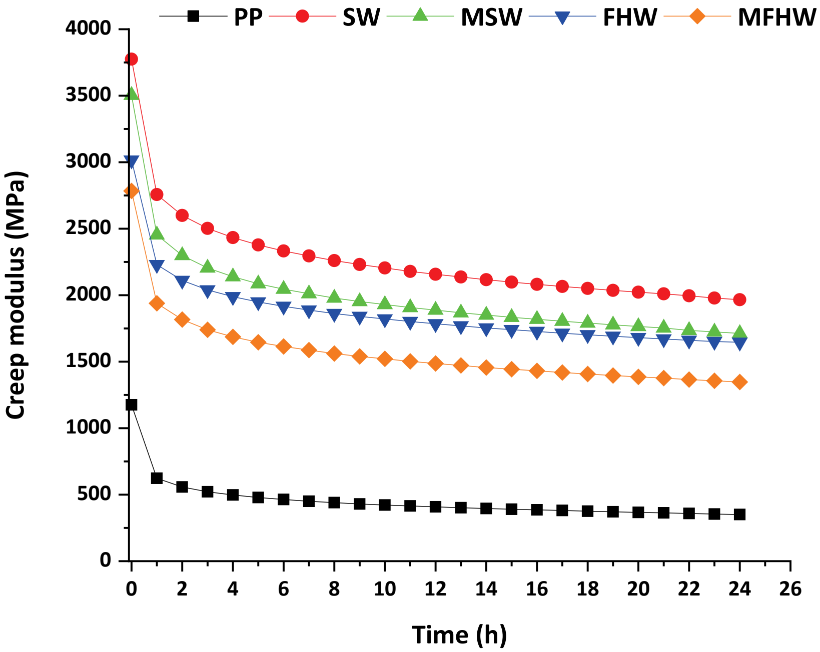


Figure 20. Influence of birch false heartwood on the WPC creep modulus.

3.3.5 Creep-recovery parameters of the WPC samples

In the Table 4 is presented the creep-recovery parameters from the experiment. As expected, it is clearly seen that the instantaneous and total deflection is highest for PP. With the addition of the wood particles, the deflection has greatly decreased, showing the growth of the material stiffness. FHW composites show a slightly higher instantaneous deflection than SW composites. However, the permanent deflection for the both, SW and FHW composites is similar. The addition of APTES has slightly increased both, the instantaneous deflection and permanent deflection indicating the reduction of the material stiffness. The percent recovery is also highest for the PP because of the high total deflection. APTES modified MSW and MFHW composites showed lower percent recovery than unmodified samples since they also had higher initial deflection and total deflections. Also, the fractional deflection was highest (3.04 mm) for the PP. Lowest fractional deflection (1.73 mm) was observed with FHW composites, indicating the higher creep resistance to long-term loading than other tested WPCs. The addition of APTES has also slightly increased the fractional deflection of the WPCs. Based on the long-term creep test, the false heartwood showed interesting results where it had the higher instantaneous deflection than SW composites, but lower total deflection and fractional deflection than SW composites. The permanent deflection after 24 h loading and 24 h recovery is also similar incense of FHW composites and SW composites (0.58 and 0.64, respectively). These results show that the false heartwood based WPCs have good durability to long-term creep loading.

Table 4. Creep-recovery parameters of studied materials.

Composites	PP	SW	MSW	FHW	MFHW
ID (mm)	3.48	1.09	1.17	1.38	1.47
TD (mm)	11.71	2.08	2.39	2.49	3.04
PR (%)	63.76	41.37	27.30	57.97	33.44
PD (mm)	1.26	0.64	0.85	0.58	0.98
FD (mm)	3.04	1.80	1.91	1.73	1.92

ID- instantaneous deflection; TD- total deflection; PR- percent recovery; PD- permanent deflection; and FD- fractional deflection.

3.4 Short-term cyclic creep

The creep-recovery curves of the short-term cyclic creep of materials are presented in Figure 21. In general, the short-term cyclic creep results show that the addition of the wood particles into the PP matrix greatly decreases the deflection of the material compared to the neat PP due to the stiffness of wood particles itself, which results in WPCs increased brittleness of. Similar effects have also been noted by Lee *et al.* (2004). The results show that increasing the load increases the creep rate for all the materials.

It can be also observed that the residual deflection of WPC increases with increasing the load. The higher the creep deflection is then the higher is also the residual deflection. The highest creep rate was observed for neat PP and the lowest creep rate was observed for the birch sapwood composites. According to Lee *et al.* (2004), Mukhopadhyay and Srikanta (2008), Najafi and Najafi (2009), Kazemi-Najafi, Nikray and Ebrahimi (2012), increasing the wood content in PP matrix decreases WPCscreep deflection . However, all WPC samples are showing similar creep deflection and differences are in the range of 1 mm. This proves that the birch false heartwood has similar mechanical properties as birch sapwood.

When comparing WPCs, then it is clearly seen that the MFHW composite samples show the highest creep deflection, which is also shown in flexural test results that the stiffness of MFHW composite samples is the lowest. There is only very little increase of creep deflection at 30% loading level after 60 min loading. The average creep deflection of WPCs samples after 60 min loading at 30% loading level is just 0.56 mm. At the same loading level, neat PP exhibits 1.74 mm of creep deflection, which is 210% higher than WPCs. After 60 min loading at 50% loading level, the MFHW composites show a little higher (1.67 mm) increase in creep deflection than other WPC samples (1.24 mm). At 70% loading level and after 60 min loading it is interestingly seen that the creep deflection of MSW composite (3.08 mm) has increased 25% more than SW composite (2.46 mm). At the same loading level, also the MFHW composite creep deflection (3.90 mm) is 56% higher than FHW composite creep deflection (2.50 mm). At the end of the 70% of loading level these composites were already significantly damaged and some of the samples broke during the test. This shows that the APTES modification of wood particles had increased the brittleness and made WPCs more fragile, which is also been confirmed from the previous results of static flexural test and tensile test.

When looking at the creep-recovery curves, one can see that when increasing the load levels then instantaneous deflections, recovery and permanent deflections are increased with increasing load levels. Instantaneous deflections are highest at the 70% loading level and at this loading level all the materials exhibit tertiary creep stage and had the creep-induced structural damages. It was also observed that during the 70% loading stage, one or two out of five specimens of each WPC sample had creep rupture before the end of loading cycle. According to Xu (2002), the creep strain in WPCs is primarily influenced by the modulus of elasticity of the composites. This shows that low modulus materials have higher instantaneous creep.

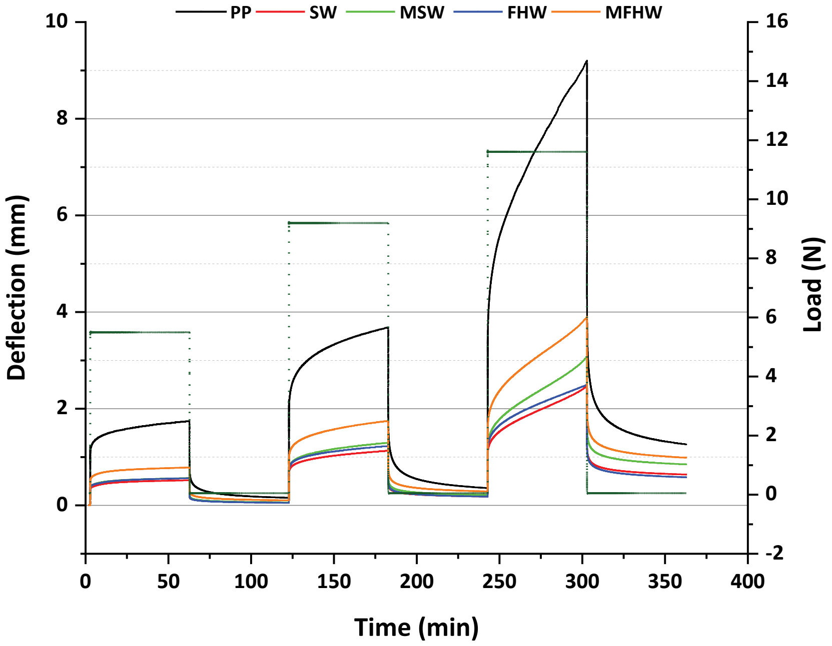


Figure 21. Influence of birch false heartwood on the WPC cyclic creep loading.

3.5 FTIR spectroscopy

The FTIR spectra of the composites are presented in and Figure 23 (see Figs. 5a and 5b in Paper III). The spectra shows a similar pattern for all the samples, except for a few peaks that were not visible in the PP spectrum, but only in composites. In the wood fingerprint region (see and Fig. 5a in Paper III), the WPC showed a difference in the band absorption intensity, which was expected. The wide peak at 3347 cm-1 in the region 3400 cm^{-1} to

3200 cm^{-1} is assigned to –OH (hydroxyl) groups mainly from cellulose. However, the peak intensity had decreased due to the polarity reduction the surface of wood particles after modification (Lv *et al.*, 2015). The hydroxyl group intensity was affected by the sodium hydroxide treatment which had decreased the absorption of hydroxyl groups for modified WPC samples and absorption peaks became narrower. According to Farsi and Ghasemi (2010), this indicates the emerging of amorphous region in the wood cellulose by removal of hydroxyl groups from its chain and reduction of the polarity on the wood surface. The intense peak at 2915 cm^{-1} was due to the C-H stretching in $–CH_2–$ groups. The key absorption bands of PP (see and Fig. 5a in Paper III) included 1457 cm^{-1}, 1374 cm^{-1}, and 981 cm^{-1} (CH_3 bending) (Morent *et al.*, 2008). The birch sapwood had the high hemicellulose carbonyl groups peaks at 1736 cm^{-1} and 1602 cm^{-1} which had decreased with NaOH treatment.

It is clearly seen that the WPC samples had very strong peaks at 1049 cm^{-1}, 668 cm^{-1} and 612 cm^{-1}. To make it clearer the magnification of these ranges of the FTIR wavenumbers for modified and unmodified birch sapwood and false heartwood composites are shown on Figure 23 (see Fig. 5b in Paper III). The peak at 1049 cm^{-1}, shown on Figure 23 (see Fig. 5b in Paper III) is attributed to primary alcohols and aromatic ether (C-O) stretching vibrations (cellulose, hemicellulose, and lignin) (Chen et al., 2017). The birch sapwood composites showed the highest absorbance, at 1049 cm^{-1} compared to false heartwood composites and modified composites, indicating that false heartwood had less hydroxyl groups available. Bankole, Rohumaa and Kers (2016) have also reported this in their research. The APTES modification effect was responsible for the peak changes at 1049 cm^{-1}, which corresponded to the Si-O-C band. The intense peaks at 1049 cm^{-1} and 668 cm^{-1} was from the reaction between the hydroxyl groups of cellulose and that of silanol on the wood surface, which created Si-O-Si- and -Si-O-C ether bonds (Ma, Wang and Chu, 2017). In Figure 23 (see Fig 5b in Paper III), it can be observed that peak intensity for the modified sapwood and false heartwood had decreased at the corresponding range of 1049 cm^{-1}, 668 cm^{-1} and 612 cm^{-1}. This can be explained with the reduced number of primary alcohols on the wood surface. In addition, the absorption peaks shapes have flattened, indicating the decrease of –OH bonds formed between the –OH groups (Lv *et al.*, 2015).

From the FTIR results, it is seen that the APTES have reacted with both sapwood and false heartwood but there is no visible reaction peak between the APTES and PP. That is also the main reason why the mechanical properties were not significantly improved by the APTES modification in this research. Also, it can be observed that the false heartwood modification was more difficult due to the lower number of available –OH groups.

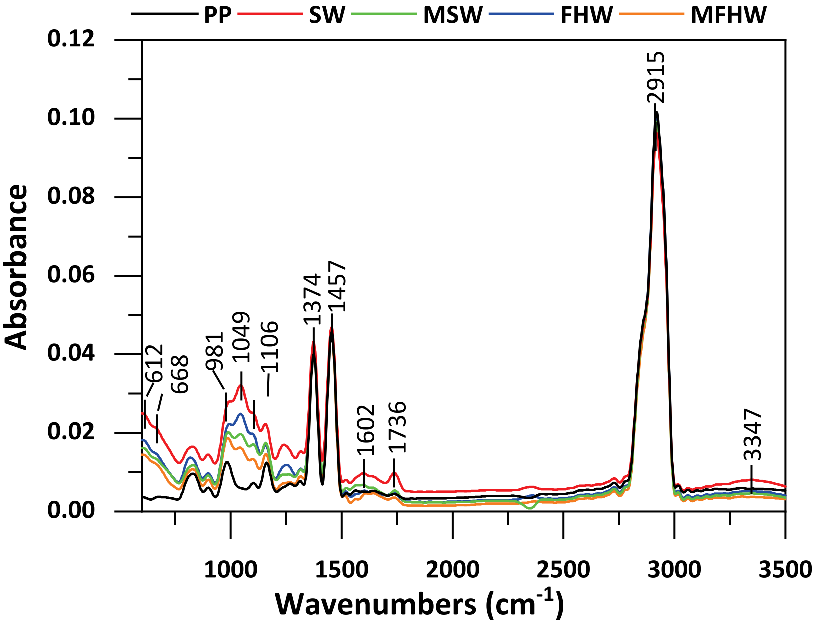


Figure 22. Influence of birch false heartwood on the WPC FTIR spectra.

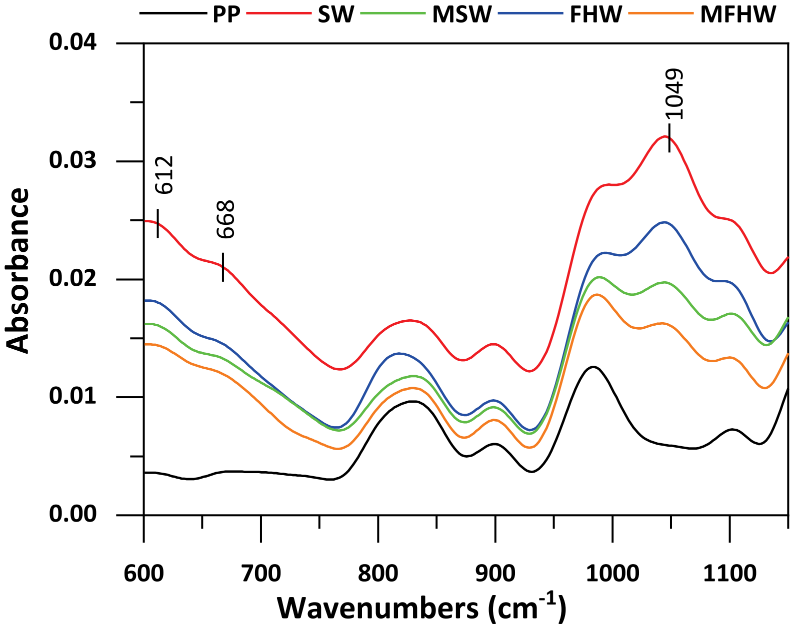


Figure 23. Influence of birch false heartwood on the fingerprint area of APTES modification in WPC.

Conclusions

The aim of this thesis was to explore the usage of birch false heartwood as filler material on the properties of wood-plastic composites. For that purpose, several chemical modifications of birch wood were tested, and birch false heartwood and sapwood filler were used in WPCs. In the analysis part, various mechanical tests such as tensile test, flexural test, long-term creep test, and short-term cyclic creep test were carried out. In addition, the density and FTIR measurements were done. Based on the study, the following conclusions can be made:

1. The addition of 60 wt% of birch false heartwood or birch sapwood decreased the tensile strength by 40% for both wood filler types. This decrease is due to the high wood loading content and random distribution of the particles that create decrease the interfacial bonding between the polymer matrix and wood filler and causing the microscopic cracks. The use of false heartwood instead of sapwood in WPCs did not have any additional decrease in tensile strength. However, the modification of birch false heartwood with APTES did not improve the tensile strength. This cause was explained with higher concentration of extractives, tyloses and phenolic compounds in the false heartwood which makes it less impregnable with chemicals.
2. In flexural properties, it was discovered that the presence of birch false heartwood did not have any negative effect on the flexural strength for the composites with 60 wt% wood loading level. The flexural strengths of birch sapwood composites and birch false heartwood composites had very similar flexural strengths (45.70 MPa and 44.24 MPa, respectively). This evidence confirms once again that birch false heartwood does not have negative influence on WPCs strength properties.
3. The MOE in tensile of the material increased 160% for both, false heartwood and sapwood composites and there was no additional influence of false heartwood on material stiffness. The stiffness in flexural was increased 219% in case of birch sapwood WPCs. The false heartwood had slightly lower increase in flexural stiffness after APTES modification, which can be explained with false heartwood structure that is hard to impregnate.
4. Studies confirmed that birch false heartwood did not have any significant negative impact on WPCs long-term flexural creep properties. The creep deflections after 24h loading were found to be in the range of 1 mm for the all WPCs. Creep rate for all the composite was highest within the first hour of loading and then became constant. FHW composites showed slightly lower (4%) decrease (83.34%) in creep modulus after 24 h loading whereas sapwood composites had 87.50% decrease in creep modulus. The permanent deflection after 24 h loading and 24 h recovery is also similar for FHW and SW composites (0.58 mm and 0.64 mm, respectively). This shows that false heartwood composites have even slightly better resistance to creep loading than sapwood composites.
5. According to the current research, the false heartwood composites had the same creep deflections and creep recovery deflections as sapwood composites at each loading level during 60 minutes of loading and 60 minutes of recovery. APTES modification of false heartwood and sapwood has increased the creep deflection in both cases. APTES modified FHW composites showed the

significant damaged after 70% of loading level confirming the more fragile behaviour of modified false heartwood composites than sapwood composites.

