TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

EFFECT OF BIRCH (*BETULA PENDULA* ROTH) FALSE HEARTWOOD ON THE THERMAL PROPERTIES AND DURABILITY OF WOOD-PLASTIC COMPOSITES IN OUTDOOR CONDITIONS

KASE (*BETULA PENDULA* ROTH) VÄÄRLÜLIPUIDU MÕJU PUITPLASTKOMPOSIITIDE TERMILISTELE OMADUSTELE JA VASTUPIDAVUSELE VÄLISTINGIMUSTES

MASTER THESIS

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Tallinn, 2020

AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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Thesis is in accordance with terms and requirements

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THESIS TASK

Student: Tanel Tumanov, 178154KVEM

Study programme: KVEM12/15 Technology of Wood, Plastic and Textiles

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Thesis topic:

Effect of birch (*Betula pendula* Roth) false heartwood on the thermal properties and durability of wood-plastic composites in outdoor conditions

Kase (*Betula pendula* Roth) väärlülipuidu mõju puitplastkomposiitide termilistele omadustele ja vastupidavusele välistingimustes

Thesis main objectives:

1. To study the effects of weathering on wood-plastic composites made with birch false heartwood.
2. To investigate the thermal properties of wood-plastic composites.
3. To study and assess the effect of modification with a coupling agent.

Thesis tasks and time schedule:

No	**Task description**	**Deadline**
1.	Milling and preparation of filler materials	April 2018
2.	Pre-treatment and modification of filler materials	May 2018
3.	Compounding and moulding the composite materials	May 2018
4.	Conducting thermal-related tests	Oct 2018
5.	Starting the weathering test, initial colouration measurement	Oct 2018
6.	Finishing the weathering test and final colouration measurement	Apr 2020
8.	Visual assessment and measuring tensile and flexural properties	Apr 2020
9.	Data analysis	May 2020
10.	Thesis pre-defence	11Th of May 2020
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PREFACE

The topic is a part of a expanded research that involves using birch false heartwood in wood – plastic composites. The research was mainly carried out in the TalTech Laboratory of Wood Technology. The aim of the work was meant to investigate the mechanical properties of wood - plastic composites made from birch sapwood filler and birch false heartwood filler to observe the differences in each batch of materials. Additionally, both materials are modified with a silane coupling agent 3-Aminopropyl-triethoxysilane (APTES) and the effects of modification are studied in this thesis. Standardised test specimens were made by mixing both birch sapwood and birch false heartwood with polypropylene. The test specimens were obtained by compounding the materials in a twin-screwed extruder and specimens were then injection moulded. The test specimens were placed on a stand outside the Laboratory of Wood Technology to expose the composites to the outdoor conditions. The composite samples were left on the stand for more than a year and afterwards the tensile and flexural strength were tested and compared with the initial pre-weathering figures. Also, the change in colouration was measured, and changes in appearance were observed. The other part is related to describing the viscoelastic properties of original(not subjected to weathering) materials, where the Vicat softening temperatures and heat deflection temperatures were determined and thermogravimetric analysis and dynamic mechanical analysis were conducted.

I would like to thank everyone who has provided help and guidance in the making of this paper, Prof Jaan Kers, Dr Triinu Poltimäe, Dr Heikko Kallakas and others. Thank you for the assistance.

Keywords: Wood-plastic composite, Birch, False heartwood, thermal properties, weathering, masters' thesis

List of abbreviations and symbols

APTES- 3-Aminopropyl-triethoxysilane

DMA- Dynamic mechanical analysis

HDT- Heat deflection temperature

FHW- False Heartwood

PP- Polypropylene

NaOH- Sodium hydroxide

MSW – Modified birch sapwood

MFHW- Modified False Heartwood

SW – Birch sapwood

UV – ultraviolet (radiation)

TGA- Thermogravimetric analysis

WPC- Wood-Plastic Composite

WP-Wood Particle

wt%- percentage by weight

INTRODUCTION

It has become apparent in the latter decades that we live in a world that has limited resources and the growth of overall world population is not slowing down soon. The demand for everyday household products and services is also increasing. The worsening state of environment and the depletion of resources has become a global issue. In the light of these problems, the more economical and sparing use of already available resources is becoming more actual day by day.

Plastics have become irreplaceable materials in our everyday life in the last half a century. The initial chemicals for the synthesis of plastics are mainly derived from crude oil, which is a nonreproducible resource. So, using natural renewable resources is increasingly becoming more popular. One option is to use natural fibres as a filler in synthetic material to make it more environmentally friendly [1]–[3]. These types of materials, where two or more different phases of materials are used, are called composite materials. Composites can combine the best of two separate materials – the most tangible everyday examples are reinforced concrete and car tyres where iron bars or in the case of tyres, steel belts are imbedded into the structure of the tyre to reinforce the structure. Composites using natural fibres like hemp fibre as fillers are already being used in the automotive industry and in construction [4].

One of the most abundant sources of cellulosic fibre is natural wood. As we all know, wood is abundant and a fantastic construction material. This implies that wood fibres or particles have a potential to be used as a filler inside a plastic material in order to substitute considerable part of plastic used in a bulk of material. But wood comes in different quality. False heartwood is a discolouration of tree trunk, usually a problem associated with birch (*Betula pendula*) and beech trees. Birch wood is extensively used in veneer industry, but false heartwood is considered being a nuisance and usually discarded as waste and burned to get heat and/or electricity. Previous research has been done in order to study the potential of using birch false heartwood fibre as a filler in polypropylene based composites [5], [6]. Using natural particles in a composite is complicated and poses many difficulties – the natural incompatibility between the interface of hydrophilic cellulosic particles and hydrophobic polypropylene chains [7]. Also due to hydrophilic nature of cellulosic particles they tend to absorb moisture and are susceptible to warping and deformation. In addition, wood particles start to degrade at around 200°C. The overall scope of this thesis is to study the weathering effects on wood-plastic composites and assess their endurance to the elements like rain, moisture, snow, heat differentials, sunrays, etc. Unlike a simple ultraviolet degradation test, this weathering test is more versatile and mimics the real-world conditions that a wood-plastic composite product must endure in real outdoor conditions. In addition to weathering tests, some thermal properties are to be studied to evaluate the thermal stability and load bearing capabilities of wood-plastic composites under elevated temperatures.

Previous studies regarding the same composites using Birch false heartwood filler have been done by H.Kallakas and G.Ayansola [5], [6], which included the determination of flexural and tensile properties, impact strength, influence of creep, FTIR spectroscopy, water absorption, the effect of accelerated weathering on mechanical properties and colouration. The effects of natural weathering and viscoelastic properties of the composites using false heartwood filler have yet to be studied. It is widely known that WPCs degrade in outdoor conditions and are prone to discolouration. According to previous papers the artificial ageing inside UV-chamber decreases the flexural modulus of elasticity and flexural strength. In addition, weathering increased the surface lightness of WPCs and scanning electron microscopy showed the presence of cracks and voids inside the degraded material.

The target of this research was to investigate the properties and behaviour of birch false heartwood particulate filler inside WPCs:

- The effects of weathering on the tensile and flexural properties of WPCs using birch false heartwood as filler.
- The effects of weathering on visual appearance, colouration and surface lightness of WPCs using birch false heartwood.
- Determine the Vicat softening temperature and heat deflection temperature of WPCs made with false heartwood filler.
- Determine the thermal stability of different WPCs.
- Give assessment to the internal structure and viscoelastic properties of WPCs using dynamic mechanical analysis.

The idea is to compare the results to birch sapwood filler and investigate whether false heartwood filler is an eligible substitute for sapwood. This work is divided into three main parts. The first one describes the general properties of wood filler, plastics, wood-plastic composites and the mechanism and effects of fibre modification with a coupling agent. The second part describes the making of WPCs and testing methods and third section is purely focused on analysing the results. The appendix contains material datasheets and previous research regarding composites made from birch false heartwood.

1 LITERATURE OVERVIEW

1.1 Birch wood and its properties

Silver birch (*Betula pendula)* is a medium-sized deciduous tree, which belongs to the Betulaceae family. The plant is native to Europe and its widespread in Siberia, China, Turkey, Caucasus and northern parts of Iran. It has spread into North America, where it is often considered as invasive species. The species is most common in northern Europe, where the distribution is fairly continuous in mixed forests. Tree has an average lifespan of 90-100 years, at most 120-150 years. [8]

Silver birch is among the most commercially important tree species in northern Europe. Its wood is used in plywood-making and carpentry as well as for pulpwood and fuel. The wood of silver birch is pale-coloured and there are no differences of any importance between the spring and summer wood or heart- and sapwood. The wood specific density is very high as shown in Table 1.1. The wood fibres are very short (kraft pulp fibre length is on average 1.1-1.5 mm [9]) and birch pulp is mixed with conifer pulp to improve paper quality. Curly birch (var. *carelica*), a special form of silver birch, is highly valued for the decorative colour pattern of the wood. There are several heritable pattern types and some of them can also be identified by visual inspection of the trunks. Silver birch (and birches in general) is an essential component of temperate and boreal forests and has a positive effect on the diversity of ecosystems. numerous herbivorous insects and symbiotic fungi are dependent on the presence of birches [10].

According to [11] all birch has a fine and uniform texture, closed pored and no significant odour. Birch dries with a fair amount of shrinkage. It loses almost 16% of its volume going from green to dry lumber and does like to warp and twist if enough weight is not applied to the green lumber as it air dries. Once dried it is stable. It is not resistant to decay, fungal and insect attack. Spalting is very common [8]. In all categories, birch exhibits good machining properties. It planes and sands to a smooth finish. It cuts and drills with limited difficulty, although it should always pre-drilled for nailing. Birch holds nails and screws relatively well and glues up easily. Some of the properties of birch wood are shown in Table 1.1.

Table 1.1 Properties of birch wood [11]

Properties	**Silver Birch *Betula Pendula***
Tree dimensions	height 20-30 m,.3-.6 m trunk diameter
Average dried weight, kg/m3	640
Specific gravity	0.5
Specific gravity, moisture content 12%	0.64
Janka hardness, N	5.360
Flexural strength, MPa	114.3
Elastic modulus, GPa	13.96

1.2 Heartwood and sapwood

Wood consists mainly from sapwood and heartwood. Heartwood is the dead, central wood of trees. The cells inside heartwood contain tannins and other extractive substances that darken its colour and sometimes make it odorous. Heartwood poses mechanical strength and is fairly decay resistant. Wood – preservative chemicals have difficulties penetrating heartwood. Sapwood is outer, living layers of the secondary wood of trees, which engage in transport of water and minerals to the crown of the tree. The cells therefore contain more water and lack the deposits of colouring substances commonly found in heartwood. Sapwood is thus paler and softer than heartwood and can usually be distinguished in cross sections of tree trunks. [12] Sapwood and heartwood are clearly visible on Figure 1.1.

Figure 1.1 Darker heartwood shown in the middle and lighter sapwood on the outside [12]

1.3 False heartwood

Some hardwood species do not have naturally occurring heartwood i.e. beech, poplar, ash, birch and others. Although, often birch and beech wood is plagued by a discolouration of the tree stem that starts from the pith and can take a significant proportion of the total wood mass. This discolouration is known by many names such as red heartwood, tension wood, false heartwood, wounded wood, protection wood, brown heart, blackheart, coloured wood [13]. False heartwood and red heartwood are one of the most common terms for this phenomenon, the latter is used mostly in industry. In this study, the term false heartwood is mostly used. The appearance and shape of false heartwood discolouration can be clearly seen on Figure 1.2.

The formation of false heartwood usually takes place in several stages. Usually the first stage is related to some kind of mechanical damage like branch or bark injuries, broken branches, stem wounds, cracks [13]. The second step involves the permeation of oxygen into the tree stem, and subsequent colouration of tree stem occurs because of polymerisation and oxidation of phenolic compounds [14]. After this, fungi and bacteria begin to grow in the region. This initiates the growth of tyloses i.e. bladder-like distensions of a parenchyma cell into the lumen of adjacent vessels which forms a barrier in order to protect healthy wood from decaying and further penetration of oxygen. Without the oxygen, fungus dies, and discolouration is the only consequence forming a region what we know as false heartwood. When tyloses fail to block the oxygen, wood may start to rot. [13],[14],[15],[16]

As it came apparent, the formation of coloured false heartwood can be quite complex in nature. A study [17] found the entry of microbes through damaged tree parts to be the main culprit for false heartwood formation. Another study [18] showed that the amount of false heartwood was correlated to the age of tree and where false heartwood became significant in trees over 40 years of age. The false heartwood region grows in diameter with aging.

Studies have shown that the properties of birch sapwood and false heartwood do not differ significantly, although false heartwood has been reported to have a higher moisture content than sapwood [14], [19]. This could inhibit the adhesion between hydrophilic wood particles and plastic polymer matrix. A study by Johansson [20] showed that the elastic modulus and compression strength of birch sapwood and false heartwood were relatively alike. False heartwood veneers had about 17% lower density than sapwood veneers. Another study [19] reported birch false heartwood veneer to have 150% higher surface roughness compared to veneer made from birch sapwood. Average tensile strength of both veneers had similar values, but the values of false heartwood varied greatly, indicating that false heartwood has more inhomogeneous properties.

The inherent inhomogeneous nature of false heartwood is one of the problems that it poses in industry apart from the visual appearance. The higher reported surface roughness of false heartwood makes it harder to glue the veneers evenly. The surface roughness probably poses a difficulty in plastic polymer and wood particle adhesion during wood-plastic composite manufacture.

Figure 1.2 Birch false heartwood shown in the middle of a wood slice [21]

1.4 Wood-plastic composites

Composite materials are such materials that are made from two or more structurally complementary materials with noticeably different physical or chemical properties, which remain distinct and separate in the final structure of the product [22], [23]. Composites can be classified based on the matrix, which could be metal, ceramics or polymers[24], [25] and also based on types of fibres/particles used inside the composite [26].

Wood-plastic composites or WPCs are composite materials made of wood fibre/wood flour and thermoplastic(s) such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), or polylactic acid (PLA). Thermoplastics are primarily used because they are relatively easy to process, mainly because they have a low melting temperature. Not all thermoplastics can be used, the melting temperature of thermoplastic material should remain below ≈210 °C, where wood degradation starts to take place. In addition to wood fibre and plastic, WPCs can also contain other ligno-cellulosic and/or inorganic filler materials. WPCs are a subset of a larger category of materials called natural fibre plastic composites (NFPCs).

WPCs are relatively new materials compared to products made from solid timber. According to [27] the most widespread use of WPCs in North America is in outdoor deck floors, but it is also used for railings, fences, landscaping timbers, cladding and siding, park benches, moulding and trim, window and door frames, and indoor furniture.

1.4.1 Advantages of WPCs

Generally, WPCs do not corrode and are resistant to decay and rot [28]. WPCs have good workability and usually can be machined using conventional woodworking tools. Unlike regular wood, WPCs can be moulded into practically any desired shape. They are also flexible and possess mechanical properties that are comparable to neat polymers, despite the high filler content. Flexibility allows to form arching curves. Another advantage over wood is that the WPC does not need to be painted, with the use of additives, the final product can be given any desired colour. Although recycling WPCs is more complicated than wood or plastic, disposed WPCs can be used to produce new WPCs.

1.4.2 Disadvantages of WPCs

Because WPCs contain wood particles, they tend to absorb moisture [28]. Increased moisture also content decreases tensile strength [6]. The plastic polymers and adhesives added into WPCs make wood-plastic composite difficult to recycle. WPCs have a lower strength and stiffness than wood, and they experience time and temperature-dependent behaviour like creep [29]. The wood particles inside the composite are susceptible to fungal attack, though less than solid wood and the polymer can be degraded by UV radiation [30]. Also, one downside is the increased fire hazard compared to solid wood. This is because plastic materials have a higher heat content, which means that plastics produce a lot of heat when burning, potentially leading to more vigorous fires.

