TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

Department of Materials and Environmental Technology

INFLUENCE OF BIRCH FALSE HEARTWOOD ON THE PHYSICAL AND MECHANICAL PROPERTIES OF WOOD-PLASTIC COMPOSITE

KASE VÄÄRLÜLIPUIDU MÕJU PUITPLASTKOMPOSIITIDE FÜÜSIKALISTELE JA MEHAANNILISTELE OMADUSTELE

MASTER THESIS

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Tallinn, 2018

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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Department of Material and Environmental Technology

THESIS TASK

Student: Gbenga Solomon Ayansola, 165574KVEM

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

Main speciality: Wood Technology

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Thesis topic:

Influence of Birch False Heartwood on the Physical and Mechanical Properties of Wood-Plastic Composite

Kase väärlülipuidu mõju puitplastkomposiitide füüsikalistele ja mehaannilistele omadustele

Thesis main objectives:

1. To access the possibility of producing WPC using birch false heartwood at 60 % wood content and 40 %
2. To study the effects of the birch false heartwood on the physical and mechanical properties of the wood-plastic composite
3. To determine the effects of silane modification on the physical and mechanical properties of birch false heartwood plastic composite

Thesis tasks and time schedule:

No	Task description	Deadline
1	Selection of project topic from the variety of available topics	Oct 2016
2	Literature review of topic and materials and method selection to get familiar with the chosen topic	Dec 2016
3	Separation of birch false heartwood from sapwood in preparation for the reduction into the chosen particle size	Feb 2017
4	Crushing of wood into desired size for usability in wood-plastic composite	Mar 2017
5	Modification of wood particle in NaOH and APTES solution	Mar 2017
6	Preliminary manufacturing of wood-plastic composite by compression moulding.	May 2017
7	Milling the test samples from the manufactured composites on the CNC machine	June 2017
8	Separation of new set of birch false heartwood from sapwood	Oct 2017
9	Crushing of more wood into the desired size	Nov 2017

10	Modification of crushed samples by NaOH and APTES	Nov 2017
11	investigation into the possibility of producing samples by injection moulding	Dec 2017
12	manufacturing of composites by injection moulding	Feb 2018
13	Testing of composites based on the preselected test methods	April 2018
14	Analysis of results	May 2018
15	Writing and compilation of thesis	May 2018

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PREFACE

This project was carried out in the laboratory of wood technology, Tallinn University of Technology, Estonia. The topic is a part of a broad research being carried out in the laboratory of wood technology.

In this work, the influence of birch false heartwood on the physical and mechanical properties of wood-plastic composites were examined. Birch false heartwood and its normal wood were made into composites. The false heartwood was modified in NaOH and APTES at room temperature and compounded in a co-rotating twin screw extruder. Bone shape composites were made by injection moulding and the samples were tested for their tensile properties, flexural properties, water and thickness absorption properties, impact strength and behaviour on exposure to UV radiation. The results of the work showed that there is a great prospect for the use of birch false heartwood in the production of WPC. Some of the mechanical properties improved and showed comparable results with the normal birch wood.

I would like to appreciate everyone who has been of great assistant to me in the cause of this work, Prof Jaan Kers, Dr Triinu Poltimae, Heikko Kallakas, Dr lllia Krasnou, Tiia Plamus and Adelola Jesutomipe. Thank you all for the help and assistance you rendered.

Keywords: Birch, False heartwood, Wood-plastic composite, Silane, masters' thesis

LIST OF ABBREVIATIONS AND SYMBOLS

WPC- Wood-Plastic Composite

WP-Wood Particle

UV- Ultra-Violet

PP- Polypropylene

PB- Pure Birch

MPB-Modified Pure Birch

MP-Modified Pure Birch

FHW- False Heartwood

MFHW- Modified False Heartwood

NaOH- Sodium hydroxide

APTES- 3-Aminopropyl-triethoxysilane

INTRODUCTION

Estonia is one of the Baltic States with an abundance of green land. Estonia forest covers about 51% of the country's landmass i.e. forest cover over one half of the landmass and the area of stands was 2.14 million hectares as at 2016. Generally, there are four most common types of tree species in the country namely pine (*Pinus sylvestris*) which is 32.6% of the total area of stands, birch (*Betula pendula* and *Betula pubescens*) 30.0%, spruce which is 17.4%, and grey alder (*Alnus incana)* stands which is 9.2% (Statistic Estonia, 2017)

As abundant as birch (*Betula pendula*) is in the country, it often develops a brown colouration referred to as false heartwood or red heartwood in its 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 aging of the tree. The use of this false heartwood has often been a concern to the wood industry in view of the problems associated with its use. False heartwood has often led to the price reduction of wood when wood is visually graded due to the difficulties in distinguishing between discoloured and altered wood (Hornfeldt *et al.* 2010) as well as wastages of wood in that, False heartwood do not yield quality veneer to be used in the production of plywood. Hence, they are used either as source of energy or stacked in between plywood layers but never at top surface. In their work, Hallaksela and Niemisto (1998) conducted on birch expressed it this way 'the alarming observation of discoloration in birch stem cut at first thinning stage have raised doubts about the quality of wood that might in future be harvested from birch plantations'. Hence, the need to research ways of maximizing birch wood products.

A possible way could be in using the birch false heartwood as a filler in the manufacturing of wood-plastic composite (WPC). WPC is a material obtained by a process of combination of wood as filler or reinforcement material with plastic. This often results into a product with enhanced material properties which is able to prolong the durability and preserve the beauty of the product. In recent times, the subject of durability of WPC has gained attention and focus is now being made towards understanding the factors and mechanisms of WPC degradation issues. Consequently, many scholars have studied false heartwood to understand its properties (Hornfeldt *et al.* 2010, Johansson and Hjelm 2013, Baettig *et al.* 2017) and possibly provide a means to its usefulness in wood technology applications. Several works have been conducted on the properties of wood and plastic combination with different authors focusing on different polymers and wood species (Bledzki and Faruk *et al.* 2006, Mat *Taibet al.* 2006, *Mijiyawa et al.* 2015). Several research areas have also been investigated such as artificial and natural weathering of WPC, effects of different particle sizes and filler materials, effects of UV radiation and the colour changes that takes place as a result of such exposures, 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 thesis therefore seeks to investigate the use of birch false heartwood as a filler material in wood-plastic composite. The aim of this master thesis is to investigate the effect of Birch false heartwood on the physical and mechanical properties of wood-plastic composites. Comparison of the results obtained will be made with pure birch wood-based composites. Assessment of the birch false heartwood properties in WPC's will also be made and the results will be analysed, and appropriate solutions offered. The objectives are:

1. To access the possibility of producing WPC using birch false heartwood at 60 % wood content and 40 % PP
2. To study the effects of the birch false heartwood on the physical and mechanical properties of the WPC's by tensile and flexural test, water absorption and swelling thickness test, weathering test and colour analysis
3. To determine the effects of silane modification on the physical and mechanical properties of birch false heartwood plastic composite
4. Analyse the results obtained with those obtained from similar studies
5. Determine the prospect of using birch false heartwood in manufacturing of the WPC

In this thesis, Chapter one is focused on the properties of WPC, the manufacturing process and materials as well as a brief report of various works conducted by different researchers on WPC and its properties. In Chapter two, the methods and materials used in this work are reported and the results obtained are presented and discussed in Chapter Three. The conclusion and summary of this research work is also given at the end of the chapters.

1 LITERATURE REVIEW

1.1 Properties of Birch Wood

Birch (*Betula pendula*) wood has a long history of use in several applications such as pulping for paper manufacture, toothpick, toy parts, construction of transport vehicles etc. Although their use for outdoor purposes is limited because of their poor biological durability (Grinins, 2016) yet, they are often used in those applications because of their ease of use. There are approximately 40 *Betula* species. Birch is a diffuse porous hardwood. It is relatively easy to saw, veneer, carve, plane, turn, nail, screw, paint, varnish and glue (Herajarva, 2005). It is susceptible to colour defects caused by stem miner *phytobia betula*. They do not possess actual heartwood. The formation of false heartwood is induced by diverse exogenous factors, including various kinds of injuries or stresses that damage the tree, triggering a succession of processes (Hörnfeldt *et al.* 2010). The extent of both normal and false heartwood increases as the tree ages. When the age of the tree exceeds ca 70-90 years, the wood material near the pith is often darkened by decay (Herajarva, 2005). A common cause of stress in birch is drought; others include breakage of branches which create openings in trees or stem injuries, thereby exposing injured cells to atmospheric conditions. Xylose is an extraction obtained from birch wood used in the production of sweetener. The bark is rich in oils and this oil is used as insulating material. The use of birch has been widely established in the manufacturing of plywood and veneer products. Most of the sawn wood is used in furniture and cabinetry manufacturing, flooring and interior decoration as well as for decorative items and musical instruments. Small birch timber is used in the production of fibre board, particleboard.

Modulus of elasticity (MOE) and modulus of rupture (MOR) test performed on yellow birch and sugar maple has been reported (Duchesne *et al*. 2016). The test was conducted at 12% moisture content and it followed the ASTM 2007 standard test method for small clear specimen. Models were built and compared to identify the main factors related to the variations of MOE and MOR in both wood species. At 95% confidence interval CI, in birch MOE and MOR models, the number of rings (CI=261.84, 707.5 and 1.06, 5.19), tree age (CI= -39.24, -4.07 and -0,39, -0,08) had significant effect on the MOE and MOR variations respectively. The work showed that in birch, the number of rings as well as tree age significantly affected MOE and MOR. Both decreased with tree age

1.2 Heartwood

Wood is composed of the sapwood and the heartwood. The sapwood is the lighter part of the wood which contains living cells and serves as a conduction medium for the uptake of plant nutrient and water from the root. Usually (but not always) the sapwood changes at a certain stage of a plants growth leaving the interior core of the wood with a dark colour part called the heartwood. The heartwood is the inner layers of wood which in the growing tree have ceased to contain living cells and in which the reserve materials (e.g. starch) have been removed or converted into heartwood substances (IAWA 1957). The heartwood is generally darker in colour than sapwood, although sometimes there is no clearly visible differentiation.

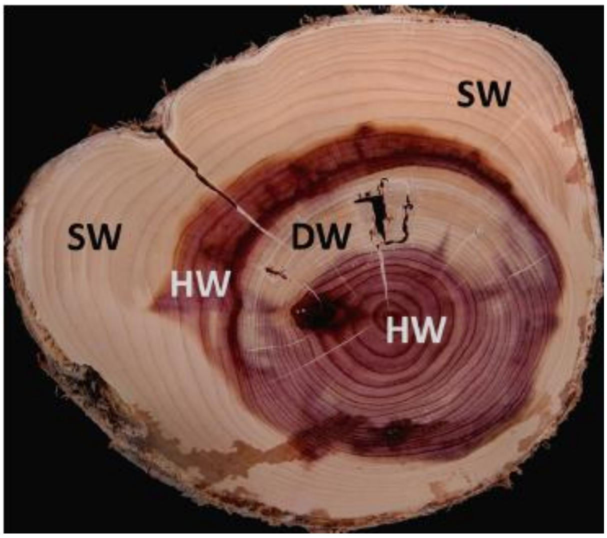


Figure 1.1 Transverse section of Juniperus Virginianum. Heartwood and Sapwood. (Smith, 2015)

HW- Heartwood, SW- Sapwood, DW- Discoloured wood

The occurrence and volumetric proportions of heartwood varies within wood species. The transition of sapwood to normal heartwood is initiated by internal processes rather than by external conditions (Shigo and Hillis 1973). Once the transition process begins, it continues such that the sapwood rings remain more or less constant during the life of the tree.

Extractives have been known to be responsible for the wide range of colours often seen in the heartwood of a tree and the quantity of these extractives usually increase from the central region of the tree- pith to the heartwood boundary. This is considered to be due to the higher amount formed at the time of heartwood formation. Phenol oxidases can cause darkening of heartwood on exposure to air (Shigo and Hillis 1973).

1.3 False Heartwood

Generally, in defining broadleaf species, their natural properties such as colour of wood is usually considered important. Naturally, some species such as black walnut, oak, elm have darkly coloured wood, and these are not classified as false heartwood. However, many other species such as birch, beech, poplar and ash have disuniform colour from the pith to the cambium. Different names have been used to describe this phenomenon of discoloured wood found in different wood species. Such names are stained wood, false heartwood, red heartwood, core wood, wet wood, black heart, pathological heartwood etc. (Shigo and Hillis, 1973; Basham, 1991). However, no common name has been officially accepted in the different terminology list (Johansson and Hjelm, 2013). The formation of false heartwood is brought about by several exogenous factors which include wounds, injuries or different stress that are capable of damaging a tree, giving rise to a succession of processes (Hornfeldt and Drouin 2010). These points to the fact that conditions such as cell death, depletion of nutrients which are visible in heartwood formation also occur in the formation of discoloured wood (Shigo and Hillis, 1973).

Several multiple factors are responsible for this discoloration and these factors are generally similar to those of the formation of normal heartwood. These include emptying of the living contents of cells of the stems, diminishing of the conductive capacity, excessive air penetration into the tree, aging of parenchyma cells, drought (low temperature), presence of fungi, generic predispositions and forest silvicultural practices (Shigo and Hillis, 1973; Marinko *et al*., 2009; Hornfeldt *et al*., 2010).

Figure 1.2 Normal birch (left) (Wulfenia *et al.* 2016), birch with false heartwood (right) (Lundqvist *et al* 2013)

False heartwood process formation has been reported not to begin with poor soil quality but only at a later stage (Shigo and Hillis, 1973). Any mechanical damages of tree with a dehydrated core zone result in oxygen absorption into the tree and the initiates the process of tylose formation which is an enzymatic process (Marinko *et al.*, 2009). This air in the ripewood zone (dehydrated zone) cause the fast dying of parenchyma cells (Racko and Cunderlik, 2010). Another factor responsible for false heartwood formation is largeness of branch.

When a tree is wounded due to any reasons, several events follow which changes the chemical processes occurring in the xylem resulting into discoloration and this process includes the oxidation as a result of exposure to air and phenols formation. The presence of false heartwood reduces the optimum use of trees.

Hallaksela and Niemisto (1998) investigated the stem discoloration of planted silver birch. Birches were planted in 160 areas and they were measured and sampled between ages 18 and 65 years. The authors reported the discolored false heartwood in young birch of ages 18-29 years in forest land to be most common in the butts of logs (less than 4.5 m), aged 30 years in the second log and in mature birches in the top section (greater than 8.5 m). They identified the increased number of bacteria and fungi in the discoloured wood compared to the normal wood as probable reasons for the discoloration. They concluded that the discoloration in the pith of birches was restricted and the quality of wood was not affected other than the colour changes. According to Shigo and Hillis (1973), false heartwood basically differs from heartwood in the way heartwood substances are stored either on the outside or inside of the parenchyma instead of the storage in the cell walls.

1.4 Wood-Plastic Composites

Wood in the form of particles, fibres or flour is one of the most common natural fibres used in the thermoplastics industry which is commercially produced from post-industrial sources as planer shavings and sawdust (Stark *et al.* 2003). Natural fibres are derived from wood and agricultural materials sources. One very important variable used to characterize wood floor is mesh size (the screen size used to distinguish between particles sizes). Wood flour/ particle is generally used as filler for plastics which tends to increase the stiffness of the composite but not necessarily strength. So far, relatively little information exists about the use of birch false heartwood composite.

1.4.1 Processing Advantage

1. Wood fibres provide a lower density of composite product than synthetic and mineral filled thermoplastics
2. Machine wear and tire of processing equipment is much higher when using synthetic and mineral fillers than with wood fibres
3. When wood is used, fibre damage is reduced and can be recycled
4. It is dimensionally stable to warp, twist, split etc
5. Offers a good colour stability to UV, sealants

1.4.2 Disadvantages

1. Water absorption and thickness swell is higher with WPC which does not occur in solid polymer
2. Interfacial adhesion is very limited with wood and thermoplastic, hence, coupling agent or surface activation is essential to be used to enhance adhesion
3. Obtaining a homogenous mixture may be difficult with the use of fillers

1.4.3 Applications

WPC applications include

1. Decking
2. Interior auto parts
3. Plastic lumber
4. Window/door
5. Railing
6. Fencing
7. Building (outdoor cladding)

1.4.4 Raw Material

Wood- In the manufacturing of wood-plastic composites, wood is often used as either a filler or a reinforcement material in combination with the polymer. Wood fibres are considered reinforcing because they bear a higher proportion of the load applied and they are often characterized with a much greater length than the cross-sectional dimension of the fibre. They offer a high aspect ratio which make way for easy transfer of stress. Generally, fillers are used to increase the mechanical properties of plastic composites and these fillers may be in form of flour or short fibre size when used for reinforcement (Walcott and Englund, 2000).

Wood fibres are natural; examples of which are Bast fibres (Hemp, Flax, jute, Kenaf), Leave fibres (Sisal, Abaca), Rice husks, straw etc and also; wood flour is obtained from granulated wood particles. When natural fibres are combined with plastics, it is called natural fibre composites (NFC) and when wood particle is used, it is called wood plastic composite (WPC).

Wood flour/particle is obtained from grinded wood and its typically characterized based on different mesh sizes. A key advantage wood flour possess is that different wood species can be used, and their use is based on the available species in different locality and regions. However, the end properties of particles or fibre obtained from a wood species can be different from the properties of the wood itself. This is often based on the processing method by which the fibre or particle are produced

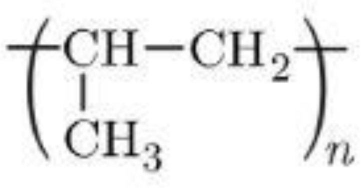
Polymers- Polymers are high molecular weight materials composed of many repeating subunits whose performance is largely dependent on its molecular architecture. Polymers can be classified into 2 based on their origin, namely

1. Natural Polymers such as Keratin, collagen, wool, silk, natural rubber etc
2. Synthetic Polymers such as nylon, polyvinyl chloride (PVC), Polystyrene, polyethylene, polypropylene, synthetic rubber etc

Further classification can be made of these synthetic polymers into thermosets and thermoplastics. Thermoset differ from thermoplastic based on the effect of heat application on their structure. Thermosets polymers increase stiffness with an initial increased temperature. They are irreversibly cured and are capable of failing after an increased application of heat following which they do not assume back to their original state. Thermoplastic on the other hand are able to withstand high temperature increase to become mouldable upon heating. On cooling, they assume the shape onto which they were made and can be further modified by heat. They are polymers with very few or no crosslink e.g. polypropylene, PET etc

Several thermoplastics are available for use in the composite industry, however not all can be used in the manufacturing of WPC. This is primarily due to temperature. Temperature is considered before a thermoplastic can be used in WPC manufacturing. Due to the limitation of the application of high temperature to wood, a thermoplastic of lower melting point which is less than the degradation temperature of wood (~200 ˚C) is selected. This thermal property criterion therefore limits the wide range of thermoplastics that can be used in WPC manufacturing. Heating wood beyond that may lead to the total collapse of the wood structure and consequently failure of the material. Commonly used low melting temperature thermoplastics are polypropylene, polystyrene, low and high-density polyethylene (LDPE and HDPE), polyvinyl chloride (PVC).