6. The APTES modification was observed with FTIR test which confirmed the peak intensity changes at 1049 cm-1, 668 cm-1 and 612 cm-1 showing the availability of hydroxyl groups for APTES modification. It was shown that false heartwood had less hydroxyl groups available to modify with APTES and therefore the modification effect is lower than for sapwood composites.

The novel WPCs with birch false heartwood filler and PP matrix were developed in this thesis. Based on the results of this thesis, it was discovered that birch false heartwood gives good results and has great potential to be used in WPCs. There was no significant decrease in mechanical properties and creep deflections when birch false heartwood was used as filler material in the composites instead of birch sapwood. Therefore, birch false heartwood can also be used in WPCs instead of just birch sapwood. However, there is a need to improve the chemical modification of false heartwood and investigate the long-term durability of the false heartwood WPCs in outdoor environment.

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References

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Abstract

The Influence of Birch (*Betula pendula*) False Heartwood on the Mechanical Properties of Wood-Plastic Composites

Birch (*Betula pendula*) often develops a brownish-reddish discoloration in its sapwood which is referred to as red heartwood or false heartwood. The utilization of this false heartwood has been a concern in the wood industry, because this discoloration is a wood defect that leads to the price reduction of the material. Therefore, there is the need to investigate ways to use birch false heartwood by giving it more value and maximizing the outcome of quality birch wood. One possible option could be utilizing the birch false heartwood as wood filler material in the wood plastic composites (WPC). There have been no studies published on the birch false heartwood usage as filler material in wood-plastic composites. Therefore, this research seeks to fill this gap and investigate the utilization of birch false heartwood as filler material in WPCs. The aim of this research was to investigate the effect of birch false heartwood on the mechanical properties of the WPCs.

In this research, the birch wood (both the sapwood and the false heartwood) was used as filler material. Polypropylene (PP) was used as matrix material. It was also investigated how the birch false heartwood chemical modification would affect the improvement of WPCs properties. For modification, the wood particles were treated with 3-aminoprophyl-triethoxysilane (APTES). The wood particles were then mixed with the PP in the ratio 60 wt% of wood to 40 wt% of PP in the co-rotating twin-screw compounder. The compounded composites were then injection moulded into standard test samples. The resulting composites were grouped into four categories: birch sapwood, modified birch sapwood, false heartwood, and modified false heartwood. Neat polypropylene samples were produced as a reference. Mechanical properties of the WPC-s were tested with tensile test, 3-point flexural test, and flexural long-term and short-term cyclic creep tests. The effect of modification was analysed using Fourier Transform Infrared Spectroscopy (FTIR).

The use of false heartwood instead of sapwood in the WPCs did not have any additional decrease in tensile strength. However, the modification of birch false heartwood with APTES did not improve the tensile strength. This cause can be explained by higher concentration of extractives, tyloses and phenolic compounds in the false heartwood which makes it less impregnable with chemicals. In flexural properties, it was found that the presence of birch false heartwood did not have any negative effect on the flexural strength for the composites with 60 wt% wood loading level. The flexural strengths of birch sapwood composites and birch false heartwood composites had very similar flexural strengths (45.70 MPa and 44.24 MPa, respectively).

Studies confirmed that birch false heartwood did not have any significant negative impact on the long-term flexural creep properties of the WPCs. The creep deflections after 24 h loading were found to be in the range of 1 mm for the all WPCs. False heartwood composites had lowest decrease (83.34%) in creep modulus after 24 h loading whereas sapwood composites had 87.50% decrease in creep modulus. The permanent deflection after 24 h loading and 24 h recovery is also similar for FHW and SW composites (0.58 mm and 0.64 mm, respectively). This shows that false heartwood composites possess even slightly better resistance to creep loading than sapwood composites. According to the current research, the false heartwood composites had the same creep deflections and creep recovery deflections as sapwood composites at each loading level

during 60 minutes of loading and 60 minutes of recovery. APTES modification of false heartwood and sapwood had increased the creep deflection in both cases. It was shown with FTIR analyses that false heartwood had less hydroxyl groups available to modify with APTES and therefore the modification effect is lower than in sapwood composites.

Based on the results of this thesis, it was found that birch false heartwood gives good results and has great potential to be used in the WPCs. There was no significant decrease in mechanical properties and creep deflections when birch false heartwood was used as filler material in the composites instead of birch sapwood. Therefore, birch false heartwood can also be used in the WPCs instead of just birch sapwood. However, there is a need to improve the chemical modification of false heartwood and investigate the long-term durability of the false heartwood WPCs in the outdoor environment.

Lühikokkuvõte

Kase (*Betula pendula*) väärlülipuidu mõju puitplastkomposiitide mehaanilistele omadustele

Kasel (*Betula pendula*) tekib tihti kasvamise käigus puidu südamikku pruunikaspunane värvimuutus mida nimetatakse punasüdamikuks või väärlülipuiduks. See väärlülipuit on puidurike, mis on puidutööstuses kasepuidu kasutamisel probleemiks ja alandab puitmaterjali hinda. Seetõttu on oluline uurida, kuidas oleks võimalik kase väärlülipuitu ära kasutada andes sellele kõrgemat väärtust ning seeläbi parandada kvaliteetse kasepuidu väljatulekut puidutööstuses. Üheks võimaluseks on kase väärlülipuidu kasutamine puitplastkomposiitide täiteainena. Seni pole kirjanduses kirjeldatud kase väärlülipuidu kasutamist puitplastkomposiitides. Täitmaks seda tühimikku, uuriti antud doktoritöös kase väärlülipuidu kasutamist puitplastkomposiitide valmistamiseks. Käesoleva doktoritöö eesmärgiks oli uurida kase väärlülipuidu mõju puitplastkomposiitide mehaanilistele omadustele ja vastupidavusele.

Antud doktoritöös kasutati puitplastkomposiitide täiteainena kasepuitu (maltspuitu ja väärlülipuitu) ja maatriksina kasutai polüpropüleeni (PP). Töös uuriti ka kase väärlülipuidu keemilise modifitseerimise võimalust puitplastkomposiitide omaduste parandamiseks. Kasepuidu modifitseerimiseks kasutati 3-aminopropüül-trietüksüsilaani (APTES). Komposiitide segud valmistati koostisega 60% massist puitu ja 40% massist PP ja segati kokku kaheteolises kompaunderis. Kompaunditud segudest valmistati seejärel survevalu seadmega standardikohased katsekehad. Valmistatud komposiidid jagati nelja gruppi: kase maltspuiduga, modifitseeritud kase maltspuiduga, väärlülipuiduga ja modifitseeritud kase väärlülipuiduga komposiidid. Lisaks kasutati etalonkatsekehana võrdluseks puhast PP-d. Puitplastkomposiitide mehaanilisi omadusi katsetati tõmbekatsel, 3-punkti paindekatsel, pikaajalisel paindekoormusega roomekatsel ja lühikesel tsüklilisel paindekoormusega roomekatsel. Keemilise modifitseerimise mõju uuriti Fourier' teisendusega infrapunaspektroskoopiaga. (FTIR).

Kase väärlülipuidu kasutamine maltspuidu asemel ei vähendanud puitplastkomposiitide tõmbetugevust. Seevastu kase väärlülipuidu modifitseerimine ei parandanud aga komposiitide tõmbetugevust nagu seda oli näha maltspuiduga komposiitide puhul. Selle põhjuseks on ekstraktiivainete, tülooside ja fenooliühendite suurem osakaal väärlülipuidus, mis takistavad immutamist erinevate kemikaalidega. Paindekatse tulemused näitasid et kase väärlülipuidu lisamine 60% massist osakaaluga ei muutnud puitplastkomposiitide omadusi kehvemaks võrreldes kase maltspuiduga komposiitide painde tulemustega. Kase maltspuiduga ja kase väärlülipuiduga puitplastkomposiitide omadused olid väga sarnased (vastavalt 45.70 MPa ja 44.24 MPa).

Pikaajalise paindekoormusega roomekatse tulemused näitasid, et kase väärlülipuidul ei olnud mingit negatiivset mõju puitplastkomposiitide roomele. Kõikide puitplastkomposiitide läbipaine peale 24 tundi koormust oli 1 mm piires. Kase väärlülipuiduga komposiidid näitasid kõige väiksema roome elastsusmooduli vähenemist (83,34%) peale 24 tundi. Võrdluseks, kase maltspuiduga komposiitide roome elastsusmooduli vähenemine oli 87,50%. Katsete tulemused näitasid, et peale 24 tundi paindekoormust ja 24 taastumist olid kase väärlülipuiduga komposiitide jääkdeformatsioon kõige väiksem ja sarnane kase maltspuiduga komposiitidele (vastavalt 0,58 mm ja 0,64 mm). Seega näitavad antud doktoritöö tulemused, et kase väärlülipuiduga komposiitidel on isegi natuke parem vastupidavus roomele kui tavalisel maltspuiduga komposiitidel. Tsüklilisel painekoormusega roomekatsel olid kase

väärlülipuiduga komposiitide ja kase maltspuiduga komposiitide läbipainded ja jääkdeformatsioonid samasugused peale vastavalt peale 60 minutit koormust ja 60 minutit taastumisperioodi. APTES-ga kasepuidu modifitseerimine suurendas väärlülipuiduga komposiitide ja ka maltspuiduga komposiitide läbipainet. Kusjuures, peale 70% koormustaset purunesid umbes pooled modifitseeritud kasepuiduga kasekehasid vahetult enne katse lõppu. Seega muutis APTES-ga puidu modifitseerimine komposiidid rabedamaks. FTIR katsetulemused näitasid, et kase väärlülipuidul on vähem hüdroksüülrühmasid, mida saab APTES-ga modifitseerida ja seetõttu on ka väärlülipuidu modifitseerimine keerulisem ja selle mõju komposiitidele väiksem.

Käesoleva doktoritöö tulemused näitasid, et kase väärlülipuit annab häid tulemusi ja omab suurt potentsiaali puitplastkomposiitides täiteainena kasutamiseks. Kase väärlülipuit ei vähendanud puitplastkomposiitide mehaanilisi omadusi ja läbipainde omadusi pikaajalisel roomekatsel võrreldes kase maltspuiduga komposiitide tulemustega. Seetõttu võib antud doktoritöö tulemuste põhjal järeldada, et kase väärlülipuitu võib kasutada ka kase maltspuidu asemel puitplastkomposiitide täiteainena. Edasisse uurimustöös tuleks keskenduda kase väärlülipuidu keemilise modifitseerimise parandamisele ja uurida kase väärlülipuiduga puitplastkomposiitide vastupidavust väliskeskkonnas.

Appendix 1

Publication I

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The influence of accelerated weathering on the mechanical and physical properties of wood-plastic composites

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Abstract. This research concentrates on the effect of moisture absorption and UV radiation on the mechanical and physical properties of wood-plastic composites (WPC). The goal is also to evaluate the importance of wood flour fraction size on the mechanical properties of WPC and their influence on the accelerated weathering results. Wood flour reinforced composites with three different fractions of wood flour made from birch (*Betula*) chips were prepared. Additionally, Bleached-Chemi-Thermo-Mechanical aspen (*Populus tremula*) pulp (Aspen BCTMP) was used. Thermoplastics (LLDPE-g-MAH, PP) were used to prepare composites. Wood flour and BCTMP surface were treated with two different coupling agents: 3-aminopropyltriethoxysilane (APTES) and polyvinylalcohol (PVA). The WPC specimens were prepared by injection molding. Accelerated weathering tests were carried out to evaluate the influence of weathering on the mechanical and physical properties of composites. Three-point bending test and Charpy impact test were used to test mechanical properties. The test results showed that using wood flour as a filler material in composites made the WPC material more rigid and brittle. Due to the water absorption and swelling of WPC, the flexural modulus (MOE) and strength decreased and impact strength increased by making the material weaker with increasing the deflection of the WPC. The UV radiation decreased the composites flexural strength and MOE, while impact strength was increased. After the accelerated weathering cycles, cracks and voids were found on the surface of the WPC materials. After the UV radiation treatment, also the WPC colour was lightened.

Key words: wood-plastic composites, wood flour, coupling agent, mechanical properties, physical properties, weathering.

1. INTRODUCTION

Wood-plastic composites (WPC), based on wood flour and polyolefins, have been of interest scientifically as well as commercially, because WPC combines the best properties of both polyolefins and wood particles. For example, compared to wood, WPC has higher moisture resistance, rot resistance, split resistance, distortion resistance, UV resistance and does not need to be painted. WPC also has better durability (8–15 years) compared to wood (3 years) [1]. WPC properties depend on the features of their constituents like the wood particle size and binding the wood particles to the polymer matrix using coupling agents. WPC material properties are also influenced by different polymer types, wood filler content, additives and processing technologies.

WPC mechanical properties are influenced by weathering conditions (moisture and UV radiation effect) and therefore using this material outdoors makes it sensitive to changes in the environment. The natural weathering or accelerated weathering of WPC materials can change their colour and mechanical properties [2]. WPC two major components, wood and polymer, are both vulnerable to weathering and, therefore, it is necessary to evaluate water absorption and UV radiation effect on WPCs.

WPC consists of hydrophobic polymer matrix and hydrophilic wood, in form of flour, fibers or particles [3]. Due to the wood hydrophilic nature, moisture absorption of WPCs will mainly occur in the wood component [3,4]. Therefore, it is very important to have

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strong bonding between wood fibers and thermoplastic polymers in order to avoid unwanted effects on the WPCs dimensional stability and mechanical properties [4]. For that reason, different surface treatments are used before improving wood/polymer adhesion in WPCs [5]. Maleic anhydride is typically used as a coupling agent in composites and different silane coupling agents are used for wood fibre surface treatments [6]. Also, polyvinyl alcohol (PVA) has been used for wood fibre surface treatment due to the strong bonding with wood [7,8]. This improves the adhesion and wetting between the polymer matrix and wood filler in the composites. On the surface of the WPC, wood particles are covered with a thin layer of the polymer matrix by making the WPC relatively water-resistant material. However, UV radiation can cause degradation of this thin polymer surface layer resulting in a decreased water resistance [2,4]. Due to the degradation of this thin surface layer, water absorption into the composites can occur through gaps and flaws at the interfaces between wood fibres and thermoplastic matrix resulting in the reduction of the mechanical properties of WPCs [4].

WPCs are also very susceptible to UV radiation degradation. Photodegradation affects all the main components of wood such as cellulose, hemicellulose, lignin, and extractives. Lignin is found to be more sensitive to degradation than other wood constituents (lignin absorbs from 80% to 95% of UV light). Photodegradation of lignin results in the discoloration of wood. Photochemical reactions in wood are initiated by the UV radiation causing the formation of free radicals, which causes the degradation of lignin and photooxidation of cellulose and hemicelluloses, leading to discoloration of wood [9]. In WPCs, UV radiation also causes photodegradation of polyolefins through the radical-based process. Due to the photodegradation, polymer dimensions change in all scales (monomer unit, chain, morphology, and on the macroscopic scale). Therefore cracks can occur and propagate on the composite surface which result in light diffusion and decrease of mechanical properties [9,10].

The aim of this study was to investigate the influence of wood particle size, UV radiation, and moisture absorption to the WPC structure, mechanical and physical properties. Therefore WPCs were made using three different wood particle fraction sizes. Wood particle surface was treated with different coupling agents (silane or polyvinyl alcohol). WPC test specimens were made by injection molding. The behaviour of these materials was studied after accelerated weathering: bending and impact tests were made to evaluate mechanical properties of the composites, and surface changes were observed by SEM and colour measurement.

2. MATERIALS AND METHODS

2.1. Polymers and wood fillers

Two different thermoplastics were used: pelletized polypropylene (PP) from the Borealis Polymers OY company and Fusabond E (MB226DE) from the DuPont enterprise. PP was heterophasic copolymer (block copolymer) and Fusabond E was maleic-anhydride-grafted linear low-density polyethylene (LLDPE-g-MAH). Physical properties of the polymers used are given in Table 1.

Two different types of wood raw material were used as a reinforcing filler in the composites. Birch (*Betula*) chips were brought from the UPM Kymmene Otepää AS firm and then refined to appropriate fractions using disintegrator device DS-A. After the refining process, three different fraction sizes of birch wood particles were obtained (Table 2). Additionally Bleached-Chemi-Thermo-Mechanical aspen (*Populus tremula*) pulp (Aspen BCTMP) from company AS Estonian Cell was used. Quality of Aspen BCTMP was HB 450/80. As Aspen BCTMP was in the form of large chips, it was ground to the fine flour (particle size ≤0.126 mm) using cutting mill Retsch SM100.