1.4.3 Plastic matrix

One of the most wide-spread commodity plastics used in everyday life, and in the manufacture of WPCs, is polypropylene (PP). PP is the second most produced synthetic thermoplastic after polyethylene (PE) and is used to produce automotive details, household products, fibre, isolation for wires etc. PP is produced via chain-growth polymerisation from the monomer propylene. Ziegler – Natta and more often metallocene catalysts are used to produce PP and regulate how the methyl group ends up in the polymer chain. The term tacticity describes for polypropylene how the methyl group is oriented in the polymer chain. PP can be either isotactic (i-PP), syndiotactic (s-PP) or atactic (a-PP). The structures of different PP forms are shown on Figure 1.3 below. Commercial polypropylene is usually isotactic, so consecutive properties are attributed mainly to i-PP.

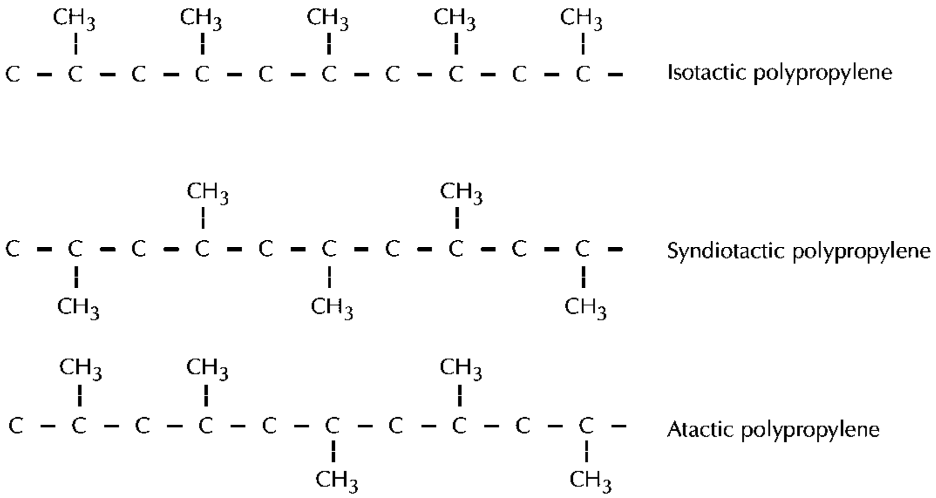

Figure 1.3 Different forms of polypropylene [31]

Both i-PP and s-PP are relatively strong and flexible, having a melting temperature of 174 °C and 217 °C. Atactic PP is an amorphous rubber-like material and is often used to make gaskets. Semi-crystalline i-PP is one of the least dense plastics having a density of 0.90-0.91 g/cm^3. Operating temperature lies between 0°C and 100°C and can be exceeded for a short period of time. Semi-crystalline PP has high impact strength, stiffness and retains its properties up to softening point. This makes it a good material for containers and pipes that come into contact with hot liquids. I-PP is relatively resistant to fatigue, relatively scratch-resistant and has high gloss. Also, it has good dielectric properties comparable to PE.[32]

Properties of PP can also be altered by regulating stereoregularity, this means adding segments with different tacticity together into PP chains. Also links from PE can be co-polymerised into PP chains, forming a copolymer. These modifications allow to greatly change the properties of PP like strength, hardness, melting temperature, etc.

1.4.4 Wood filler

Many natural wooden materials like wood chips, flakes, fibres, shavings and sawdust can be used to make a WPC. These can be transformed into suitable filler materials like wood flour (WF) with little effort. What makes these fillers especially desirable, is their low cost, and often these fillers are considered as waste. So, it makes sense to use these eco-friendly reproducible resources in a WPC and it helps to decrease the total amount of waste. Apart from the overall quality of raw materials, the size distribution and content percentage of wood flour particles are crucial in shaping out the mechanical properties of WPCs. The result in a study [33] showed that the particle size distribution influences the mechanical properties of WPC. An excessive percentage of small particles decreased the mechanical properties of WPC. Typical filler particle/fibre sizes in WPCs are chosen between 0.18 to 0.35 mm [22]. Fillers larger than these are usually considered as "oversize" and are seldom used for making WPCs, especially via injection moulding [22], [34]. Despite this, several studies have shown polypropylene based WPCs to have improved mechanical properties when the length and aspect ratio (ratio of length to diameter) of particle/fibre was high [35]–[37]. This promises to make wood fillers with a length of several millimetres to be usable in making WPCs.

1.4.5 Improving the interface between plastic and filler

The interface between the fibre and matrix is critical for the function of the composite material and as such is considered as a crucial factor [38], [39]. The major factors that determine the properties of WPCs are fibre dispersion, fibre length distribution, fibre orientation and fibre-matrix adhesion [22],[40],[25]. WPCs possesses difficulties regarding to the poor interfacial adhesion between polar hydrophilic wood particles and non-polar hydrophobic polymer, which is usually very poor and needs to be enhanced with the help of coupling agents [22], [41]. The idea behind coupling agent or compatibilizer is creating an interphase between wood filler and plastic matrix in a way that the compatibilizer has a way of interacting with both the hydrophilic wood filler and hydrophobic plastic matrix [42]. Coupling agents are usually added in small quantities to bond different otherwise incompatible materials. The bonding takes place via the formation of covalent bonds, secondary bonding, polymer molecular entanglement or mechanical interlocking [43]. The main methods of modification applied for wood fillers are esterification, graft copolymerisation and treatment with silanes [44].

Compounds known as silanes are one of the most common coupling agents for improving the adhesion of different wood fillers and other natural fibre fillers as well. Silane coupling agents have different functional groups at either end which allows reaction to take place with OH groups of cellulose whilst the other end can interact and form a bond between the functional groups of polymer matrix [45]–[47]. (3-Aminopropyl)triethoxysilane or abbreviated as APTES is one of the most commonly used silanes due to its simplistic structure and relatively minimal cost [48]. APTES has been used widely, including the previous studies regarding the exact same WPCs used in this thesis(included in appendix). The general scheme of APTES grafting onto cellulose based surface is depicted on Figure 1.4 below. The process normally involves three steps [49]–[52]:

- The hydrolysis of the alkoxy groups of the silane in the presence of water to give the respective silanol.
- Adsorption of the silanol groups onto surface of cellulose through hydrogen bonding between silanol and OH groups.
- Chemical condensation leading to siloxane bridges (S-O-Si) and adhesion onto the surface through Si-O-C bonds.

The siloxane bridges resulting from condensation contribute to the formation of polysiloxane network on the surface of cellulose filler.

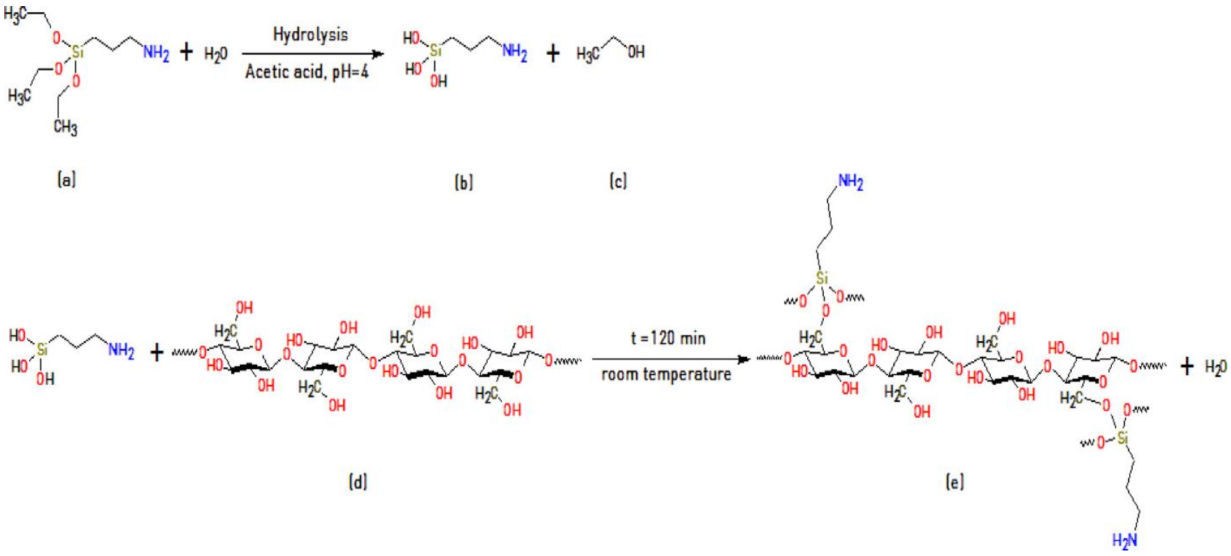

Figure 1.4 (a) APTES;(b) silanol;(c) ethanol;(d) cellulose;(e) surface-modified cellulose [53]

2 MATERIALS AND METHODS

2.1 Materials

2.1.1 Filler material

The filler materials were made from scrap veneer obtained from Kohila Veneer AS (seen on Figure 2.1). Both birch sapwood and false heartwood parts were separated by hand and crushed into smaller pieces. The materials were visually inspected to ensure quality before sending them to be milled in TalTech, Department of Mechanical and Industrial Engineering, Powder Metallurgy laboratory. Initially, the wooden chips were crushed with disintegrator DSA-3 so they would be equal in size. The crushed veneers were further milled, using DSL-115 disintegrator. The particles were sieved with sieve sizes from 0.63 mm to 1.25 mm to get wood particles with an average size of 1 mm.

Figure 2.1 Birch false heartwood and sapwood veneer as raw material

2.1.2 Plastic matrix

The plastic used in this research was polypropylene PPH 11012 by Total. It is a nucleated controlled rheology homopolymer with antistatic properties and a high melt flow index of 55 g/10 min. Density is 0.905 g/cm^3. Melting point is at 165˚C. PPH 11012 is characterised by high fluidity for high speed injection. Suitable for making thin wall products like dairy pots, salad trays, food packaging, etc. Also has a high antistatic nature allowing shorter cycle times and makes demoulding easier. The data sheet for PPH 11012 can be found in appendix 1.

2.2 Pre-treatment with alkali

The purpose of pre-treatment in alkaline environment is to remove waxes, oils, excess lignin and hemicelluloses from the surface of the filler material to improve the adhesion between cellulose fibre and polymer plastic. The removal of excess substances from the fibre surfaces increases the amount of hydroxyl groups on the fibre surface and improves wetting and adhesion with thermoplastic polymers [54], [7]. It is a widely used chemical treatment otherwise known as mercerisation. This helps to prepare the filler for subsequent modification with the silane coupling agent.

Pre-treatment was done with NaOH solution that was made by measuring 5% of the mass of treatable wood filler and dissolving the weighed NaOH in distilled water. The solution was thoroughly mixed with the wood filler inside a container at room temperature (22°C) to guarantee even distribution. After waiting 90 minutes, the filler material was rinsed in large amount of tap water in order to wash off excessive NaOH and ensure neutral or near-neutral environment ($pH \approx 7$). The pH tester strips were used to check the pH of the filler material. The rinsing process was done in a vacuum pump to make the extraction of rinsing water easier. After obtaining neutral pH, the pre-treated filler was put into oven to dry at 60°C for 24 hours. The dried material was stored in a plastic bag until further treatment.

2.3 Modification with coupling agent

The purpose of modification is to improve the interfacial adhesion between hydrophilic cellulose fibres and hydrophobic plastic polymer. The modification was done in TalTech Laboratory of Wood Technology. Wood filler was modified with 3-Aminoprophl-triethoxysilane or APTES by Sigma-Aldrich (datasheet in appendix) at 23°C. 5% wt% of APTES was weighed and dissolved in solution of pure medical grade ethanol and distilled water in volumetric ratio of 6:4 and stirred constantly for at least an hour. At the same time the pH of the solution was brought down to a value of 4-5 with droplets of acetic acid. The filler during modification can be seen on Figure 2.2. The solution was then mixed thoroughly with corresponding amounts of birch sapwood and birch false heartwood filler inside a plastic container. The mixture was left to react for 120 minutes. After this, the obtained fillers were dried in an oven at 60˚C for 24 hours. Upon drying, the fillers were sealed in plastic bags until further use.

Figure 2.2 Wooden filler during modification with APTES

2.4 Making of composites

The composites were made at TalTech Laboratory of Polymers and Textile Technology via injection moulding. Before the production, wooden fillers are dried in an oven at 60˚C for an hour to remove any excess moisture that interferes with the compounding. For every filler batch, the filler content is chosen to be 60% by weight. The remaining 40% is neat polypropylene. Wood filler and neat PP are mixed in a laboratory rotary roller for 3-5 minutes. After this the mixtures were compounded in Brabender Plasti-Corder PLE 651 extruder, which has a co-rotating twin-screw. The extruder die on the compounder had 4 different heating sections that were set to 180˚C, 185˚C, 190˚C ,190˚C. The compounder screw rotation velocity was set to approximately 60 turns per minute. After the extrusion the materials were cooled to room temperature and granulated in Retsch SM 100 miller. The granulated composites are stored in plastic bags up until injection moulding.

The injection moulding was done with Battenfeld BA 230E injection moulding machine (Figure 2.3) in accordance with EN ISO 527-2. The specimen type was 1A (shown on Figure 2.5). The sector temperatures were set to 170 ^{o}C and 180 ^{o}C, rotating screw speed to 40 rpm. The injection pressure was set to 7 MPa and cooling time to 15 seconds. The entire process is described by schematic on Figure 2.4 and Table 2.1 shows the amount of used materials and received test specimens.

Figure 2.3 Battenfeld BA 230E used for injection moulding

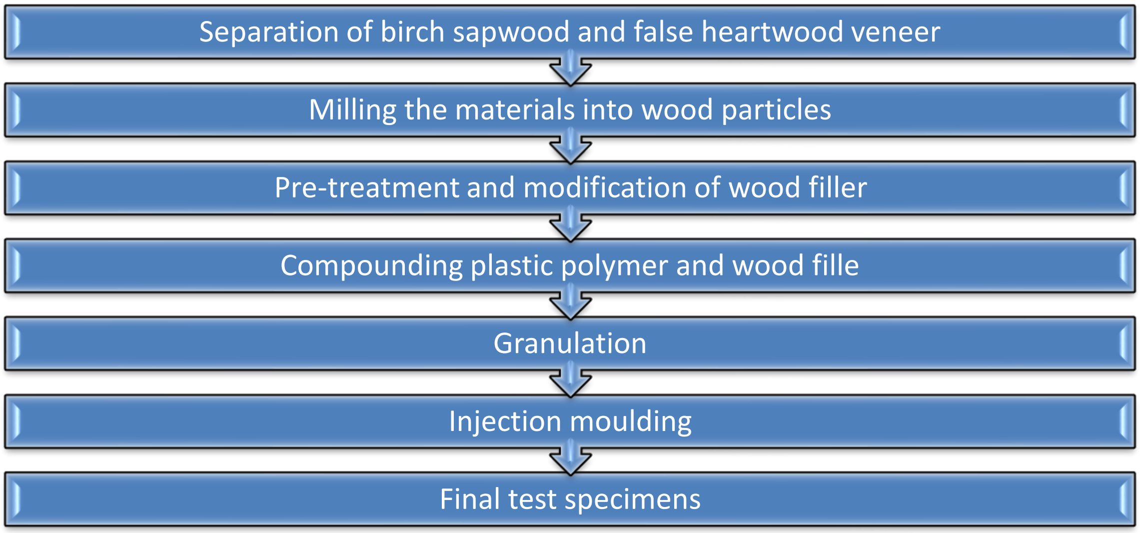

Figure 2.4 The process of making a WPC

2.1 Materials used

Material	**PP (wt%)**	**Filler(wt%)**	**NaOH(wt%)**	**APTES (wt%)**	**No of specimen.**
PP	100	0	0	0	17
SW	40	60	0	0	17
MSW	40	60	5	5	11
FHW	40	60	0	0	18
MFHW	40	60	5	5	17

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

2.5 Testing methods

The methods are summarised in Table 2.2. Weathering, tensile test and flexural test were done in Tallinn University of Technology. Heat deflection temperature, thermogravimetric analysis, Vicat test and dynamic mechanical analysis were done in Montanuniversität Leoben, Austria. The weathering was done using specimen type 1A from EN ISO 527-2. The tensile and flexural test included only weathered WPCs whereas all the other test were done with undegraded materials.