In recent times, the use of polypropylene has been on the raise. This can be said to be mainly due to the higher property it exhibits (Kallakas *et al*. 2016). Polypropylene is one of the most important polyolefins with a wide range of applications. Polyolefin are any polymer produced from a simple olefin-alkene group



$$\left(\underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 \right)_n$$

Figure 1.3 Monomer Structure of Polypropylene (Chawla *et al* 2017)

The use of wood-plastic composite (WPC) has found such a wide application in the modern world. From the automotive industry to decking in ship, profiles in building and construction etc. Over the years, the processes leading to the production of WPC has been improved. The raw materials used are basically wood flour, particles or fibres and thermoplastics such as polypropylene (PP) and polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC). The consideration for Sustainability of the thermoplastic polymer has brought about the implementation of biogenic matrix polymers (Faruk *et al*. 2012; Patrick *et al*. 2015).

The use of bio-based plastics as reinforced matrices for biocomposites is gaining more and more approvals daily as the average annual growth rate was 38% from 2003 to 2007 and 48% in Europe in the same period (Faruk *et al*. 2012). Biopolymers can be divided into biodegradables and non-biodegradable. Several new polymers from renewable energy sources such as starch have been developed. Starch, a naturally occurring polymers was re-discovered as a plastic material. Others include poly lactic(PLA) from sugar and polyhydroxyalkanoate (PHAs) produced from vegetable oils. Bio-based polyethylene obtained from sugarcane and bio-based polyamides from castor oil are commercially available and they represent some very interesting alternatives to their fossil-based counterparts (Endres *et al*. 2011). The problem identified in producing WPC based on polyamides is there relatively high temperature which is capable of causing wood fibre degradation as a result of the heat. Bio-based polyamides such as polyamide 10.10 (PA 10.10) and polyamide 6.10 (PA 6.10 and polyamide 11 (PA 11) have lower melting temperatures than conventional polyamide 6 (PA 6) (Feldmann *et al*. 2014). However, the market prices of bio-based polyamides are up to five times higher than conventional PA 6 due to lower production capacities (Shen *et al*. 2009)

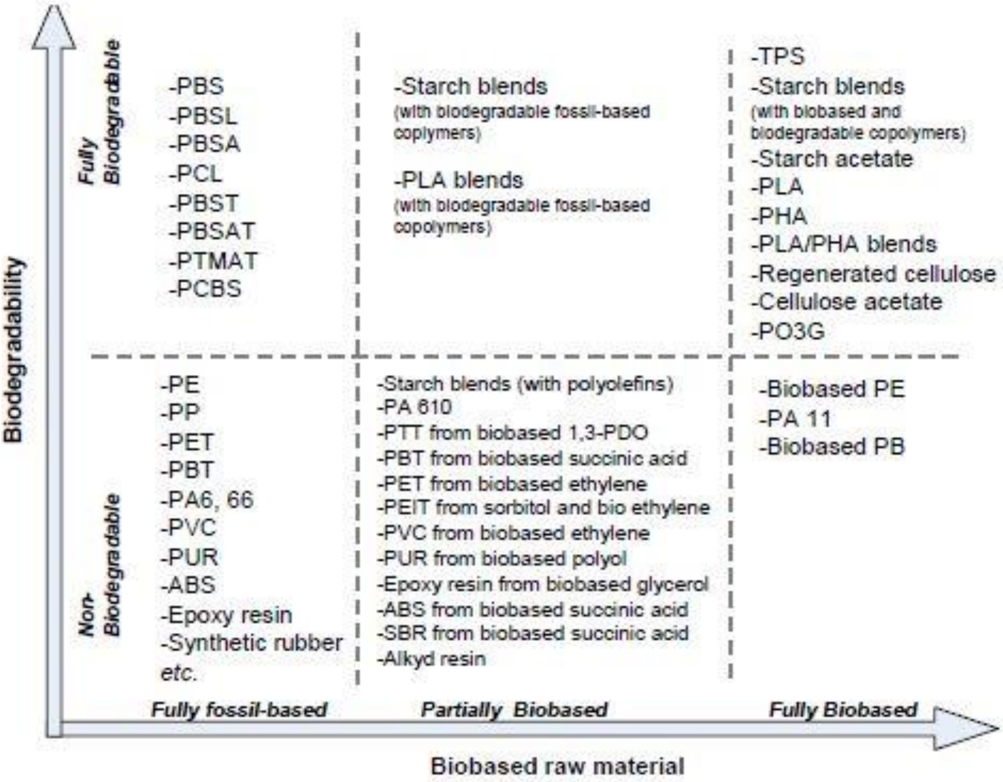


Figure 1.4 Current and emerging(partially) bio-based plastic and their biodegradability (Shen et al.2009)

Bledzki *et al*. (2009) investigated the properties of PLA bio-composites with abaca and man-made cellulose fibres. They made comparison of the result with the composites of PP. With man-made cellulose of 30wt%, the tensile strength and modulus was shown to increase by factors of 1.45 and 1.75 times in comparison to PLA.

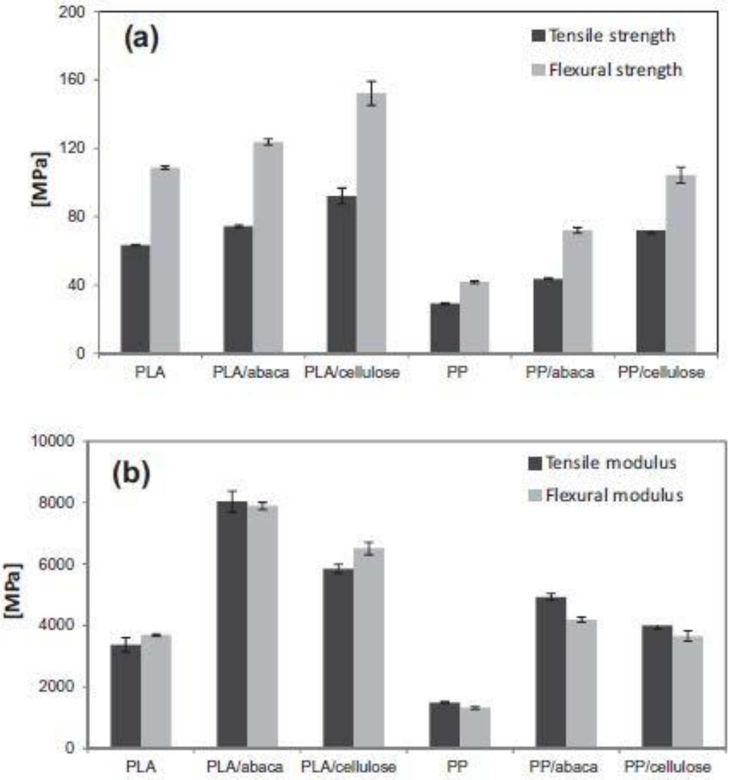


Figure 1.5 Tensile and flexural properties [(a) Strength and (b) modulus] of PLA and PP composites (fibre content 30wt%) Bledzki et al. (2009)

Bledzki and Jaszkiewicz (2010) conducted a similar work and reported that the tested biopolymer-based composites showed comparable and, in some cases, better mechanical characteristics than the common natural fibre reinforced PP composite as can be seen in the table 1.

Table 1.1 Mechanical properties of PLA, PHBV and PP based natural fibre reinforced composites (Bledzki and Jaszkiewicz, 2010)

Matrix	**Fiber**	**Tensile E-modulus (Gpa)**	**Tensile strength (Mpa)**	**Tensile elongation-at-break (%)**
PLA	-	3.4±0.23	63.5±0.4	3.3±0.5
	Man-made cellulose	5.8±0.15	92.0±4.7	1.9±0.3
	Abaca	8.0±0.34	74.0±0.7	1.44±0.1
	Jute	9.6±0.36	81.9±2.9	1.8±0.0
PHBV/ecoflex	-	2.14±0.07	27.3±0.3	7.0±1.1
	Man-made cellulose	4.4±0.34	41.7±3.8	2.3±1.0
	Abaca	4.4±0.06	28.0±1.3	0.9±0.1
	Jute	7.0±0.26	35.2±1.3	0.8±0.0
PP	-	1.5±0.03	29.2±0.4	>50
	Man-made cellulose	3.7±0.11	71.6±2.7	3.5±0.5
	Abaca	4.9±0.11	42.0±0.5	1.7±0.2
	Jute	5.8±0.47	47.9±2.7	1.4±0.1

Additives- The physical and mechanical properties of WPC can be generally said to depend on the interfacial interaction between the word surface and the thermoplastic surface. Several additives are applied to achieve different purposes. A very important additive used is the coupling agent. The coupling agent is used to improve the surface interaction between the wood which is primarily hydrophilic and the thermoplastic which is primarily hydrophobic. Adding a coupling agent ensures that the dissimilar sections of one molecule will be compatible with another component of the composite matrix. They are also called compatibilizer. Commonly used coupling agents are maleic anhydride grafted polypropylene (MAPP), (3-Aminopropyl)triethoxysilane APTES, titanates etc. Kallakas *et al*. (2015) showed that APTES offers a better surface compatibility.

The chemical modification of wood has been in use for a while to alter the structure of wood and improve the interfacial adhesion between wood and polymer matrix. This consequently leads to the improvement of the mechanical and physical structure of composites (Gwon et al. 2010). Several researches have been conducted on different modification process. This process includes alkaline modification, silynation, esterification, maleated, acetylation, cyanoethylation etc (Kallakas *et al.* 2015). Silane treatment has been shown to decrease the water absorption of composites, increase the crystallization temperature and crystallization enthalpy while decreasing the crystallinity of composites (Kim *et al.* 2010).

Various additives are added to achieve different end results

1. Stabilizers such as antioxidants, UV stabilizers and heat stabilizer are added to prevent or reduce the chemical reactions capable of degrading the composite
2. Chemical or physical blowing agent to reduce density of material
3. Biocides for prevention of microbial species which may want to feed on the fibre. Usually important for product to be exposed to moisture.
4. Additives that enhance the aesthetic of product
5. Fire or flame retardants etc.

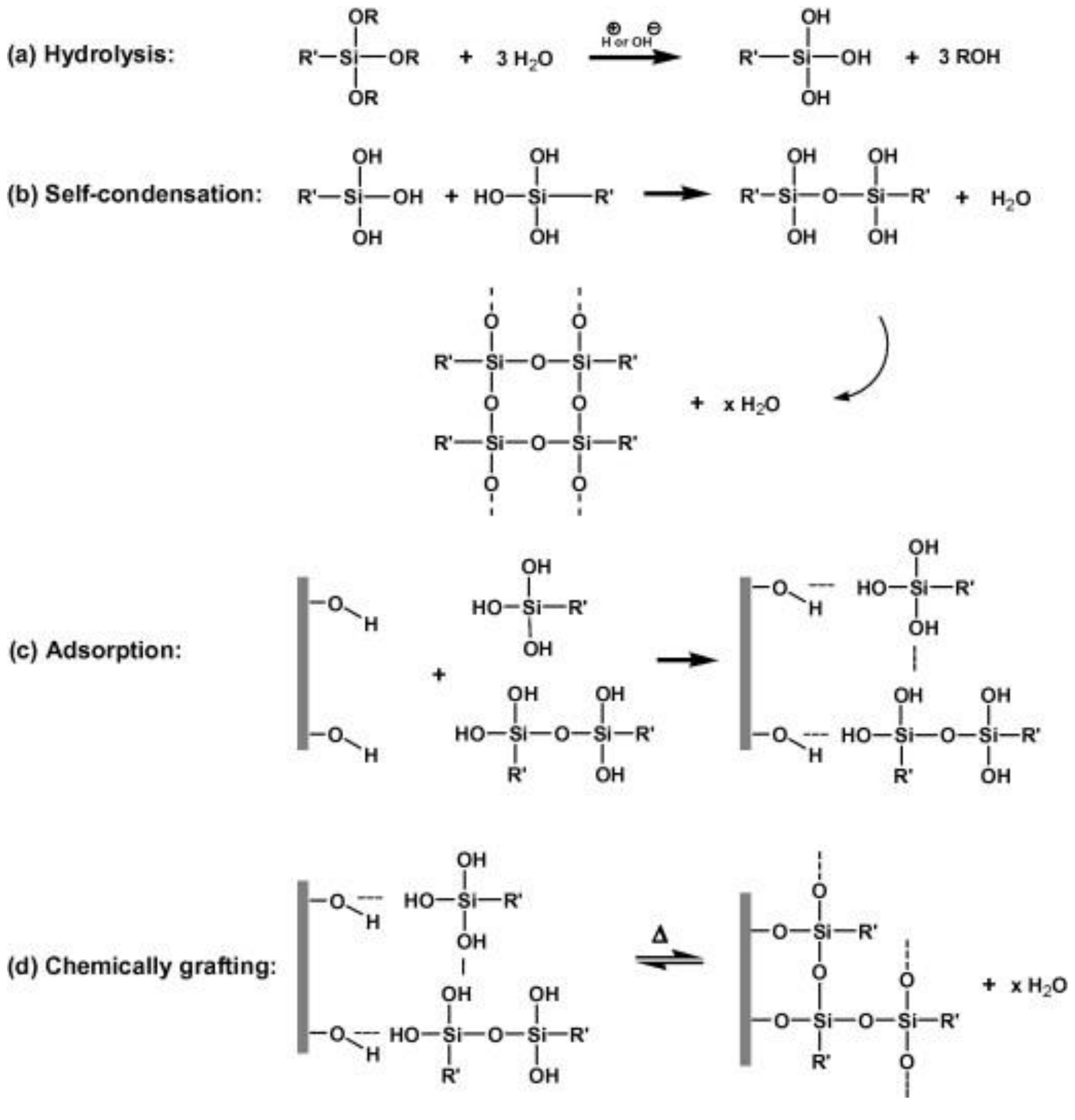


Figure 1.6 Interaction of APTES with natural fibres by hydrolysis process (Xie *et al.*2010)

1.4.5 Wood-Plastic Composite Manufacturing Process

The manufacturing process of wood-plastic composite includes extrusion, injection moulding or thermoforming (pressing) and injection moulding. Newer WPC manufacturing processes now exist, and these includes additive manufacturing via fused layer modelling and laser sintering (Gardner *et al.* 2015). A very important consideration in the manufacturing process is the type of polymer used. The type of polymer to be used is limited to the temperature by which wood degrades. Wood degrades around 220 °C; consequently, polymers with lesser melting temperatures are only used. Wood fibres are hydrophilic in nature due to the hydroxyl group in their cellulose and hemicellulose. Thus, wood fibres used in the process are modified using chemical or physical treatments. This is to ensure the adhesion of the wood fibre and polymer. Wood log is debarked, dried and then crushed into the required mesh size. The fibre is then mixed with polymer pellets and then they are compounded in the extruder after which they can be moulded into desired shape based on the final product

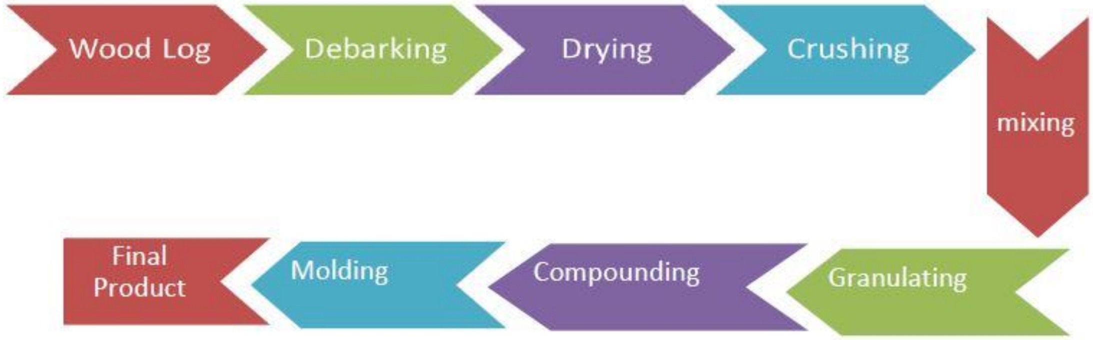


Figure 1.7 Schematic diagram showing the manufacturing process of WPC

Compounding Technology- Extrusion Process: Extrusion process is a very important process in WPC manufacturing. It is a compounding technology in which both the WF and polymer are melted and passed along a heated rotary screw of high temperature. It is the process of converting solid polymer into vicious liquid states and then reconstituting them into finished product. Many extruders are used in processing WPC. Some of the common extruders are the single screw extruder and twin-screw extruder. The key components of the extrusion process are

The Extruder: The extruder can be (a) Single screw extruder (b) Twin- screw extruder (c) Planetary rolling extruder (d) Muiti- corotation screw extruder. The advantage screw extruder has over the other types of extruder is that it is able to continuously process and mix polymers.