2.2. Coupling agents

Three different coupling agents were used to improve adhesion between the polymer matrix and the filler. LLDPE-g-MAH was added to the PP composites, 5% of the wood fibre content (Table 3). Wood flour was treated with two different coupling agents: 3-aminopropyltriethoxysilane (APTES) and PVA. Both coupling agents bond to the wood through OH-groups creating a hydrogen bond. APTES was mixed (5% of the wood fibre content) with solution of ethanol and destilled water (ratio of the substances was 9 : 1) and sprayed over wood flour. For PVA, water solution was made, 5% PVA was added to the wood fibre content and solution was sprayed on wood flour.

Table 1. Physical properties of polymers

Properties	Fusabond E (MB226DE)	PP (BC245MO)
Density, g/cm^3	0.93	0.905
Melt flow rate, g/10 min	1.75	3.5
Metling point, °C	120	166
Conditions of use, °C/2.16 kg	190	230

Table 2. Measurements of birch wood particles

Fraction	Size, mm
I	≤0.63
II	0.63–1.25
III	1.25–2

Table 3. Composition of WPC samples

Sample	Polymer	Coupling agent	Polymer coupling agent, wt%	WF fraction, mm	WF coupling agent	WF coupling agent, wt%	Polymer/ wood, %
PP1	PP	LLDPE-g-MAH	5				100
PP2	PP	LLDPE-g-MAH	5	BCTMP			80/20
PP3	PP	LLDPE-g-MAH	5	BCTMP	APTES	5	80/20
PP4	PP	LLDPE-g-MAH	5	BCTMP	PVA	5	80/20
PP5	PP	LLDPE-g-MAH	5	I	APTES	5	65/35
PP6	PP	LLDPE-g-MAH	5	II			65/35
PP7	PP	LLDPE-g-MAH	5	II	APTES	5	65/35
PP8	PP	LLDPE-g-MAH	5	II	PVA	5	65/35
PP9	PP	LLDPE-g-MAH	5	III	APTES	5	65/35
LLDPE1	LLDPE-g-MAH						100
LLDPE2	LLDPE-g-MAH			BCTMP			80/20
LLDPE3	LLDPE-g-MAH			BCTMP	APTES	5	80/20
LLDPE4	LLDPE-g-MAH			BCTMP	PVA	5	80/20
LLDPE5	LLDPE-g-MAH			I	APTES	5	65/35
LLDPE6	LLDPE-g-MAH			II			65/35
LLDPE7	LLDPE-g-MAH			II	APTES	5	65/35
LLDPE8	LLDPE-g-MAH			II	PVA	5	65/35
LLDPE9	LLDPE-g-MAH			III	APTES	5	65/35

2.3. Composite processing

After mixing the wood particles with coupling agents, wood flour was dried at 110 °C in an air-circulating oven for 2 h and then mixed thoroughly with polymer matrix in mortar. All composites made of wood flour as a filler were prepared with 65% polymer and 35% wood flour (WF). Aspen BCTMP composites were prepared with 80% polymer and 20% wood flour. Also 3% (by weight of the mixture) calcium stearate and silicone oil were added to the mixture in order to improve the fluidity of the mixture in the extruder. Mixture of composites is shown in Table 3.

The mixture was then compounded in twin-screw extruder Brabender Plasti-Conder PLE 651 at 175 °C for LLDPE-g-MAH and 185 °C for PP to produce homogeneous composite pellets. The screw speed was 30–40 rpm. Test samples were prepared by injection molding of the WPC pellets according to ISO 178:2010. Battenfeld BA 230 E device was used for injection molding. Test samples dimensions were 60 mm × 10 mm × 4 mm, cross-section area was 40 mm^2.

2.4. Methods of testing

2.4.1. Weathering

Water absorption, swelling, and resistance to the UV radiation of the composites were tested. For testing the resistance to UV radiation, at least five test samples were selected from each experimental group. Composite resistance to the UV radiation was tested according to the EN ISO 4892-3:2006. The composite samples were placed in the UV radiation chamber that was equipped with two UVC radiation lamps: Philips 30 W, G30T8 UV-C and 15 W, G15T8 UV-C. Wavelength of UV lamps was in the range of 250 nm. Test was carried out at room temperature, 23 °C. Composite samples were placed in the UV radiation chamber and the exposure cycle was carried out for 3 weeks (500 h). After the exposure cycle ended, the samples were removed for colour measurements and mechanical testing.

For water absorption and swelling experiments a minimum of five samples were tested for each composite. Tests were carried out according to EN ISO 322 and EN ISO 317. First, samples were weighed and measurements were taken and then immersed in distilled water at room temperature for 3 weeks. Samples were weighed and measured each week. Before weighing and measuring, the samples were wiped with paper tissue to eliminate the excess of water on the sample surfaces. The change in mass of the samples was measured to an accuracy of 0.01 g and their dimensions to an accuracy of 0.01 mm. After the soaking cycle ended, the samples were removed for colour measurements and mechanical testing.

2.4.2. Mechanical testing

Flexural tests were carried out with three-point loading system according to ISO 178:2010. Flexural strength was measured at room temperature with crosshead speed of 20 mm/min, test span 60 mm. For testing, Instron 5866 tensile tester was used. Five test samples were used for every composite. Before testing, width and thickness of each test sample were measured. The flexural strength and modulus of elasticity (MOE) were calculated during the bending testing.

Also Charpy impact strength for single-notched samples were tested in edgewise position according to ISO 179-1. Test was carried out with a Zwick 5102 pendulum impact tester at room temperature. The nominal pendulum energy was 4 J. Thickness and remaining width in the centre from the notch, to the nearest 0.02 mm was measured before Charpy impact test was performed. Energy, absorbed by breaking the test sample, was measured and Charpy impact strength was calculated.

2.4.3. Colour analysis

Surface colour was measured to evaluate the colour changes of the treated and untreated composites. Colour was measured with Minolta Chroma Meter CR-121, according to EN ISO 4582. Composites surface colour was measured by using the CIELAB colour system. In CIELAB system, colour is measured in L^*, a^*, b^* coordinates, where L^* is the lightness coordinate in the range between 0 (black) and 100 (white), a^* is red/green coordinate ($+a^*$ to red and $-a^*$ to green), b^* is yellow/blue coordinate ($+b^*$ to yellow and $-b^*$ to blue). The colour difference is expressed as a single numerical value, ΔE^*, which indicates the size of the colour difference. ΔE^* is defined as

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}, \qquad (1)$$

where ΔL, Δa, and Δb are the differences between the initial and after weathering values of L^*, a^*, and b^*, respectively.

3. RESULTS AND DISCUSSION

3.1. Flexural properties

The changes in flexural strength of different wood flour fraction size (modified with APTES) and polymers (LLDPE-g-MAH and PP) are described in Fig. 1. The results show that addition of wood flour to the LLDPE-g-MAH increased flexural strength twice. However, addition of wood flour to the PP reduces the flexural strength, because PP is a more rigid polymer than LLDPE-g-MAH and therefore wood flour makes PP more flexible. Test results show that biggest flexural strength results were obtained with wood flour fraction I. Increasing the wood flour fraction size decreased the flexural strength of WPCs slightly up to 8%. A similar trend has also been shown in other studies [11,12]. Decreasing flexural strength with increasing the wood flour fraction size can be explained with the fact that composites with smaller wood particles were more homogeneous than composites with larger wood fibres. WPC mechanical properties are more influenced by the fibre length to diameter ratio, which significantly improves the flexural strength [11,12].

The change in flexural MOE according to wood flour fraction size is shown in Table 4. The results demonstrate, that increasing the wood flour fraction size has little effect on flexural MOE (best results are obtained with fraction I). It is seen that the addition of wood flour to the polymer matrix increases the flexural MOE of the composite and makes the material more brittle (up to 80%).

For improving the mechanical properties of WPCs, it is very important to have strong bonding between the polymer matrix and wood filler. Therefore, the influence of coupling agents on the mechanical properties was investigated and the results are given in Table 4 and Fig. 2. From Fig. 2 it can be seen that

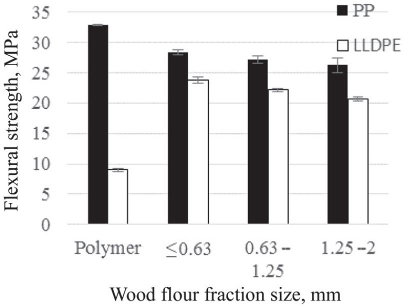

Fig. 1. APTES modified wood flour fraction size impact to the flexural strength of WPCs.

Table 4. Flexural and impact properties of WPCs

Sample	Flexural strength, MPa	Flexural MOE, GPa	Impact strength, kJ/m^2
PP1	32.8	1.01	14.53
PP2	23.5	1.30	6.41
PP3	23.8	0.87	7.26
PP4	25.4	1.20	7.69
PP5	28.3	2.34	4.03
PP6	25.6	1.82	5.57
PP7	27.1	2.07	4.99
PP8	27.4	1.74	8.08
PP9	26.2	1.91	4.67
LLDPE1	9.0	0.23	74.59
LLDPE2	20.7	0.76	8.13
LLDPE3	16.3	0.51	16.97
LLDPE4	15.3	0.49	14.71
LLDPE5	23.8	1.00	7.57
LLDPE6	18.2	0.65	11.31
LLDPE7	22.2	0.92	9.25
LLDPE8	21.8	0.91	10.29
LLDPE9	20.7	0.83	8.59

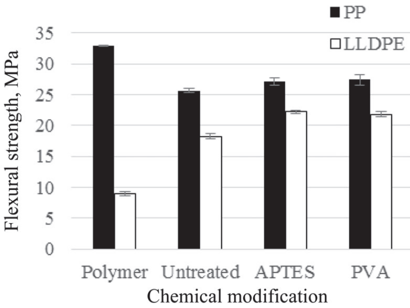

Fig. 2. Coupling agent influence to the flexural strength of WPC (fraction II).

chemically pretreated wood flour gives better coupling with the polymer matrix and thereby better flexural strength values than composites with untreated wood flour. Lower flexural strength values with untreated wood flour composites can be explained by poor bonding between hydrophilic wood flour and hydrophobic polymer and therefore by poor wood flour dispersion into the polymer matrix [13]. Poor coupling of the polymer and wood flour may also be the reason why the flexural strength decreased with increasing the dimensions of the wood fibres.

With consideration of the flexural strength and influence of additives, the wood flour processed with APTES gives WPC the best flexural strength values. The results from Table 4 and Fig. 2 show that the addition of APTES to the wood flour increased the flexural strength 6% of PP/wood flour composite and 22% of LLDPE-g-MAH/wood flour composite. The flexural MOE also increased with APTES modified wood flour composites resulting in a stiffer material (Table 4). With APTES, flexural strength increased most (22%) with the flour/LLDPE-g-MAH composite. PVA gave best flexural strength increase of 7% with wood flour/PP composite. However, flexural MOE decreased while modifying wood flour with PVA.

WPCs were also prepared with Aspen BCTMP. From Table 4 it can be seen that Aspen BCTMP gave similar results to wood flour composites. Adding 20% of Aspen BCTMP to LLDPE-g-MAH polymer matrix increased flexural strength of composite for 23%, almost as much as the wood flour fraction I. Since Aspen BCTMP was refined to very fine flour (≤0.126 mm), then it was distributed evenly into the polymer matrix and therefore flexural properties increased significantly. Previous studies have shown that wood particle size over 1 mm increases significantly mechanical properties of WPCs and size under 1 mm decreases the influence on mechanical properties [14].

3.2. Charpy impact strength

The results of Charpy impact strength are shown in Figs 3 and 4 and Table 4. The results show that addition of wood flour to the polymer matrix decreased impact strength more than 7 times, which correlates with other studies [15,16]. The addition of wood flour to the polymer generates stress concentration regions in composites which require less energy for cracking the composite, and thereby reducing the impact strength. Therefore, the addition of wood flour makes the composite material more brittle.

WPC material impact properties are influenced by the size of wood fibres. From Fig. 3 it can be seen that the lowest impact strength was with wood flour fraction I. Highest impact strength values were obtained with wood flour fractions II and III, which correlates with other studies [15–19]. This can be explained by the fact that larger wood particles have greater strength and thereby the strength of the composite increases. The results of this research suggest that addition of wood flour to the LLDPE-g-MAH makes it almost as brittle as the PP composite. In the composite, wood flour reduces the mobility of polymer chains, thereby reducing their energy-absorption capability by impact test. Poor linkage

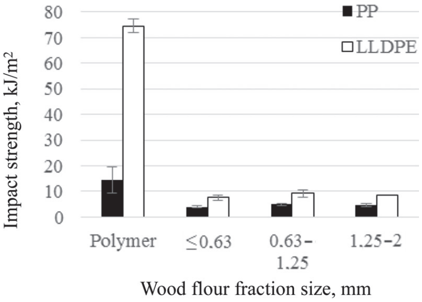

Fig. 3. APTES modified wood flour fraction size influence to the impact strength of WPCs.

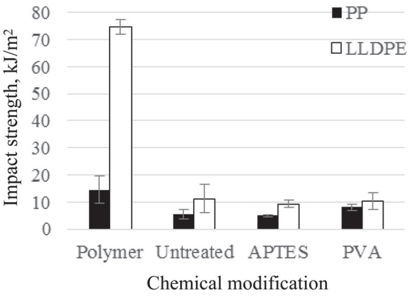

Fig. 4. Coupling agent influence to the impact strength of WPC (fraction II).

between the wood fibres and polymer matrix leads to microcracks in the impact test, which grow rapidly into large cracks leading test samples to break. Therefore it is important to have strong bonding between wood fibres and polymer matrix, what can be improved with coupling agents. Figure 4 shows that wood flour, processed with APTES, reduces impact strength the most, 10% for the PP composite and 17% for the LLDPE-g-MAH composite. PVA influenced less, reducing impact strength up to 10%. The largest decrease in impact strength of APTES modified wood flour composites is due to the fact that APTES bonds wood fibres with the polymer matrix better than PVA. With weaker bonding between polymer and wood fibres, impact force influenced more the polymer matrix. Therefore impact strength with PVA was lower than with APTES. Increasing impact strength values of PVA modified wood flour/PP composites are due to the poor interfacial bonding between polymer and wood flour, which results in different cracks in the composite during the impact testing (Fig. 4) [20].

The results of Aspen BCTMP are shown in Table 4 and are similar to the wood flour based composites. Adding only 20% of Aspen BCTMP fine flour, decreased impact strength almost as much as adding 35% wood flour.

3.3. Influence of water absorption and swelling

Water absorption and swelling of the composites during the accelerated weathering are shown in Table 5. The highest water absorption values were obtained with wood flour fraction II, 2.8% for PP composite and 1.2% for LLDPE-g-MAH composite. Water absorption was lowest with wood flour fraction I. Higher water absorption values with PP composite can be explained with the fact that the PP composite had lower amount of MAH coupling agent than the LLDPE-g-MAH. Therefore PP composites had weaker bonding between the polymer matrix and wood flour, which allowed water more easily to impact wood fibres in the composite. The results show that increasing the wood flour fraction size increases the water absorption of the composites, which also correlates with other studies [21,22]. Larger wood particles have an uneven interfacial layer what makes them more vulnerable to moisture.

Table 5. Water absorption and swelling of WPCs after 3 weeks of soaking in water

Sample	Absorption, %			Swelling, %		
	After 1 week	After 2 weeks	After 3 weeks	After 1 week	After 2 weeks	After 3 weeks
PP3	0.0	0.0	0.9	2.5	2.4	2.2
PP4	0.3	0.1	0.9	2.1	2.1	1.9
PP5	1.5	2.3	2.4	2.3	2.6	2.5
PP7	1.6	2.1	2.8	2.9	3.4	2.7
PP8	1.5	2.6	3.1	3.2	3.4	2.7
PP9	1.1	1.8	2.1	2.9	3.4	2.9
LLDPE3	0.5	0.3	0.7	0.6	1.2	0.8
LLDPE4	0.6	1.0	0.7	1.8	1.6	1.6
LLDPE5	0.2	1.4	1.1	1.9	2.0	1.8
LLDPE6	0.3	1.3	1.2	1.4	1.8	1.7
LLDPE7	0.6	1.1	1.2	1.8	1.3	1.5
LLDPE9	1.1	1.0	1.0	1.3	0.8	1.0

In Table 5, there is a clear difference in swelling the two different polymers. With PP composites the swelling increases when wood flour fraction size increase. Highest swelling of 2.9% was obtained with wood flour fraction III. However, with LLDPE-g-MAH there is the opposite situation. This can be explained by the inhomogeneity of LLDPE-g-MAH samples.

Table 5 shows that PVA modified wood flour/PP composite swelling increased 3% and water absorption up to 10% more than APTES modified wood flour/PP composites. The reason for this is that, PVA is a water-soluble polymer, which links with water through hydrogen bonding, and therefore reduces moisture resistance of composites. APTES molecules can react with cellulose OH group through amine groups, resulting in a strong bond [23]. To improve moisture resistance of WPC, it is very important to have strong bonding between wood fibres and polymer matrix.