Table 2.2 Testing methods

Testing method	**Standard**	**No of test specimen used**
Weathering	EN ISO 877	11-18
Colouration measurement	Laboratory method	6
Tensile test	EN ISO 527-2	5-8
Flexural test	EN ISO 178	5-9
Heat deflection temperature	ISO 75-1	2-4
Thermogravimetric analysis	Laboratory method	Small samples (10-15 mg)
Vicat Test	ISO 306	2-4
Dynamic Mechanical Analysis	Laboratory method	2

2.6 Weathering

The test specimens were placed on stand (Figure 2.5) angled 45 degrees facing south in Tallinn, Estonia (latitude N 59° 25'). The weathering was meant to take place for at least a year to imitate the effects of four seasons. In contrast to artificial weathering, in outdoor conditions the materials were subjected to the elements - varying intensity of sunrays, temperature differentials, changing moisture content, freezing and thawing, rain, snow, etc. This is to simulate the degradation in actual outdoor conditions. The setup is according to specifications in EN ISO 877.

Figure 2.5 Test samples on a stand

2.7 Colouration analysis and visual assessment

The colouration measurement was carried out on the test specimens before and after the weathering test. In order to measure the differences in colouration CIELAB colour, space system is used. Since 1976, the CIELAB system has become the universally accepted colorimetric reference system for quantifying and communicating colour. Figure 2.6 illustrates the colour space concept. The CIELAB colour system contains one axis for lightness (L*) and two channels for colour (a* and b*). In the three-dimensional model, the chromatic a* axis extends from green (-a*) to red (+a*), and the chromatic b* axis extends from blue (-b*) to yellow (+b*). The lightness dimension, represented by L*, ranges from 0 (pure black) to 100 (diffuse white). Colour differences can be computed as the relative distance between two reference points within a colour space. This difference is typically expressed as delta E (ΔE) and is calculated by comparing reference and sample L*a*b* values to pinpoint how far apart two colours reside within a colour space. [20]

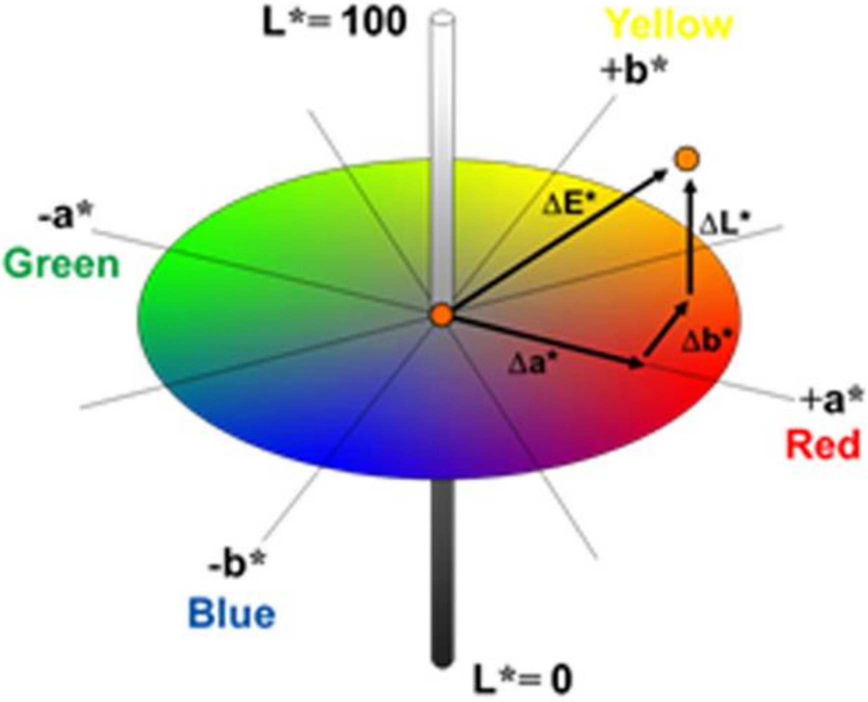

Figure 2.6 CIELAB colour space [55]

The colouration difference ΔE can be calculated using the equation:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{1}$$

Where ΔE is the total colouration difference, ΔL, Δa and Δb are the differences of the parameters measured before and after the weathering test.

The measurement was done with Minolta Chroma Meter CR-121 (Figure 2.7) before the weathering test and at the end of the test 451 days later. Each test specimen was measured from 3 different points sufficiently apart from each other. The measurement was done on D65 daylight setting and parameters L, a and b were noted.

Figure 2.7 Colouration measurement with Minolta CR-121

In addition, the degraded surface of the test samples was investigated and photographed with a DM-01 digital microscope.

2.8 Tensile testing

The tensile test was done after the end of degradation period in outdoor conditions with test specimen 1A (Figure 2.8) in accordance with the specifications in EN ISO 527-2:2012. The test was done with Instron 5866 using a 5kg 10 kN static load cell (shown on Figure 2.9). The test speed was set to 1 mm/minute specified in standard. At the time of testing air temperature was 24˚C and humidity 15%.

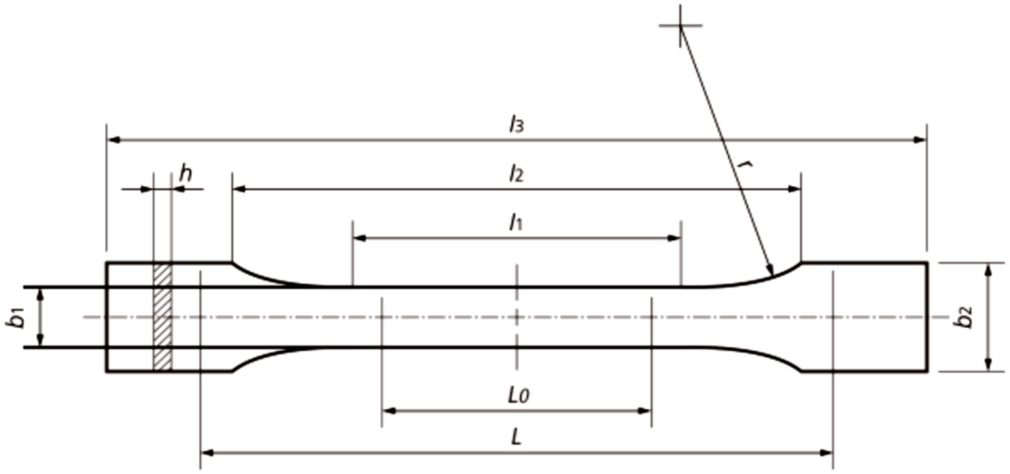

Figure 2.8 Test specimen ISO 527-2

Where,

l1 - length of narrow portion, mm

l2 - distance between broader portions, mm

l3 - Total length, mm

r - radius, mm

b1 - width at narrow portion, mm

b2 - width at ends, mm

L0 - gauge length, mm

L - initial distance between grips, mm

Tensile strength is calculated using the equation 2 below

$$\sigma = \frac{F}{A} \tag{2}$$

Where

σ is the tensile strength, MPa

F is the measured force, in N

A is the initial cross-sectional area of the specimen, mm^2

The tensile modulus is calculated using the equation as given below

$$\mathrm{Et} = \frac{\sigma_{t2} - \sigma_{t1}}{\varepsilon_{t2} - \varepsilon_{t1}} \tag{3}$$

Where,

E_t tensile modulus, MPa

σ_{t1} tensile strength at deflection s1, MPa

σ_{t2} flexural stress at deflection s2, MPa

εti corresponding flexural strain $\varepsilon_{t1} = 0.0005$ and $\varepsilon_{t2} = 0.0025$

Figure 2.9 Tensile test with Instron 5866

2.9 Flexural testing

The flexural properties were also determined using Instron 5866 by conducting a 3-point bend test (Figure 2.10). A 10 kN load cell according to ISO 178:2010 was used. The span length was 64 mm. Air temperature was 24°C and air humidity 15%. The testing speed was set to 1mm/min. The test specimen was placed in a way where the bending load contacted the centre of the specimen. For each material up to 9 specimens were tested but the minimum number of tests was 5. The flexural strength and flexural modulus are calculated by equations 4 and 5 below.

$$\sigma_f = \frac{3FL}{2bh^2} \tag{4}$$

Where,

σ_f flexural strength, MPa

F applied force, N

L span, mm

b width of the specimens, mm

h thickness of the specimens, mm

$$S_i = \frac{\varepsilon f i L^2}{6h} \tag{5}$$

Where,

S_i deflection, mm

ε_{fi} flexural strain $\varepsilon_{f1} = 0.0005$ and $\varepsilon_{f2} = 0.0025$

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}} \tag{6}$$

Where

E_f is modulus of elasticity, MPa

σ_{f1} flexural stress at deflection s1, MPa

σ_{f2} flexural stress at deflection s2, MPa

Figure 2.10 Flexural test with Instron 5866

2.10 Vicat softening point

Vicat softening point is the temperature at which the specimen is penetrated to a depth of 1 mm by a flat-ended needle with a 1 mm² circular or square cross-section. The Vicat softening temperature can be used to compare the heat-characteristics of different materials. The test was done with CEAST 6510/517 VICAT/HDT testing machine (Figure 2.11) in Montanuniversität Leoben, Austria and was conducted according to ISO 306 with a smaller test specimen with dimensions of 80x10x4 mm. The temperature gradient was set to 120˚C per minute and the tests were conducted both with 1kg (10N) and 5kg (50N) load (methods A120 and B120). For each type of WPC at least two samples with thickness of 4 mm were tested. The softening point was registered when the needle penetrated 1 mm into the material. The test was conducted in bath filled with silicon oil.

Figure 2.11 CEAST 6510/517 VICAT/HDT testing machine

2.11 Heat deflection temperature

Heat deflection temperature was determined with the same CEAST 6510/517 VICAT/HDT testing equipment as the Vicat test shown on Figure 2.11 and 2.12. The specification for conducting the determination of heat deflection temperature are specified in ISO 75. The test specimen is loaded in three-point bending in the edgewise direction and had dimensions of 80x10x4 mm. It was placed on the supports in a way that the longitudinal axis of the specimen was perpendicular to the supports. To compensate for any asymmetry effects, such as warpage of the specimen, test specimen was tested pairwise. The test specimens were submerged at least 50 mm into the heating oil, and the heating rate during the test was 120°C per minute. The span between the supports were 64 mm. The starting temperature of the test was 24°C. According to ISO-75-2 the constant flexural stress chosen was 1.80 MPa referred to as method A. The applicable force is calculated as below.

$$F = \frac{2\sigma_f bh^2}{3L} \tag{7}$$

Where,

F   is the load, in newtons;

σ_f is the flexural stress at the surface of a test-specimen, MPa;

b is the width of the test sample, mm;

h is the thickness of the test sample, mm;

L   is the span between the supports, mm.

The needed force in instance for a specimen with a thickness of 4mm and flexural stress of 1.8 MPa is 3 N. The weights are chosen accordingly, so the overall force exerted upon the specimen is 3 N.

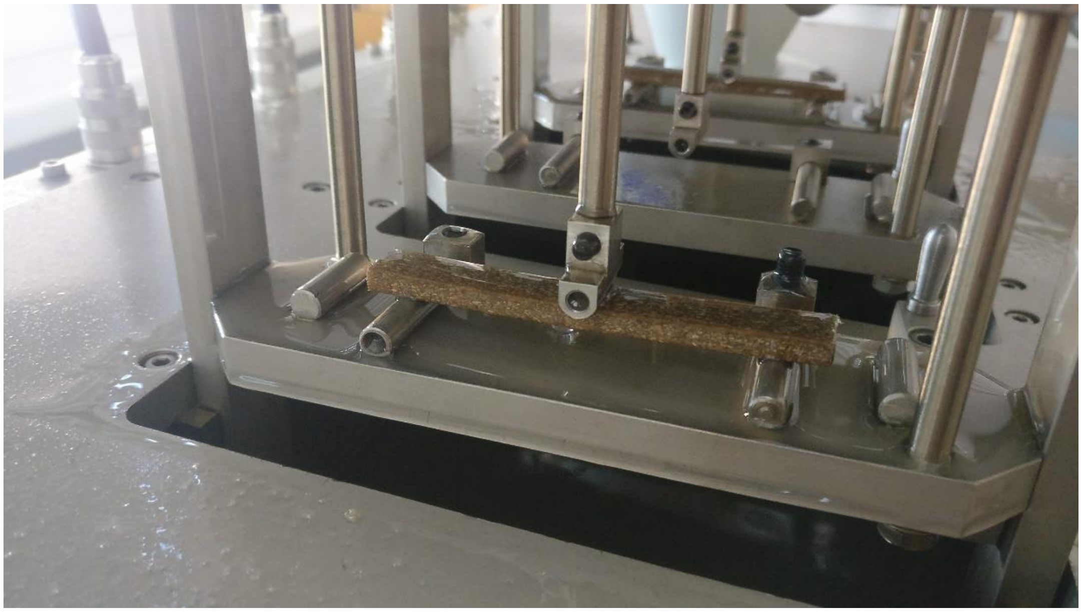

Figure 2.12 HDT test with CEAST 6510/517

The flexural stress-strain increase value specified in ISO-75-2 is 0.2%. The deflection temperature value is recorded when the initial deflection of the bar has increased by the standard deflection Δs which in this case has the value of 0.341 is calculated as follows by formula:

$$\Delta s = \frac{L^2 \Delta \varepsilon f}{600h} \tag{8}$$

Where,

Δs is the standard deflection, in millimetres;

L is the span, in millimetres, between the lines of contact of the test specimen and the specimen supports;

$\Delta \varepsilon_f$ is the flexural-strain increase, in percentage;

h is the thickness, in millimetres, of the test specimen.

2.12 Thermogravimetric analysis

This test method is used to assess changes in the mass of a material as a function of temperature and time. The thermogravimetric analysis or TGA determines the weight loss of a plastic specimen when the temperature is increased under defined atmospheric conditions. This measurement provides information about physical phenomena, such as phase transitions, absorption, adsorption and desorption; as well as chemical phenomena including chemisorption, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction).

The TGA analysis was conducted with METTLER TOLEDEO TGA/DSC 1 test machine shown on Figure 2.13. The rate of temperature increase was set to 5 °C/min and a small sample of every WPC with a weight of 10 to 15 mg was used. The heating took place in pure nitrogen (N_2) atmosphere and a gas flow of 50 mL/min. Thermal decomposition of each sample occurred in a programmed temperature range of 24–600 °C.

Figure 2.13 Mettler Toledo TGA/DSC 1

2.13 Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) is a technique that is widely used to characterise a material's properties as a function of temperature, time, frequency, stress, atmosphere or a combination of these parameters. It is a material characterisation method that provides information on bulk properties and thermal transitions. At frequencies and temperatures of interest, an oscillatory strain or stress is applied to the material, and the resulting stress or strain developed in the material is measured. DMA allows to assess the viscoelastic properties of plastic and composite materials. In the process storage modulus, loss modulus and damping ratio of WPCs are determined to give insight to the internal structure of the materials.

Dynamic mechanical properties of the composites were measured by using METTLER TOLEDO DMA861 (Figure 2.14). The frequency was set to 1 Hz. The temperature range was from -50 to 150°C and the heating rate was set to 2 °C per minute.

Figure 2.14 Mettler Toledo DMA861

3 RESULTS AND DISCUSSION

3.1 Colouration measurement and visual assessment

The test specimens were place onto a stand for 451 days. Over that period the visual appearance of WPCs changed considerably. A comparison is shown on Figure 3.1 below. The initial colours of WPCs ranged from slightly different tones reddish-brown. All WPCs had a bleached appearance that differed significantly from their initial looks after the weathering. The WPCs had grainy surface and overall chalky appearance. The sides, which were not exposed to direct sunlight, lacked the granular chalky appearance but were nevertheless lightened in colour. The appearance of neat PP had not changed much – rather transparent samples had obtained an opaque exterior.