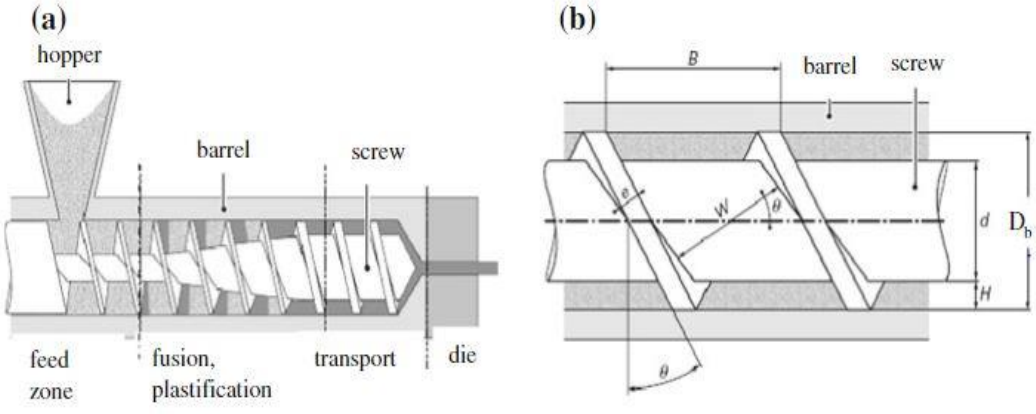


Figure 1.8 Scheme of the extruder. The extruder(a) Geometry of the screw (b) (Berthiaux and Mizonov. 2004)

Single Screw Extruder: The single screw extruders are cheaper to acquire than the twin screw extruders and are mechanically very simple (Riaz, 2000). They are often useful in academic research. They contain a single rotating screw which makes their mixing ability poor. It is the most commonly used and does not require a feeder since the polymer intake is directly through the hopper. It has its speed screw directly related to its output. Any increase in its screw speed, consequently leads to more output. The materials are pushed forward and not simply rotate with the screw as a result of fractional force on the barrel and screw surface (Martelli, 1983).

Twin Screw Extruder: This is made of two rotating screws which may be in opposite direction (counter rotating) or in the same direction, in this case called (co-rotating). The counter rotating twin screw extruders are used in the processing of polyvinyl chloride. It has a good product intake capacity. They are equipped with feeder which makes the rate of output independent on the screw speed. They can be intermeshing or non-intermeshing. Non-intermeshing extruders are similar in operation to the single-screw extruder where the forward conveyance movement is essentially dependent on the friction between extrusions and the barrel (Walcott and Englund, 2000). However, in intermeshing twin screw extruder, the conveyance of the material is not fractional force dependent because of the displacement of the material in the screw channel caused by the adjacent screw (Walcott and Englund, 2000).

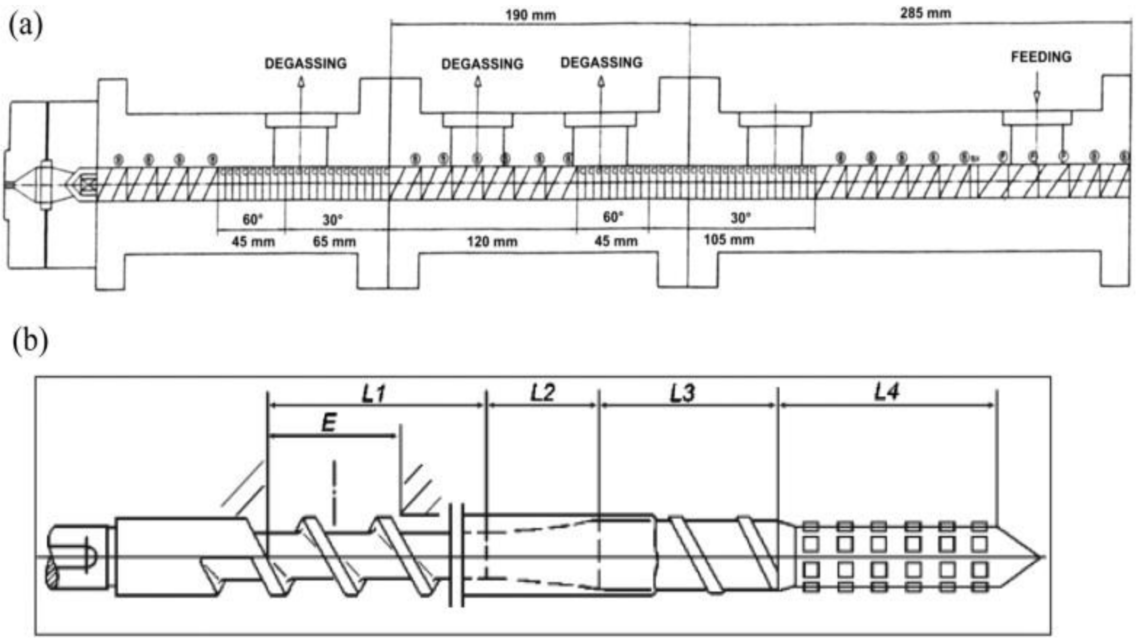


Figure 1.9 Screw profile scheme for twin screw extruder (a) and screw image for the single-screw extruder (b) (Mistretta *et al.* 2014)

Injection Molding: Injection moulding is a well-used process in the manufacturing of plastic part with different shapes and contours. It requires the use of a mould raw material and the injection moulding machine. The mixed polymer is feed into the hopper of the machine and they are melted in the machine at high temperature and then injected into the mould. It solidifies upon cooling in the mould. Injection moulding is used to produce thin walled parts useful in various application. To obtain a good WPC injection from the machine it is essential to ensure that the moisture content of the raw material is very low, and the temperature profile of the machine must be adapted to the WPC (Custompartnet, 2007). Injection moulding has a very short process cycle and basically contain 4 stages: Clamping, Injection, Cooling and Ejection.

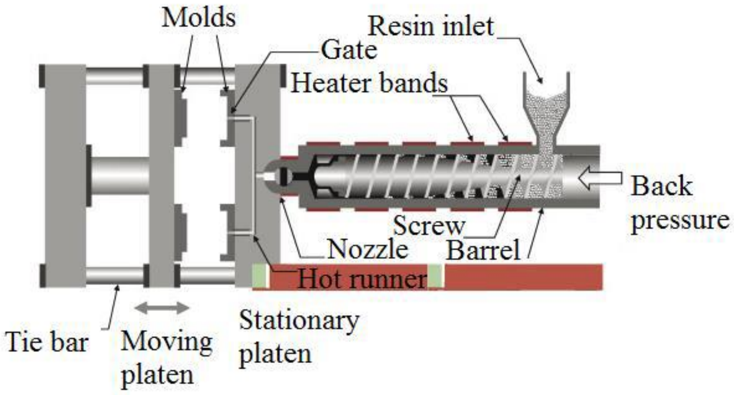


Figure 1.10 Scheme of Injection moulding (Lim *et al.* 2008)

1.5 Properties of Wood-Plastic Composite

1.5.1 Mechanical Properties

Several studies have been conducted to determine the impact of wood flour/particle on the mechanical properties of WPC. Kallakas *et al*. (2016) examined the flexural properties of WPC with thermally treated and untreated silane modified and unmodified WF. It was reported that the WF addition caused a flexural strength increase by 9-21%. Modification of WF with APTES at 5wt% has also shown an increased flexural property than unmodified WF composite (Kallakas *et al*. 2015; Kim *et al*., 2011). MOE increased with chemical modification such as NaOH, PVA (Polyvinyl alcohol), APTES and AA (acetic anhydride). Several authors have reported increase in flexural strength of wood- polypropylene composites (Muslim *et al*. 2015; Stark and Rowlands 2003; Gallagher and McDonald 2013). The tensile strength of WPC samples of PP, recycled HDPE and Polysterene PS has been shown to decreased with wood fibre addition (Wolcottt and Englund, 2000). Gallagher *et al*. (2013) showed that the Modulus of rupture (MOR) increased with a reduction in WF size and increased with the addition of coupling agent Malleated Polyethylene (MAPE). WF thus improves stiffness of WPC.

Addition of wood flour/particle to polypropylene matrix has showed lowered impact properties compared to the pure PP. Impact strength decreased as stated by Kallakas *et al*. (2016) because of the stress concentration regions in the WPC which do not need high energy to break, thus making the material brittle. As reported by Dalvag *et al*. 1985, tensile strength, Charpy impact and elongation at break improved when the compatibilizer MAPP was used in PP/WF composites. Start and Rowlands, 2003 also concluded that the larger particle size has the greater notched impact energy and a lower unnotched impact energy as a result of higher stress concentration. Stark *et al*. (2003) carried out an investigation to determine the influence of pine wood flour particle size on the mechanical properties of wood flour/ polypropylene at 40% by weight and melted at temperature below 190 ˚C. Tensile tests, flexural tests and the notched and unnotched Izod impact strength tests were performed to determine the energy needed to cause the composite failure (ASTM 2000c). Mesh sizes of 35, 70, 120 and 235 were used. The energy required to initiate crack in the composite was measured with an unnotched specimen and crack propagation with a notched Izod specimen. Comparison was also made between the wood flour and wood fibre component. It was concluded that aspect ratio and not particle size had the greatest effect on strength and stiffness but has significance on the impact energy. The larger the particle size, the greater the notched impact energy and the larger the particle size, the lower the unnotched impact energy. The authors' recommended the addition of the coupling agent MAPP to wood fibre composites for increase in strength and stiffness of the composites. This was further confirmed by Mijiyawa *et al*. (2014)

1.5.2 Water Absorption Properties

The hydrophilic nature of wood and hydrophobic nature of polymer makes it suitable to study the water absorption ability of the material for outdoor applications. Silane coupling treatment of WF in WPC has shown a reduction in the amount of water absorbed to about 2.5 times lower than the untreated composites. Kim et al. 2010 subjected PP/WF composite to water soaking for 30 days and it was reported from the investigation that APTES showed the lowest water absorption WA. This result is similar to that obtained by Liang (1995) where wood-fibre/polystyrene composites were subjected to water absorption. The water absorption rate decreased when the polymer content was increased so also does thickness swelling. However, the increase performance did not directly correspond to the polystyrene content change. Benthien and Ohlmeyer, (2013) preconditioned WPC samples at 20 ˚C and 65% relative humidity and afterwards submerged the samples in cold water at 20 ˚C for 24-672 h. They reported an increase in water absorption and thickness swelling with increasing time of immersion and WF content.

1.5.3 Effect of wood particle size and filler content on WPC properties

The wood content influences the mechanical properties of extruded WPC. Yam *at al.* (1990) produced an HDPE/wood fibre composite using a co-rotating twin screw extruder. The authors submitted that an increase in flexure and tensile modulus with increase in fibre loading for acetylate treated, heat treated and the untreated fibres. They also reported a decrease in tensile and impact strength in the composites as the fibre content increased.

Muslim *et al*. (2015) investigated the mechanical and thermal properties of the polypropylene composite at various wood filler contents (0-60 wt%) and different particle sizes. The tensile strength of polypropylene composites was observed to increase with increases in wood filler content and particle size. In all three samples (sizes 200 µm, 400 µm and 800 µm) it was observed that the smaller sample size had the better tensile strength at higher filler compositions. The better dispersion and filler-matrix interaction between the two compounds was identified to be the main reasons or factors responsible for the observed trend.

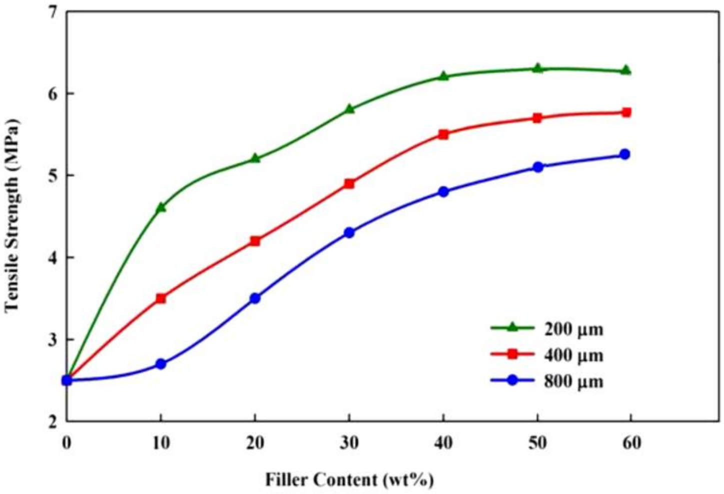


Figure 1.11 Relation between tensile strength and filler content of wood-polypropylene composites. Muslim et al. (2015).

The impact strength of polypropylene composites was observed to increase with increases in wood filler content. However, the impact strength of the prepared composites was observed to decrease with lower sample sizes. Hence it was concluded that increasing the particle size of wood filler would significantly decrease the level of stress concentration in the composites with a resultant increase in impact strength. The flexural strength of polypropylene composites increases with the filler content increment but decreases with filler particle size increment. Similar result is reported by Nihat *et al.* (2014) and Tazi *et al.* (2016).

1.5.4 Melt Flow Index

Melt flow index (MFI) represent an aspect of the rheological properties of the resin such as its flow ability (Tabkhpaz *et al*. 2012). It is a very quick method to determine the flow characteristics of WPC systems in the molten state (Gallagher *et al*. 2013). Matrix melt flow behaviour plays an important role on the structure- property relationship of the WPC. Gallagher *et al.* examined the melt flow rate of some WPC witth wood contents between 10 and 50%. They found the WPC melt as a function of wood content to decrease as the wood content increased. They reported a 84% decrease in MFR when WF content increased from 30 to 50%. The result also showed that WPC melt viscocity increased with increase in wod loading and the decrease in WF size showed an increase in the MFR (decrease in melt viscosity) of the WPC. Generally, MFR increased while viscosity decrease for all samples. However, Stark *et al.* 1997 reported the melt index for the range of wood flour they examined to increase as particle size increased. Four screened particle size and four commercial aprticle size wood flour were examined. The authors explained that this is due to the fact that as the particle size increased, the unfilled volume of the polymer regions increased which consequently resulted in greater flow mobility for the polymer and a higher melt index

1.5.5 Weathering Properties

Exposure of plastic materials to ultra-violet radiation has been shown to have effects on the mechanical and physical properties such as the appearance and colour change of such materials. It is one of the main causes of the changes in mechanical and visual properties of WPC that have been reported. Badji *et al.* (2017) investigated the influence of weathering on visual and surface aspect of WPC under natural and artificial weathering conditions by a simultaneous analysis of the changes and surface topography. The authors reported that wood flour is responsible for the bleaching of composites under aging test due to the photodegradation of the wood flour lignin whose chromophoric groups are able to form free radicals upon absorption of UV rays. Photobleaching of lignin is easier and faster than cellulose (Peng *et al*. 2014). Lightness (L*) of WPC specimens have been shown to increase and b* decreased after exposure to UV rays. Wood content and weight decrease with prolong exposure of WPC to weathering which causes an increase in the degradation of wood as well as erosion which creates cracks on the composite surface (Fabiyi and McDonald, 2014). Prolong exposure of WPC to weathering has been shown to decrease wood content wood content (Fabiyi and MCDonaid, 2009). Weathering cause wood particle bleaching and crack formation on WPC surfaces (Soccalingame *et al.* 2015)

1.6 Fourier Transform Infrared Spectroscopy-FTIR

FTIR is a known technique for the analysis of materials. FTIR spectrometer are often equipped with an attenuated total reflectance (ATR) useful mainly in applications such as the investigation of material surfaces and coatings. By this technique, several mixed material samples can be identified at once without necessarily separating them. It is most useful for the study of polymeric materials which involves identification and characterization of polymers as well as determination of their molecular structures. The stretching vibration peak at 1730 cm^{-1} has been attributed to C=O stretching of carboxylic groups in acetyl group in hemicelluloses (Silverstein *et al.* 2014, Ma *et al.* 2017). It works by obtaining in a spectrum, the absorption of infrared radiation by a material. It is capable of analysing liquid, gaseous and solid samples. A typical FTIR spectrometer consists of a source, sample compartment, amplifier, convertor, interferometer etc. Radiation is generated by the source through the interferometer to the detector. The generated signal is then amplified and converted to digital signal which is transferred to a computer. A portion of lignin and hemicellulose can be extracted through the washing with Alkaline solution (Lu *et al.* 2005). It is important to obtain a background spectrum before commencing analysis because of dissolved gas traces which must be subtracted from the sample spectrum in other to have a true information about the sample been analysed. It is a faster, less expensive and more accurate and simple in performance than thermos-analytical methods (Li *et al.*2015). Acetyl group may hydrolyse into acetic acid which in turn reduce the number of hydrophilic C=O groups as a result of higher temperature and moist environment in hot air (Chen *et al.* 2017).

1.7 Price Comparison of WPC and Solid Timber

The price comparison between WPC and solid timber in Tallinn is shown in the table below. The table shows the price range with product dimensions as obtained locally from sales outlets in Tallinn

Table 1.2 Price comparison of WPC and solid timber (Onewood)

WPC		Solid Timber	
Dimension (mm)	Price (euro)	Dimension (mm)	Price (euro)
22 x 300 x 300	3.99	50 x 50 x 2400	2.26
30 x50 x 3000	13.2	50 x 50 x 3000	2.82
6 x 60 x 3000	10.7	50 x 150 x 3000	7.74
25 x 160 x 3000	23.2	50 x 150 x 4800	11.47

WPC as can be seen is more expensive. This is so in view of the value addition of WPC as against solid timber. However, in the long run, WPC will compensate for the price difference because of the improved properties it offers such as durability and longer service life.

The cost of paints and lacquer varies based on manufacturers and the product itself. However, the starting price for 1L of oil primer/undercoat starts at 50 euros (finepaintofeurope).

2 MATERIALS AND METHODS

2.1 Materials

2.1.1 Filler Material

The birch wood (both the pure wood and the false heartwood) was supplied as veneers by Kohila Vineer OÜ. The experimental work began with the separation of Birch false heartwood from the pure wood. The false heartwood was separated from birch veneer. The veneers were carefully sorted and checked for quality assurance in the laboratory before proceeding with crushing them into the desired particle size. Birch veneers were initially crushed mechanically in the Tallinn University of Technology, Department of Mechanical and Industrial Engineering, Powder Metallurgy laboratory, using disintegrator DS-A to particles after which the wood particles were then mechanically refined into the specific wood size particles using separation grinding with disintegrator DSL-115. The wood particle length and distribution were measured using analytical sieve shaker method with Fritsch Analysette c3. The used sieve sizes were from 25 to 0.025 mm and the samples were crush into the particle size of 1mm.