Moisture affects also the mechanical properties of WPC. Table 6 shows that flexural strength and MOE decrease during the water soaking cycle. After 3 weeks of water soaking, the WPCs flexural strength decreased for 3% and flexural MOE for 14%. It shows that flexural strength decreased most with the PVA modified wood flour fraction II/LLDPE-g-MAH composite, about 5%. Best results were obtained with APTES modified wood flour fraction I composites, 1.2% for PP composite and 2.1% for LLDPE-g-MAH composite. It can be concluded that APTES binds wood fibres through OH groups and makes them hydrophobic, thus the moisture resistance is greater than the PVA modified wood flour composites. Moisture causes swelling of wood particles in WPC which then causes microcracks in the matrix, and therefore the flexural strength and MOE decrease.

Moisture also affects the impact properties of WPCs. Based on the results of Table 6, it can be seen that impact strength increases 17% on average after 3 weeks of water soaking cycle. This can be explained by the plasticizing effect on wood fibre and polymer interface during the moisture impact [4]. During the further absorption of water into composite, the wood fibre and polymer interface weakens, and as a result the impact strength also starts to decrease. Figure 5 shows scanning electron microscope (SEM) micrograph of the surface change of a WPC sample after 3 weeks of water soaking. Micrograph shows separation between wood flour and polymer, which indicates the lack of interfacial adhesion. Figure 5b shows a WPC specimen after 3

Table 6. Accelerated weathering influence on the mechanical properties of WPCs

Sample	Flexural strength, MPa			Flexural MOE, GPa			Impact strength, kJ/m^2		
	Untreated	After 3 weeks of water soaking	After 3 weeks of UV radiation	Untreated	After 3 weeks of water soaking	After 3 weeks of UV radiation	Untreated	After 3 weeks of water soaking	After 3 weeks of UV radiation
PP3	23.80	23.42	25.54	0.87	0.90	0.97	7.26	8.94	8.81
PP4	25.42	25.13	26.00	1.20	0.97	1.26	7.69	8.01	7.11
PP5	28.33	27.97	27.55	2.34	2.18	2.41	4.03	4.61	4.17
PP7	27.08	26.45	25.38	2.07	1.67	2.08	4.99	6.65	4.66
PP8	27.41	26.71	25.85	1.74	1.49	1.74	8.08	7.19	6.56
PP9	26.22	25.04	24.79	1.91	1.68	1.88	4.67	5.26	4.52
LLDPE3	16.27	14.18	15.99	0.51	0.46	0.48	16.97	22.07	17.84
LLDPE4	15.31	13.38	15.02	0.49	0.42	0.46	14.71	15.19	13.55
LLDPE5	23.78	23.27	22.22	1.00	0.53	0.88	7.57	9.08	8.28
LLDPE6	22.17	21.40	21.86	0.92	0.89	0.89	9.25	11.36	9.48
LLDPE7	21.76	20.76	21.17	0.91	0.87	0.88	10.29	10.64	8.84
LLDPE9	20.71	20.16	20.42	0.83	0.77	0.84	8.59	9.88	9.60

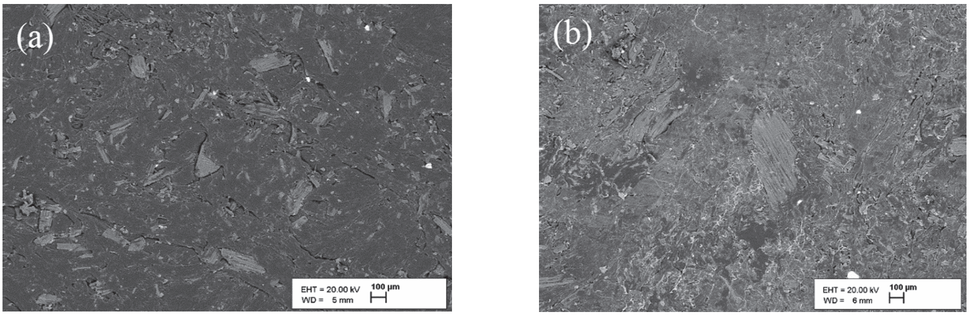

Fig. 5. SEM micrographs of the WPC surface: composite LLDPE-g-MAH surface (a), and composite LLDPE-g-MAH surface after water soaking (b).

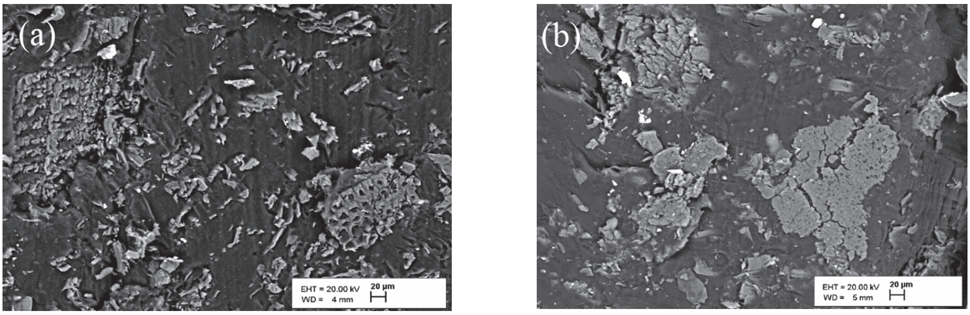

Fig. 6. SEM micrographs of WPC cross-section: composite PP cross-section (a), and composite LLDPE-g-MAH cross-section (b).

weeks of water soaking, where cracks can be observed in the polymer matrix as well as wood-matrix delamination. Figure 6 shows cross-section areas of PP and LLDPE-g-MAH composites. It can be seen that the LLDPE-g-MAH composite has smoother surface than the PP composite and it is caused by better interfacial adhesion between wood filler and polymer matrix on the LLDPE-g-MAH composite.

In addition, Aspen BCTMP (20% of Aspen BCTMP fine flour added to the polymer) composites were also tested, which gave similar results to the 35% wood flour based composites. This indicates that fine flour composite properties are more homogeneous. The results of the tests are shown in Table 6. It can be concluded that after 3 weeks of water soaking cycle, WPC becomes weaker and more elastic.

3.4. Influence of UV radiation

UV radiation influence on the flexural and impact properties of WPCs are shown in Table 6. The results show that after the UV radiation exposure for 3 weeks (500 h), flexural strength of WPCs decreases about 4%. The greatest flexural strength decrease, of 6.5%, was obtained with APTES modified wood flour fraction I/LLDPE-g-MAH composite. The smallest change in flexural strength, 1.4%, was obtained with the APTES modified wood flour fraction II and II/LLDPE-g-MAH composites. However, the results show differences in flexural strength changes for PP and LLDPE-g-MAH composites after UV radiation exposure. UV radiation has strong influence on the wood fibres, which causes photodegradation, causing a decrease in WPCs mechanical properties.

Table 6 shows that flexural MOE decreases after UV radiation exposure to LLDPE-g-MAH composites. However, for PP composites, flexural MOE slightly increases after exposure. This difference may be due to the fact that, when composites are exposed to UV radiation, the crystallinity of PP initially increases, then decreases [24]. Therefore, the results show that PP composite structure tolerates the influence of UV radiation much longer than the LLDPE-g-MAH composite, which will degrade already after 500 h. For different wood flour fraction sizes, best results were achieved with fraction I and UV radiation influence increase when the fraction size was increased. Results also show that PVA modified wood flour composites had slightly better resistance to UV radiation exposure than the APTES modified wood flour composites.

As for the impact strength, the UV radiation exposure increased the impact strength of composites. Impact strength increased most (11.8%) with wood flour fraction III and LLDPE-g-MAH based composites.

In addition, Aspen BCTMP based composites were also tested. The results were similar to the wood flour based composites. Based on this research, it can be said that UV radiation exposure makes WPC material more elastic.

3.5. Colour analysis

The lightness (L^*) and colour coordinates (a^* and b^*) as well as the total change of colour ΔE^* of the WPCs are shown in Figs 7 and 8. Figure 7 shows that lightness of the composites increased for most of the composites after 3 weeks of the water soaking cycle. The biggest lightness change occurred in the composite LLDPE9, the most significant total colour change occurred in the composite LLDPE6, where colour changed from yellow to blue (9.9 units). Colour measuring shows the loss of red and yellow colour during water soaking, which makes composites faint and turn into grey tone. However, some test samples shifted towards yellow and red, and made composites darker.

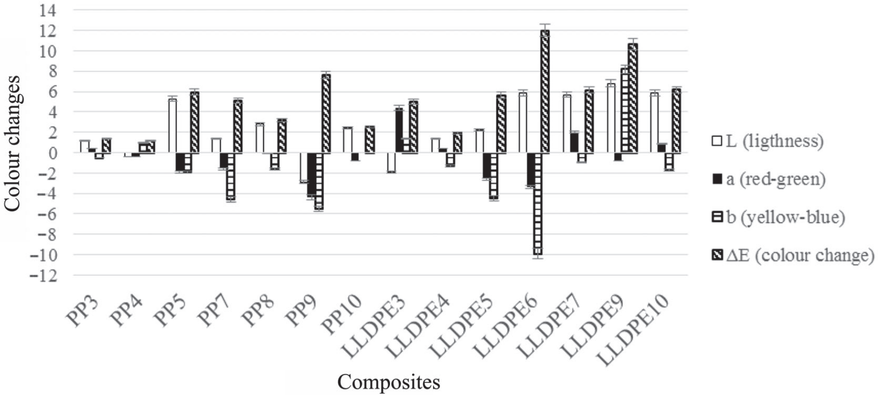

Fig. 7. Colour changes after 3 weeks of water soaking.

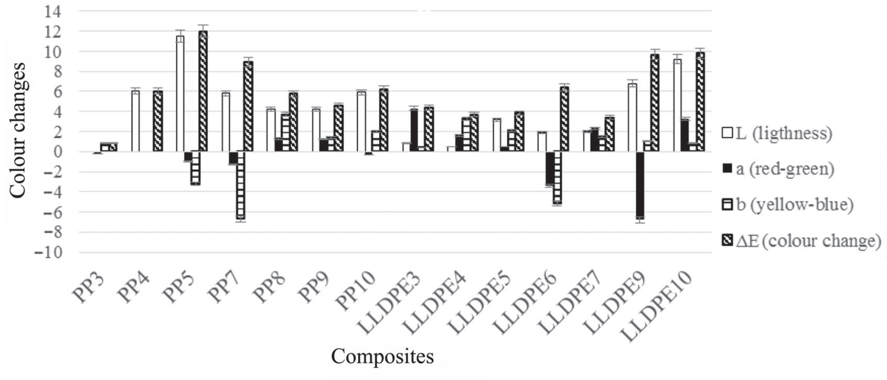

Fig. 8. Colour changes after 3 weeks of UV radiation exposure.

In case of UV radiation exposure, all the test samples turned lighter, as shown in Fig. 8. This is also in accordance with other studies [24,25]. During the UV radiation, most of the samples also shifted to more red. There is also a noticeable change towards green colour in many composites. The lightness and yellowness of the composites during weathering is caused by the lignin component decomposition in wood fibres. Redness is determined with the extractives content of the wood. Discoloration of WPCs during UV radiation exposure is a combination of both chemical and physical changes. Photooxidation of wood components initiate chemical changes in WPCs, which determine the primary colour change. If the adhesion between wood flour and polymer is strong enough to anticipate surface erosion and removal of wood particles, then composites turn darker and yellowish. However, the loss of the degraded wood component and combination with degradation of the polymer matrix leads to fading of the WPC surface [9].

Based on colour analysis results, visual colour changes were not observed, but with colorimeter the colour changes were present.

4. CONCLUSIONS

The influence of UV radiation and moisture content on the mechanical and physical properties of WPCs were investigated. The effect of coupling agents and wood flour fractions size on the mechanical and physical behaviour of WPCs were also experimentally determined. The following conclusions can be drawn from the study.

- WPC mechanical properties depend mostly on the wood fraction size. Smaller wood fraction size gives better flexural properties than the larger wood fraction size.
- It is very important to choose right coupling agent. Best test results were obtained with composites made of APTES modified wood flour and LLDPE-g-MAH.
- Adding wood flour to the thermoplastic polymers decreased impact strength and made WPC more rigid and brittle.
- Water absorption and swelling increase with increasing the wood flour fractions size in the composites because of the decreasing interface between the polymer matrix and wood flour.
- Water absorption and swelling of WPC decreased the flexural MOE and strength while impact strength increased by making material weaker and increasing the deflection of WPC materials.
- UV-radiation decreases the flexural MOE and strength, while impact strength increases by making WPC material properties weaker.
- Weathering of WPC also changes material colours. UV-radiation increased the lightness of all specimens. However, SEM analysis showed cracks and voids on the cross-section area of WPC specimens after weathering tests.

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Kunstliku vanandamise mõju puitplastkomposiitide mehaanilistele ja füüsikalistele omadustele

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Käesolevas töös uuriti kunstliku vanandamise (niiskuse ja UV-kiirguse) mõju puitplastkomposiitide (PPK) mehaanilistele ning füüsikalistele omadustele. Uurimistöö eesmärgiks oli hinnata ka puidujahu fraktsiooni suuruse mõju PPK mehaanilistele omadustele ja kunstlikule vanandamisele. Komposiitide valmistamiseks kasutati kolme erinevat kase (*Betula*) puidujahu fraktsiooni ja kemi-termo-mehaanilist (KTM) haava (*Populus tremula*) puitmassi. Polümeerse maatriksina kasutati kaht erinevat termoplastilist polümeeri: Fusabond E MB226DE (maleiinhappe anhüdriidiga modifitseeritud LLDPE) ja polüpropüleeni (PP). Puidujahu ja KTM-i modifitseerimiseks kasutati kaht erinevat sidusagensit: 3-aminopropüül-trietüksüsilaani (APTES) ning polüvinüülalkoholi (PVA). Komposiidid valmistati kaheteolises ekstruuderis ja katsekehad tehti survevalumeetodiga. Viidi läbi kiirendatud vanandamise katsed (UV-kiirguskamber ja vees leotamine), et hinnata vanandamise mõju PPK omadustele. Mehaanilisi omadusi testiti kolme punkti paindekatsega ja Charpy pendliga löögikatsega. Lisaks uuriti ka PPK värvuse muutust peale vanandamist.

Mehaanilistest katsetest järeldus, et PPK materjali mehaanilised omadused sõltuvad kõige rohkem puidujahu sisaldusest ja fraktsiooni suurusest. Puidu lisamine tõstis materjali paindeelastsusmoodulit ja vähendas löögitugevust, muutes materjali jäigemaks ning rabedamaks. Kõige paremad paindeomadused andis puidujahu fraktsioon I, sest see oli komposiidis kõige ühtlasemalt jaotunud. Puiduosakeste suuruse kasvades muutus materjal elastsemaks, vähenes paindetugevus ja kasvas löögitugevus. Niiskus vähendas puidukiudude tugevust ja muutis need elastsemaks, mistõttu PPK tugevusomadused muutusid nõrgemaks ning läbipaine suurenes. UV-kiirguse toimel vähenesid mehaanilised omadused, paindeelastsusmoodul ja paindetugevus, löögitugevus kasvas. PPK materjal muutus elastsemaks. Lisaks muutus PPK materjal UV-kiirguse toimel heledamaks.

Appendix 2

Publication II

Kallakas, H.; Shamim, M.A.; Olutubo, T.; Poltimäe, T.; Süld, T.M.; Krumme, A.; Kers, J. (2015). Effect of chemical modification of wood flour on the mechanical properties of wood-plastic composites. Agronomy Research, 13 (3), 639−653.

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Effect of chemical modification of wood flour on the mechanical properties of wood-plastic composites

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Abstract. The poor compatibility between the highly hydrophilic wood fibres and the hydrophobic polymers is associated with a loss of mechanical properties. Therefore, to improve the interfacial adhesion between the polymer matrix and wood flour (WF), a chemical modification of WF is an appropriate solution. This study analyzes the influence of different chemical modifications of WF on the mechanical properties of wood-plastic composites (WPCs). WPC test samples were prepared from birch (*Betula*) WF with a mesh size of 0.63 mm as the filler material and polypropylene (PP) as the matrix material. WF was chemically modified by six different methods to increase its adhesion to, and compatibility with, the polymer matrix. The six chemical methods used were: alkaline (NaOH) modification, polyvinyl alcohol (PVA) modification, silane treatment with 3-aminopropyltriethoxysilane (APTES), acetylation with acetic anhydride, cyanoethylation, and wood fibre esterification. The composites were produced using a twin-screw extruder and the test samples were prepared by injection moulding. The composites' mechanical properties (three-point bending test), Charpy impact strength and thermal properties were tested. In addition, SEM micrographs of WPC surfaces were generated. WF as a filler material enhanced the flexural properties, while impact strength decreased, making the material more rigid and brittle. The test results revealed that the chemical modifications of WF improved the mechanical properties and crystallinity of WPC materials, while the melting temperature decreased. However, the influence of the chemical modification on the mechanical and thermal properties of WPC varied by method.

Key words: wood-plastic composite, wood flour, chemical modification, mechanical properties, thermal properties.