Figure 3.1 Left - test specimens before weathering; right - after weathering

All WPCs had roughly the same appearance after degradation. The discolouration problem seems to be caused by photodegradation of wood components inside the WPCs [56];[57]. It is widely known that the resistance to the elements of WPCs is generally poor, and discolouration, chalking, and dimensional change caused by outdoor exposure are major problems for their use outdoors [56]. Lignin in wood strongly absorbs ultraviolet light, and this leads to radical induced depolymerisation of both lignin and cellulose at wood surfaces [58], [59]. Photodegraded components are washed away by rain and the wood surfaces become lighter [60]. It is reported in several studies that WPCs with a lower 40% plastic content suffer from incomplete encapsulation of wood flour in the plastic matrix and give poorer resistance to natural weathering than WPCs that have a higher than 50% plastic content [61]–[63]. This implies that lower 40% plastic content will lead to higher loss of physical and mechanical properties. During exposure to natural weathering, the ultraviolet radiation causes scissions of the polymer chains which decrease the crystallinity inside the PP plastic matrix. This leads to the formation of fractures [64], [65]. Although both UV radiation and moisture can degrade WPCs, exposure to the combination of UV radiation and moisture is more detrimental to WPCs than is exposure to UV radiation alone [66]. There are several contributing reasons for this. The presence of water accelerates oxidation reactions and swelling of wood facilitates the light to penetration into the WPC. Rain also washes away the degraded layer and removes natural wood extractives [66].

All the WPC samples had degraded in similar fashion and there were no significant visual differences between WPCs. Figure 3.2 shows a close-up of the degraded WPC sample. Close up of the sample shows a grainy appearance of the front side that was exposed to direct sunlight. The backsides of samples were much smoother and lacked the granular appearance, although they were also significantly lightened in colour. This is because the backsides of the samples were not exposed to direct sunlight to the same extent and therefore did not undergo the same amount of degradation.

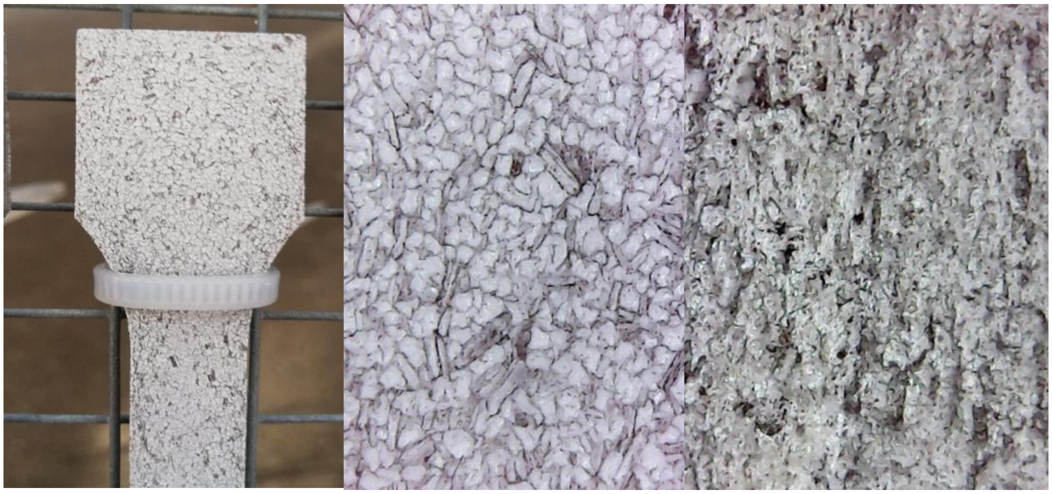

Figure 3.2 Left - WPC surface; centre WPC front side; right - WPC backside after weathering

The total colouration difference was calculated, and the results are shown on Figure 3.3. The delta E value for WPCs ranged from 32.19 to 39.33. Neat PP showed the least amount of colouration ($\Delta E=15.38$). MSW and FHW composite showed nearly the same amount of change (36.36 and 36.78 respectively). MFHW composite showed the highest amount of change with a value of 39.33. SW composite showed somewhat smaller change in colour than the rest of WPCs. This is in accordance with a similar study by G. Ayansola [6], where weathering was done in a UV-chamber for 84 days. This study also showed that SW-composite underwent the least amount of change in colour. The increased difference of colour for other composites could be attributed to the effects of modification and the amount of depolymerized phenolic extractive substances in false heartwood particles. It is possible that some amount of lignin gets degraded during modification with the coupling agent. Absorption of UV light initiated the photodegradation of lignin to form free radicals and chromophore groups, resulting in colour changes after weathering [67],[68],[69]. The highest colouration for MFHW can be explained with the combined effects of modification and the presence of phenolic compounds that formed during false heartwood formation. It is difficult to assess the exact influence of these compounds because their exact composition and structure are unclear. It is possible that UV radiation lead to the decomposition of these phenolic substances and they got consumed during the natural weathering process, leading to an overall higher difference in colouration.

The initial and final values of lightness are represented on Figure 3.4. Lightness L* value describes the lightness of colour. As can be seen, after 451 days all the WPCs obtained similar final lightness values and had only little differences. SW had the highest initial lightness value (52.49) followed by FHW (48.29), MSW (42.95) and MFHW (36.89). It is probable that wood components got degraded during modification and this resulted in darkening of the particles, this explains why MSW has lower initial lightness. FHW has particles already containing extractive substances responsible for the darkening of the material. MFHW represents the combined effects of modification and the presence of these extractives, so the lowest initial lightness value makes sense. The nearly identical final lightness of WPCs showed that despite the modification and presence of extractives, the surface degraded in similar fashion. For comparison, PP showed the least amount of change in lightness.

The research conducted by G. Ayansola [6] showed that the accelerated weathering for 84 days in UV chamber resulted in little more than half of the ΔE attained during natural weathering for all WPCs. During natural weathering, the ΔE for PP (15.38) was far greater than in UV chamber (2.16). Although FHW had somewhat larger change in colouration than SW, it can be said that FHW is comparable to SW regarding both the colouration and visual appearance after weathering.

Table 3.1 Change in colour and surface lightness according to CIE Lab colour system

Material	**Colour change ΔE**	**Initial lightness L***	**Final lightness L***
PP	15.38 (0.96)	26.63 (1.52)	40.51 (0.97)
SW	32.19 (1.45)	52.49 (2.19)	73.67 (1.38)
MSW	36.36 (1.91)	42.95 (1.77)	70.58 (1.23)
FHW	36.78 (2.14)	48.29 (2.13)	74.17 (1.44)
MFHW	39.33 (1.98)	36.89 (1.76)	71.44 (1.52)

The value in brackets indicates the standard deviation

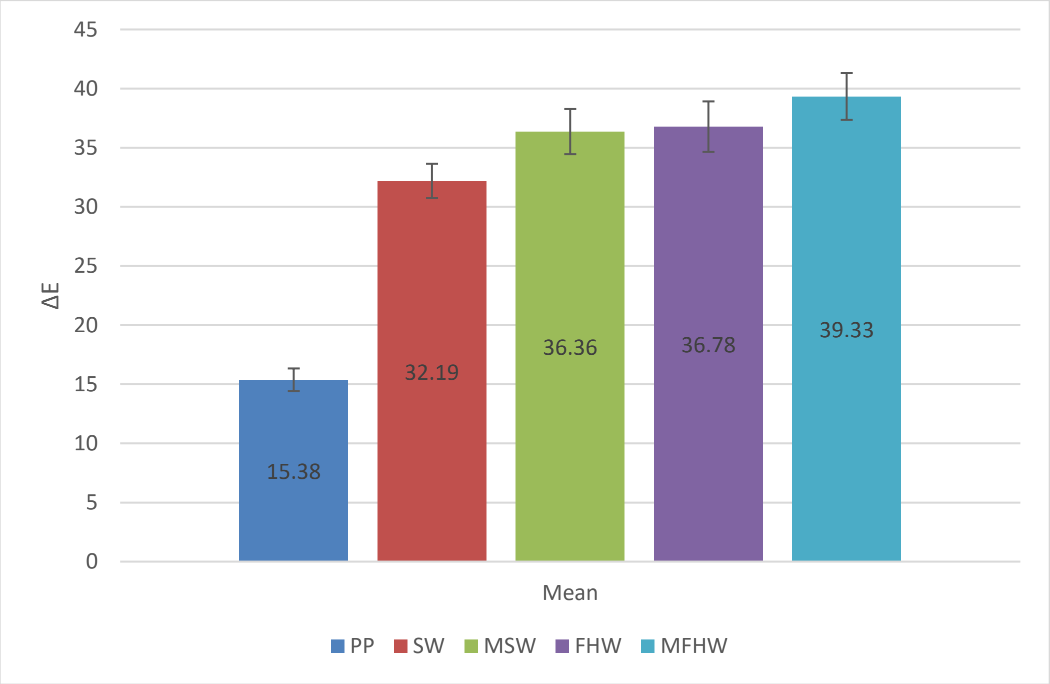

Figure 3.3 Colouration differences

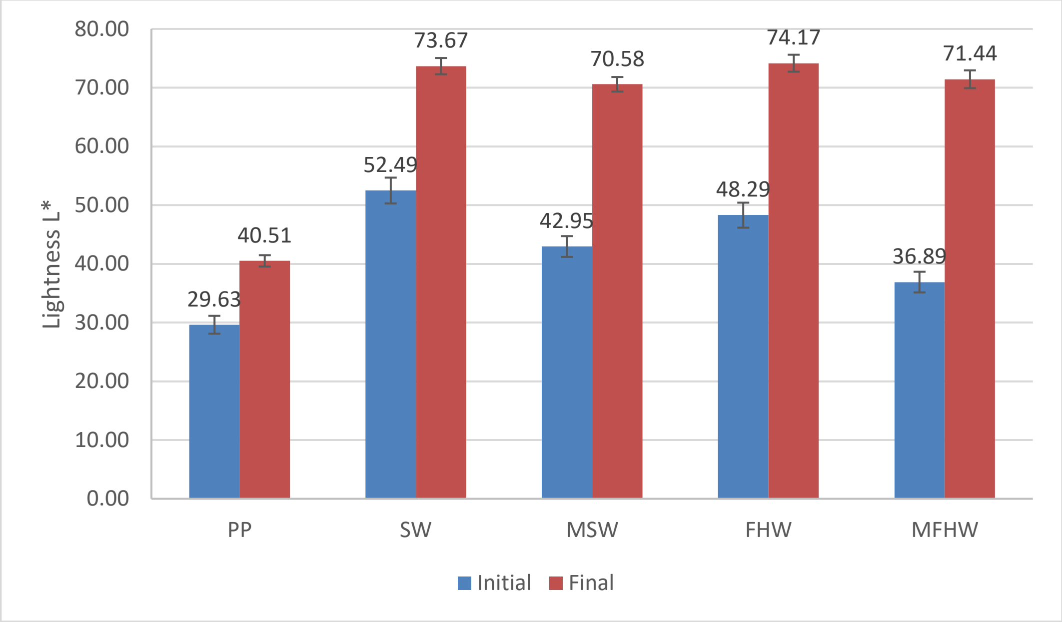

Figure 3.4 Change in lightness L*

3.2 Tensile properties

Tensile strength describes the maximum stress that a material can withstand while being stretched or pulled before breaking. In addition, the initial original values of the WPCs before weathering and accelerated weathering in UV chamber were added to the graphs. These results describe the same WPCs made from the exact same materials and were taken from the works of H. Kallakas and G. Ayansola [5], [6], [70]. The tensile strength and modulus are described on Figures 3.5 and 3.6 and in Table 3.2.

The samples from neat PP act as comparison to the WPCs made with fillers. The drastic 58% decrease in tensile strength from the original strength can be seen. This decrease in strength is identical to results obtained by Badji [68], where PP lost 60% of its initial tensile strength. Interestingly, the accelerated weathering resulted in the same strength value as natural weathering, even though accelerated weathering lasted for a far shorter amount of time. The decrease in strength is due to scission of polymer chains after exposure to UV-radiation [71]. The tensile strength of SW and FHW composite decreased 6% and 7%. There was not a noticeable difference with accelerated weathering. The strength of MSW decreased by 15% and the decrease was greater than with accelerated weathering. MFHW composite practically retained its strength compared to initial value (21.30 and 21.34 MPa respectively) and showed slightly higher value than that was obtained after artificial weathering.

Tensile modulus is a measure of the resistance along the axis of strain to elastic deformation that a material has, simply describing the stiffness of a material. The modulus of neat PP stayed virtually unchanged compared to initial and artificially weathered values. But when it comes to WPCs, the modulus decreased by a considerable amount for all composites. The fractures caused by the scission of plastic polymer chains and the exposed wooden filler allows humidity to penetrate the WPC surface and cause large gaps between the phases [62]. Thus the absorbed humidity decreases the tensile and also flexural modulus of the composite [72], [73]. Also, humidity can also interfere with the compatibility between phases.

Also, all values were lower than of artificially weathered ones. This can be explained by the much longer exposure time to the elements and sunrays. The modulus of SW lowered the least amount – 18%. An analogous study by Badji [68] showed a similar drop in stiffness. FHW showed a slightly higher drop with 24%. Both modified sapwood and false heartwood composites showed a nearly 30% drop in tensile modulus. There is a possibility that the pre-treatment or modification process removes excessive hemicelluloses, lignin and other extractives allowing voids and cracks to form and makes the WPCs more susceptible to outdoor degradation. The tensile properties of FHW and SW are very similar and FHW does not seem to have a negative effect on the WPC.

Table 3.2 Tensile properties of weathered WPCs and loss from initial values

Material	**Tensile strength, MPa**	**Tensile modulus, GPa**	**Loss in strength, %**	**Loss in modulus, %**
PP	12.99 (0.87)	1.65 (0.03)	58%	1%
SW	19.95 (0.29)	3.54 (0.04)	6%	18%
MSW	19.38 (0.28)	3.17 (0.03)	15%	30%
FHW	20.07 (0.43)	3.39 (0.07)	8%	24%
MFHW	21.30 (0.62)	3.00 (0.12)	0%	30%

The value in brackets indicates the standard deviation

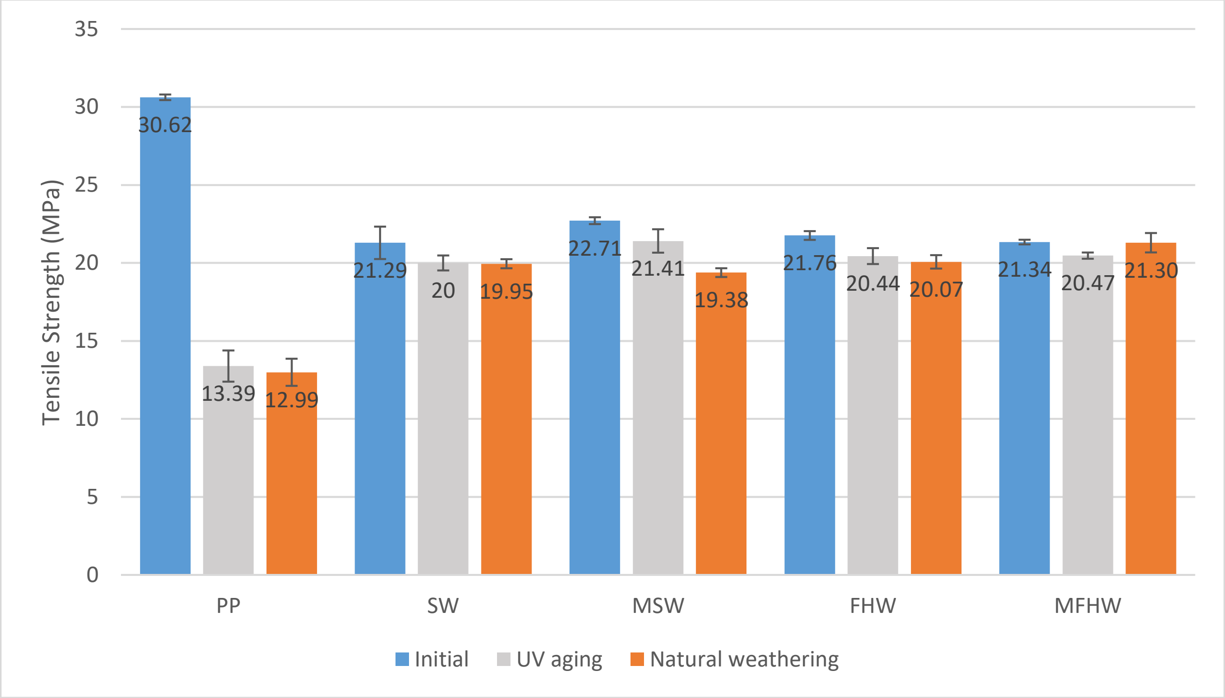

Figure 3.5 Tensile strength of WPCs [5], [6]