2.1.2 Polymer Material

The PP used (PPH 11012) is manufactured by Total Petrochemical. 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 diary pots and tubs, salad trays, caps and closures and video cassette boxed. Polypropylene PPH 11012 has a highly antistatic nature that allows for shorter cycle times and easy demoulding. It has a melting point of 165 ˚C.

2.2 Modification by NaOH

The wood particles were modified in the TTU Laboratory of Wood Technology using alkaline solution with NaOH (min. 98%, p.a. 1 kg, CAS 1310-73-2) at 5 wt% (by wood content). NaOH supplied by Keemiakaubandus AS, Estonia. The WF was treated in NaOH solution at room temperature and left for about 90 min. The WF was then rinsed with distilled water to neutralize the excess NaOH and then oven dried at 60 ˚C for 24 h. The effect of the alkaline is to cause a disruption of the hydrogen bonds present on the fibre surface. This leads to the removal of certain amount of lignin, hemicellulose, waxes and oils. It also increases the adhesion ability of thermoplastic with the fibre surface.

Figure 2.1 Modification of wood with NaOH

The rinsing of the NaOH modified WF was done in a vacuum pump. The WF was washed at least four times for every batch and was tested using a litmus paper to determine their neutrality. This was done using the handsheet former LA-1 vacuum machine shown in figure 2.2. The handsheet former LA-1 vacuum machine is commonly used in paper industry laboratories. It worked such that modified wood flour is poured into the handsheet former's drainer cylinder and diluted with water up to volume of 8:1. The diluted mixture is manually mixed for about 3 mins to homogenize the concentration and then the water is drained instantly. This was repeated about four times until the NaOH modified wood becomes neutral.

Figure 2.2 Rinsing of WF modified in NaOH using a vacuum

2.3 Modification by Silane (APTES)

The WF was treated with APTES (3-Aminoprophl-triethoxysilane) solution at room temperature (23 ˚C). APTES was supplied by Sigma-Aldrich (assay: 98%, density 0.946 g/mL, bp: 217 ˚C/760 mmHg). 5wt% (based on WF) of APTES was used. APTES was immersed in a solution of ethanol and distilled water in the ratio 6:4 and continuously stirred for 1 h for silane hydrolysis, thereafter, the pH of the solution was adjusted to 4-5 with acetic acid supplied by lach-ner (99.8%, M: 60.05 g/mol). The APTES solution was poured on the WF and left for 2 h. The WF was then oven dried at 60 ˚C for 24 h. Upon drying, the modified WF were collected and placed in a sealed air proof plastic bag to prevent their moisture absorption.

Figure 2.3 Modification by Silane (left), fully modified samples ready for drying (right)

2.4 Material Calculations

The breakdown of the materials consumption used in the manufacturing of the composites is given below

Table 2.1 Materials calculations for composites making

Process	Pure birch wood	Birch false heartwood
Total wood mass available	6.5 kg	4.75 kg
Mass of wood modified	3.25 kg	2.4 kg
Mass of NaOH (5 wt%) used in modification	162.5 g	120 g
Mass of APTES (5 wt%) used in modification	172.75 g	156.5 g
Quantity of acetic acid	60 mL	50 mL
Quantity of ethanol	3 L	2.4 L
Quantity of water	2 L	1.6 L

2.5 Composite processing

The wood particles (both modified and unmodified) were mixed with the polypropylene polymer in the ratio 60 wt% of wood to 40 wt% of polypropylene for all samples made. The fractional sample size of the wood particles is 1 mm. The mixture was done in batches of 500g each and each batch was mixed in the laboratory rotary mixer for 5 minutes. The composites were compounded in the co-rotating twin-screw Brabender Plasti-Corder PLE 651 extruder located in the TTU Laboratory of Polymers and Textile Technology. The barrel has four melting temperatures zones which were set at 180 ˚C,185 ˚C, 190 ˚C and 190 ˚C respectively. The rotation screw speed was set at 60 rpm throughout the process. The extruded materials were allowed to cool naturally and thereafter granulated in Retsch SM 100 miller. The mesh size of 1mm was used in the machine. The compounded composites were placed in tightly sealed plastic bags to prevent moisture impact before they were moulded into standard samples (figure 2.5)

Figure 2.4 Compounded samples sealed in plastic bags awaiting injection moulding

The test samples were made by injection moulding in Battenfeld BA 230E (see figure 2.6) according to EN ISO 527-2. The injection moulding machine was set at temperatures between 170 ˚C and 180 ˚C, injection pressure of 7 MPa and screw speed of 40 rpm with cooling time of 15 s. table 2.1 gives the composite composition plan.

Figure 2.5 Battenfeid BA 230 E injection moulding machine

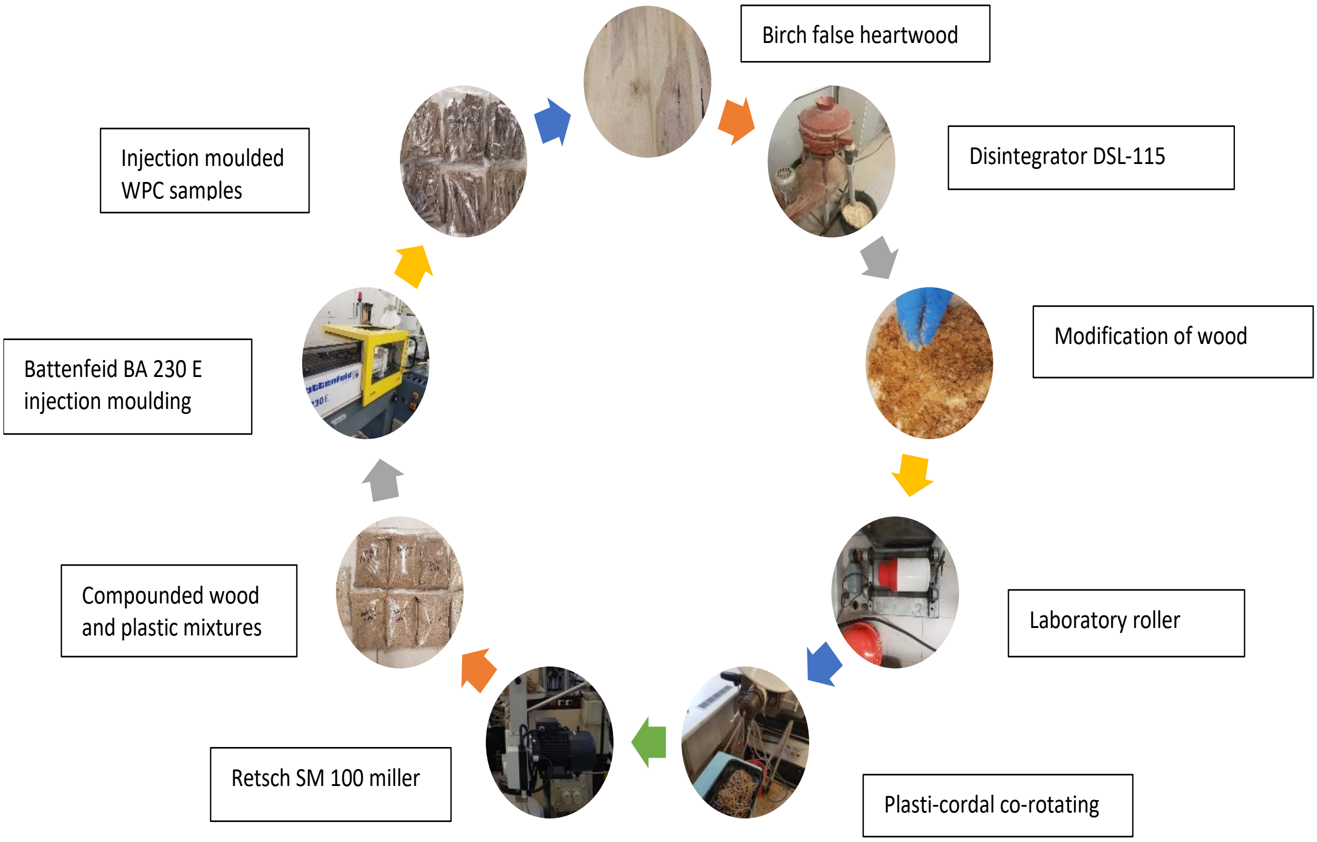


Figure 2.6 Scheme of manufacturing process of WPC

Table 2.2 NaOH and APTES concentration on the Composite

Sample	**PP (wt%)**	**Birch (wt%)**	**NaOH (wt%)**	**APTES**
PP	100	-	-	-
PB	40	60	-	-
MP	40	60	5	5
FHW	40	60		
MFHW	40	60	5	5

PP- Polypropylene
PB- Pure Birch
MP- Modified Pure Birch
FHW- False Heartwood
MFHW- Modified False heartwood

2.6 Testing

A total of 306 samples were tested and these were distributed according to table 2.3. The specimens were grouped in to 5 namely polypropylene PP, pure birch PB, modified pure birch MP, false heartwood FHW and modified false heartwood MFHW. All the testing were conducted in accordance with their respective standards

Table 2.3 Distribution and number of test samples based on tests performed with the appropriate standard used

No.	Test	Method	No. of Specimen				
			PP	PB	MP	FHW	MFHW
1	Tensile	EN ISO 527-2	6	6	6	8	8
2	Bending	EN ISO 178	6	6	6	8	8
3	Charpy Impact	EN ISO 179-1	6	6	6	8	8
4	Water Absorption and Thickness swelling	EN 15534:2014	18	18	18	24	24
5	UV properties	EN ISO 4892-3:2006 and EN 927-6:2006	18	18	18	24	24
6	FTIR	Laboratory method					

2.7 Mechanical Properties

2.7.1 Tensile Test

The tensile test was determined on the Instron 5866 with 10 kN load cell in accordance to EN ISO 527-2. The test speed was set at 5 mm/min and the tensile strength and modulus was calculated. The test was conducted at room temperature 23 ˚C and relative humidity of 50%. The test specimen is type 1A. The thicknesses of the specimens were measured with a micrometre screw gauge and at least six test specimens were examined

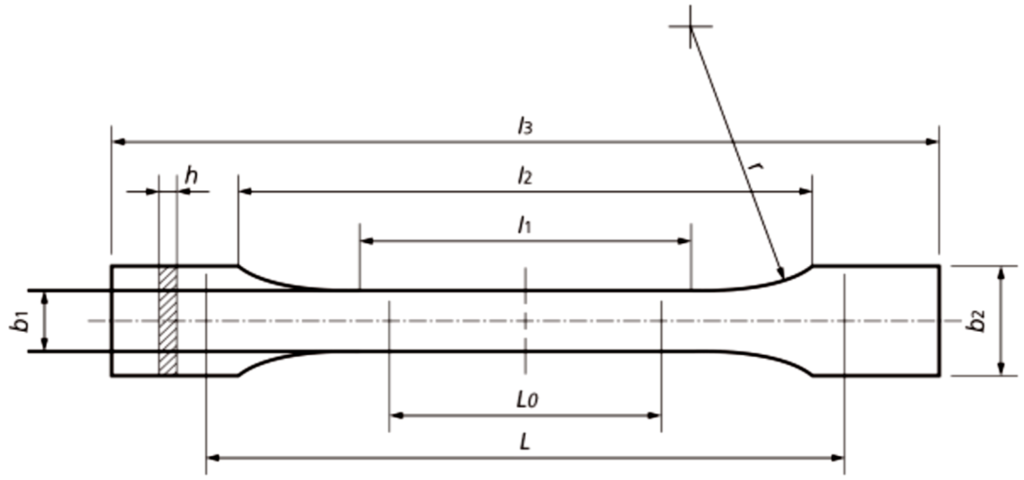


Figure 2.7 Test specimen (type 1A)

Where

l_3- Overall length, mm
l_2- distance between broad parallel-sided portions, mm
h- thickness, mm
r- radius, mm
l_1- length of narrow parallel-sided portion, mm
b_2- width at ends, mm
b_1- width at narrow portion, mm
L_0- gauge length, mm
L- initial distance between grips, mm

The tensile strength is calculated using the equation 2.1 as given below

$$\sigma = \frac{F}{A} \tag{2.1}$$

Where

σ	is the tensile strength value in question, expressed in MPa
F	is the measured force concerned, in newton's
A	is the initial cross-sectional area of the specimen, expressed in square millimetres

The tensile modulus is calculated using the equation as given below

$$E_t = \frac{\sigma_{t2} - \sigma_{t1}}{\varepsilon_{t2} - \varepsilon_{t1}} \tag{2.2}$$

Where

E_t	tensile modulus, MPa

σ_{t2}	tensile strength at deflection, s_1, MPa
σ_{t2}	flexural stress at deflection, s_2, MPa
ε_{ti}	corresponding flexural strain ε_{t1}= 0.0005 and ε_{t2} = 0.0025

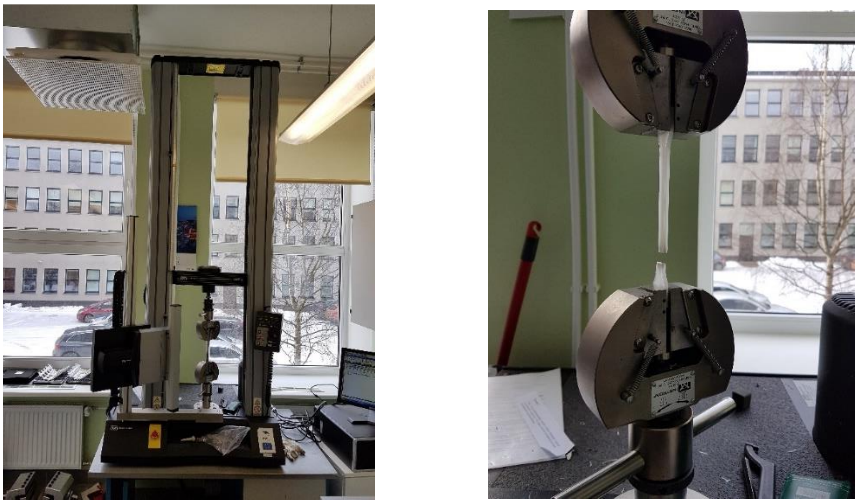


Figure 2.8 Instron machine during testing of specimen (left), PP specimen undergoing tensile test (right)

2.7.2 Flexural Test

The flexural properties of the composites were conducted by means of Instron 5866 three-point loading system with 10 kN load cell according to ISO 178:2010 at room temperature of 23 ˚C. The testing speed was set at 5 mm/min for the test and the span length was 64 mm. The thicknesses of the samples were measured and accordingly recorded. The test specimens were marked at mid-point and positioned on the support such that the middle mark falls directly under the point of pressure. For each sample, at least six test specimens were examined. The flexural strength and modulus is calculated using the equations as given below

$$\sigma_f = \frac{3FL}{2bh^2} \tag{2.3}$$

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

$$S_i = \frac{\varepsilon_{fi} L^2}{6h} \ (i=1 \ or \ 2) \tag{2.4}$$

where

Si	deflection, mm
ε_{fi}	corresponding flexural strain ε_{f1}=0.0005 and ε_{f2} = 0.0025

$$E_t = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}} \tag{2.5}$$

Where

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

Figure 2.9 Flexural test of a specimen

2.7.3 Impact Test

The impact test was conducted on Zwick Charpy 5102 pendulum impact tester in accordance with EN ISO 179-1 at room temperature of 23 ˚C. The test specimens were machined notched (type A) to have edgewise impact so that the line of impact is directly opposite the notch. The Charpy impact strength of the notched specimens were calculated using the equation

$$a_C N = \frac{E_c}{h.b_N} \times 10^3 \tag{2.1}$$

Where

E_c is the corrected energy, in joules, absorbed by breaking the test specimen;
h is the thickness, n millimetres, of the test specimen
b_N is the remaining width, in millimetres, of the test specimen.

The type of failure of each specimen was noted.

Figure 2.10 Zwick Charpy 5102 pendulum impact tester

2.8 Physical Properties

2.8.1 Water Absorption and Thickness Swelling

The water absorption and thickness swelling were done according to EN 15534-1:2014. Each test specimens were weighed, and their thicknesses recorded. They were completely immersed in water placed in containers at room temperature 23 ˚C for 28 days, with the measurements taken at interval 24 h, 48 h, 96 h, 168 h, 336 h and 672 h and the amount of water absorbed was measured on weighing balance according to the interval as laid out in EN 15534-1:2014. For each sample, at least six specimens were examined, and the water level was daily monitored to ensure constant complete immersion in water. The specimens were cleaned with a dry towel before weighing to removed surface water and weighed immediately afterwards. The process was repeated for each measurement time interval. The percentage change in mass c relative to the initial mass and the percentage thickness in swelling k relative to the initial mass were calculated using the formula

$$c = \frac{m_2 - m_1}{m_1} \times 100\ \% \qquad (2.2a)$$

And

$$k = \frac{t_2 - t_1}{t_1} \times 100\ \% \tag{2.2b}$$

Where

m_1 is the mass of the test specimen, in milligrams (mg), after initial drying and before immersion;

m_2 is the mass of the test specimen, in milligrams (mg), after immersion.

t_1 is the thickness of the test specimen, in millimetres (mm), after initial drying and before immersion;

t_2 is the thickness of the test specimen, in millimetres (mm), after immersion.

At the end of the water absorption test, the specimens were tested mechanically (tensile, flexural and Impact test) to determine the behaviour of the WPC's after exposure to water.