INTRODUCTION

In recent years, wood-based renewable composites have garnered much attention, both scientific and commercial, due to their light weight, eco-friendliness and low cost, as well as worldwide environmental awareness. Natural fibres are considered potential alternatives to glass or carbon fibres in fibre-reinforced thermoplastic composites because of their nature-friendliness, recyclability, biodegradability and low cost compared to mineral fillers (Ashori, 2008; Lu et al., 2008). According to previous research, natural fibres are less abrasive than inorganic mineral fillers and therefore cause little damage to moulding and mixing equipment (Acha et al., 2006).

However, the usability of natural fibres in composite materials is still limited due to their hydrophilic nature, which leads to poor compatibility with the hydrophobic polymer matrix. This may also result in composites with poor mechanical properties and decreased durability. Here, chemical modification of wood is used to alter its structure, enhancing interfacial adhesion between the polymer matrix and wood fibres and thus improving the physical and mechanical properties of the composite material (Gwon et al., 2010b; Těšinová, 2011). The chemical modification of wood flour (WF) has been studied by many authors. It has been reported that chemical modification can clean the wood fibre surface, stop the moisture absorption process, and increase the surface roughness. Different chemical modification techniques have been used, such as alkaline treatment, benzoylation, silylation, peroxide, acetylation, esterification, maleated coupling, etc. (Kalia et al., 2011). With alkaline treatment, the amount of crystalline cellulose is increased, impurities and swelling of the wood fibres are reduced, resulting in a smaller number of hydroxyl groups. The swelling of the wood fibres depends on the alkali concentration (Kim et al., 2011). Silanes efficiently connect with the superficial hydroxyl groups of the wood fibres and induce hydrolysis, condensation, and bond formation, producing chains between the polymer matrix and wood fibres. It is reported that silane modification enhances the properties of composite materials (Farsi, 2010; Kim et al., 2011).

Acetylation of wood has been widely used for modifying wood with acetic anhydride, which results in the esterification of accessible hydroxyl groups in the cell wall with acetyl groups. Previous research has shown that acetylated wood fibre based WPC materials exhibit enhanced mechanical properties, decreased moisture content and an improved resistance to brown-rot decay compared with unmodified WPC materials (Khalil et al., 2002; Segerholm et al., 2005). Generally, these chemical modification methods all improve the overall properties of WPC materials compared with unmodified composites. Based on previous studies it is also believed that the interfacial adhesion between the polymer matrix and the chemically modified WF is significantly increased (Gwon et al., 2010a).

The aim of this study was to investigate the influence of the chemical modification of WF on the interfacial strength of WPC. Therefore, WF was modified with six different chemical agents. Chemically modified WF was compounded with polypropylene (PP) resin and WPC test specimens were prepared by injection moulding. The mechanical behaviour of these composites was evaluated after the flexural and impact test.

MATERIALS AND METHODS

Materials

In this study, PP was used as a matrix material for WPCs. The PP obtained from the company Borealis Polymers OY is a heterophasic copolymer (block copolymer) with a density of 0.905 g cm^{-3} and a melt flow index (MFI) of 3.5 g 10 min^{-1}. The wood filler from hardwood (birch (*Betula*)) chips was supplied by the firm UPM Kymmene Otepää AS and then refined to a mesh size of 0.63 mm using the disintegrator device DS-A. For a chemical modification of the WF, a reagent grade sodium hydroxide (NaOH), 98%; polyvinyl alcohol (PVA); 3-aminopropyltriethoxysilane (APTES), 98%; acrylonitrile, 99%; dimethylformamide (DMF), 99%; and acetone, 99.5%, were purchased from Sigma Aldrich Chemical Co. For acetylation, acetic anhydride (AA), 98.5%, acquired from Merck Millipore chemicals, vinyl acetate (VA), 99%, from Fluka Chemical Corp, toluene from LACH-NER, s.r.o. and ethanol were used.

Alkaline modification of WF

Different concentrations of NaOH were selected based on previous studies (Doczekalska & Zborowska, 2010; Doczekalska et al., 2014) to investigate the effect of removing impurities and increasing crystalline cellulose content on the mechanical properties of WPCs. The chosen concentrations of NaOH for WF treatment were 5 wt% and 17.5 wt% (based on the mass of the WF). WF was treated in the chosen solutions of NaOH at room temperature (25 °C) for 90 min. The NaOH solution was prepared in the laboratory by dissolving NaOH granules in water and the solution was then poured onto the WF. After activating, the WF was rinsed with distilled water to neutralize the excess NaOH and then oven-dried at 60 °C for 24 h.

Polyvinyl alcohol modification of WF

PVA has excellent adhesive properties and therefore could be used for cross-linking wood fibres to polymer matrix. In this experimental method, an aqueous solution was prepared with 5 wt% of PVA (based on the mass of the WF) to compare it with other modifications. WF was treated with the PVA solution at room temperature (25 °C). The PVA solution was prepared in the laboratory by dissolving PVA powder in distilled water and then poured onto the WF. After treatment the WF was oven-dried at 60 °C for 24 h.

Silane modification of WF

For silane modification, the WF was treated at room temperature (25 °C) with an aqueous APTES solution. The concentration of APTES chosen for comparison with other modification methods was 5 wt%. On the basis of previous research in WF modification (Gwon et al., 2010a), 5 wt% of APTES (based on the mass of the WF) was added, prior to treatment, for the purpose of hydrolysis in a solution of ethanol/distilled water at a ratio of 9:1 (where ethanol is highly volatile and the objective was to obtain fast-drying WF) and at a pH value of 5. The stirring time was 10 min. A silane solution was then poured onto the WF and treated for 2 h; after the treatment the WF was oven-dried at 60 °C for 24 h.

Acetylation of WF

The acetylation of WF was carried out by two different methods to compare acetylation by boiling and acetylation using a co-solvent and a catalyst to increase the reaction rate. The effect of the two different acetylation methods and using the catalyst on the mechanical and physical properties of WPCs were investigated. The first method, based on a previous study (Ibach & Clemons, 2006), was straightforward and consisted in boiling the WF in AA. The WF was boiled in AA in a 1 l round-bottom flask with a stirrer for 4 h. The modified WF was then washed with distilled water and oven-dried at 60 °C for 24 h.

In the second method (Cetin et al., 2011), the WF was transferred to a round-bottom flask with a condenser containing a DMF solution with AA. The reaction was carried out using potassium carbonate (K_2CO_3) as a catalyst for 1.45 mmol g^{-1}dry wood. The amount of AA used in the solution was 70 mmol g^{-1} dry wood. The reaction was performed at 100 °C for 4 h. After the reaction, the modified WF was Soxhlet extracted by means of distilled water for 6 h and then by means of toluene/acetone/ethanol solution (at a ratio of 4:1:1 vol/vol) for 6 h to remove unreacted chemicals and by-products. After extraction the WF was oven-dried at 60 °C for 24 h.

Esterification of WF

WF esterification was carried out at the conditions established in a previous study (Wei et al., 2013). WF was weighed into a 3-neck round-bottom flask fitted with a condenser, an overhead stirrer and a thermometer. WF was reacted with VA at an amount of 12.5 mmol g^{-1} dry wood, 15 g of K_2CO_3 and 600 ml of DMF. Heat was then applied using sand as the heating medium because of the high temperature; the reaction mixture was stirred continuously at 120 °C for 6 h. After this, the reaction mixture was filtered to remove any excess reagents and the WF was then washed with distilled water and rinsed with acetone. After washing, the WF was oven-dried at 60 °C for 24 h.

Cyanoethylation

WF was cyanoethylated according to a method found in previous research (Ghali et al., 2011). Prior to cyanoethylation, the WF was treated with a NaOH solution (5 wt% based on the mass of the WF) for 2 min at room temperature to about 90% wet pickup. After the alkaline treatment, the WF was put into a round-bottom flask containing acrylonitrile/toluene solution (at a ratio of 50:50). The reaction was performed at 60 °C for 60 min. When the reaction was finished, the WF was thoroughly washed with 5% acetic acid solution and then with distilled water. After washing, the WF was oven-dried at 60 °C for 24 h.

Composite processing

After modification, the WF was weighed and the composite mixtures for all the samples were calculated at a ratio of 65% polymer and 35% WF. The mixture of the composites is shown in Table 1. The composites were compounded in a twin-screw extruder Brabender Plasti-Conder PLE 651 at 195 °C at a screw speed of 40 rpm. The compounded materials were then ground to produce granules. Test samples were prepared by injection moulding (Battenfeld BA 230 E) using the previously made granules according to standard ISO 178:2010. The conditions for injection moulding were as follows: temperature 170–185 °C from feed zone to die zone; injection pressure 7 MPa; screw speed 40 rpm; cooling time 15 s. The molten mixture was injected into two-bar shape moulds to produce flexural and impact test samples. The dimensions of the test samples were 63 x 10 x 4 mm.

Table 1. Make-up of the composites

Sample	PP (wt%)	WF (wt%)	Modification	Modification (wt%)
1	100	0	–	–
2	65	35	–	–
3	65	35	NaOH	5
4	65	35	NaOH	17.5
5	65	35	PVA	5
6	65	35	APTES	5
7	65	35	AA	5
8	65	35	AA and DMF	5
9	65	35	VA and DMF	5
10	65	35	Acrylonitrile	5

Mechanical properties

The flexural properties were determined with the three-point loading system Instron 5866 according to ISO 178:2010. The testing was carried out at room temperature 20 °C, at a crosshead speed of 20 mm min^{-1} and a test span of 60 mm. Five samples were used for each composite. For each composite, its flexural strength and modulus of elasticity (MOE) were calculated. In addition, Charpy impact strength was determined for single-notched samples according to ISO 179-1. Notched impact strength was tested with a Zwick 5102 pendulum impact tester at room temperature 20 °C and nominal pendulum energy of 4 J. The energy absorbed by breaking the test sample was measured and Charpy impact strength was calculated.

Differential scanning calorimetry

WPC samples were tested by differential scanning calorimetry (DSC) to measure the thermal transition of the composites. DSC was performed by means of the Mettler Toledo FP900 Thermosystem with FP90 Central Processor (control and evaluation unit) and FP85 Measuring Cell fitted with cooler system using a nitrogen atmosphere at a flow rate of 20 mL min^{-1}. WPC samples were weighed at about 10 mg, placed in a small aluminium crucible and subjected to a temperature program. The heating and cooling conditions for WPC samples were 30 to 250 °C and 250 to 30 °C with heating and cooling rates of 10 °C min^{-1}, respectively. For each WPC sample its melting temperature (T_m), melting enthalpy (ΔH_m), crystallization temperature (T_c), crystallization enthalpy (ΔH_c) and crystallinity (X_c) were determined.

Scanning electron microscopy

The unmodified and modified composite surfaces and cross-sections were evaluated microscopically by means of the field emission scanning electron microscope (FE-SEM) ZEISS Ultra-55 with GEMINI In-lens SE detector. The acceleration voltage used was 20 kV. Samples were prepared by cutting and mounting a microtomed cross-section. After that, the samples were coated with gold.

RESULTS AND DISCUSSION

Flexural properties

The flexural strength of WPCs with different wood modifications is presented in Fig. 1. The results show that the addition of WF to the PP matrix increased the flexural strength; this effect is enhanced by different chemical modifications of the WF, which make the material more rigid and brittle. However, some chemical modifications demonstrated a decrease in the flexural strength compared to unmodified WF composites. 5% NaOH, PVA and AA modified PP/WF composites showed the lowest values of flexural strength (33.1 MPa, 33.3 MPa, and 33.4 MPa, respectively), which indicates poor interfacial adhesion between the PP matrix and WF. Adding 35% WF to the PP matrix increased the flexural strength of the composites by about 10% with unmodified WF. A similar increase in flexural strength with 30–40% unmodified WF has also been noted in previous studies (Stark & Rowlands, 2003; Karmakar et al., 2007; Ndiaye et al., 2012). However, these previous studies also show that when adding a maleic anhydride grafted polypropylene (MAPP) coupling agent to the composite mixture the increase in flexural strength is significantly higher. The best flexural strength values were obtained by the WF esterification method (38.5 MPa), which increased flexural strength by about 7% compared to unmodified WF (36.2 MPa). The conclusion here is that interfacial adhesion between PP and WF improved with the esterification of WF.

As seen from Fig. 1, an increase in the NaOH concentration from 5% to 17.5% results in a 12% higher flexural strength (from 33.1 MPa to 36.9 MPa, respectively). Alkaline treatment increases the fibre surface roughness and possible reaction sites on the fibre surface, which helps to improve the mechanical properties of WPC through mechanical interlocking and chemical bonding (Gwon et al., 2010a). The mechanical properties of WPC materials are influenced by removing impurities from WF. Based on the results presented in Fig. 1, it can be concluded that at an increased alkaline content the mechanical properties of WPC are also enhanced. However, previous research has shown that at an alkaline content increased to more than 10 wt%, the flexural strength starts to decrease slightly as a result of corrosive interactions between wood fibres in the composites caused by excessive alkali that weakens the WF surface (John et al., 2008; Gwon et al., 2010a). Therefore it is important to choose an optimum amount of NaOH to achieve strong mechanical properties of WPCs.

Two different methods of WF acetylation were also tested and the mechanical properties were compared. The flexural strength results in Fig. 1 show that just boiling the WF in AA even decreases the flexural strength of WPC compared to unmodified WF-based composites. However, another method using the solution of AA and DMF with a catalyst (K_2CO_3) gave better results, increasing the flexural strength slightly, by 2%, compared with unmodified WF (from 36.2 MPa to 37.1 MPa, respectively) and by 11% compared with acetylation by boiling in AA (from 33.4 MPa to 37.1 MPa, respectively). Therefore, acetylation with the AA and DMF solution with a catalyst (K_2CO_3) was found more effective with regard to enhancing the mechanical properties of WPCs. An enhanced acetylation of wood in the presence of a catalyst and an improvement in the mechanical properties of WPCs has also been shown in previous studies (Cetin, et al., 2011; Özmen et al., 2013). Acetylation replaces the OH groups of wood cell wall polymers with acetyl groups, so that they become hydrophobic and thus compatible with thermoplastics.

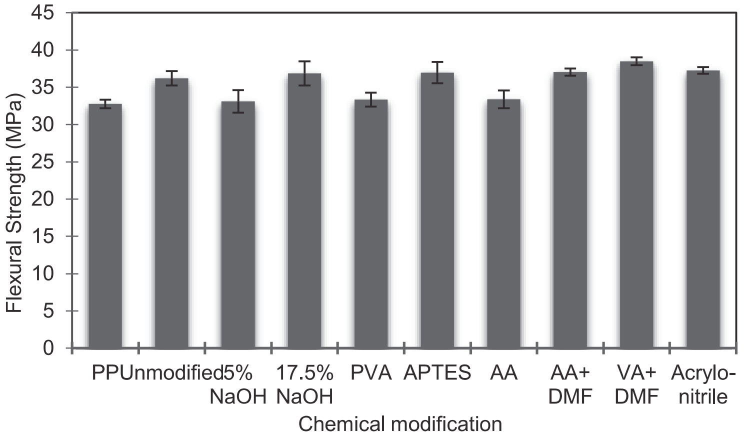

Figure 1. Flexural strength of chemically modified and unmodified WF/PP composites.

With acrylonitrile and APTES modification of WF, the flexural strength was also higher than with unmodified WF composites. With cyanoethylation, the wood OH groups are modified with acrylonitrile and wood is made hydrophobic and compatible with polymers. With acrylonitrile, the composites' flexural strength (37.3 MPa) was increased by 3%, and with APTES (37.0 MPa), it was 2% higher than with unmodified WF composites. However, previous research (Kim et al., 2011) has shown a significantly higher improvement in flexural properties with APTES modified PP/WF composites (about 80% compared to unmodified composites) when the WF is modified with NaOH prior to silane modification. The increase in flexural properties with APTES modification is explained by a stronger interface between WF and PP compared to unmodified composites. This enhances flexural stress distribution in the composites. Silane-reactive chemical groups provide covalent bonding with the OH groups of wood fibres and another chemical group connects with the polymer by creating interfacial adhesion between the polymer and WF.

The flexural MOE values of different composites are shown in Fig. 2. The results demonstrate that significantly higher values of flexural MOE were achieved by four different chemical modifications: 5% NaOH, PVA, APTES and AA. APTES gave the highest flexural MOE value (2.6 GPa) and compared to unmodified WF composites, the value increased from 1.00 GPa to 2.56 GPa, respectively, making the composite stiffer. On the other hand, WF esterification gave the lowest values of flexural MOE (0.91 GPa).

Therefore, it can be concluded from the flexural properties that most of the chemical modification methods tested in this study improved the flexural strength values, which indicates that interfacial adhesion between WF and PP was increased. The increase in bonding between WF and PP may be due to the fact that chemical modification reduces the number of hydroxyl groups in WF and modification with NaOH leads to the removal of extractives and hemicellulose from the WF.