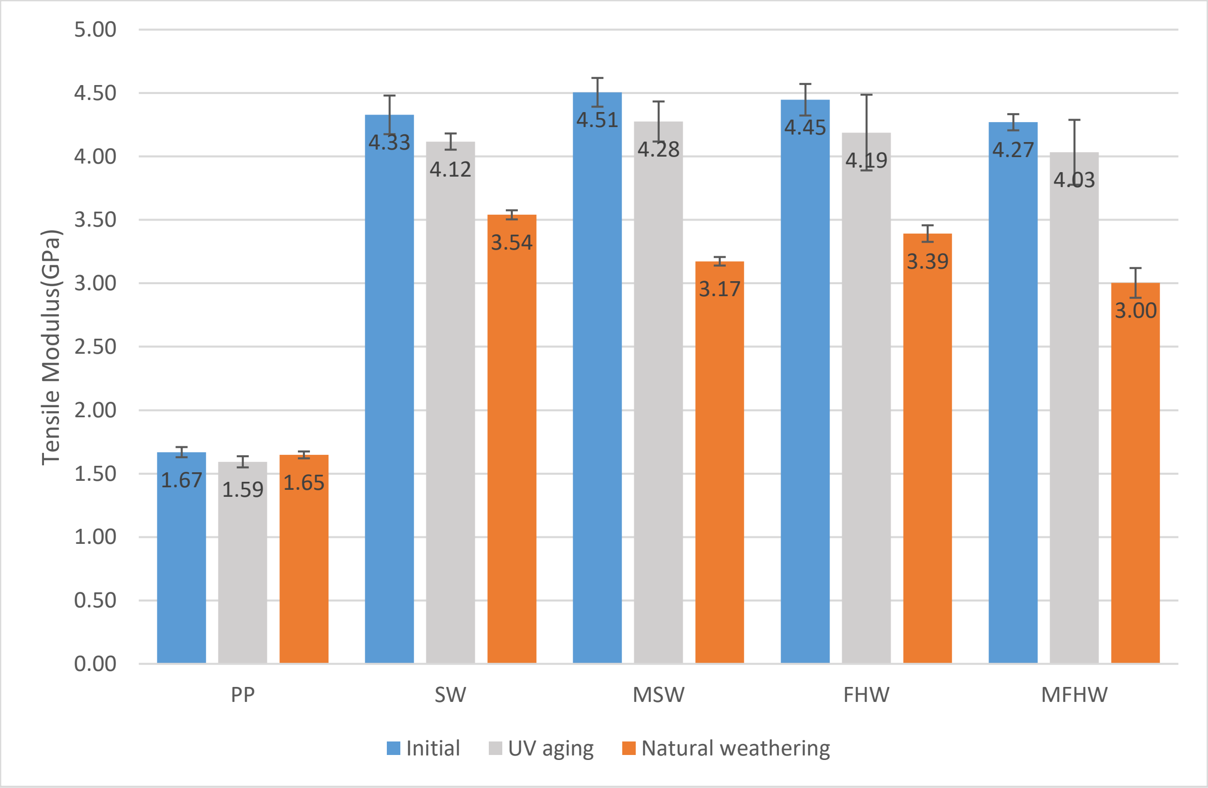

Figure 3.6 Tensile Modulus of WPCs [5], [6]

3.3 Flexural properties

Flexural strength represents the highest stress experienced within the material at its moment of yield. All of WPCs and PP showed a significant decrease in strength. Also, the decrease in strength was greater than that of accelerated weathering. This is sensible because the test duration was much longer and outdoor conditions subject the material to larger variety of elements like temperature differentials, changing air moisture, freezing and thawing, etc.

The results are summarised in Table 3.3 and visualised on Figures 3.7 and 3.8. Polypropylene lost 58% of its initial strength and suffered the greatest drop. The strength was just slightly lower from that obtained from accelerated weathering. Both SW and MSW lost 17% and 21% respectively. FHW lost about 13% of its strength and MFHW had the lowest drop in strength with 10%. The lower strength strop could be explained that the higher concentration of extractives present in false heartwood could behave as UV-absorbers. The protective ability of extractives is due to the presence of unsaturated phenolics in the heartwood showed in a study [74]. These phenolic compounds absorb light energy and are consequently degraded in themselves.

Seems like the modification did not have the desired effect for MSW as its flexural strength dropped more than that of unmodified SW. The modification or pre-treatment process possibly damaged the sapwood filler. Generally, the strength of FHW dropped less than SW and MSW. The extractive materials in false heartwood could have offered some protection against UV-degradation. The modification also could possibly have played a role in stabilising the MFHW composite as it suffered only a 10% strength decrease.

Flexural modulus of elasticity changed drastically for all WPCs, the modulus for PP stayed practically unchanged. The drop for SW was 29% to the value of 3.35 GPa. MSW suffered a larger 36% drop. FHW and MHFW dropped 20% and 39% respectively. The reason for the decrease is probably related to the surface defects that have formed after degradation. As mentioned before, the components of wood, especially lignin degrade after exposure to radiation. The degraded material comes loose and is washed off by rain, leaving voids on the surface of test samples [58], [59]. The presence of small voids or cracks on the surface relieve the stresses during flexing, therefore decreasing the flexural modulus. As mentioned in the tensile properties section, the absorbed humidity decreases the tensile and also flexural modulus of the composite [72], [73]. Interestingly, the modified versions suffered an overall greater drop in modulus, indicating that wood filler suffered from excessive removal of material during pre-treatment or modification, allowing larger voids and fractures to form inside the WPC.

FHW seems to have slightly smaller loss in strength and modulus compared to SW and can be deemed to be equivalent or even superior in retaining the flexural properties of WPCs after weathering.

Table 3.3 Flexural properties of weathered WPCs and loss from initial values

Material	**Flexural strength, MPa**	**Flexural modulus, GPa**	**Loss in strength, %**	**Loss in modulus, %**
PP	18.73 (0.87)	1.30 (0.09)	58%	0%
SW	38.05 (0.61)	3.35 (0.13)	17%	29%
MSW	37.23 (0.83)	3.14 (0.08)	21%	36%
FHW	38.61 (0.83)	3.31 (0.12)	13%	20%
MFHW	40.19 (0.98)	2.65 (0.27)	10%	39%

The value in brackets indicates the standard deviation

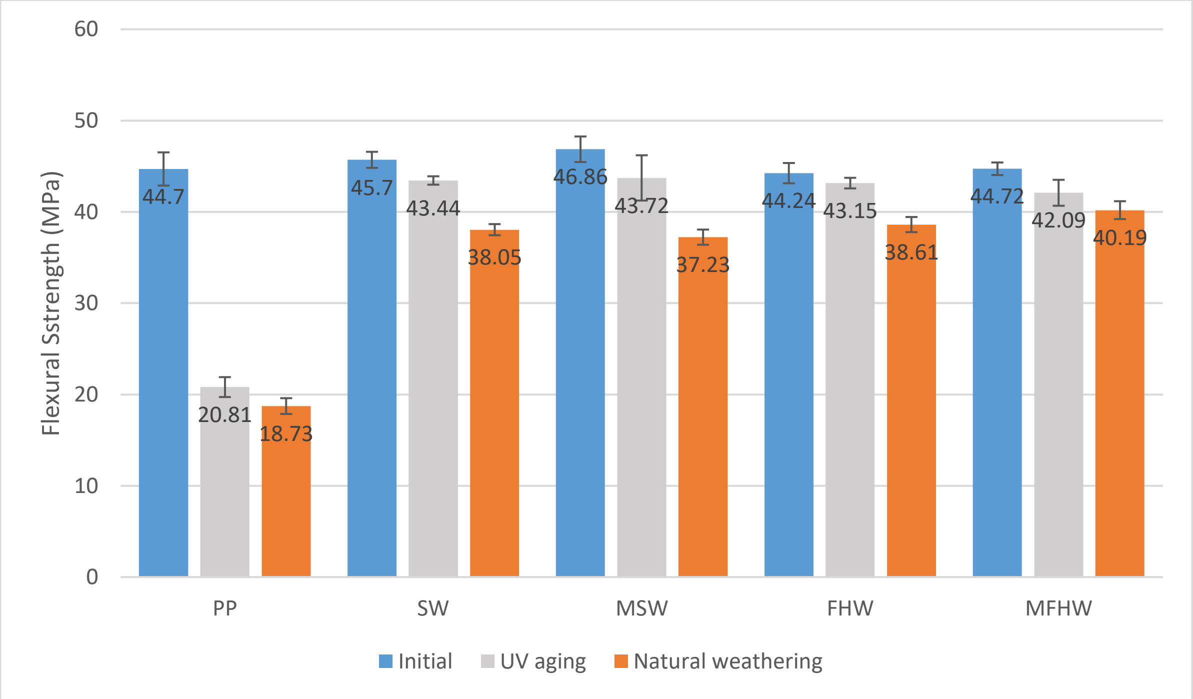

Figure 3.7 Flexural strength of WPCs [5], [6]

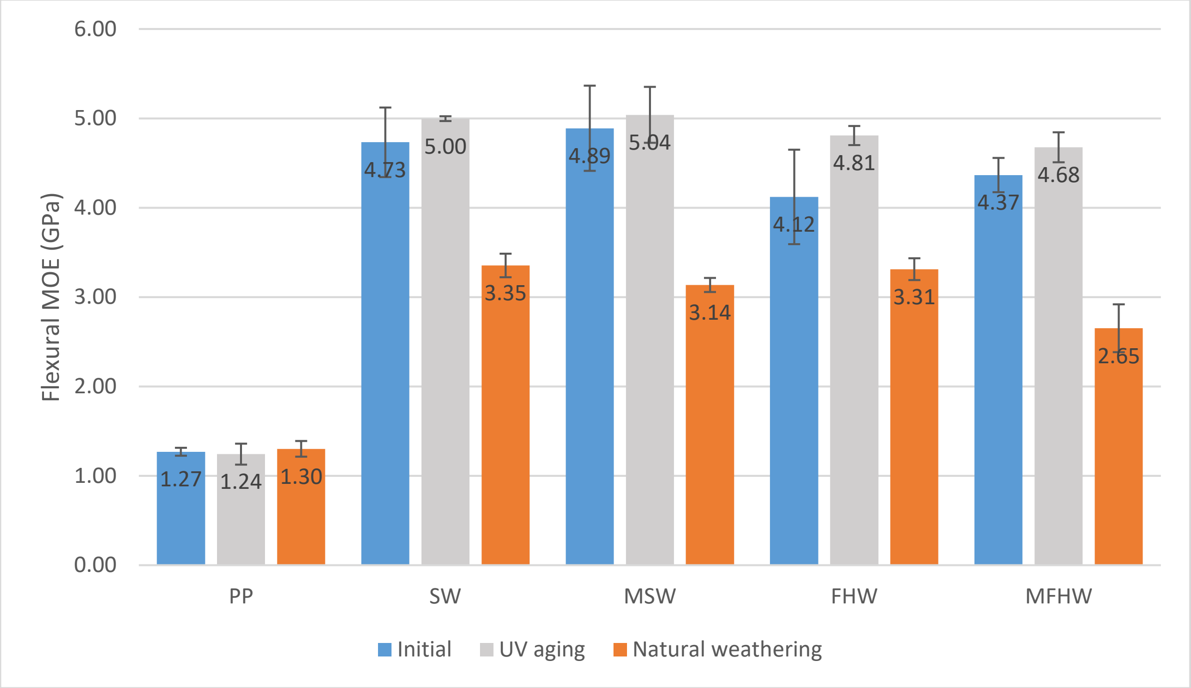

Figure 3.8 Flexural Modulus of Elasticity of WPCs [5], [6]

3.4 Vicat softening point

Vicat test was conducted in two sets, first one with a load of 1kg and the second one with a load of 5kg, the results are shown in Table 3.4 and Figure 3.9. Under 1 kg load all the composite materials sustained nearly identical softening points around 160 -161 °C. PP had a softening point near 156°C, it lacks the reinforcing fillers, so it is easier for the needle to penetrate the material. This is consistent with figures shown in literature [75] for both PP and WPC, which has a filler content of 60%. Results with a 5kg load resulted in penetration at a temperature approximately 35 degrees lower than with a 1 kg load. Softening point of PP was around 106°C and WPCs ranged from 120 to 129 °C Composites had an average of 18% higher softening point than pure PP. Nevertheless, there was not a significant variance between different batches of WPCs. Considering the standard deviations, MPB had a softening point of 120°C which is roughly 5 degrees lower than the average of other WPCs. The reasons behind MPBs slightly lower softening point could be related to inhomogeneous material distribution or matter removal during modification. Also, small sample size could play a role here. With a 1kg load there was no practical difference between any of the WPCs. With the increased 5 kg load, the WPC had noticeably higher softening point from PP. There are no major differences between WPCs and the effect of modification does not seem to play any significant role. On the contrary, the removal of material during pre-treatment or modification could offer less reinforcement for WPCs. FHW has identical properties to SW regarding the shape-retention capability of WPCs.

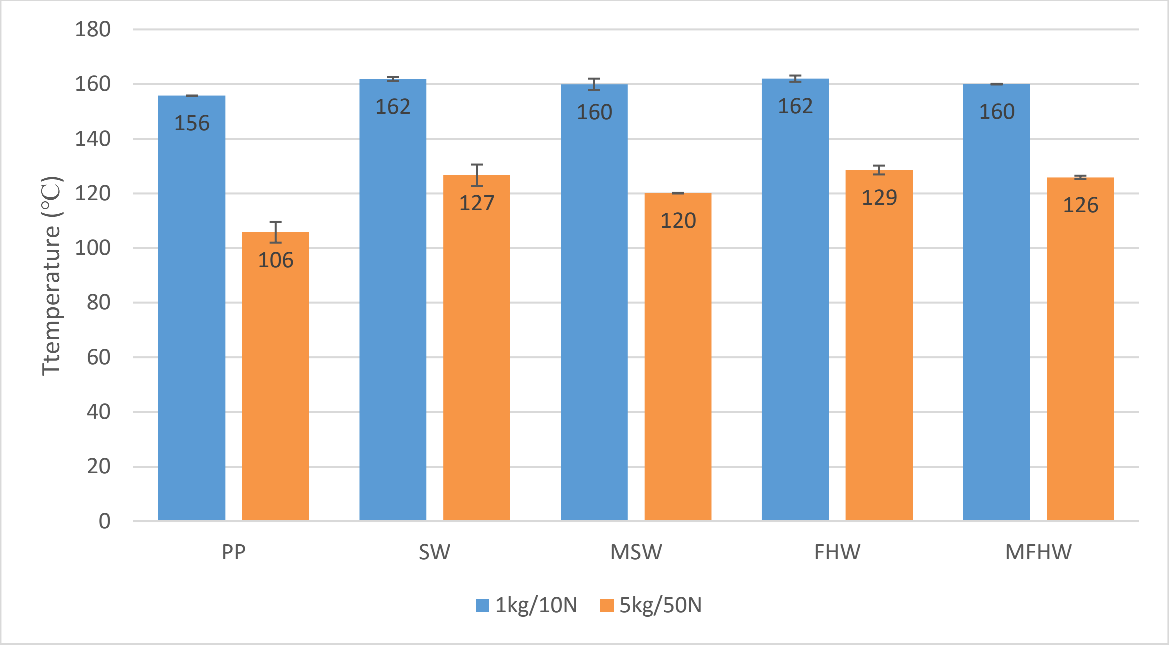

Figure 3.9 Vicat softening points of WPCs

3.5 Heat deflection temperature

The results are represented in Table 3.4 and on Figure 3.10 and they show that the heat deflection temperature of WPC samples is about 40 °C higher than of neat PP. This is logical because the cellulosic filler acts as reinforcement against the deflection and does not soften as the temperature rises. Similar values are found in literature [75]. It is noted that increasing the wood filler content increases the HDT compared to neat PP and makes it stiffer [76][77]. On average, the composites had 70.8% higher deflection temperature than pure PP ranging from 94 to 115 degrees Celsius. FHW, MPB, MFHW composites had relatively similar values that fit into standard deviation. Composite made from birch sapwood (SW) had up to 20 degrees higher deflection temperature than other composites. This could be from inhomogeneous distribution inside the composite or from the fact that birch sapwood did not undergo mercerisation, therefore got to keep the excessive lignin and hemicelluloses on the surface that may have played a role in retaining the load-bearing properties. The extractive materials inside false heartwood could somehow inhibit the interaction between filler and polymer and therefore result in lower deflection temperature.