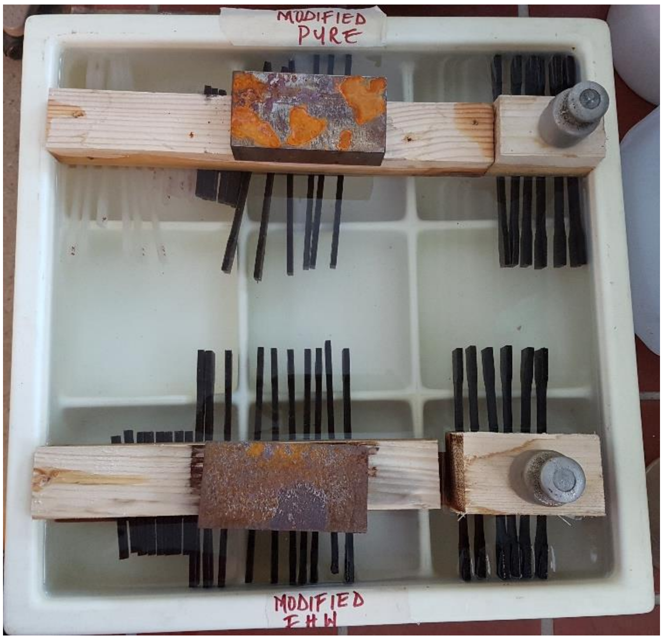


Figure 2.11 Specimens immersed in water for 28 days

2.8.2 Weathering - UV Exposure

The UV-exposure was performed in the UV chamber of the laboratory of wood technology. The WPC samples were irradiated with UVA-351 type fluorescent lamps (PHILIPS TL-D 36W/08 T8 blacklight) whose peak wavelength of the tube was 351nm. The blacklight Blue lamps are low-pressure mercury vapour fluorescent lamps with inner envelop coated with fluorescent powder which emits long-wave UV radiation to excite luminescence. It has the power rating of 36, lamp current of 0.44 A and voltage of 103 V. it has the life at 50% failures estimated at 15000. The test was conducted at room temperature, 23 ˚C. According to EN ISO 4892-1 the UV irradiation was in every position of the bottom surface of the UV-chamber a minimum of at least 70% of the maximum irradiation value obtained from the central area of the UV-chamber bottom surface.

During the UV irradiation test intensities of irradiation at a wavelength of 350nm were recorded with a radiometer Delta OHM HD 2102.2 and with lux-meter probe SICRAM, UVA. Intensity was 5 W/m^2. The chamber is equipped with 6 of those lamps. A total of 102 specimens were exposed to UV radiation. The specimens were properly marked in the un-exposed surface and the exposure cycle was carried out for 2016 h. The specimens were occasionally removed from the chamber and colour measurements were made at the intervals of 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 in accordance to standard. At the end of the exposure cycle, the specimens were placed in plastic bags and tested for their mechanical properties namely tensile, flexural and impact properties. For each testing, at least six specimens were tested according to their appropriate standards. The UV peak diagram is shown in fig 2.14. It shows that the optimum wavelength is about 350 nm.

Figure 2.12 Specimens in the UV chamber ready for artificial weathering

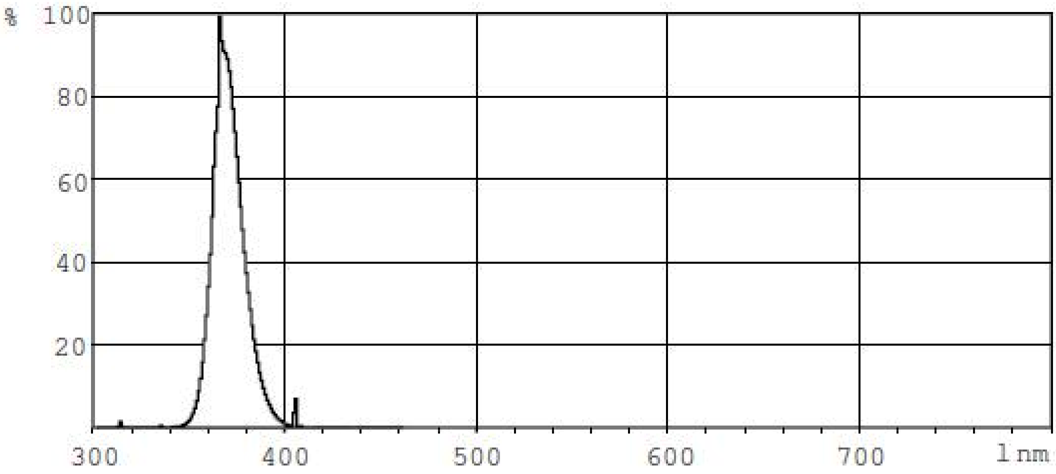


Figure 2.13 UV peak diagram (www.lighting.philips.com)

2.8.3 Colour Analysis

Colour analysis of composite surface was carried out on the specimens placed under UV. The measurement was conducted using the CIELAB colour system. The CIELAB colour system gives the measurement of colour in three coordinates namely L*, a* and b* and the distance between two points in the colour space is equivalent to the visual colour difference of the two samples. L axis running from top to bottom represent lightness on dark L*= 0 to light L*= 100 scale, a* coordinate represent red/green (+a* to red and -a* to green), b* correspond to yellow /blue coordinate (+b* to yellow and -b* to blue).

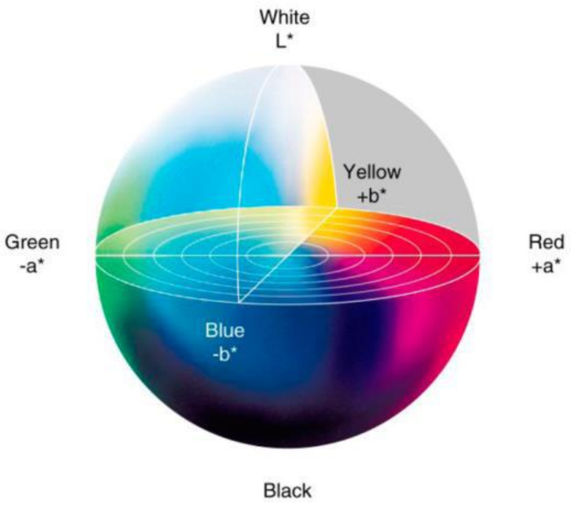


Figure 2.14 CIELAB colour measurement method

The total colour difference ΔE which indicates the size of the colour difference can be calculated using the equation

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{2.3}$$

Where

ΔL, Δa, and Δb represents the differences between the sample initial and after weathering values of L*, a*, and b* respectively.
The measurement was conducted with Minolta Chroma Meter CR-121 in accordance with EN ISO 4582 for 2016 h. Light markings were made on the surface of each specimen to enjoy that readings are taken about the same points always. Measurements were taken 3 times each on the surface of each specimen and the mean value was recorded.

2.8.4 FTIR Analysis

The FTIR analysis of the specimens was carried out in the polymer materials laboratory of the department of chemical and materials technology to determine the efficiency of the chemical modification. The analysis was carried out using Interspectrum FTIR spectrometer (model Interspec 200-X) with KBr disc method in taking the infrared spectra. The spectral resolution used was 4cm^{-1} and the spectral was recorded in the range 3000 cm^{-1} to 500 cm^{-1}. A scalpel was used to cut out thin pieces from the already produced composite samples and positioned in the window of the sample compartment

3 RESULTS AND DISCUSSION

3.1 Tensile Strength

Tensile strength indicates the tensile stress a material can withstand before failure. It is a measure of the force needed to pull or stretch apart a material before its failure. The results of the mechanical tests are presented in table 3.1. For each sample, at least six replicate specimens were tested, and the average recorded as in figure 3.1 and 3.2.

The results obtained for PP which serves as the control reference; in the two cases of before soaking in water and that obtained after immersion in water shows the highest tensile strength of 30.62 and 30.67 MPa respectively. This shows a similarity between the two results which indicates that water did not have impact on the polymer tensile strength and consequently no absorption took place in the PP samples. Similar report is given by Stark, 2001. The tensile strength of all samples reduced after absorption of water **(**fig 3.3).

The modified pure birch sample showed slightly higher tensile strength by 6.67% than the pure birch samples in all cases; 22.71 and 21.3MPa respectively. The addition of 5 wt% silane to the PP/WF composites coupled with the 5 wt% pre-treatment with NaOH is responsible for the increase in the tensile strength of the composites. Kim *et al*.2010 and Kallakas *et al*.2015 also reported this. The modified and the unmodified heartwood samples have very close tensile strength average values of 21.34 and 21.76 MPa before immersion and 16.34 and 18.19 MPa after immersion. This shows about 2% difference before immersion.

The addition of 5wt% APTES and 5 wt% NaOH did not affect the tensile strength of the false heartwood at 60% wood content before soaking. Rather, there was 10.17% decrease in the tensile strength of the modified false heartwood after immersion in water. This suggest that the silane was not able to penetrate through the bonds of the heartwood to enable the interfacial adhesion of the composite. A possibility could be that the modification process opened the PP/WF interface to water degradation which consequently led to reduction in the strength property of the false heartwood composite This result confirms the previous investigation by Kallakas *et al.* 2017*.* Composite immersion in water has been shown to cause dimensional instability and inferior mechanical properties (Mat Taib *et al.2006).* In all cases, apart from the control, the false heartwood composites after immersion showed higher value than the others. This can be explained that the heartwood contains non-living core and non-conducting tracheary elements which inhibits to an extent, the absorption of water unlike the other samples (Smith 2015).

According to Stark 2001, the tensile strength and tensile modulus of wood flour with polypropylene composite decreased by 14% and 29% after water absorption at 40 wt% wood composition. However, in this work, 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 pure birch, modified pure, false heartwood and modified false heartwood respectively. This is comparable to the 46-50% reduction for tensile modulus reported by Taib *et al.* 2006. One reason the modulus showed greater decrease may be because of the high wood content of 60 wt% used in this work. Other reason which could have attributed to these reductions is the wood which is hydrophilic in nature absorbs water which leads to swelling and eventual formation of microcracks resulting from the swelling.

The control sample PP showed the lowest modulus of elasticity (1.67 GPa) for all samples examined. Modified pure birch has the highest modulus of 4.5GPa before immersion while the modified false heartwood has the lowest modulus of 4.2GPa before and after water absorption. It was affected mostly by water because it had the greatest absorption. Again, the false heartwood has a 27% higher modulus than the modified false heartwood after soaking in water. This indicates that silane had no effect on the false heartwood in improving its properties but opened the composite to more degradation. It may be assumed that silane coupling between the PP matrix and WF did not increase the interfacial bonding nor resulted in improved stress propagation (Kim *et al.* 2010).

3.1.1 Impact of accelerated weathering on the tensile properties of composites

As can be observed in table 3.1, PP lost its tensile strength to become very brittle. PP lost 56% of its tensile strength to UV radiation. This value of lost strength is close to the 60% value reported by Badji *et al.* 2017 after natural weathering. This is due to the crystallization of PP resulting from chain scission reaction of polymer in the process of UV weathering (Fayolle *et al.* 2007).

With the addition of wood to the plastic, stiffer materials were obtained, and the tensile strength of the resultant composites are far better than the PP. Modified pure composites had the highest tensile strength after exposure to UV (21.41 MPa). Both the false heartwood and modified false heartwood composites have about the same tensile strength (20.44 MPa and 20.47 MPa respectively) which translates to a reduction of 6% and 4% respectively. Pure birch composite with a tensile strength of 20 MPa reduced by 6%. Hence, the modification with APTES at 5wt% wood content seems not to have effect on the tensile strengths of the modified composites on exposure to UV. Similar trend is observed for the modulus of elasticity as shown in fig 3.2

The MOE in general decreased for PP and all WPCs. Interestingly, a reduction of approximately 5% was observed for PP, PB and MP and 6% for FHW and MFHW for MOE of the composites. Of all the composites, MP has the highest MOE 4.28GPa and MFHW has the lowest MOE 4.03 GPa. Soccalingame *et al.* 2015, reported that for tensile characteristics, WPC at 30wt % wood content is not so very much sensitive to weathering.

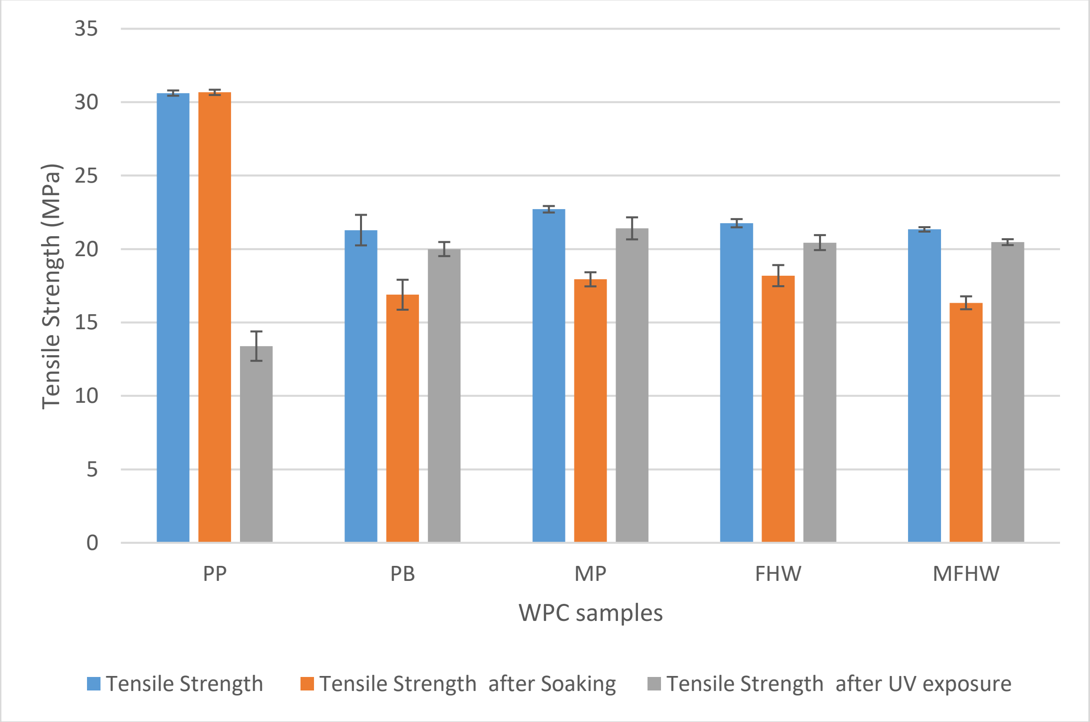


Figure 3.1 Tensile strength of WPC samples on exposure to UV and before and after immersion in water

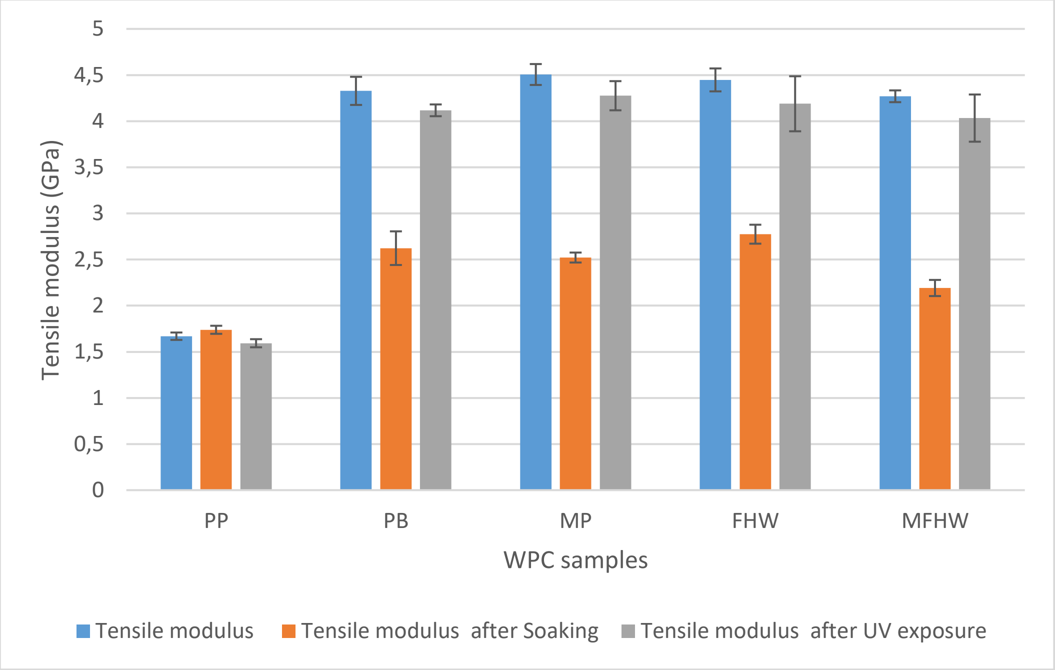


Figure 3.2 Tensile modulus of WPC samples on exposure to UV and before and after immersion in water

Table 3.1 Tensile properties of composites before soaking, after water immersion and on exposure to UV

Sample	Maximum Load (N)			Tensile strength (MPa)			Modulus of Elasticity (MPa)			Extension at maximum load (mm)		
	Before Soaking	After Soaking	UV	Before Soaking	After Soaking	UV	Before Soaking	After Soaking	UV	Before Soaking	After Soaking	UV
PP	1224.87 (7.01)	1238.6 (16.04)	535.67 (40.02)	30.62 (0.18)	30.67 (0.20)	13.39 (1.00)	1669.06 (40.04)	1738.57 (43.64)	1592.78 (43.97)	9.02 (0.21)	8.35 (0.32)	1.42 (0.20)
PB	851.56 (41.62)	737.84 (44.53)	800.11 (19.28)	21.29 (1.04)	16.89 (1.02)	20.00 (0.48)	4328.24 (152.28)	2623.25 (182.41)	4117.61 (63.89)	1.20 (0.45)	1.85 (0.38)	0.97 (0.12)
MP	908.47 (8.86)	782.26 (19.52)	856.34 (30.19)	22.71 (0.22)	17.94 (0.48)	21.41 (0.75)	4505.69 (113.37)	2521.58 (54.15)	4275.78 (158.07)	1.29 (0.09)	3.07 (1.39)	1.18 (0.13)
FHW	870.25 (11.13)	788.79 (28.06)	817.44 (20.39)	21.76 (0.28)	18.19 (0.72	20.44 (0.51)	4447.31 (124.39)	2774.58 (102.79)	4188.61 (298.40)	1.24 (0.09)	2.13 (0.84)	1.00 (0.07)
MFHW	853.56 (5.88)	702.09 (30.12)	818.81 (8.16)	21.34 (0.15)	16.34 (0.44)	20.47 (0.20)	4269.82 (63.74)	2191.48 (87.41)	4033.02 (255.77)	1.41 (0.10)	2.33 (0.10)	1.28 (0.09)

Displayed data are mean values and those in bracket indicates the standard deviation

3.2 Flexural Properties

The flexural strength is the stress at failure in bending. It is also called Modulus of Rupture(MOR) or bending strength. Table 3.2 shows the results of the flexural strength and modulus of the composites before soaking in water, after soaking and on exposure to UV rays for 2016 h. Figure 3.2 and 3.3 shows the comparison of the flexural strength and flexural modulus (MOE) of all composites and the neat PP before and after WPCs were immersed in water and upon exposure to UV rays.