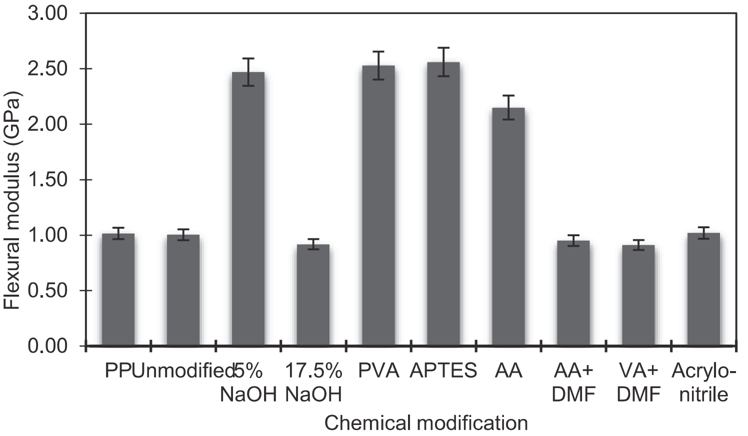

Figure 2. Flexural modulus of chemically modified and unmodified WF/PP composites.

Impact strength

The Charpy impact strength of single-notched specimens of unmodified and modified WPC samples is shown in Fig. 3. The single-notched impact test was chosen because the pendulum impact tester did not provide sufficient energy to break un-notched PP samples due to the high elasticity of the PP matrix. This is the reason why many other researches have also previously used the single-notched impact test for WPC impact testing. With all the composites, the addition of WF to the PP matrix lowered the impact properties significantly (about threefold) compared to pure PP; this is also in accordance with previous research (Bledzki & Frauk, 2004; Bledzki et al., 2009). When incorporating WF in the PP matrix, impact strength is decreased due to the stress concentration regions in WPC that require less energy to break the composite, making the material more brittle. The results show that only the PVA and acrylonitrile modifications of WF had a slightly higher impact strength (4.72 kJ m^{-2} and 4.56 kJ m^{-2}, respectively) compared with unmodified WF composites (4.44 kJ m^{-2}). All the other modified composites exhibited a lower impact strength compared with the unmodified ones. The lowest impact strength was demonstrated by APTES modified WF composites (3.56 kJ m^{-2}) – 25% lower than that of unmodified WPC samples. APTES silanol groups can create strong bonds with the hydroxyl groups of WF and thus improve interfacial adhesion between WF and the polymer matrix.

The chemical modification of WF improves the interaction between WF and the polymer matrix, resulting in strong bonding, and therefore the breaking of the composites needs relatively low impact energy. Composites with weaker interfacial bonding have higher impact strength because micro-cracks can occur in the impact test, propagating along the fibre/matrix interface and causing debonding, which leads to a higher energy-absorption capacity of the WPC (Ray et al., 2001; Nourbakhsh & Ashori, 2010). Therefore, an impact test shows the effect of chemical modification on the interfacial bond in the composites, which also affects the mechanical properties of WPC materials.

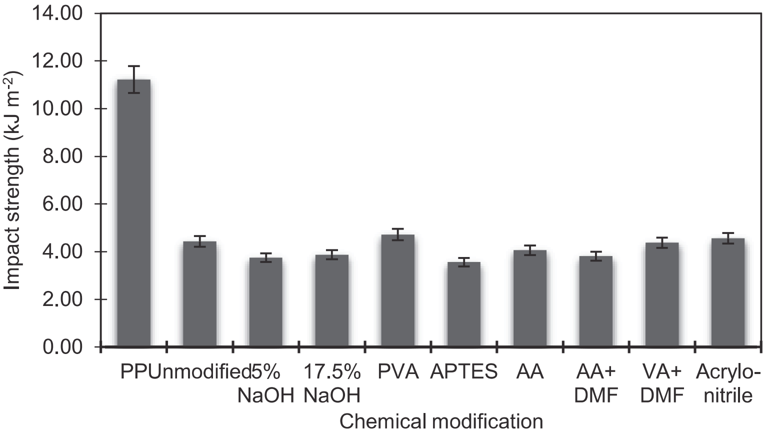

Figure 3. Impact strength of chemically modified and unmodified WF/PP composites.

Differential scanning calorimetry

All the WPC samples (unmodified and modified) were measured with the DSC system and the data of the composites is shown in Table 2. Thermal analysis demonstrates that the addition of WF to the polymer matrix decreased the T_m by 1.3–4.3 °C. The addition of 35% unmodified WF to the polymer matrix decreased the T_m by 1.7 °C, while the largest decrease, by 4.3 °C, was provided by NaOH (17.5 wt%) modified WF composites. ΔH_m values decreased significantly when WF was added to the polymer matrix. It was interesting that PVA modified WF composites gave only 14.1 J g^{-1} of ΔH_m compared to pure PP (54.6 J g^{-1} of ΔH_m) and therefore a lot less energy is required to melt the composite. With WPC samples, the highest ΔH_m was obtained with APTES – it was just 17% lower than pure PP. Therefore, the APTES modification of WF requires a lot more energy than other modifications to melt the composite. The same trend was also noted in a previous study (Kim et al., 2011).

The T_c of the WPCs with PVA and NaOH (5 wt%) modified PP/WF composites was higher than with other modifications and unmodified composites, indicating a better nucleation ability of PVA and NaOH (5 wt%) modified WPCs. Accordingly, these act as nucleating agents, increasing the rate of crystallization of polymers and thereby also the crystallization temperature (Ayrilmis et al., 2014). Other WF modifications show lower T_c values (0.6–5.8 °C), which indicates a weakened nucleation ability with these modified WF composites, resulting in a better interfacial adhesion between PP and WF. Wood consists of cellulose with a crystalline structure, and hemicellulose and lignin with an amorphous structure, thus reducing the crystallinity of composites. Therefore, the improved interfacial adhesion in these composites is explained by the hindered movement of PP chains, decreasing the crystallization rate of PP in the WPCs (Ndiaye & Tidjani, 2012).

All WPC samples except AA+DMF modified WF composites show a decrease in the ΔH_c results compared to pure PP. Most of the WF modifications decreased the ΔH_c compared to unmodified composites. However, APTES, AA and AA+DMF modified composites increased the ΔH_c by 7%, 1%, and 36% respectively, compared to unmodified WPCs. Previous research (Ayrilmis et al., 2014) has shown that the modification of WF can increase the ΔH_c by inducing a formation of crystals in heterogeneous nucleation spots. This increases the crystallization rate in the WPCs.

The crystallinity X_c of all the composites was reduced with the addition of WF to the polymer matrix. The lowest X_c was obtained with the PVA modified composite of only 6.2% crystallinity. Most of the modified composites increased the X_c compared to unmodified composites. The highest X_c was achieved with APTES (X_c = 21.3%) and 17.5% NaOH (X_c = 20.2%) modified composites – just 19% and 26% lower than pure PP, respectively. The decreased crystallinity of WPCs shows that the formation of polymer crystals is hindered by WF in the composites. However, the higher crystallinity of APTES modified composites may be explained by the better interfacial adhesion between WF and the PP matrix. Previously it has been reported that APTES modification provides the highest increase in X_c (Kim et al., 2011).

Table 2. DSC results of the unmodified and modified WPC samples

Sample	PP/WF (wt%)	Modification	Modification (wt%)	T_m^a (°C)	ΔH_m^b (J g^{-1})	T_c^c (°C)	ΔH_c^d (J g^{-1})	X_c^e (%)
1	100/0	–	–	173.0	54.6	107.5	1,950	25.4
2	65/35	–	–	171.3	32.6	107.6	1,760	15.3
3	65/35	NaOH	5	171.7	36.0	109.2	1,420	18.9
4	65/35	NaOH	17.5	168.7	40.5	102.4	1,380	20.2
5	65/35	PVA	5	169.5	14.1	116.3	868	6.2
6	65/35	APTES	5	171.5	46.7	103.3	1,880	21.3
7	65/35	AA	5	171.3	40.4	107.5	1,780	19.2
8	65/35	AA and DMF	5	172.1	22.6	106.9	2,400	10.5
9	65/35	VA and DMF	5	170.1	38.2	101.7	1,620	19.0
10	65/35	Acrylonitrile	5	169.6	34.5	103.8	1,520	15.4

^{a}Melting temperature; ^{b}melting enthalpy; ^{c}crystallization temperature; ^{d}crystallization enthalpy; ^{e}crystallinity

Scanning electron microscopy

SEM pictures of the surfaces and cross-sections of modified and unmodified WPC samples are shown in Fig. 3. With a chemical modification of WF there is a better dispersion of wood and adhesion with the polymer matrix. With unmodified composite samples (Fig. 4a and 4b) cavities and voids are present in the composite surfaces. Also PVA modified composite surfaces (Fig. 4g and 4h) reveal voids and separate wood particles, representing a non-compatibilized system. Therefore, these composites have poor interfacial adhesion between WF and the PP matrix. With modified composites, micrographs show fewer cavities and voids and more homogenous surfaces, which also indicate an improved interfacial adhesion between WF and the PP matrix. Smooth and uniform surfaces with a good dispersion of WF in the PP matrix can be seen in Fig. 4m, 4n, 4q and 4r, which shows a strong compatibility between WF and the PP matrix with AA+DMF and Acrylonitrile modifications. With other chemical modifications, minor cavities and voids are present on the surfaces of WPCs, reducing the interfacial bonding of PP and WF. These SEM observations clearly explain the enhanced mechanical properties of modified WPCs, so that the stronger interaction between WF and PP also improves the mechanical properties of WPCs.

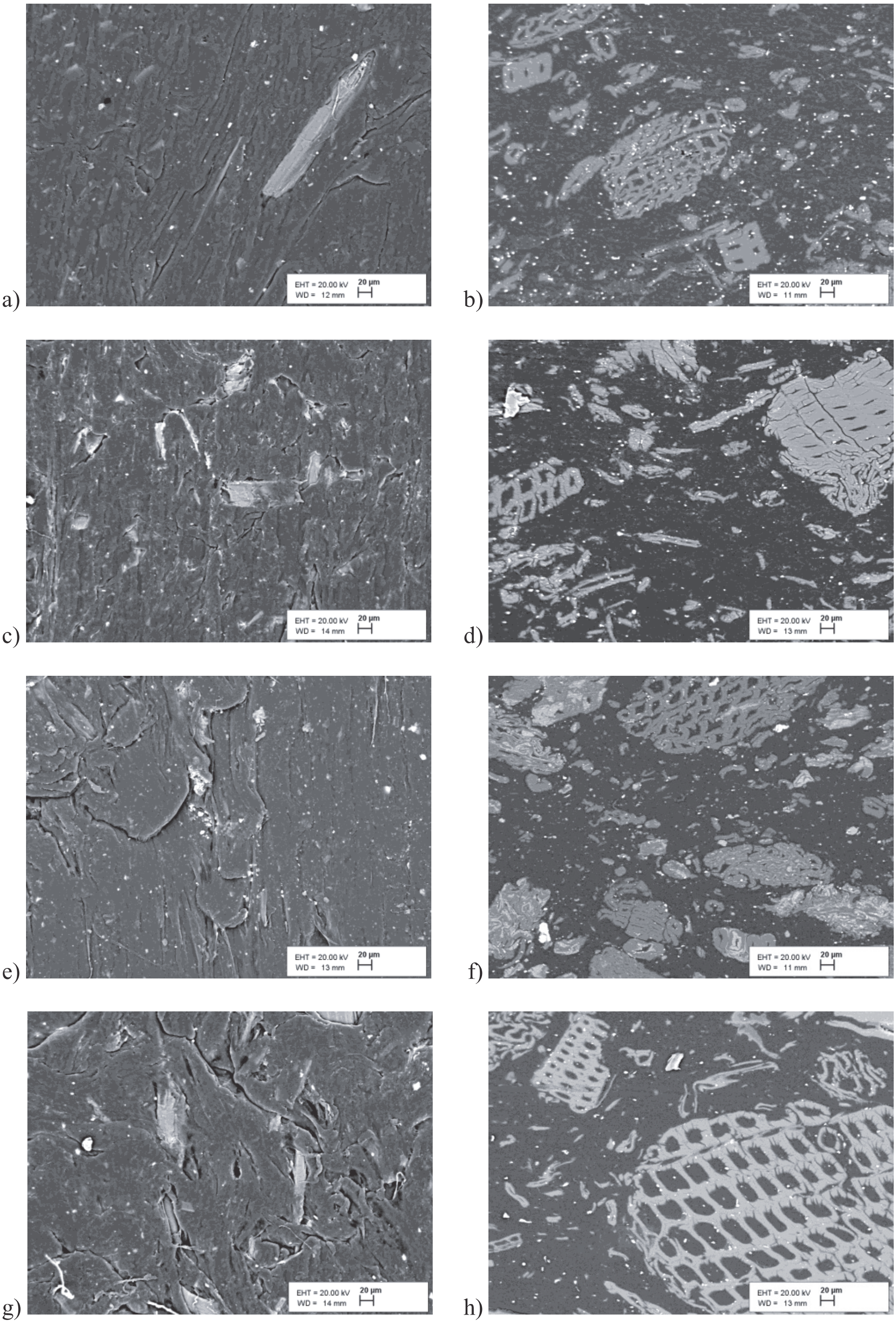
a)
EHT = 20.00 kV
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Fig.4 (continued)

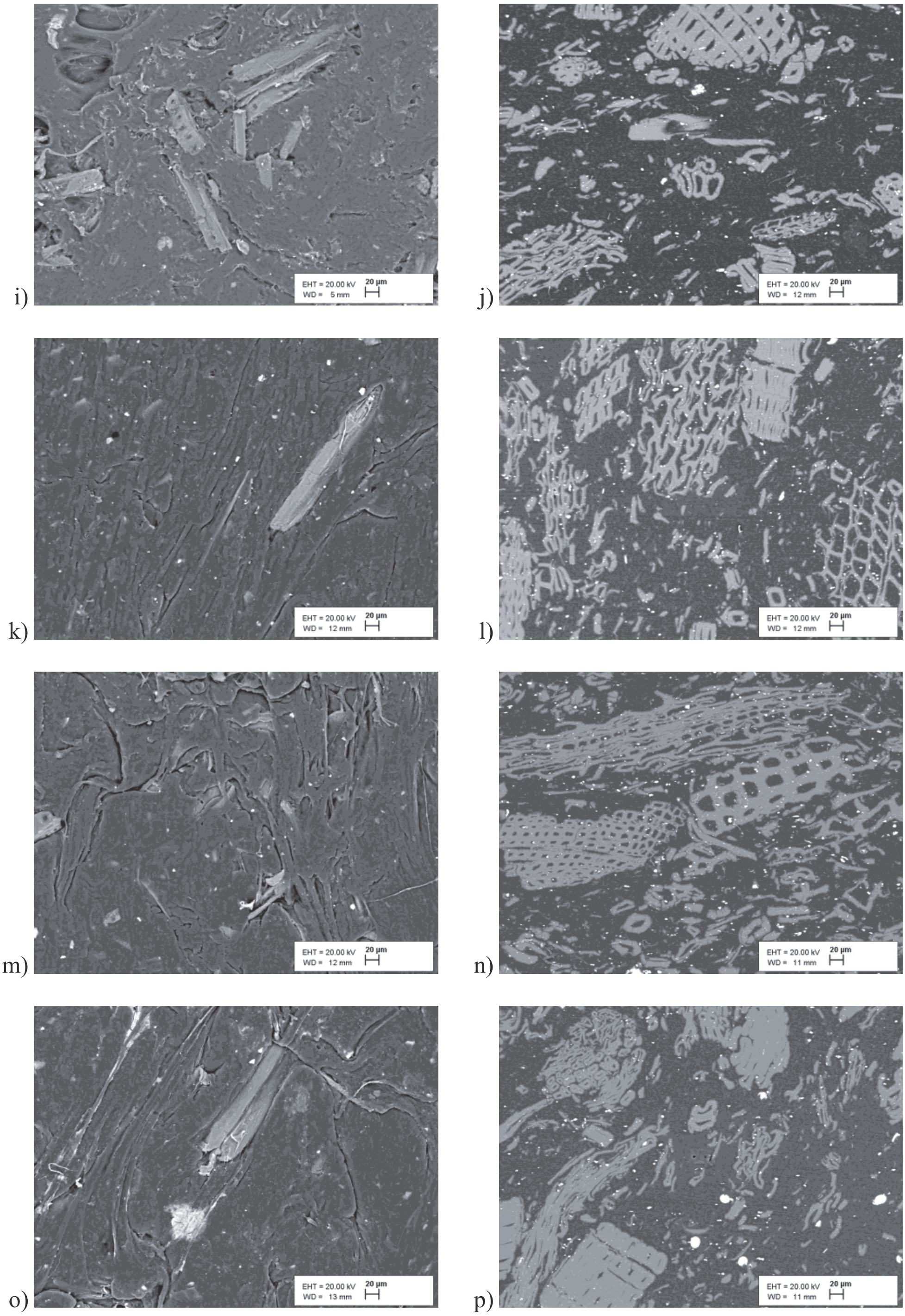
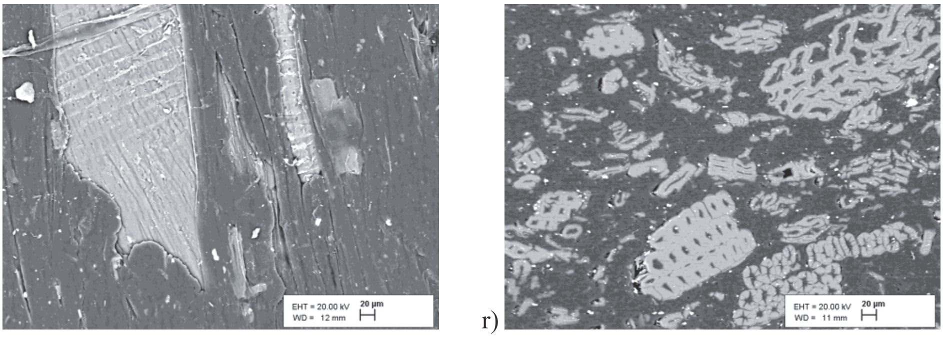


Fig.4 (continued)



q) r)

Figure 4. SEM micrographs of the surfaces and cross-sections of unmodified and modified composites: a) unmodified WPC surface; b) unmodified WPC cross-section; c) 5% NaOH modified WPC surface; d) 5% NaOH modified WPC cross-section; e) 17.5% NaOH modified WPC surface; f) 17.5% NaOH modified WPC cross-section; g) PVA modified WPC surface; h) PVA modified WPC cross-section; i) APTES modified WPC surface; j) APTES modified WPC cross-section; k) AA modified WPC surface; l) AA modified WPC cross-section; m) AA+DMF modified WPC surface; n) AA+DM modified WPC cross-section; o) VA+DMF modified WPC surface; p) VA+DMF modified WPC cross-section; q) Acrylonitrile modified WPC surface; r) Acrylonitrile modified WPC cross-section.