The effects of modification are not apparent. FHW has a slightly lower load bearing capability than SW but is still comparable to it.

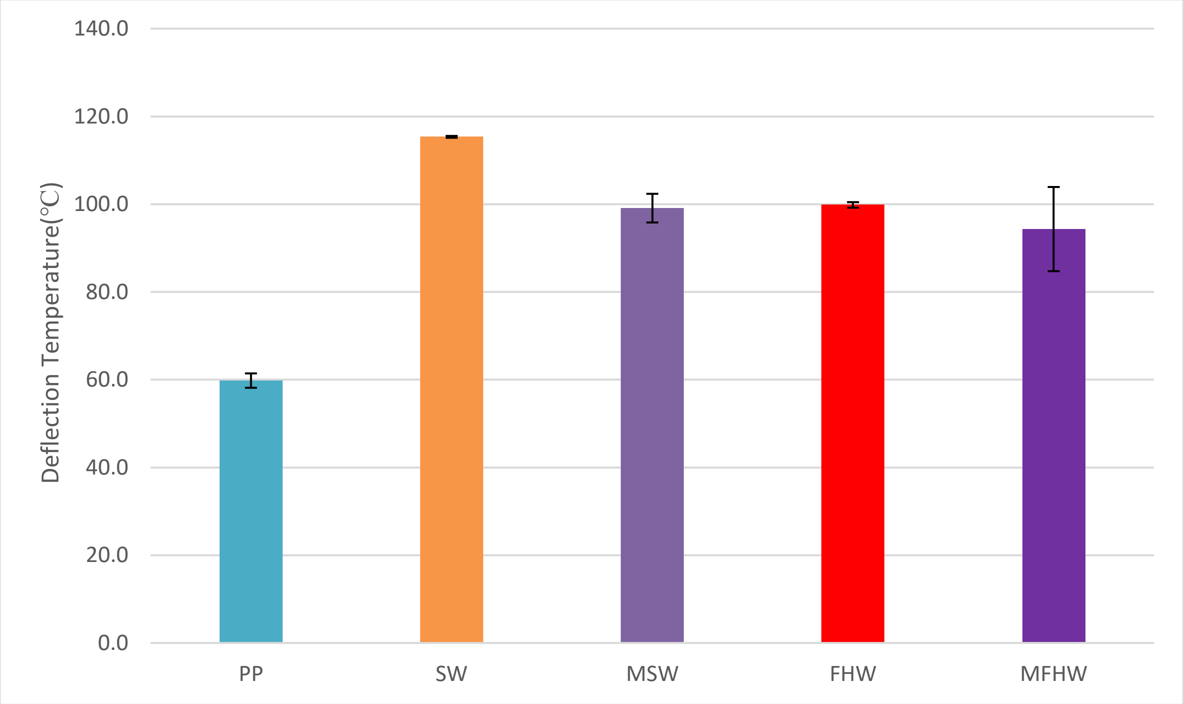

Figure 3.10 Heat deflection temperature of WPCs

Table 3.4 Vicat tests and heat deflection temperatures of WPCs

Material	**Vicat 10N, ˚C**	**Vicat 50N, ˚C**	**HDT, ˚C**
PP	156 (0.07)	106 (3.82)	60 (1.64)
SW	162 (0.71)	127 (3.96)	115 (0.21)
MSW	160 (2.05)	120 (0.14)	99 (3.27)
FHW	162 (1.13)	129 (1.63)	100 (0.64)
MFHW	160 (0.14)	126 (0.64)	94 (9.59)

The value in brackets indicates the standard deviation

3.6 Thermogravimetric analysis

The obtained TGA curves are shown on Figure 3.11 and curve peak results are shown in Table 4. It is visible that the thermal degradation of neat PP occurs in a narrow temperature region between 350˚C and 450˚C. The mass loss for PP was nearly 100%. This was because PP degraded into gaseous products at a higher temperature. We can see that the TGA curves of WPCs degraded in steps in contrast to PP. The thermal decomposition behaviour of WPCs primarily depends on its chemical constituents, namely: cellulose, hemicelluloses, and lignin[78]. According to research [78] the minute change below or around 100 ˚C can be contributed to evaporating moisture. The next mass loss stage in the temperature domain from 170°C to 550°C occurring through decomposition process of the major constituents present in wood: cellulose, hemicelluloses and lignin. Hemicelluloses decompose mainly between 150 °C and 350°C, cellulose between 275°C and 350°C and lignin between 250°C and 500°C [79][80][81]. Another study says that the decomposition of lignin ranges between 180˚C and 900˚C[82]. Lignin starts to decompose sooner than cellulose, but its rate of decomposition is slower than that of cellulose[82]. Aromatic ether linkages present in lignin have high thermal stability. It is also reported that crystalline cellulose with its intra-chain hydrogen bonds has a higher thermal stability compared with hemicelluloses [83].

From the TGA graph on Figure 3.11 can be seen that all the WPCs decompose in a similar fashion and at 200 ˚C all had lost roughly the same amount of mass (2.5%) which can be accounted to excretion of moisture and other volatile compounds. From 250°C to 350°C the mass loss of WPCs becomes substantial. This is more clearly visible on first-order derivative of thermogravimetric curves or DTG curves (Figure 3.12), where the peak of first derivative shows the point of greatest rate of change on the weight loss curve. For all WPCs there are two clearly visible peaks. The peak temperatures D_{max} and corresponding mass loss are in Table 3.5. The first peak corresponds to decomposition of hemicellulose, cellulose and lignin constituents. The second peak at around 450˚C involved the degradation of PP inside the WPC. It becomes noticeable that both modified WPCs suffered a smaller mass loss in the 250-350°C region than the unmodified ones. This could be related to overall loss of excessive lignin and hemicelluloses during pre-treatment with sodium hydroxide or it can be a sign of successful improved adhesion between the particles and polymer matrix leading to minuscule improvement in thermal stability compared to unmodified WPCs.

To summarise, it can be said that FHW and SW have very similar thermal stability.

Table 3.5 TGA/DTG results

Material	**First peak** **D_{max}, ˚C**	**Second peak** **D_{max}, ˚C**	**Mass loss To 360˚C, %**	**Mass loss** **From 360 to 600˚C, %**
PP	none	453	0	99.8
SW	350	460	40	47.7
MSW	339	458	31.9	54.6
FHW	351	461	37.6	50.1
MFHW	337	456	30.8	56.4

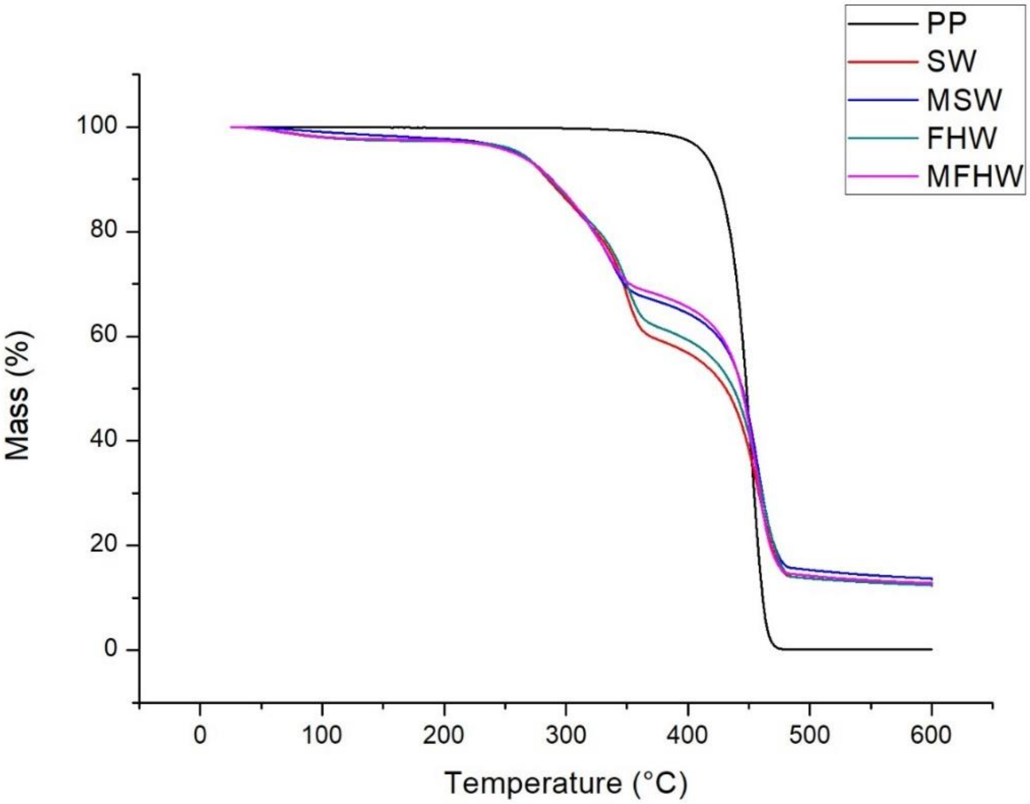

Figure 3.11 TGA curves of PP and WPCs

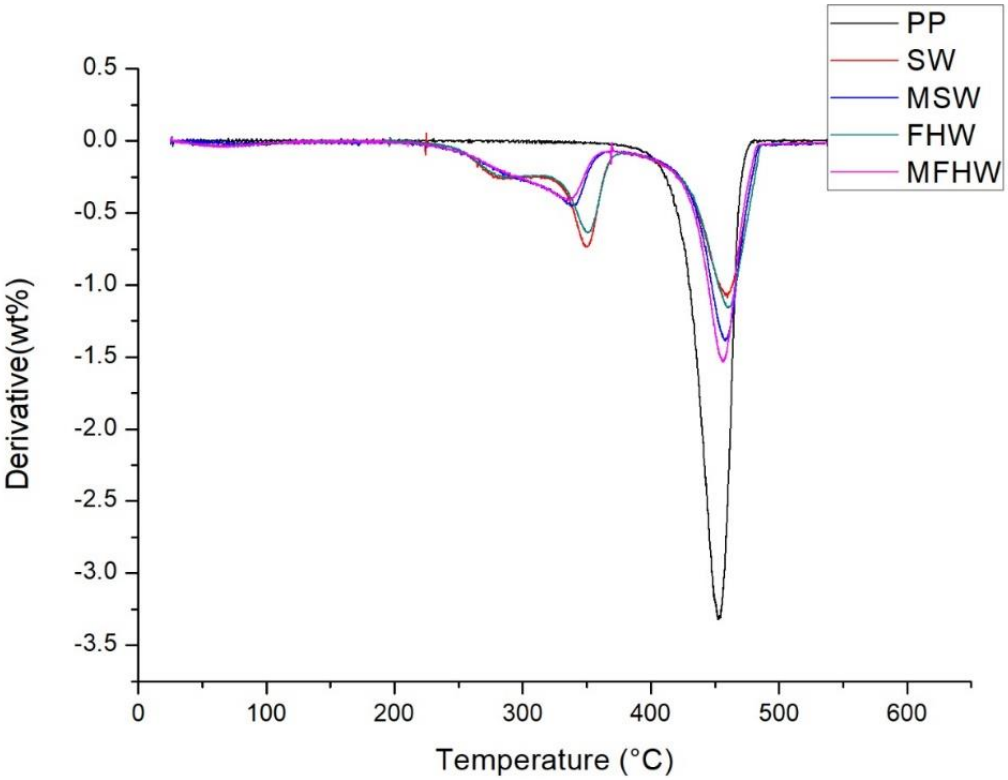

Figure 3.12 Derivative of TGA curves

3.7 Dynamic mechanical analysis

Dynamic mechanical analysis allows to determine characteristics such as storage modulus (E′), loss modulus (E′′), and loss factor (tan δ). These parameters are temperature dependent and provide information about interfacial bonding between the reinforced filler and polymer matrix of composite material [84],[85],[86]. The storage modulus represents the elastic part of the sample and a higher storage modulus corresponds to higher resistance to deformation while the loss modulus represents the viscous part of the sample. E′′ indicates the energy converted into heat and can thus be used as a measurement of viscous component or unrecoverable oscillation energy dissipated per cycle [84].

The storage modulus, loss modulus and loss factor of the composites as a function of temperature are shown on Figures 3.13, 3.14 and 3.15. In addition, values at 20˚C are shown in Table 3.6. From the Figure 3.13 we can see that the initial storage modulus of WPCs was much higher than it was for neat PP. The increased modulus can be attributed to evenly dispersed wood particles which lead to even distribution of applied stresses throughout the composites [87] and to a stiffening effect of reinforcing particles and significantly reduced viscous constituent [88]. As a result, the composite remains stiffer and the polymer flow is restricted. The increase of storage modulus with the introduction of natural particles have been reported in several studies [89],[90].

As the temperature rose, the modulus of every WPC started to decrease in similar fashion. From -50 °C to 50 °C the modified MSW composite showed a slightly higher storage modulus than unmodified SW composite which could indicate the improved adhesion between filler and polymer after modification with silane coupling agent. From 50 °C to 150°C MSW lost its higher modulus to SW. The storage modulus of FHW stayed higher over the entire temperature range compared to MFHW. This could show that the modification did not have the desired effect on improving the adhesion between two materials. It is possible that the depolymerized phenolic compounds or other extractive materials present in false heartwood fibres could somehow inhibit the formation of bonds during modification process.

The loss modulus E′′ also increased for all the WPCs which means that the damping properties of WPCs became significantly higher than that of PP. Loss modulus E′′ is a sensitive indicator of molecular differences and is often used in failure investigations. The increased loss modulus corresponds to enlarged friction between fibre and matrix during cycling–loading. In addition, fibre–fibre interaction takes place, further increasing the friction, and in consequence enhancing the dissipative energy [88]. According to DMA characterisation of polymers [91] the peak maximum of E′′ corresponds to the beginning of significant segmental motion of polymer chains. The mechanical energy is dispersed as heat through molecular chain motions. The peaks of MSW and FHW occur at about 10˚C whereas PP, SW and MFHW had a peak at around 5˚C. This could show that there is less internal resistance inside the SW and MFHW during the test. The higher peak for MSW and FHW could be an indication of somewhat stronger internal structure and show the effects of modification for MSW composite. PP is reported to have three relaxation points on tanδ curve which are near the vicinity of -80˚C(γ), 10˚C (β) and 100˚C (α) [92]. On figure 3.15 both β and α-relaxations are visible around 13˚C and 90 to 100˚C. Here the β-relaxation of PP corresponded to the glass rubber transition of the amorphous portion. The temperature at the maximum peak corresponds to the glass transition temperature (T_g). Within rising temperature from -50˚C to 10˚C E′ rapidly fell and E′′ rapidly rose which resulted in tanδ forming a peak around 12˚C. The temperature corresponding to the peak is considered to be glass transition temperature T_g. A similar relaxation process can also be seen for WPCs, but the loss factor tanδ is lower at the same transition temperature. It is noted that there is a relation between tanδ and interface adhesion and a lower tanδ value can indirectly show a better interface adhesion [93].