The modified pure birch composite before soaking in water has the highest flexural strength of 46.86 MPa, a value which is 4.8% higher than the pure polymer with 44.7 MPa and 2.5% higher than the pure birch composite indicating a strong interface of adhesion between the WF and APTES. APTES at 5 wt% wood content seems not to have effect on the flexural strength of modified false heartwood as both FHW and MFHW have about the same strength before soaking in water (44.24 and 44.72 MPa). However, the effect of APTES 5 wt% modification is visible in the flexural strength of MFHW composites after soaking in water.

All samples, apart from the pure polymer, shows a reduction in the flexural strength of the composites after immersion for 28 days as can be observed in figure 3.2. PB reduced in flexural strength by 12.19% and MP by 14.43%. The false heartwood composite after absorption of water, showed the lowest reduction of 10.6% in flexural strength and the modified false heartwood showed the highest reduction of 16.6% in flexural strength. This indicate that MFHW absorbed water more than the FHW. This may be explained in part, as because false heartwood is known to differ from sapwood amongst other things, in having a reduced moisture content (Torelli, 1984, Baettig *et al.* 2017)), hence, APTES may be said to increase the permeability of birch false heartwood. Thus, indicating the impact of the modification on the rate of water absorption of the composites.

In general, the samples have comparable strength after immersion in water ranging from 37.29 MPa to 40.13 MPa. The modification of the false heartwood with 5 wt% silane has no effect in increasing the flexural strength before and after water absorption. This may be due to the reasons as explained for the tensile strength. The bond quality at the interface of the polymer matrix and the filler, has impact on the strength of composites (Stark, 2001). The hydrophilic nature of wood leads to the absorption of more water which leads to swelling and the formation of microcracks.

The addition of wood to the polymer improved the flexural MOE of the polymer making the composites more rigid and at the same time brittle. MP composites has the highest flexural MOE (4.89 GPa) before immersion in water which is higher than PB, FHW and MFHW composites by 3.3%, 18.7% and 12% respectively. After absorption of water, all the composites decreased in flexural modulus by 46.3%, 66.4%, 18% and 72.3% for PB, MP, FHW and MFHW composites respectively. Again, the highest decrease is seen with MFHW (2.9 GPa) and the lowest is found with FHW (18% decrease). Just as explained in flexural strength, APTES modification of the MFHW composite can be attributed for this. It increased the water permeability of birch false heartwood.

3.2.1 Effects of UV radiation on the flexural properties

The most visible effect of UV radiation is seen on the neat PP. The ductile PP before exposure to UV rays turned brittle after exposure in UV for 2016 h and the degradation of the plastic could easily be noticed as they were picked up for testing. Badji *et al.* 2017 reported the change in the of the composite to brittleness. All composites slightly decreased in flexural strength of between 2.5% and 7.2% for all composites. This result obtained is similar to that obtained by Kallakas *et al.* 2015 where the greatest flexural strength decreases of 6.5% was recorded.

The flexural MOE is seen to increase after exposure to UV for all composites. This indicates that the material becomes ductile. The increase ranges from 3.1% for MP to 16.7% for FHW composites. The flexural MOE obtained for FHW (4.8 GPa) is higher than that obtained for MFHW (4.68GPa). Similar trend is obtained for the flexural strength after UV exposure with FHW composite (43.15 MPa) having flexural strength higher than that of MFHW composite (42.09 MPa). Thus, APTES at 5wt% wood content can be said to have effect on the modified false heartwood on exposure to UV radiation.

Table 3.2 Flexural properties of composites before and after soaking in water

Sample	Maximum Load (N)			Flexural strength (MPa)			Flexural modulus (MPa)		
	Before Soaking	After Soaking	UV	Before Soaking	After Soaking	UV	Before Soaking	After Soaking	UV
PP	79.47 (3.24)	79.63 (5.69)	36.99 (1.94)	44.70 (1.82)	44.79 (3.20)	20.81 (1.09)	1269.06 (44.38)	1271 (45.02)	1242.45 (117.25)
PB	81.25 (1.57)	71.35 (1.34)	77.23 (0.81)	45.70 (0.88)	40.13 (0.75)	43.44 (0.46)	4731.83 (389.20)	3234.53 (69.09)	4996.60 (26.93)
MP	83.30 (2.49)	71.30 (2.04)	77.72 (4.41)	46.86 (1.4)	40.10 (1.14)	43.72 (2.48)	4889.17 (476.52)	2937.57 (112.19)	5039.29 (312.87)
FHW	78.66 (1.97)	70.28 (1.72)	76.71 (1.03)	44.24 (1.11)	39.53 (0.97)	43.15 (0.58)	4120.76 (528.58)	3090.46 (84.09)	4807.75 (106.92)
MFHW	79.50 (1.24)	66.30 (4.27)	74.83 (2.53)	44.72 (0.69)	37.29 (2.40)	42.09 (1.42)	4365.26 (191.69)	2534.07 (126.66)	4676.19 (167.84)

Displayed data are mean values and those in bracket indicates the standard deviation

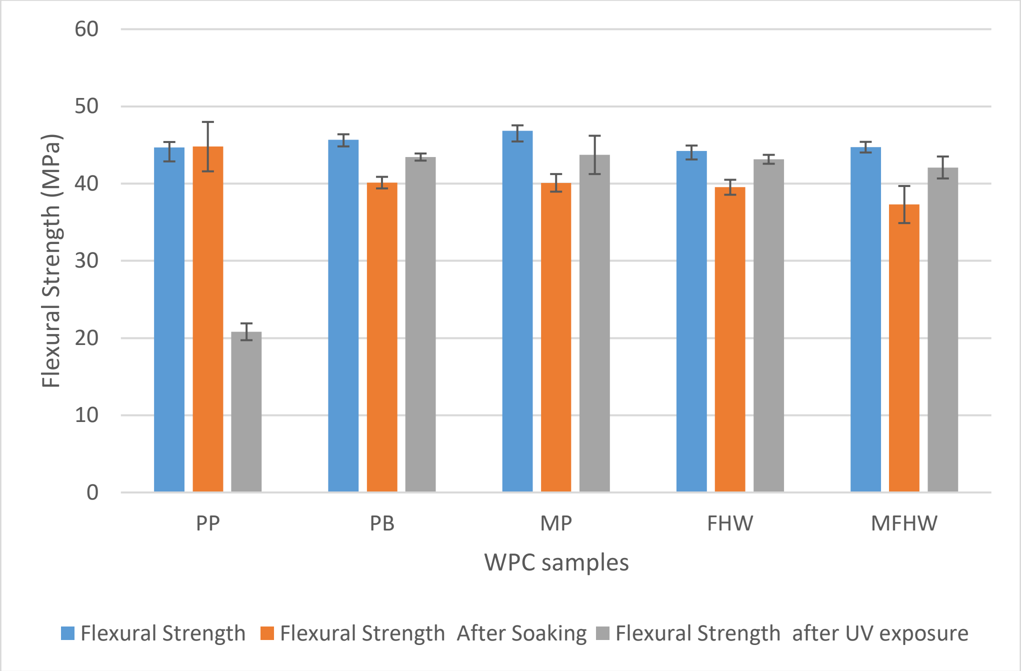


Figure 3.3 Flexural strength of composites before soaking, after soaking and on exposure to UV

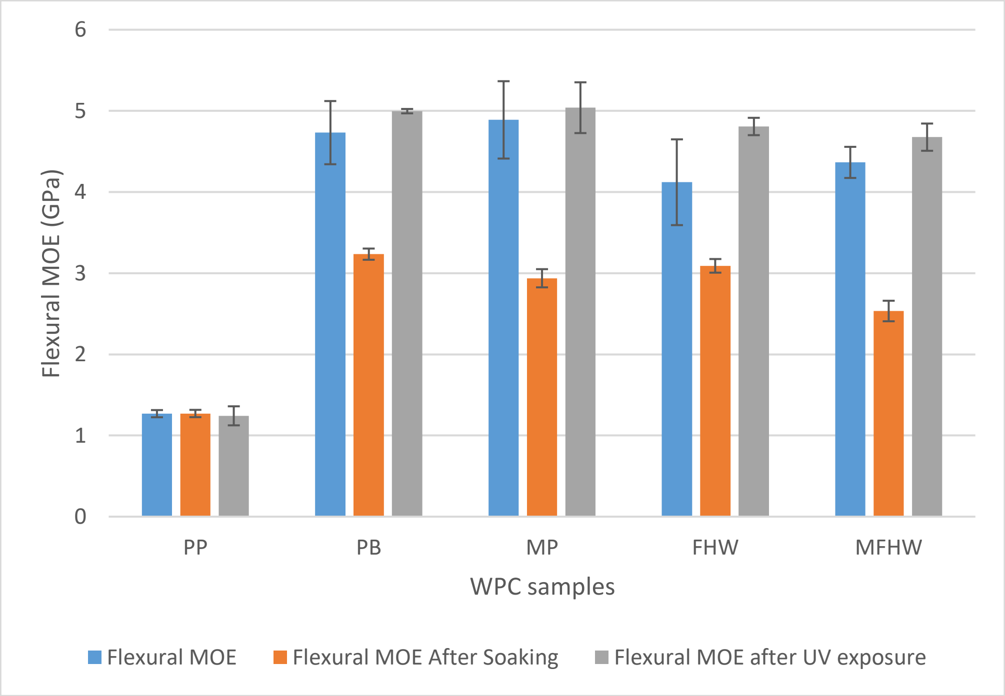


Figure 3.4 Flexural MOE of composites before soaking, after soaking and on exposure to UV

3.3 Impact Tests

The results obtained from the notched impact test carried out on all specimens before and after immersion is given in table 3.31. Figure 3.31 shows the impact strength of the composites before and after immersion in water and fig 3.32 shows the comparison between them. The notched impact energy is a measure of crack propagation.

The effect of water can be clearly seen to affect the impact strength of all the composites. The absorption of water reduced the impact strength for all samples. This is because when WPC absorbs water, moisture is built up in the fibre cell wall which caused fibre swelling and results into dimensional instability of the composite material (Mat Taib *et al.* 2006). Fibre swelling in turn may lead to the breakage of polymer bond leading to crack formation which open the composite to greater water penetration (Gassan and Bledzki, 1999). These may have been responsible for the reduced impact strengths of the composites. Pure and false heartwood wood samples have the greatest loss of 70.5% and 70% respectively. PP has the least impact strength loss of 11.5 kJ/m^2 and generally ranges from 64.5% to 70.5% for other samples. Stark, 2001, Upadhyaya *et al.* 2012 all showed a decrease in the impact strength of the composites. According to the works of Kim *et al.* 2010*,* different results were obtained at different wood contents for the result of the impact test. This implies that the wood content can affect the impact strength of composites. The modification treatment improved the impact strength of the false heartwood composite. The impact strength of the modified false heartwood in both cases of before and after immersion is higher than that of the FHW by 2.4% and 12.9%.

3.4 Effect of UV exposure on the Impact strength of composites

As can be observed in table 3.3, PP lost its strength to become very brittle from its ductile state after exposure to accelerated weathering. For all the composites, decrease in impact strength is recorded which implies they become brittle and this decrease is attributed to degradation as a result of chain scission and increase in crystallinity. Similar finding is reported by Soccalingame *et al.* 2015. Modified pure composite showed the greatest impact strength (3.41 kJ/m^2) after exposure.

Table 3.3 Impact strength of WPCs on exposure to UV and immersion in water

Sample	Energy J			Impact Strength (kJ/m²)			Std dev		
	Before soaking	After	UV	Before soaking	After soaking	UV	Before soaking	After soaking	UV
PP	0.41	0.39	0.06	12.91	11.42	1.88	0.03	0.01	0.001
PB	0.35	0.11	0.11	10.91	3.22	3.29	0.04	0.01	0.01
MPB	0.33	0.12	0.11	10.29	3.65	3.41	0.003	0.013	0.003
FHW	0.32	0.10	0.11	10.10	3.03	3.30	0.005	0.003	0.01
MFHW	0.33	0.12	0.10	10.34	3.42	3.16	0.006	0.008	0.01

Displayed data are mean values

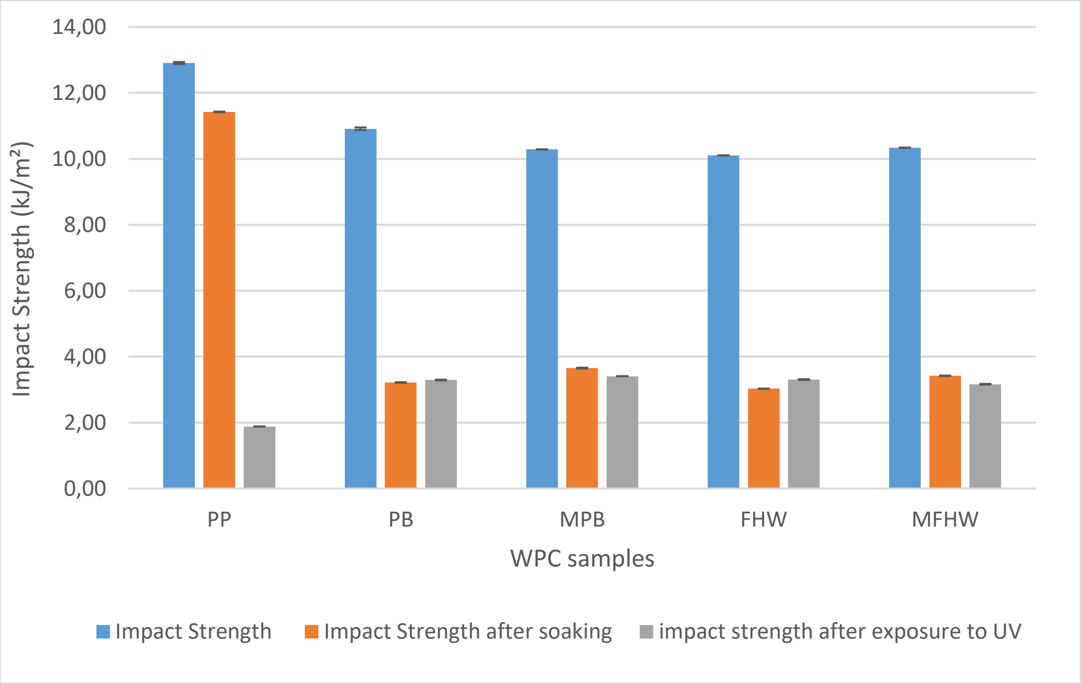


Figure 3.5 Influence of water absorption and UV on the impact strength of WPC

3.5 Water Absorption and Thickness Swelling

The water absorption and thickness swelling of the composites are presented in table 3.41 and 3.42 respectively. The table shows the water uptake and swelling of all the composites as a function of immersion time in hours. For each sample, an average of at least six specimens are recorded.

The water absorption of the composites was observed to increase with time at every level of immersion. Similar result has been shown in previous research (Bouafif *et al* 2008). Likewise, the thickness swelling of the composites increased with the time of immersion (figures 3.41 and 3.42). Total immersion time was 672 h. Modification with 5 wt% silane and 5 wt% NaOH increased the water absorption of the modified false heartwood WPC's and modified pure WPC's specimens. False heartwood WPC's water absorption increased more by 28% than modified pure birch WPC's (4.3%). The modified false heartwood WPC has the highest absorption of 17.26**%** and the false heartwood WPC has the lowest water absorption of 13.47%. Again, this may be explained as a result of the nature of the heartwood which contain non-living cells and extractives. According to Olsson *et al.*2001, the extractives of the heartwood are the main source of low water permeability. The age and growth rate of the tree affect the content and composition of extractives (Kortelainen, 2011). Kortelainen *et al.* (2005) has demonstrated that significant difference exists between the water absorption of sapwood and heartwood in Scot pine and Spruce, of which the sapwood absorbs greater water than the heartwood and, that heat treatment decreases the water absorption of heartwood. In addition, the mechanism of capillary action at the edges of wood fibre in the composites, could be 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 interface (George *et al.* 1998*,* Mat Taib *et al.* 2006).