CONCLUSIONS

This study focused on the influence of WF modification on the mechanical properties of WPC. The chemical modification of WF with seven different chemicals was evaluated. It was found that chemical modification enhances the flexural properties of WPC materials due to an improved compatibility between WF and the polymer matrix. WF esterification showed the best flexural properties, indicating strong interfacial adhesion between WF and the PP matrix. The results of an impact strength test showed that the chemical modification of WF lowers the impact strength needed for breaking the WPC material. This is due to the fact that the debonding effect of the WF/PP matrix absorbs more impact energy with modified composites than with unmodified ones. The largest decrease in impact energy was observed with APTES modified composites. It can be concluded that the chemical modification of WF results in improved mechanical properties of WPCs. The results varied slightly by method but it is possible to choose an optimal modification method for the best mechanical performance of the composites.

In the DSC analysis, T_m, ΔH_m and X_c decreased with chemically modified composites. Most of the composites with chemical modifications showed higher values of X_c compared to unmodified composites, suggesting better interfacial adhesion between WF and PP. SEM micrographs showed that the surfaces of the modified composites had fewer voids and cavities, resulting in a more homogeneous material with improved mechanical properties.

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Appendix 3

Publication III

Kallakas, H.; Ayansola, S. G.; Tumanov, T.; Goljandin, D.; Poltimäe, T.; Krumme, A., Kers, J. (2019). Influence of Birch False Heartwood on the Physical and Mechanical Properties of Wood-plastic Composites. BioResources, 14 (2), 3554−3566.

Influence of Birch False Heartwood on the Physical and Mechanical Properties of Wood-plastic Composites

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The influence of birch false heartwood was investigated relative to the physical and mechanical properties of wood-plastic composites. Birch wood (sapwood and false heartwood) particles were modified with 5 wt% NaOH (by wood content) and 5 wt% 3-aminopropyl-triethoxysilane (by wood content) before being compounded with polypropylene in a co-rotating twin-screw extruder. The compounded composites were then injection moulded into standard test samples. The resulting composites were grouped into four categories: birch sapwood, modified birch sapwood, false heartwood, and modified false heartwood. Neat polypropylene samples were produced as a reference. The samples were tested for their tensile and flexural properties, water absorption, thickness swelling, and ultraviolet aging. The compositions of the composites were analysed using Fourier transform infrared spectroscopy. The results showed that the tensile strength of all of the samples decreased after water absorption. Water absorption decreased the impact strength of all of the composites. Ultraviolet radiation degraded the neat polypropylene and lowered the mechanical properties of all of the composites. Surface chalking was observed in all of the wood-plastic composites exposed to ultraviolet aging, with colours ranging from brown and brownish black to white.

Keywords: Birch; False heartwood; Wood-plastic composite; Polypropylene; Mechanical properties; Water absorption; UV radiation

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INTRODUCTION

Birch (*Betula pendula*) is abundant and it often develops a brown colouration in its heartwood that is referred to as false heartwood or red heartwood. This is a wood defect common to birch and other wood species, such as beech, maple, ash, poplar, linden, *etc.*, and its occurrence increases with the tree age. The formation of false heartwood is induced by diverse exogenous factors, including various kinds of injuries or stresses that damage the tree, which trigger a succession of processes (Hörnfeldt *et al*. 2010). The extent of both normal and false heartwood increases as the tree ages. When the tree age exceeds approximately 70 years to 90 years, the wood material near the pith is often darkened by decay. A common cause of stress in birch is drought; another is the breakage of branches, which creates openings or stem injuries, thereby exposing injured cells to atmospheric conditions. Several factors are responsible for this type of discolouration and these factors are generally similar to those of the formation of normal heartwood. These include the emptying of the living contents of cells in the stems, decrease in the conductive capacity, excessive air penetration into the tree, aging of the parenchyma cells, drought (low temperature), presence of fungi, genetic predispositions, and forest silvicultural practices (Shigo and Hillis 1973; Prka *et al.* 2009; Hörnfeldt *et al.* 2010).

The formation process of false heartwood has been reported to begin in later stages, rather than beginning with poor soil quality (Shigo and Hillis 1973). Any mechanical damage inflicted on a tree with a dehydrated core zone results in oxygen absorption into the tree and initiates the process of tylose formation, which is an enzymatic process (Prka *et al.* 2009). Air in the ripewood (dehydrated) zone causes the parenchyma cells to die quickly. According to Shigo and Hillis (1973), false heartwood differs from heartwood in that heartwood substances are stored either on the outside or inside of the parenchyma, instead of being stored in the cell walls.

Problems associated with the use of false heartwood has often been a concern in the wood industry. False heartwood has often led to a reduction in the price of wood when wood is visually graded because of the difficulties in distinguishing between discoloured and altered wood (Hörnfeldt *et al.* 2010), as well as wood waste because false heartwood does not yield quality veneer that can be used in plywood production. Hence, false heartwood is used either as an energy source or is utilized as internal plywood layers, but never at the top of the surface. A possible use of false birch heartwood is as a filler in the manufacturing of wood-plastic composites (WPC). Wood-plastic composite is a material obtained by combining wood as a filler or reinforcement material with plastic. This often results in a product with enhanced material properties, which prolongs the durability and preserves the beauty of the product. Several works have been conducted on the properties of wood and plastic combinations, with different researchers focusing on different polymers and wood species (Bledzki and Faruk 2006; Taib *et al.* 2006; Mijiyawa *et al.* 2015). Several research areas have also been investigated for WPCs, such as artificial and natural weathering of WPC, the effects of different particle sizes and filler materials, the effects of ultraviolet (UV) radiation and resulting colour changes, the physical and mechanical properties of WPC, *etc.* (Gwon *et al.* 2010; Gallagher and McDonald 2013; Fabiyi and McDonald 2014; Peng *et al.* 2014).

This research investigated the use of false birch heartwood as a filler material in WPC. The specific objective of this study was to investigate the effect of false birch heartwood on the physical and mechanical properties of WPCs. The results were compared with birch sapwood wood-based composites.

EXPERIMENTAL

Materials

The birch wood (sapwood and false heartwood) was supplied in the form of veneers by Kohila Vineer OÜ (Kohila, Estonia). The experimental work began with the separation of the birch false heartwood from the sapwood. The false heartwood veneer pieces were separated from the birch veneer by hand crushing, after which they were carefully visually inspected to remove any sapwood veneer leftovers. The birch veneers were then initially crushed mechanically to particles using a DS-A disintegrator (Tallinn University of Technology, Tallinn, Estonia), after which the wood particles were mechanically refined into wood particles with a specific size using separation grinding with a DSL-115 disintegrator (Tallinn University of Technology, Tallinn, Estonia). The wood particle length and distribution were measured using the analytical sieve shaker method with a Fritsch Analysette c3 (Weimar, Germany). The sieve sizes ranged from 25 mm to 0.025 mm and the samples were crushed into a particle size of 1 mm.

Polypropylene (PP) (PPH 11012 homopolymer, Total Petrochemicals, Feluy, Belgium) was used as the matrix material. The PP had a density of 0.905 g/cm^3 and a high melt flow index of 55 g/10 min. To modify the wood particles, sodium hydroxide (NaOH) with a minimum purity of 98% and 3-aminopropyl-triethoxysilane (APTES) (assay = 98%, density = 0.946 g/mL) were obtained from Sigma-Aldrich Chemical Co. (St. Louis, Missouri, USA), and acetic acid (99.8%, M = 60.05 g/mol) was obtained from Lach-Ner (Neratovice, Czech Republic).

Wood Modification

The wood particles were first treated with a 5.0 wt% (by wood content) NaOH solution at room temperature (23 °C) and left for approximately 90 min. The wood was then thoroughly washed with distilled water to neutralize the excess NaOH and then oven-dried at 60 °C for 24 h. The alkaline disrupted the hydrogen bonds that were present on the fibre surface. Before silane modification of the wood particles, APTES (5.0 wt% by wood content) was immersed in a solution of ethanol and distilled water at a ratio of 6:4 and continuously stirred for 1 h for silane hydrolysis. At the same time, the pH of the solution was adjusted to a range of 4 to 5 with acetic acid while stirring. Thereafter, the silane solution was poured onto the wood particles and left for 2 h at room temperature. The wood particles were then oven-dried at 60 °C for 24 h. Then, the modified wood particles were collected and placed in a sealed airproof plastic bag to prevent moisture absorption.

Composite Processing

The wood particles were mixed with PP at a ratio of 60 wt% wood to 40 wt% PP for all of the samples. The composites were compounded in a Brabender Plasti-Corder PLE 651 co-rotating twin-screw extruder (Duisburg, Germany). The barrel had four melting temperature zones that were set to 180 °C, 185 °C, 190 °C, and 190 °C. The rotation screw speed was 60 rpm throughout the process. The extruded materials were allowed to cool naturally and granulated afterwards. The test samples were made by injection moulding (Battenfeld BA 230E, Vienna, Austria), according to ISO 527-2 (2012). Prior to injection moulding, the composite granules were oven-dried at 80 °C for 24 h to remove any moisture in the material. The injection moulding machine was set to temperatures between 170 °C and 180 °C, with an injection pressure of 7 MPa. Table 1 shows the composition of the raw materials in the composites.

Table 1. Composition of the Composites

Sample	PP (wt.%)	Birch (wt.%)	NaOH (wt.%)	APTES (wt.%)
PP	100	-	-	-
SW	40	60	-	-
MSW	40	60	5	5
FHW	40	60	-	-
MFHW	40	60	5	5

SW – sapwood; MSW – modified sapwood; FHW – false heartwood; and MFHW – modified false heartwood

Methods

Mechanical properties

The tensile and flexural tests were performed on an Instron 5866 (Norwood, Massachusetts, USA) in accordance with ISO 527-2 (2012) and ISO 178 (2010), respectively. The test speed was 5 mm/min, and the tensile strength, flexural strength, and modulus were calculated. The test was conducted at room temperature and a relative humidity of 50%. The thicknesses of the specimens were measured with a calliper and at least six test specimens were tested. The notched Charpy impact strength was tested with a Zwick 5102 pendulum impact tester (Ulm, Germany) in accordance with ISO 179-1 (2010) at room temperature.

Water absorption and thickness swelling

The water absorption and thickness swelling were measured according to EN 15534-1 (2014). Each test specimen was weighed, and its thickness was recorded. The samples were completely immersed in water at room temperature for 672 hours, with measurements taken at 24 h, 48 h, 96 h, 168 h, 336 h, and 672 h. For each sample, at least six specimens were examined, and the water level was monitored daily to ensure constant and complete immersion in water. The percentage change in the mass relative to the initial mass was calculated. At the end of the water absorption test, the specimens were tested mechanically (tensile, flexural, and impact tests) to determine the behaviour of the WPCs after exposure to water.

UV exposure and colour analysis

Ultraviolet exposure was performed in a UV chamber. The WPC samples were irradiated with UVA-351 type fluorescent lamps (TL-D 36W/08 T8 blacklight, PHILIPS, Amsterdam, Netherlands). The peak wavelength of the tube was 351 nm. The exposure cycle was performed for 2016 h, and the intensity was 5 W/m^2. The specimens were occasionally removed from the chamber and colour measurements were taken at 24 h, 48 h, 96 h, 168 h, 336 h, 840 h, 1008 h, 1176 h, 1344 h, 1512 h, 1680 h, 1848 h, and 2016 h. The colour measurement was conducted with a Minolta Chroma Meter CR-121 (Osaka, Japan) in accordance with ISO 4582 (2017) after 2016 h using the CIELAB colour system. The total colour difference (ΔE), which indicated the change in the colour, was calculated using Eq. 1,

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)} \qquad (1)$$

where ΔL, Δa, and Δb are the differences between the initial values and values after weathering of the L* (lightness), a* (green-red colour), and b* (blue-yellow colour), respectively.

FTIR analysis

The efficiency of the chemical modification was verified using Fourier transform infrared (FTIR) spectroscopy with a Brucker LUMOS FTIR microscope with an integrated FTIR spectrometer (Billerica, Massachusetts, United States) using the ATR-FTIR method. The spectral resolution used was 4 cm^{-1}, and the spectra were recorded over the range of 3500 cm^{-1} to 500 cm^{-1}. Thin wafers were cut from the previously produced test specimens using a scalpel. The thin wafers were placed under a clamp, and then the spectra were measured, and the peaks were marked.

RESULTS AND DISCUSSION

Tensile Strength

The results of the tensile tests are presented in Figs. 1a and 1b. The results showed that the modified birch sapwood samples had tensile strengths that were slightly higher by 6.67% than the unmodified birch sapwood samples, which were 22.71 MPa and 21.3 MPa, respectively. The modification of the wood particles with 5 wt% APTES and 5 wt% NaOH increased the tensile strength of the composites, which was also reported by Kim *et al.* (2010) and Kallakas *et al*. (2015). The modified and unmodified birch false heartwood samples had similar average tensile strength values of 21.34 MPa and 21.76 MPa before immersion and 16.34 MPa and 18.19 MPa after immersion, respectively. The addition of 5 wt% APTES and 5 wt% NaOH did not affect the tensile strength of the false heartwood at a 60% wood content before soaking. Instead, there was a 10.17% decrease in the tensile strength of the modified false heartwood after immersion in water. This suggested that silane was not able to penetrate the bonds of the heartwood to enable interfacial adhesion of the composite. The reason for this could have been that the modification process opened the PP/wood particle interface to water degradation, which consequently led to a reduction in the strength of the false heartwood composite. Other than the control sample, the false heartwood composites had higher strength values than the other composites after immersion. This was because the heartwood contained a non-living core and non-conducting tracheary elements, which inhibited the absorption of water to an extent, unlike the other samples (Smith 2015).

The results showed that after water absorption, the tensile strength decreased by 20.67%, 21%, 11.8%, and 23.4%, whereas the modulus decreased by 39.4%, 44%, 37.6%, and 48.7% for the birch sapwood, modified birch sapwood, false heartwood, and modified false heartwood, respectively. This was comparable to the 46% to 50% reduction in the tensile modulus reported by Taib *et al.* (2006). One reason the modulus showed a greater decrease may have been the high wood content (60 wt%) used in this work. Another reason for these reductions could have been that the wood, which is hydrophilic in nature, absorbed water. This led to swelling and the eventual formation of microcracks. The modified birch sapwood had the highest modulus of 4.5 GPa before immersion, while the modified false heartwood had the lowest modulus of 4.2 GPa before and after water absorption. The modified false heartwood was affected mostly by water because it had the greatest absorption. The false heartwood had a 27% higher modulus than the modified false heartwood after soaking in water. This indicated that silane had no effect on the false heartwood for improving its properties, but caused the composite to degrade more.

After exposure to UV for 2016 h, the PP lost 56% of its tensile strength and became brittle. This was because of the crystallization of PP, which resulted from a chain scission reaction of the polymers during UV weathering (Fayolle *et al.* 2008). The modified birch sapwood composites had the highest tensile strength after exposure to UV (21.41 MPa). Both the false heartwood and modified false heartwood composites had almost the same tensile strength (20.44 MPa and 20.47 MPa, respectively), which translated to a reduction of 6% and 4%, respectively. The birch sapwood composite had a tensile strength of 20 MPa, which was a reduction of 6%. Hence, the modification with 5 wt% APTES did not influence the tensile strengths of the modified composites that were exposed to UV. Similar trends were observed for the tensile modulus, as is shown in Fig. 1b. The tensile modulus, in general, decreased for the PP and all of the WPCs.