The tanδ curves peaked at a nearly similar temperature for all materials. When temperature is below T_g the molecules are not as mobile and therefore tanδ has a lower value. When temperature is risen to glass transition temperature, tanδ forms a peak indicating that molecules have regained their mobility. Tanδ is influenced by the type of matrix, wood flour content, the type and presence of compatibilizer, and processing parameters [91]. Graph shoes that MSW composite had the lowest value of tanδ up to 50°C. This could indicate superior adhesion between filler and polymer matrix. From there up to 140°C all WPCs obtained a similar value and continued to increase in similar fashion without major differences. Modified false heartwood composite showed a higher tanδ value compared to unmodified false heartwood composite. In contrast to sapwood composites, the increased damping ratio implied that the modification did not improve the adhesion between false heartwood fibre and polypropylene and even may have worsened it. This could be because of the additional compounds present in false heartwood that interfere with the modification. Nevertheless, the differences between damping ratios of WPCs become rather insignificant from 60°C.

FHW has very similar effects compared to SW and could effectively be used as a substitute in WPCs.

Table 3.6 Storage modulus, loss modulus and damping ratio of WPCs at 20°C

Material	**E′ (GPa)**	**E″ (MPa)**	**tan δ**
PP	2.57	267	0.1037
SW	6.44	469	0.0725
MSW	6.85	491	0.0711
FHW	5.83	452	0.0777
MFHW	5.50	487	0.0870

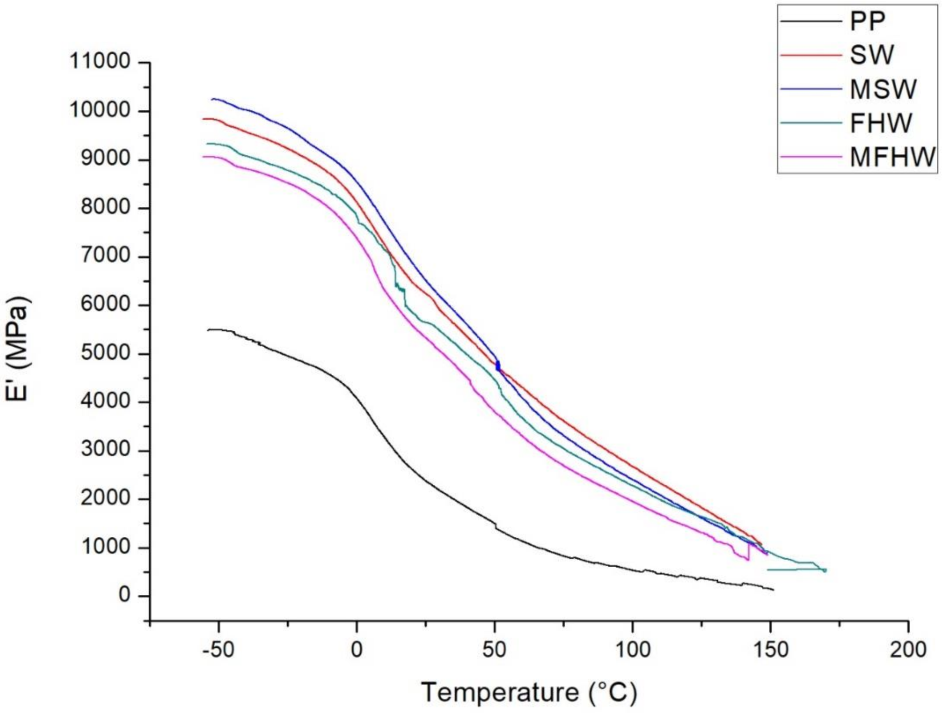

Figure 3.13 Storage modulus of PP and WPCs

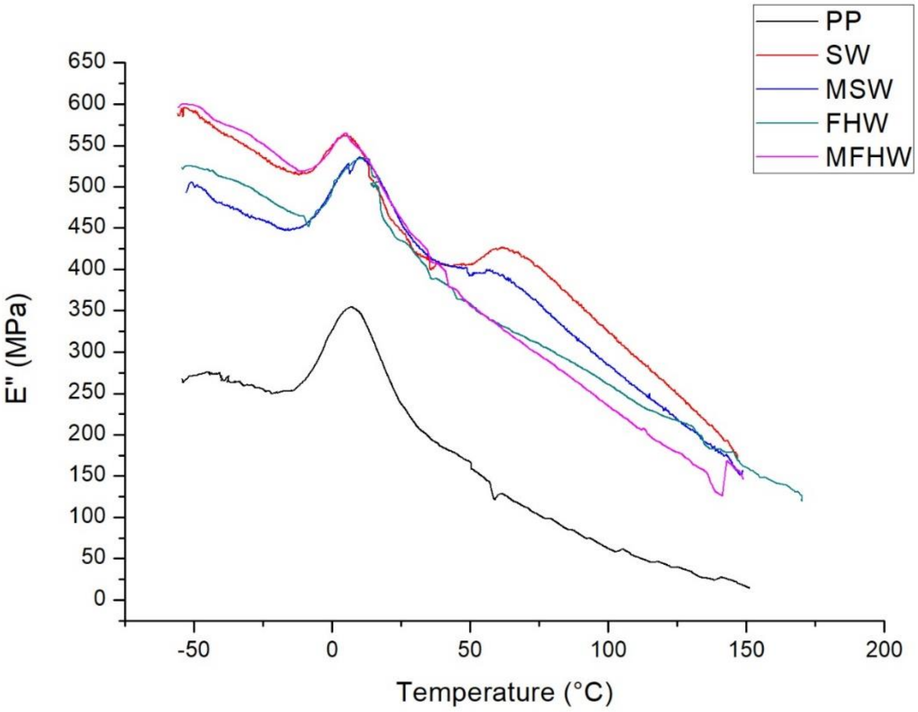

Figure 3.14 Loss modulus of PP and WPCs

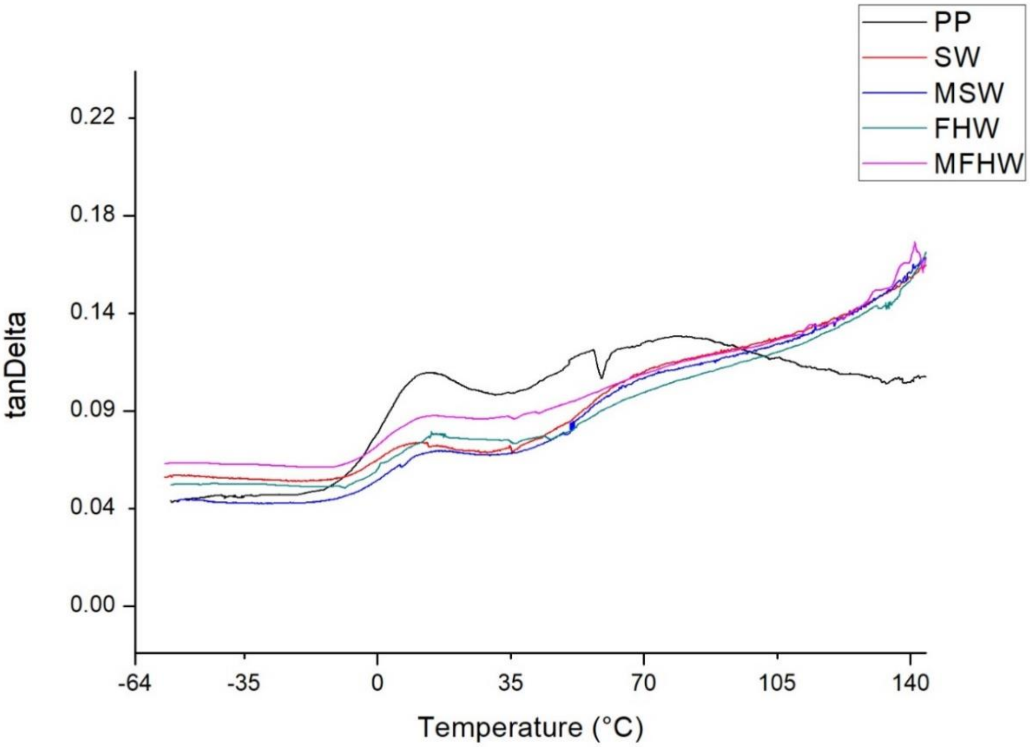

Figure 3.15 Damping factor of PP and WPCs

CONCLUSIONS

The aim of the thesis was to study the behaviour of birch false heartwood as filler in wood-plastic composites and investigate its weathering durability and thermal properties. In this research, different batches of wood-plastic composites were made using birch sapwood (SW) and birch false heartwood (FHW) and polypropylene with a wood filler content of 60%. Additionally, separate batches were subjected to modification with APTES coupling agent to observe possible effects on properties of the composites (MSW and MFHW). The Vicat point measurement, heat deflection temperature, thermogravimetric analysis and dynamic mechanical analysis was done. Also, the materials were naturally weathered for more than a year and the change in colour and lightness was measured. The weathered materials underwent tensile and flexural tests and the obtained results were compared to the results of original undegraded materials.

1. All WPCs suffered considerable changes in colour and appearance. By the end of weathering, all WPCs had obtained a very similar pale chalky look. The surfaces of test samples had developed grainy surface due to degraded materials washed away by rain. FHW and MFHW showed an overall greater colouration change, and this is probably caused by the initial darker appearance due to the presence of extractive compounds. All composites showed nearly identical values surface lightness i.e. the surface's ability to reflect light. FHW is comparable to SW regarding the colouration and appearance after 1 year of weathering.

2. The tensile strength of WPCs changed relatively little after weathering. FHW had practically identical drop (7%) compared to SW (6%), MFHW showed practically no change in strength. False heartwood seems to be equal in retaining its tensile strength with regular sapwood. Both modified composites showed greater loss in tensile modulus although this is probably because of removal of excess hemicelluloses and other substances during pre-treatment in preparation for modification.

3. Flexural tests showed that the flexural strength and modulus of elasticity (MOE) degraded similarly for all WPCs. FHW and MFHW showed smaller loss in flexural strength than SW and MSW composites, 13% and 10% respectively. FHW composite showed the smallest loss in MOE with 20%. This implies that using false heartwood

has a positive effect in sustaining the flexural properties after weathering and has equal or even slightly better weathering durability than SW.

4. When introducing fillers into the composite the Vicat softening temperature showed a slight increase from 156°C to about 160°C and there were no significant differences between different fillers. Under higher 5kg load the reinforcing nature of fillers became more apparent and increased from 13% to 22% compared to polypropylene. FHW had identical behaviour to SW.

5. The heat deflection temperature of WPCs was significantly higher that of neat polypropylene (60°C) ranging from 94°C to 115°C. This showed that all types of fillers showed similar structural reinforcing capabilities. Birch sapwood showed the highest temperature of deflection (115°C) which indicates that sapwood particles could possess a greater structural integrity than the other fillers. FHW had somewhat lower deflection temperature and could imply a slight decrease on reinforcing the structure of a WPC.

6. Thermogravimetric analysis showed that WPCs had inferior thermal stability compared to polypropylene. The mass loss of WPCs became noticeable around 100°C and became substantial from 250°C and onwards. Both modified sapwood and modified false heartwood composites showed better thermal stability around 350°C. One possibility is that this is an indication of a successful modification with a coupling agent. It is still more likely that the increased thermal stability in that region is due to the partially removed hemicelluloses during pre-treatment with NaOH. Removal of hemicelluloses increases the percentage of cellulose and lignin which prove to be more thermally stable. In conclusion, FHW nearly identical thermal stability compared to SW.

7. Dynamic mechanical analysis showed that all composites had significantly increased storage modulus compared to neat polypropylene, and overall stiffness of composite materials was higher. Composite with modified birch sapwood particles showed the highest modulus up to 50°C. MFHW composite showed the lowest stiffness among composites. Shifted peaks of storage modulus and lower damping ratio tanδ curves showed that MSW and FHW composites could have somewhat improved adhesion between filler and polymer. This could also imply that in MFHW composite pre-treatment and modification could have a rather detrimental effect on polymer-filler interface. It is possible that the depolymerized phenolic compounds and other

extractive substances in birch false heartwood could inhibit the modification reaction from taking place. Also, tyloses formed in false heartwood could prevent the coupling agent from penetrating into the material. Both SW and FHW had similar viscoelastic properties.

Based on this research, false heartwood proves to be equivalent filler material to birch sapwood and shows even better results in retaining the flexural and tensile strength during natural weathering probably because of higher concentration of phenolic extractive compounds. The modification seemed to be more viable for sapwood and somewhat less useful for false heartwood. The process of preparing false heartwood for modification and applying a modifier can do more harm than good and countervail the benefits of modification. Probably due to extractives and tyloses in false heartwood the positive effects of modification are inhibited. When it comes to making wood-plastic composites from birch wood particles, false heartwood offers great potential in replacing it as an economically viable alternative and could be regarded more than just burnable waste material.

KOKKUVÕTE

Antud uurimuse eesmärk oli uurida kase väärlülipuidu kasutamist täidismaterjalina puitplastkomposiitide valmistamisel ja saadud komposiitide termilisi omadusi ning vastupidavust välistingimustes vanandamisele. Erinevad partiid puitplastkomposiite valmistati kasutades kase (*Betula pendula*) maltspuitu ja väärlülipuitu (vastavalt SW ja FHW) ning segati kokku polüpropüleeniga. Puidu kogus komposiidis oli 60%. Lisaks eelmainitud komposiitidele valmistati modifitseeritud komposiidid, kus mõlemat puidujahu töödeldi APTES sidusagensiga, et parendada hüdrofiilse puitmaterjali ja hüdrofoobse plastiku omavahelist nakkuvust (MSW ja MFHW). Katsekehad valmistati survevalumeetodil. Seejärel määrati komposiitide Vicat pehmenemistemperatuur, läbipainde temperatuur ning teostati termogravimeetriline ja dünaamiline mehaaniline analüüs. Lisaks selle vanandati igat komposiitide partiid välistingimustes rohkem kui aasta ja hinnati komposiitide välimuse ja värvuse muutust ning tõmbe – ja paindeomadusi vanandamiseelsete omadustega.

- Kõikide komposiitide välimus ja värvus muutusid märkimisväärselt, kus komposiidid omandasid heleda pleekinud värvuse. Komposiitide pind muutus teraliseks, peamiselt vihma poolt ärauhutud lagunenud hemitsellulooside ja ligniini tõttu. Väärlülikomposiidid näitasid mõnevõrra suuremat värvuse muutust kui maltspuidu omad. Pinna lõplik heledus oli kõikidel komposiitidel väga sarnane. Võib öelda, et väärlülipuit muudab mõnevõrra rohkem värvust kui maltspuit, aga lõpptulemus on väga sarnane maltspuiduga.
- Komposiitide tõmbetugevused muutusid vanandamisega suhteliselt vähe. FHW ja SW tõmbetugevuste langus oli praktiliselt identne ja tõmbeelastsumoodulite langus oli samuti üpris sarnane. Võib öelda, et väärlülipuit käitub väga saranselt maltspuidule.
- Paindekatsed näitasid, et paindetugevuse ja paindeelastsusmooduli langus vanandamisega oli kõikide komposiitide puhul üpris sarnane. FHW puhul oli tugevuse ja mooduli langus väiksem kui SW puhul, mis viitab, et väärlülipuit on sama hea või isegi natukene vastupidavam paindeomaduste säilitamisel kui maltspuit.
- Kõikide komposiitide Vicat pehmenemistemperatuur tõusis täidise lisamise tagajärjel sarnasel viisil nii 1kg kui ka 5kg raskusega. Väärlülipuidukomposiidi omadused pehmenemisel olid sisuliselt identsed maltspuidu omaga.
- Kõikide komposiitide läbipainde temperatuur tõusis täidiste lisamisel. SW näitas 15℃ suuremat läbipainde temperatuuri kui FHW ja seega ilmneb, et väärlülipuidul

võib komposiidis olla natukene halvem kandmisvõime temperatuuri tõustes kui maltspuidul, siiski võib omadusi lugeda üpris lähedasteks.