The modified pure birch WPC also showed a greater absorption of 4.3% than the pure birch WPC sample. The absorption of water by the composites can be assumed to be caused by the hydrophilic wood flour and not the hydrophobic PP since PP did not show any water absorption. Similar results have also been shown in previous research by Stark, 2001. This result differs from that obtained by Cui *et al.* 2008 where modification reduced the water absorption after alkaline and silane treatment of wood-fibre-reinforced recycled plastic composite. The very large wood content (60 wt%) may be responsible for the absorption results obtained as well as the heartwood. Kim *et al.* 2010 reported 2.5 times reduction values in the silane treated composites than the untreated one. This was explained may be due to the limitation of water molecules to WF which may be caused by the hydrogen bond between the hydroxyl and siloxane groups

Table 3.4 Summary of the water absorption of all samples after 672 h of immersion

Samples	**Water Absorption %**					
	24 h	**48 h**	**96 h**	**168 h**	**336 h**	**672h**
PB	1.79 (0.04)	2.61 (0.04)	4.53 (0.05)	6.16 (0.05)	9.72 (0.06)	16.3(0.05)
MPB	2.1 (0.05)	3.13 (0.05)	5.16 (0.05)	7.17 (0.05)	11.41 (0.05)	17 (0.06)
FHW	1.25 (0.14)	1.77 (0.15)	3.16 (0.18)	4.24 (0.19)	6.62 (0.24)	13.47 (0.36)
MFHW	2.45 (0.27)	3.2 (0.27)	5.46 (0.27)	7.6 (0.26)	12.08 (0.26)	17.26 (0.32)

Displayed data are mean values and those in bracket indicates the standard deviation

Table 3.5 Summary of thickness swelling of all samples after 672 h of immersion

Samples	**Thickness Swelling %**					
	24 h	**48 h**	**96 h**	**168 h**	**336 h**	**672h**
PB	1.27 (0.02)	2.7 (0.03)	3.93 (0.02)	5.15 (0.01)	6.18 (0.02)	7.20 (0.02)
MPB	2.45 (0.01)	2.73 (0.03)	4.32 (0.01)	5.22 (0.01)	5.79 (0.02)	6.52 (0.01)
FHW	0.28 (0.02)	1.94 (0.03)	2.55 (0.02)	3.73 (0.01)	4.74 (0.02)	5.31 (0.03)
MFHW	1.95 (0.13)	2.52 (0.10)	4.35 (0.11)	5.38 (0.11)	6.37 (0.11)	6.66 (0.11)

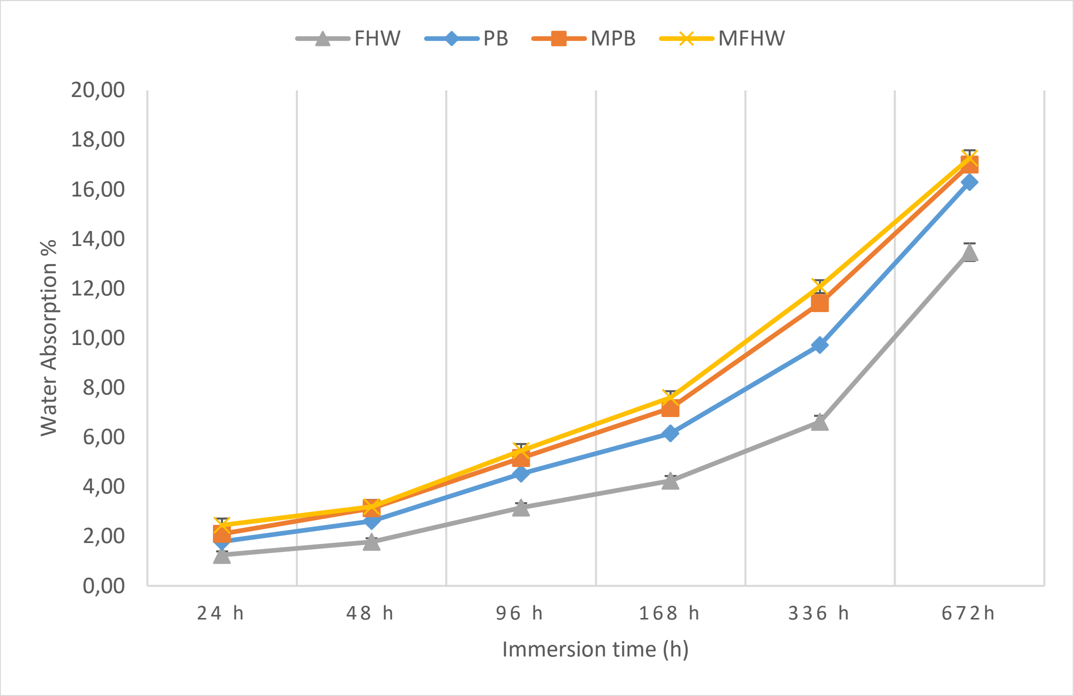


Figure 3.6 Water absorption trend for all composite samples immersed in water at 60 wt% WF

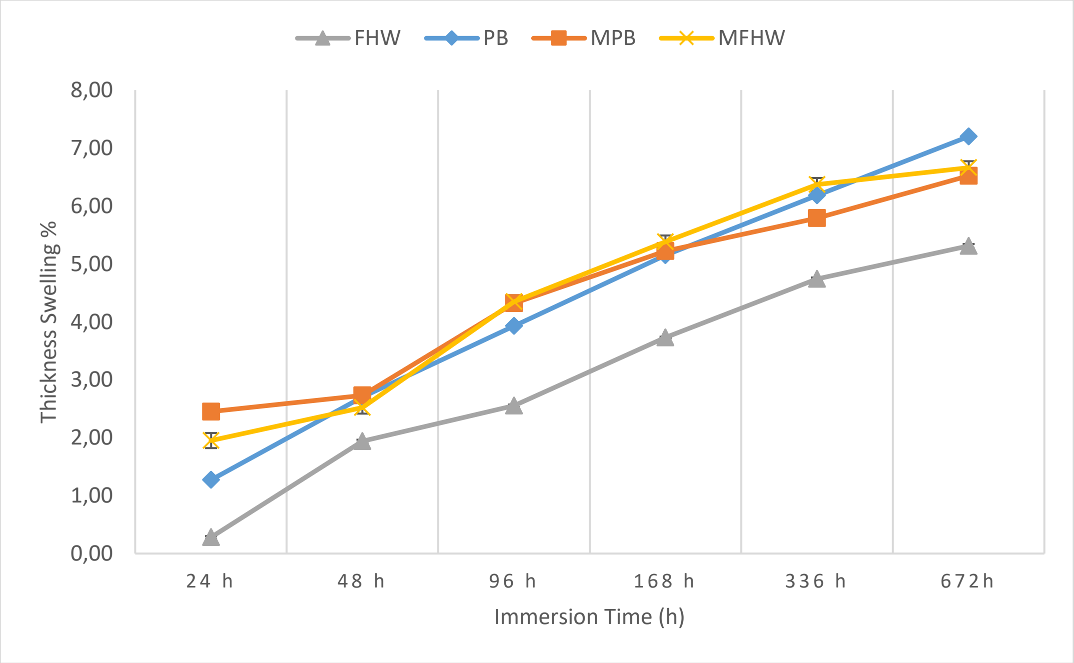


Figure 3.7 Thickness swelling trend for all composite samples immersed in water at 60 wt% WF

3.6 Colour Analysis

The colour variations of the parameters L*, a* and b* of the neat PP and the WPCs after exposure to artificial weathering compared to the initial colour before exposure are presented in table 3.6. For all composites examined, colour changes were noted, and all composites turned lighter. This is in accordance with other studies previously conducted (Kiguchi *et al.* 2007, Stark and Mueller, 2008). It is observed that weathering induced the composite bleaching. This bleaching as a result of weathering has been reported to be due to the lignin component in wood (Peng *et al.* 2014).

Surface chalking was observed in all WPCs exposed to artificial weathering with colour ranging from brown and brownish black to white. This may be attributed to the leaching of lignin and cellulose from the exposed surface and thus, as observed by Kiguchi *et al.* 2007, cellulose which is whitish and comparatively stable against UV may be the main chemical component. According to Fabiyi and McDonald, 2014 and Peng *et al.* 2014, chain scission reaction of lignin can lead to the forming of paraquinonic structure which can reduce to hydroquinone that gives the whitish colour to WPCs on exposure to weathering. Degradation of neat PP was observed as particles were seen to fall off the surface showing the effect of weathering.

The colour differences of the composites and neat PP are presented in figure 3.6. Modified pure birch and modified false heartwood had about the same colour change at the end of the 2016 h (20.03 and 20.69 respectively) which were the greatest change in colour among the composites. This could be attributed to the effect of the modification with APTES on the wood. During the process of modification, some of the lignin content of the wood is already degraded to enhance the adhesion with the polymer, and upon exposure to artificial weathering, photo-degradation of the remaining lignin whose chromophoric groups are able to absorb UV rays and form free radical groups takes place (Peng *et al.*2014, Badji *et al.* 2017). Neat PP has the lowest colour change of 2.16. Similar trend is observed for the brightness of all composites with all composites becoming brighter as shown in fig 3.7. The highest change in brightness is observed for pure birch at 59.40 and the lowest for PP at 38.28. The composites before and after exposure to UV radiation are shown in figures 3.9 and 3.10

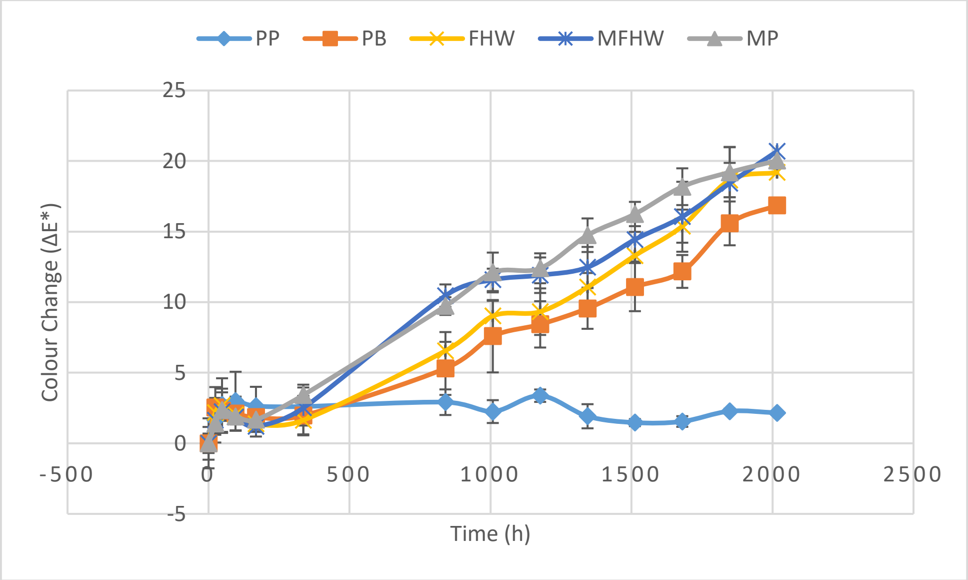


Figure 3.8 Colour change of composites at the end of 2016 h of UV exposure

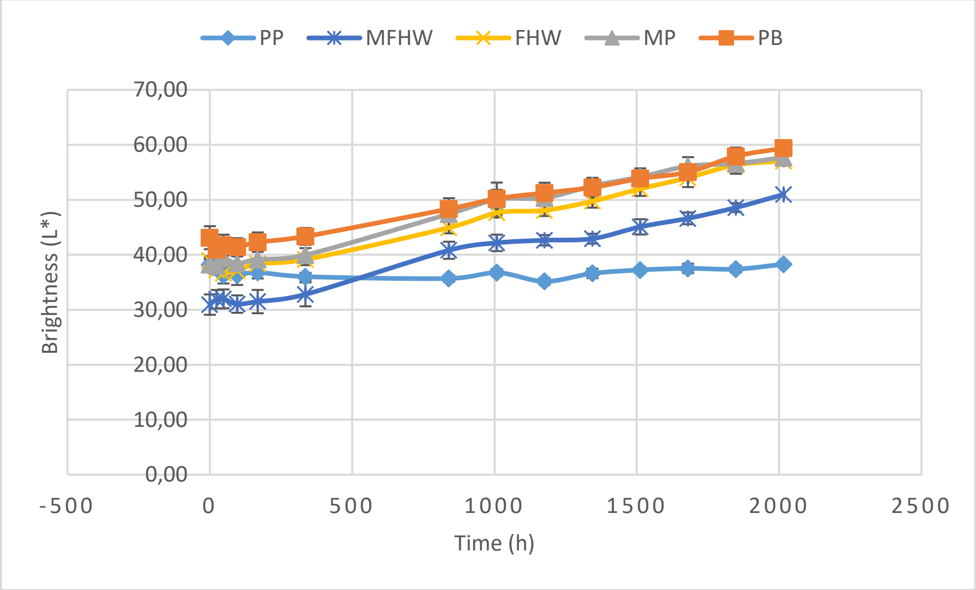


Figure 3.9 change in brightness of composites at the end of exposure to 2016 h of UV radiation

Figure 3.10 Neat PP and composites before (left) and after exposure (right) to UV radiation for 2016 h in the UV chamber

Table 3.6 Colour variation of composites on exposure to 2016 h of UV radiation

Samples		**Time (h)**													
		0	**24**	**48**	**96**	**168**	**336**	**840**	**1008**	**1176**	**1344**	**1512**	**1680**	**1848**	**2016**
PP	L*	38.17	38.41	36.29	36.32	36.80	36.02	35.69	36.77	35.16	36.62	37.24	37.53	37.39	38.28
	a*	-0.64	0.01	-1.06	0.50	0.33	-1.11	-1.09	-1.03	-0.52	-1.16	-0.91	-1.46	-2.58	-2.66
	b*	2.19	1.23	0.61	0.68	0.63	1.23	1.27	1.27	0.73	1.51	1.59	1.57	1.64	1.82
	ΔE*	0.00	1.64	2.71	3.00	2.64	2.61	2.91	2.25	3.38	1.92	1.47	1.55	2.28	2.16
PB	L*	43.11	40.97	41.75	41.41	42.29	43.34	48.34	50.22	51.24	52.25	53.88	55.02	57.93	59.40
	a*	1.08	1.73	1.23	1.33	1.18	0.22	0.72	-0.24	0.21	-0.98	-0.54	-0.85	-3.50	-2.94
	b*	10.87	11.16	9.67	11.13	12.02	11.20	11.17	12.62	12.57	12.43	12.44	12.09	11.96	12.08
	ΔE*	0.00	2.53	2.31	2.10	1.85	1.96	5.31	7.59	8.43	9.56	11.07	12.18	15.58	16.86
MP	L*	38.22	37.97	39.31	38.42	39.17	39.96	47.43	50.09	50.35	52.53	54.15	56.12	56.60	57.69
	a*	1.94	2.16	1.48	1.38	1.28	0.41	-0.72	-0.10	0.00	-1.15	-0.85	-1.05	-3.49	-2.63
	b*	12.57	11.63	10.79	11.21	12.29	10.56	11.32	11.77	11.15	11.04	11.29	11.66	11.72	11.69
	ΔE*	0.00	1.39	2.36	1.91	1.67	3.42	9.73	12.10	12.40	14.75	16.25	18.18	19.20	20.03
FHW	L*	38.96	37.20	36.66	37.10	38.38	39.13	44.93	47.65	48.07	49.73	52.00	54.03	56.34	57.04
	a*	1.89	2.58	1.89	1.97	1.83	0.69	-0.49	-0.22	0.28	-0.48	-0.43	-0.94	-3.21	-2.73
	b*	8.61	8.83	7.84	8.86	9.00	8.58	9.68	9.66	9.58	9.32	9.53	9.53	9.95	9.94
	ΔE*	0.00	2.18	2.67	2.02	1.38	1.64	6.56	9.02	9.33	11.06	13.30	15.39	18.66	19.19
MFHW	L*	30.94	31.92	31.98	31.03	31.49	32.80	40.82	42.17	42.64	42.93	45.09	46.63	48.59	50.98
	a*	2.08	1.17	1.17	0.68	1.37	0.55	-1.19	-0.68	0.26	-1.28	-0.58	-1.04	-2.92	-2.59
	b*	7.46	6.99	5.86	6.43	7.29	7.20	8.08	7.76	8.42	7.85	8.38	8.66	9.07	9.58
	ΔE*	0.00	1.64	2.23	1.85	1.21	2.51	10.46	11.58	11.91	12.47	14.44	16.05	18.43	20.69

3.7 FTIR Analysis

The FTIR is a simple characterization technique which is used for WPC to characterize the distribution of wood and plastic in WPC material. The FTIR spectra of all composites are presented in fig 3.11 and 3.12. The line spectra show similar pattern for all samples except for some few peaks which are not visible in PP. In the fingerprint region, as expected, the WPC showed difference in band absorption intensity. Modified False heartwood composites showed the highest absorbance especially at 1035 cm^{-1}. This is also reported by Bankole *et al.* 2016. The characteristic peaks 1162 cm^{-1}-1103 cm^{-1} can be seen to have higher intensity for all samples when compared with the pure PP. Silane modification effect is responsible for the peak changes at 1103 cm^{-1} and 1035 cm^{-1} corresponding to the Si-O-C band. The key absorption bands of PP as seen in fig 3.11 include 841, 974, 997, 1162, 1376 (CH_3 bending) (Morent *et al.* 2008). The peak at 1245 cm^{-1} correspond to C-O-C group in cellulose. The strong peak at 1035 cm^{-1} is attributed to secondary alcohols and aromatic ether (C-O) stretching vibration (cellulose, hemicellulose and lignin) (Chan *et al.* 2017). The enhanced peak at 1035 and 1376 cm^{-1} is due to the reaction between the hydroxyl groups of cellulose and that of silanol on the wood surface, thus creating an ether bonds of Si-O-Si- and -Si-O-C (Ma *et al.* 2017). The wavenumber of marked peaks as well as their structure and functional groups are given in table 3.6

Table 3.7 FTIR peaks and structures

Wavenumber (cm-1)	Bond	Functional group
841	substituted aromatic	Aromatic
898	S-OR	Ether
974	R2C=CHR	Alkane
997	P-OR	Ester
1035	C-O	Alcohol & ether
1103	Si-O-C	Silyl ether
1162	RCOOR	Ester
1245	Si-CH3	Silyl ether
1360	C-H	Alkanes
1376	CH2CH3	Alkane
2837	RCOOH	Carboxylic acid
2868	CH3	Alkane
2837	RCOOH	Carboxylic acid
2868	CH3	Alkane