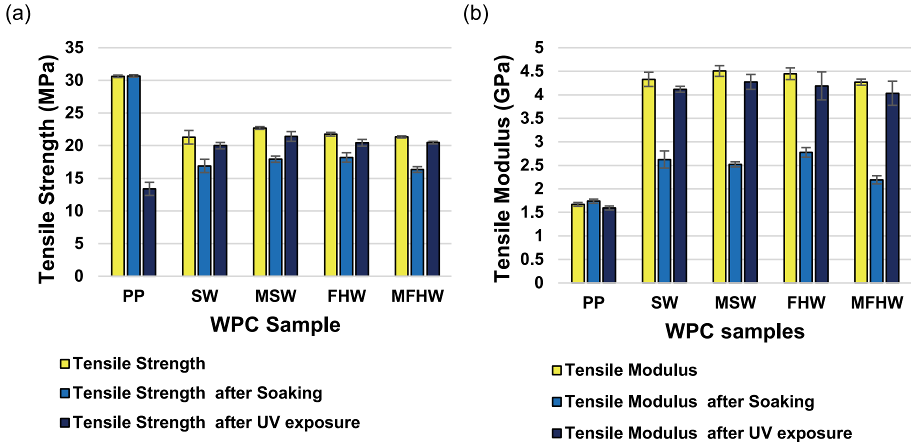

Fig. 1. Tensile Properties of the WPC samples before and after soaking in water and exposure to UV; SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

Flexural Strength

Figures 2a and 2b show the comparison of the flexural strength and flexural modulus (MOE) of all of the composites and the neat PP before and after WPCs were immersed in water and exposed to UV irradiation. The modified birch sapwood composite before soaking in water had the highest flexural strength of 46.9 MPa, which was 4.8% higher than that of the neat PP (44.7 MPa) and 2.5% higher than that of the unmodified birch sapwood composite. This indicated a strong adhesion interface between the wood fibre and APTES. An addition of 5 wt% APTES did not affect the flexural strength of the modified false heartwood as both the false heartwood and modified false heartwood had about the same strength before being soaked in water (44.2 MPa and 44.7 MPa, respectively).

However, the effect of the APTES modification was visible in the flexural strength of the modified false heartwood composites after they were soaked in water. All of the samples, apart from the neat PP, showed a reduction in the flexural strength of the composites after immersion for 28 d (Fig. 2a). The flexural strength in the birch sapwood and modified birch sapwood composites was reduced by 12.2% and 14.4%, respectively. After water absorption, the false heartwood composite showed the lowest reduction in the flexural strength of 10.6% and the modified false heartwood showed the highest reduction in the flexural strength of 16.6%. This indicated that the modified false heartwood absorbed more water than the false heartwood. This may have been because false heartwood is known to have a reduced moisture content compared with sapwood (Torelli 1984; Baettig *et al.* 2017); hence, it may be concluded that APTES can increase the permeability of false birch heartwood. This indicated the impact of modification on the rate of water absorption of the composites. The bond quality at the interface of the polymer matrix and filler impacted the strength of the composites (Stark 2001). The hydrophilic nature of wood led to the absorption of more water, which led to swelling and the formation of microcracks. The modified birch sapwood composites had the highest MOE (4.89 GPa) before immersion in water, which was higher than that of the unmodified birch saw wood, false heartwood, and modified false heartwood composites by 3.3%, 18.7%, and 12%, respectively. After water absorption, the MOE decreased by 46.3%, 66.4%, 18%, and 72.3% for the birch sapwood, modified birch sapwood, false heartwood, and modified false heartwood composites, respectively.

The ductile PP turned brittle after exposure to UV for 2016 h and the degradation of the plastic was easily noticed as they were picked up for testing. Badji *et al*. (2017) also reported this brittleness. There was a slight decrease of 2.5% to 7.2% in the flexural strength for all of the composites. A similar result was obtained by Kallakas *et al.* (2015), who recorded a maximum decrease in the flexural strength of 6.5%. The flexural MOE for all of the composites increased after exposure to UV. This indicated that the material became ductile. The increase ranged from 3.1% for the modified birch sapwood to 16.7% for the false heartwood composites. The flexural MOE that was obtained for the false heartwood (4.8 GPa) was higher than that obtained for the modified false heartwood (4.68 GPa). A similar trend was obtained for the flexural strength of the false heartwood composite after UV exposure (43.2 MPa), which was higher than the flexural strength of the modified false heartwood composite (42.1 MPa).

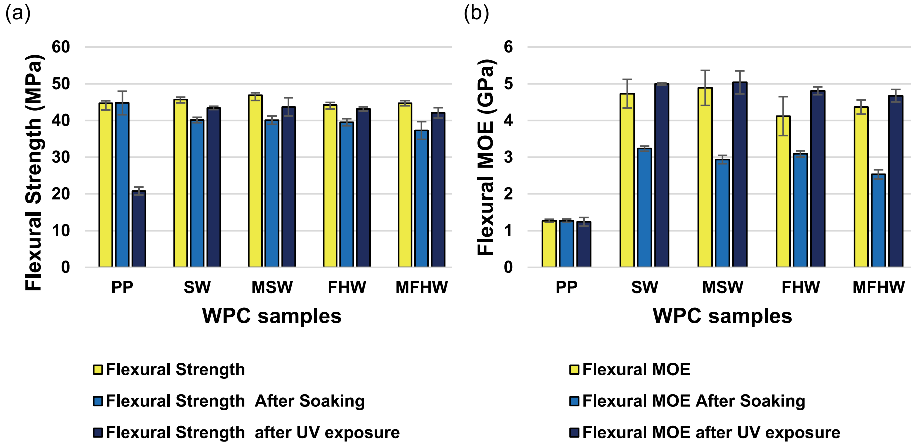

Fig. 2. Flexural Properties of the WPC samples before and after soaking in water and exposure to UV; SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

Water Absorption and Thickness Swelling

The water absorption and thickness swelling of the composites are presented in Figs. 3a and 3b, respectively. The water absorption of the composites was observed to increase with the immersion time. A similar result was reported by Bouafif *et al.* (2008). Likewise, the thickness swelling of the composites increased with the immersion time (Fig. 3b). The total immersion time was 672 h. Modification with 5 wt% APTES and 5 wt.% NaOH increased the water absorption of the modified false heartwood WPCs. The water absorption of the false heartwood WPC increased by 28%, which was greater than the increase seen for the water absorption of the modified birch sapwood WPC (4.3%). The modified false heartwood WPC had the highest absorption of 17.26% and the false heartwood WPC had the lowest water absorption of 13.47%. This was explained by the nature of heartwood, which contains non-living cells and extractives. According to Olsson *et al.* (2001), the extractives in heartwood are the main source of low water permeability.

The age and growth rate of the tree affect the content and composition of the extractives (Metsä-Kortelainen 2011).

Metsä-Kortelainen *et al.* (2006) demonstrated that a significant difference exists between the water absorption of sapwood and heartwood in Scots pine and spruce. Sapwood absorbs more water than heartwood, and heat treatment decreases water absorption in heartwood (Metsä-Kortelainen *et al.* 2006). Also, the mechanism of capillary action at the edges of the wood fibre in the composites could have been responsible for the transportation of water molecules along the fibre-polymer matrix interface of specimen cuts, taking advantage of the flaws and voids that may exist around such an interface (Taib *et al.* 2006). The absorption of water by the composites was assumed to be caused by the hydrophilic wood flour and not the hydrophobic PP because PP did not show any water absorption. Similar results have also been shown in previous research (Stark 2001). Kim *et al.* (2010) reported that the reduction values of silane-treated composites were 2.5 times greater than the values of untreated composites. This was explained by the limited exposure of water molecules to wood particles, which may have been caused by the hydrogen bonds between the hydroxyl and siloxane groups.

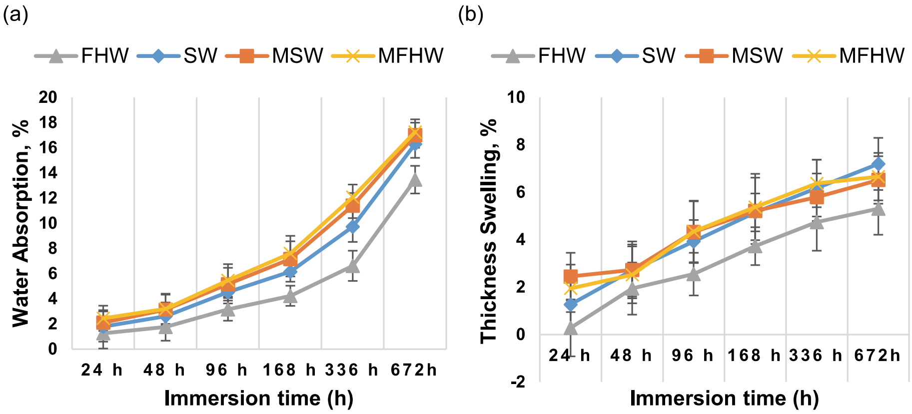

Fig. 3. Water absorption and thickness swelling of the WPC samples: SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

Colour Analysis

The colour change (ΔE) and change in brightness (L) of the neat PP and WPCs after exposure to artificial weathering compared with the initial colour before exposure are presented in Figs. 4a and 4b. No significant change was observed in colour parameters a^* and b^*. Colour changes were noted for the composites, all of which had turned lighter. This was in accordance with previous studies (Kiguchi *et al*. 2007; Stark and Mueller 2008). It was observed that weathering induced bleaching in the composites. Bleaching as a result of weathering has been reported to be caused by the lignin component in wood (Peng *et al.* 2014). Surface chalking such as the formation of a whitish, chalky powdery, friable layer was observed in all the WPCs exposed to artificial weathering, with colours ranging from brown and brownish black to white. This can be attributed to the decomposition of the lignin in the surface wood cells (Feist and Hon 1984). As was observed by Kiguchi *et al.*

(2007), cellulose, which is whitish and comparatively stable against UV, may have been the main chemical component. According to Fabiyi and McDonald (2014) and Peng *et al.* (2014), the chain scission reaction of lignin can lead to the formation of a paraquinonic structure, which can reduce to hydroquinone that causes the whitish colour of WPCs after weathering.

The colour differences of the composites and neat PP are presented in Fig. 4a. The modified birch sapwood and modified false heartwood had about the same colour change at the end of 2016 h (20.03 and 20.69, respectively), which were the greatest changes in colour among the composites. This was attributed to the effect of the modification with APTES on the wood. During modification, some of the lignin content in the wood was already degraded, which enhanced the adhesion with the polymer. Upon exposure to artificial weathering, photo-degradation of the remaining lignin, whose chromophoric groups were able to absorb UV rays and form free radical groups, took place (Peng *et al.* 2014; Badji *et al.* 2017). The neat PP had the lowest colour change of 2.16. A similar trend was observed for the brightness of all of the composites, with all of them becoming brighter, as is shown in Fig. 4b.

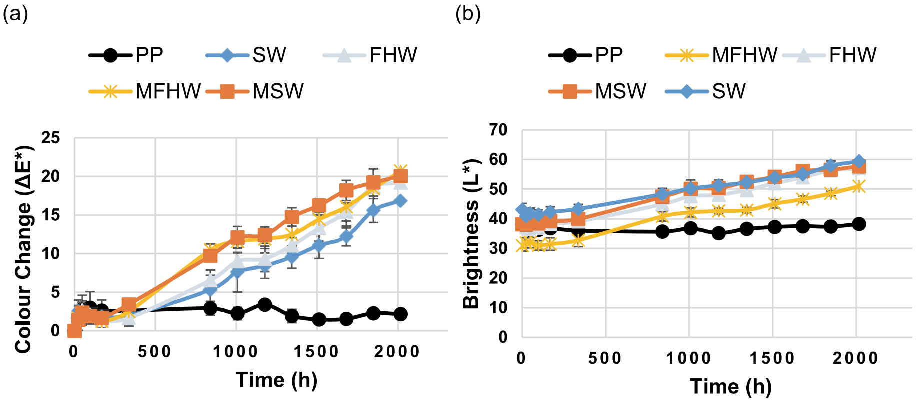

Fig. 4. Colour and brightness change of the WPC samples: SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

FTIR Analysis

The FTIR spectra of the composites are presented in Figs. 5a and 5b. The spectra showed a similar pattern for all of the samples, except for a few peaks that were not visible in the PP spectrum, but only in composites. In the fingerprint region (see Fig. 5a), the WPC showed a difference in the band absorption intensity, which was expected. The wide peak at 3347 cm^{-1} in the region 3400 cm^{-1} to 3200 cm^{-1} is assigned to –OH (hydroxyl) groups mainly from cellulose. However, the peak intensity has decreased due to the polarity reduction the surface of wood particles after modification (Lv *et al.* 2015). It can be seen that the hydroxyl group intensity is affected by the sodium hydroxide treatment which has decreased the absorption of hydroxyl groups for modified WPC samples and absorption peaks became narrower. According to Ghasemi and Farsi 2010, this indicates the emerging of amorphous region in the wood cellulose by removal of hydroxyl groups from its chain and reduction of the polarity on the wood surface. The intense peak at 2915 cm^{-1} was due to the C-H stretching in –CH_2– groups. The key absorption bands of PP (Fig. 5a) included

1457 cm^{-1}, 1374 cm^{-1}, and 981 cm^{-1} (CH$_3$ bending) (Morent *et al.* 2008). The birch sapwood has the high hemicellulose carbonyl groups peaks at 1736 cm^{-1} and 1602 cm^{-1} which have decreased with NaOH treatment.

It can be clearly seen that the WPC samples had very strong peaks at 1049 cm^{-1}, 668 cm^{-1}, and 612 cm^{-1}. To make it clearer, enlargements of these ranges of the FTIR wavenumbers for modified and unmodified birch sapwood and false heartwood composites are shown on Fig. 5b. The peak at 1049 cm^{-1}, shown on Fig. 5b is attributed to primary alcohols and aromatic ether (C-O) stretching vibrations (cellulose, hemicellulose, and lignin) (Chen *et al*. 2017). The birch sapwood composites showed the highest absorbance, at 1049 cm^{-1} compared to false heartwood composites and modified composites, indicating that false heartwood has less hydroxyl groups available. Bankole *et al.* (2016) also reported this. The APTES modification effect was responsible for the peak changes at 1049 cm^{-1}, which corresponded to the Si-O-C band. The intense peaks at 1049 cm^{-1} and 608 cm^{-1} was from the reaction between the hydroxyl groups of cellulose and that of silanol on the wood surface, which created Si-O-Si- and -Si-O-C ether bonds (Ma *et al.* 2017). In Fig 5b, it can be observed that peak intensity for the modified sapwood and false heartwood has decreased at the corresponding range of 1049 cm^{-1}, 612 cm^{-1}, and 608 cm^{-1}. This can be explained with the reduced number of primary alcohols on the wood surface. In addition, the absorption peaks shapes have flattened, indicating the decrease of –OH bonds formed between the –OH groups (Lv *et al*. 2015).

From the FTIR results, it can be seen that the APTES had reacted with both sapwood and false heartwood, but there was no visible reaction peak between the APTES and PP. That is also the main reason why the mechanical properties were not significantly improved by the APTES modification in this research. Also, it can be observed that the false heartwood modification had been more difficult due to the lower number of available –OH groups.

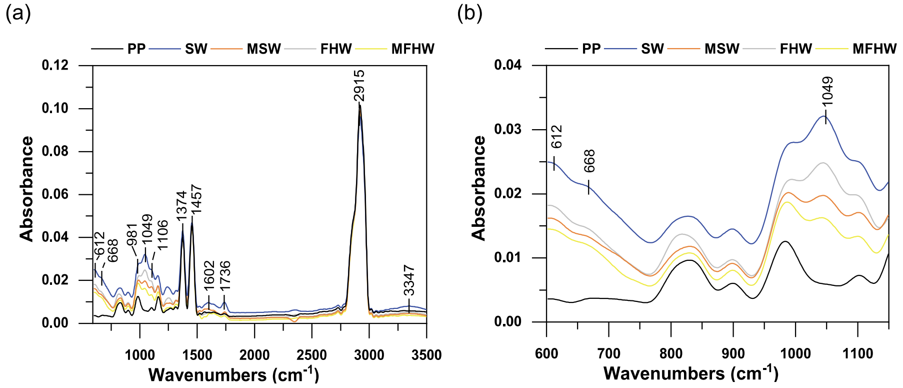

Fig. 5. FTIR spectra of the composites and neat PP: SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

CONCLUSIONS

1. The tensile strength of all of the samples was reduced after water absorption. The false heartwood and modified false heartwood had similar tensile strengths before soaking in water. After water absorption, the modified false heartwood had a 10.17% higher decrease in the tensile strength than the false heartwood.
2. The flexural strength of the false heartwood and modified false heartwood were about the same before soaking in water. However, the effect of APTES modification was visible in the flexural strength of the modified false heartwood composites after soaking in water.
3. The false heartwood composite showed the lowest reduction in the flexural strength of 10.6% and the modified false heartwood showed the highest reduction in the flexural strength of 16.6% after water absorption. This indicated that the modified false heartwood absorbed more water than the false heartwood.
4. The UV radiation degraded the neat PP and all of the composites. Surface chalking was observed in all of the WPCs exposed to artificial weathering, with colours ranging from brown and brownish black to white.
5. The use of false birch heartwood in the manufacturing of WPCs was shown to be possible. However, the modification of false birch heartwood should be improved in further studies to maximize its capabilities in WPC production.

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