- Termogravimeetriline analüüs näitas, et kõikide komposiitide terimiline stabiilsus langes võrreldes puhta polüpropüleeniga. Mõlemad modifitseeritud komposiidid näitasid natukene väiksemat massikadu 350 ℃ piirkonnas, mis on ilmselt tingitud termiliselt stabiilsema tselluloosi osakaalu tõusuga. Väärlülipuidu ja maltspuidu vahel ei ole märkimisväärseid erinevusi termilise stabiilsuse seisukohalt.
- Dünaamiline mehaaniline analüüs näitas, et kõikide komposiitide reaalmoodul kasvas täidiste lisamisel s.t kõik muutusid jäigemaks. Samuti kasvas komposiitide imaginaarmoodul. Mõnevõrra madalam sumbuvustegur tanδ MSW puhul võis viidata paremale adhesioonile plastiku ja puidu vahel, MFHW suurenenud sumbuvustegur võis viidata, et modifitseerimine ei andud väärlülipuidule oodatuid tulemusi. FHW ja SW vahel ei olnud drastilisi erinevusi.

Selle uurimuse tulemusena võib öelda, et kase väärlülipuit on samaväärne täitematerjal kui kase maltspuit ja näitas isegi mõnevõrra suuremat vastupidavust paindeomaduste kahanemisele vanandamise käigus. Modifitseerimine tundus olevat efektiivsem pigem maltspuidu puhul. Kokkuvõtteks võib öelda, et kase väärlülipuit pakub endas suurt potentsiaali kasutamaks teda täitematerjalina puitplastkomposiitide tootmiseks ja teda võib käsitada enamana kui lihtsalt jäätmena.

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Appendix 1 Polypropylene datasheet

TOTAL PETROCHEMICALS

Polypropylene PPH 11012

Technical data sheet
Polypropylene – Homopolymer
Produced in Europe

Description

Polypropylene PPH 11012 is a nucleated controlled-rheology antistatic homopolymer with a high Melt Flow Index of 55 g/10 min.

Polypropylene PPH 11012 is characterized by high fluidity for high speed injection of thin wall articles such as dairy pots & tubs, salad trays, caps & closures and video cassette boxes.

Polypropylene PPH 11012 has a highly antistatic nature that allows for shorter cycle times and easy demoulding.

Characteristics

	Method	Unit	Typical Value
Rheological properties			
Melt Flow Index 230°C/2.16 kg	ISO 1133	g/10 min	55
Mechanical properties			
Tensile Strength at Yield	ISO 527-2	MPa	34
Elongation at Yield	ISO 527-2	%	9
Tensile modulus	ISO 527-2	MPa	1700
Flexural modulus	ISO 178	MPa	1600
Izod Impact Strength (notched) at 23°C	ISO 180	kJ/m²	2.5
Charpy Impact Strength (notched) at 23°C	ISO 179	kJ/m²	3
Hardness Rockwell - R-scale	ISO 2039-2		100
Thermal properties			
Melting Point	ISO 3146	°C	165
Vicat Softening Point	ISO 306	°C	
50N-50°C per hour			87
10N-50°C per hour			152
Heat Deflection Temperature	ISO 752	°C	
1.80 MPa - 120°C per hour			58
0.45 MPa - 120°C per hour			105
Other physical properties			
Density	ISO 1183	g/cm³	0.905
Bulk Density	ISO 1183	g/cm³	0.525

Safety and Product Stewardship

For safe use and handling, please refer to the Safety Data Sheet. A Product Stewardship certificate giving the conformity to various regulations or statements on absence of certain chemicals is also available on our web site www.polypropylene.totalpetrochemicals.com

An Injection Moulding troubleshooting guide is available upon request.

TOTAL
TOTAL PETROCHEMICALS RESEARCH FELUY
Zone Industrielle C
B-7181 Feluy
Belgium

Rev : July 07

mailto : polypropylene@total.com
website : www.polypropylene.totalpetrochemicals.com

Polypropylene

Appendix 2 APTES datasheet

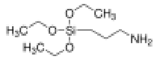
SIGMA-ALDRICH sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA
Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

Product Specification

Product Name:
(3-Aminopropyl)triethoxysilane - 99%

Product Number:	**440140**
CAS Number:	919-30-2
MDL:	MFCD00008207
Formula:	C9H23NO3Si
Formula Weight:	221.37 g/mol



TEST	Specification
Appearance (Color)	Colorless
Appearance (Form)	Liquid
Infrared Spectrum	Conforms to Structure
Color Test	≤ 25 APHA
Purity (GC)	≥ 98.5 %
Expiration Date Period 2 Years	-------------------------

Specification: PRD 1.ZQ5.10000027944

Appendix 3 Publication

PEER-REVIEWED ARTICLE **bioresources.com**

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

Heikko Kallakas,[a,]* Gbenga S. Ayansola,[a] Tanel Tumanov,[a] Dmitri Goljandin,[b]
Triinu Poltimäe,[a] Andres Krumme,[c] and Jaan Kers [a]

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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1. 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.

2. 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).

3. 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.

4. 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

5. 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.

6. 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.

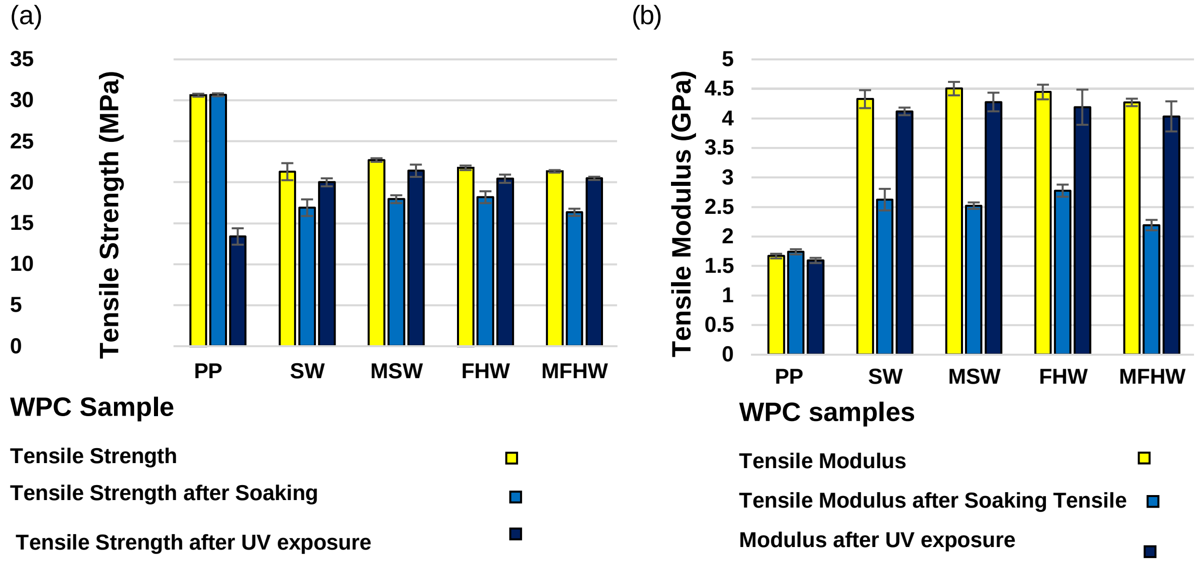

Fig. 1. Tensile Properties of the WPC samples before and after soaking in water and exposure to UV; SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

7. 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).

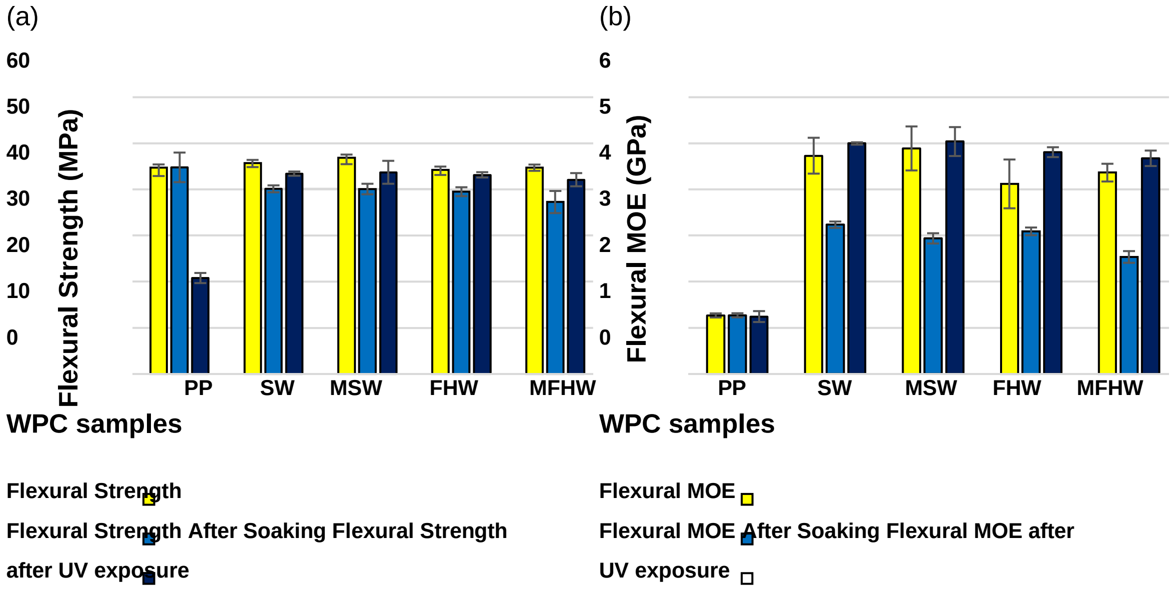

Fig. 2. Flexural Properties of the WPC samples before and after soaking in water and exposure to UV; SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

8. 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.

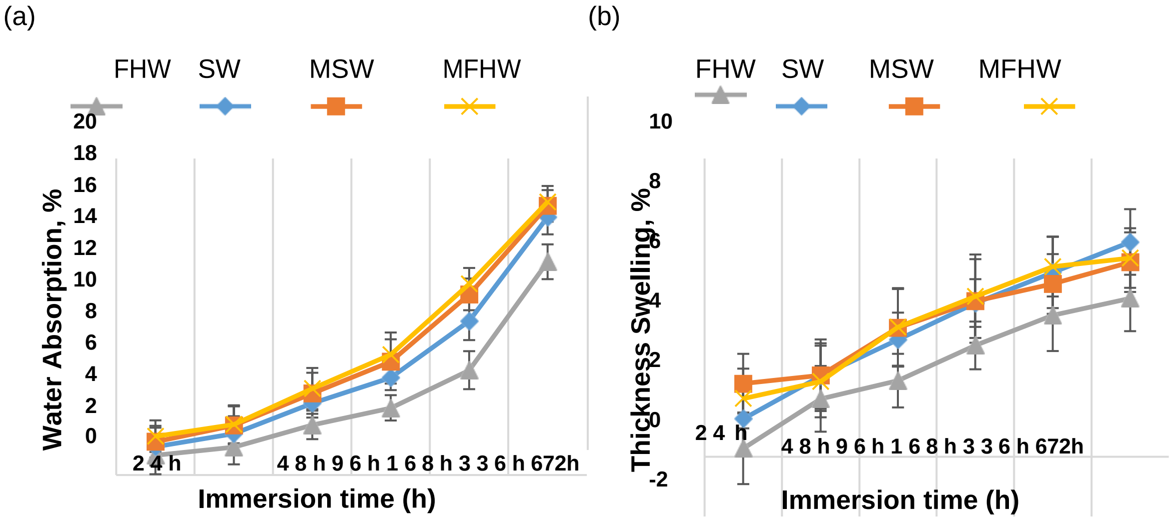

Fig. 3. Water absorption and thickness swelling of the WPC samples: SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

9. 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.

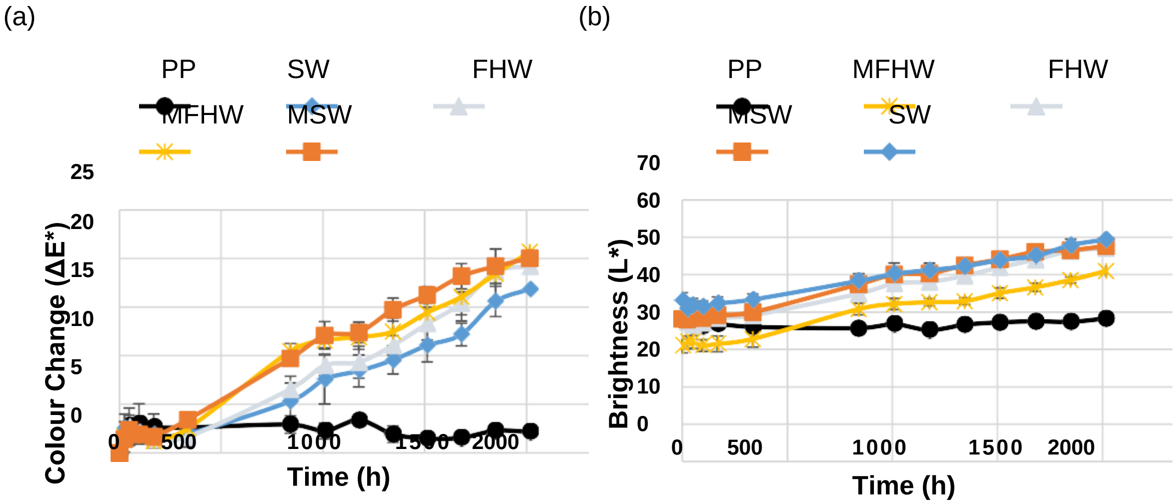

Fig. 4. Colour and brightness change of the WPC samples: SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

10. 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.

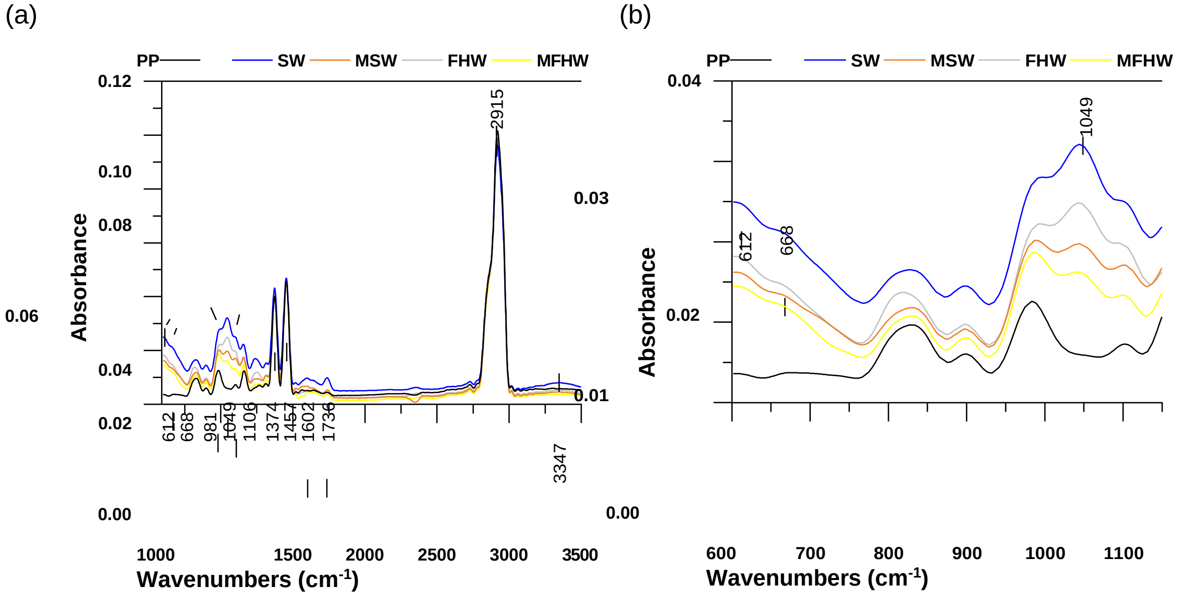

Fig. 5. FTIR spectra of the composites and neat PP: SW – birch sapwood; MSW – modified birch sapwood; FHW – false heartwood; and MFHW – modified false heartwood

11. CONCLUSIONS

12. 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.
13. 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.
14. 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.
15. 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.
16. 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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