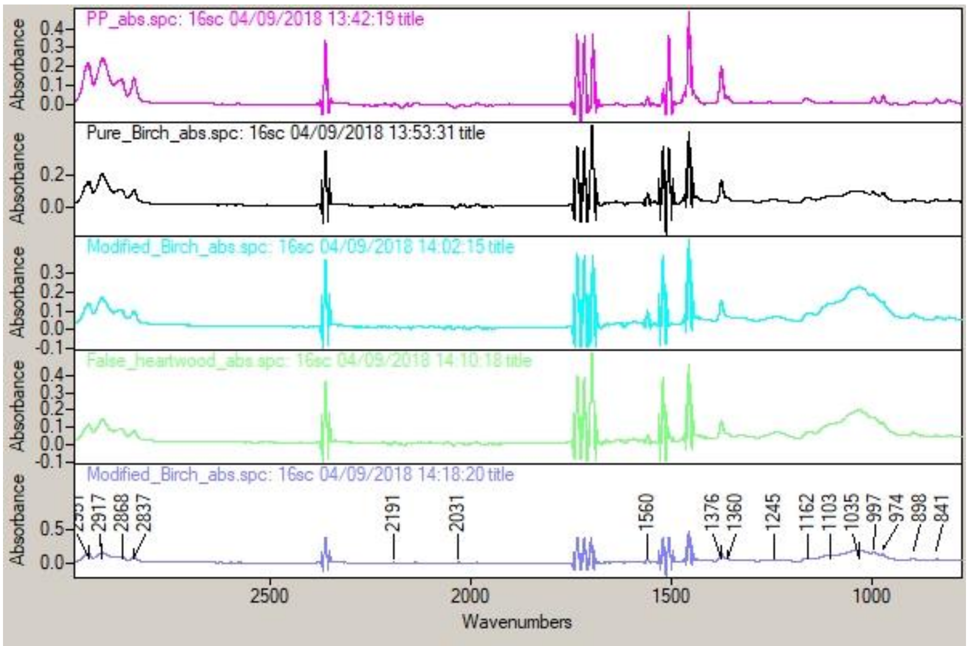


Figure 3.11 FTIR spectra of composites and neat PP

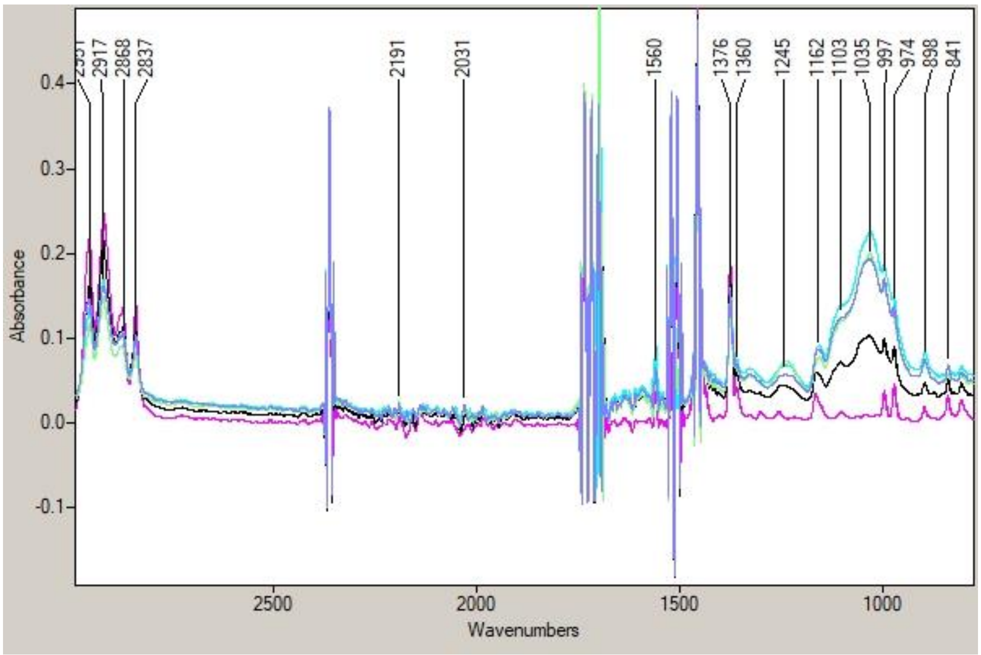


Figure 3.12 FTIR spectra of composites and neat PP

SUMMARY

This master thesis describes the research work conducted in the investigation of the influence of birch false heartwood on the physical and mechanical properties of wood-plastic composite. Thesis also focuses on accessing the possibility of producing WPC using birch wood at 60% wood content and at 40% of polypropylene (PP) polymer content. The results obtained were analysed and compared with other similar studies.

Birch wood (pure and false heartwood) particles were modified with NaOH at 5wt% (by wood content) and 3-Aminopropyl-triethoxysilane (APTES) also at 5wt% (by wood content) before compounding with PP in a co-rotating twin screw extruder at temperatures between 180 ˚C and 190 ˚C with the screw speed set at 60 rpm. The compounded composites were then injection moulded into standard test samples at temperatures between 170 ˚C and 180 ˚C and pressure of 7 MPa. The made composites were grouped into 4 categories namely, pure birch (PB), modified pure birch (MP), false heartwood (FHW) and modified false heartwood (MFHW) and neat PP samples were produced as reference. The samples were tested for their tensile and flexural properties, notched impact, water absorption and thickness swelling and UV properties. The chemical properties were analysed using Fourier Transform Infrared Spectroscopy (FTIR).

The results showed that the tensile strength of all the samples reduced after absorption of water. FHW and MFHW had close tensile strength before soaking in water but after absorption of water, MFHW had a 10.17% higher decrease in tensile strength than the FHW. This shows that the addition of 5 wt% NaOH and APTES did not affect the tensile strength of the FHW to cause an increase and it suggest that the silane was not able to penetrate through the bonds of the false heartwood to enable the interfacial adhesion of the composite. Silane did not also increase the tensile strength of the MFHW on exposure to UV. However, the false heartwood composite showed higher value than the others after water immersion.

The flexural strength of FHW and MFHW were about the same before soaking in water. However, the effect of APTES 5 wt% modification is visible in the flexural strength of MFHW composites after soaking in water. The false heartwood composite showed the lowest reduction of 10.6% in flexural strength and the modified false heartwood showed the highest reduction of 16.6% in flexural strength after absorption of water. This indicates that MFHW absorbed water more than FHW. MFHW had the highest decrease in flexural MOE. The flexural strength and MOE of MFHW was lower than that of FHW after the UV exposure. Thus, APTES can be said to

have effect on the MFHW on exposure to UV. APTES also decreased the flexural MOE of the false heartwood on exposure to UV.

Modification with 5wt% silane and NaOH increased the water absorption of MFHW and MP composites. This increase is more for MFHW by 28% and less for modified pure at 4.3%. The modified false heartwood has the highest absorption of 17.26. Absorption of water reduced the impact strength of all composites.

UV radiation degraded the neat PP and all the composites. Surface chalking was observed in all WPCs exposed to artificial weathering with colour ranging from brown and brownish black to white. Modified pure birch and modified false heartwood had about the same colour change at the end of the 2016 h which were the greatest change in colour among the composites.

The use of birch false heartwood in the manufacturing of WPCs has been shown to be possible. However, the modification of the false heartwood should be improved in further studies to maximize its capabilities in the production of WPCs.

KOKKUVÕTE

Antud magistritöö uurib kase väärlülipuidu mõju puitplastkomposiitide füüsikalistele ja mehaanilistele omadustele. Magistritöös keskendutakse kase väärlülipuidu silaaniga modifitseerimise mõjule puitplastkomposiitide omadustele. Lõputöö keskendub ka suure puidu osakaalu kasutamisele puitplastkomposiitides, kasutades 60% puitu ja 40% polüpropüleeni. Tulemusi analüüsitakse ja võrreldakse teiste sarnaste uurimustega.

Töös modifitseeritakse kasepuitu 5 % (puidu massi järgi) naatriumhüdroksiidi (NaOH) lahusega ja 5 % (puidu massi järgi) 3-aminopropüül-trietoksüsilaani (APTES) lahusega. Seejärel segatakse puit polüpropüleeni graanulitega kokku kaheteolises ekstruuderis temperatuuridel 180 ˚C ja 190 ˚C ning kruvide pöörlemiskiirusel 60 rpm. Peale puidu ja plasti segamist valmistatakse survevalumeetodil standardsed katsekehad temperatuuridel 170 ˚C ja 180 ˚C ning survel 7 MPa. Valmistati kokku neli erinevat puitplastkomposiiti: kasepuiduga puitplastkomposiidid (PB), modifitseeritud kasepuiduga komposiidid (MP), kase väärlülipuiduga puitplastkomposiidid (FHW) ja modifitseeritud kase väärlülipuiduga puitplastkomposiidid (MFHW). Kontrollkatsekehana kasutati ka puhast polüpropüleeni. Valmistatud puitplastkomposiitidel katsetati tõmbe omadusi, painde omadusi, sälguga löögikatsekeha omadusi, veeimavust ja pundumist ning UV kiirgusega vanandamist. Keemilist struktuuri uuriti Fourier Transform infrapuna spektroskoopiaga (FTIR).

Katsetulemused näitasid, et tõmbetugevus vähenes kõikidel katsekehadel pärast vees leotamist. FHW ja MFHW olid sarnaste tõmbetugevustega, aga peale vees leotamist vähenes MFHW tõmbetugevus 10,17% võrrelduna FHW komposiitidega. See näitab, et 5% NaOH aja APTES modifitseerimine ei mõjutanud FHW komposiitide omadusi kuna silaanil ei olnud võimalik ühilduda kase väärlülipuidu struktuuriga ja luua keemilisi sidemeid polüpropüleeniga. Silaaniga modifitseerimine ei parandanud ka UV-kiirgusega vanandatud katsekehade tõmbetugevust. Samas olid ka kase väärlülipuiduga komposiitide tõmbetugevused suuremad teistes komposiidite tõmbetugevustest peale vees leotamist.

Paindetugevused oli FHW ja MFHW komposiitidel peaaegu sarnased. Kase väärlülipuiduga komposiidid näitasid kõige väiksemat paindetugevuse vähenemist (10,6%) peale vees leotamise katset ja modifitseeritud kase väärlülipuiduga komposiidid näitasid kõige suuremat paindetugevuse vähenemist (16,6%). See näitab, et keemiliselt modifitseeritud kase väärlülipuiduga komposiidid imasid rohkem vett kui modifitseerimata kase väärlülipuiduga komposiidid. MFHW komposiitidel oli ka kõige suurem paindeelastsusmooduli vähenemine.

Peale UV kiirgusega vanandamist oli paindetugevus ja paindeelastsumoodul MFHW komposiitidel väiksem kui FHW komposiitidel. Seetõttu saab öelda, et silaaniga modifitseerimine ei aidanud tõsta kase väärlülipuiduga komposiitide omadusi.

Puidu modifitseerimine 5% silaani ja NaOH lahusega suurendas MFHW ja MP komposiitide veeimavust. Kõige suurem veeimavus oli MFHW komposiitidel – 28%. Veeimavus vähendas ka kõikide komposiitide löögitugevust.

UV kiirgusega vanandamine muutis kõikide komposiitide pealispinna halliks. Kõige rohkem muutsid värvi modifitseeritud kasepuiduga ja modifitseeritud kase väärlülipuiduga komposiidid peale 2016 tundi UV kiirgust.

Antud töö näitas, et kase väärlülipuidu kasutamine puitplastkomposiitide valmistamiseks on võimalik, kuid kase väärlülipuidu modifitseerimine vajab edasist uurimist ja parandamist, et parandada puitplastkomposiitide tootmist.

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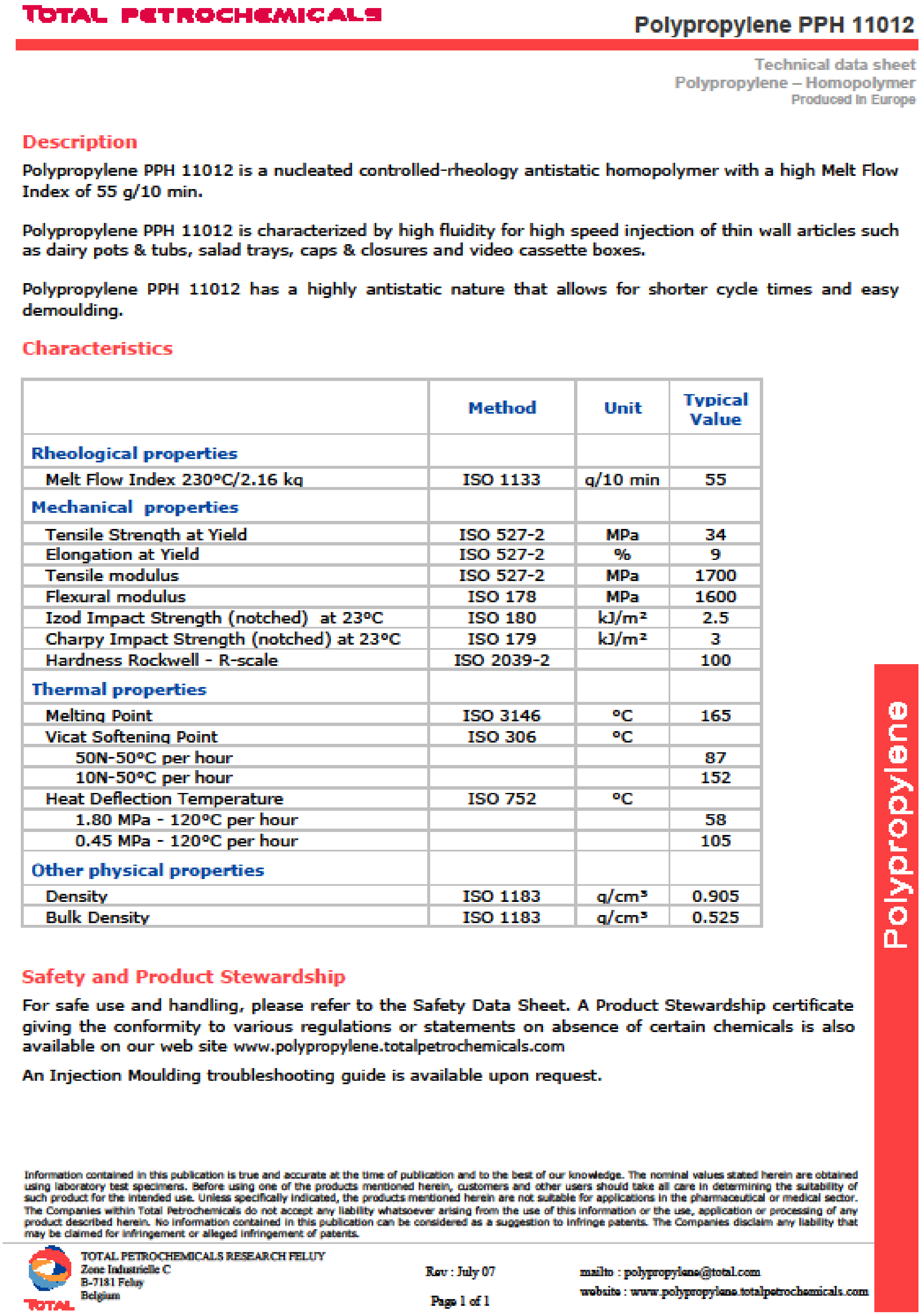
APPENDICES

Appendix 1- Data sheet of polypropylene polymer



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.

Polypropylene

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

Rev : July 07

Page 1 of 1

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website : www.polypropylene.totalpetrochemicals.com

Appendix 2- Results of tensile properties of PP

First our test method for plastics bones.

Rate 1	5.00000 mm/min
Humidity (%)	28.00000
Temperature (deg C)	23.00

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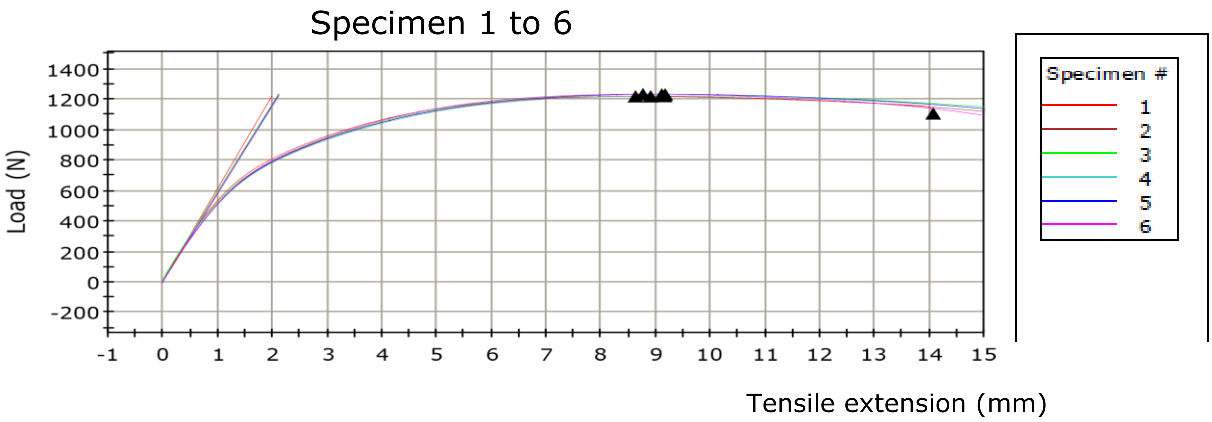

	Specimen label	Thickness (mm)	Load at Break (Standard) (N)	Maximum Load (N)	Tensile stress at Maximum Load (MPa)
1		4.00	1106.30	1217.54	30.44
2		4.00	993.45	1217.76	30.44
3		4.00	1022.07	1231.32	30.78
4		4.00	960.69	1220.32	30.51
5		4.00	811.28	1230.80	30.77
6		4.00	942.39	1231.48	30.79
Mean		4.00	972.70	1224.87	30.62
Range		0.00	295.02	13.94	0.35
Standard Deviation		0.00	97.81	7.01	0.18

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
1	27.66	1749.88	1749.88	8.72	14.15
2	24.84	1651.51	1651.51	8.96	16.19
3	25.55	1647.98	1647.98	9.16	16.28
4	24.02	1645.48	1645.48	9.22	16.05
5	20.28	1658.95	1658.95	9.23	17.51

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
6	23.56	1660.56	1660.56	8.84	15.59
Mean	24.32	1669.06	1669.06	9.02	15.96
Range	7.38	104.41	104.41	0.51	3.36
Standard Deviation	2.45	40.04	40.04	0.21	1.09

	Tensile extension at Maximum Load (mm)	Tensile extension at Break (Standard) (mm)	Nominal Strain at break	Tensile strain at Break (Standard) (%)	Nominal Strain at max Load
1	8.62	14.05	1.12	12.21	1.07
2	8.90	16.13	1.14	14.02	1.08
3	9.10	16.22	1.14	14.10	1.08
4	9.16	15.99	1.14	13.90	1.08
5	9.16	17.44	1.15	15.16	1.08
6	8.76	15.51	1.14	13.48	1.08
Mean	8.95	15.89	1.14	13.81	1.08
Range	0.54	3.39	0.03	2.95	0.00
Standard Deviation	0.23	1.11	0.01	0.96	0.00

	Tensile strain at Maximum Load (%)	Tensile stress at Preset Point (Tensile strain 0.0025 mm/mm) (MPa)	Tensile stress at Preset Point (Tensile strain 0.0005 mm/mm) (MPa)
1	7.49	4.45	0.96
2	7.73	4.23	0.92
3	7.91	4.62	1.32
4	7.96	4.22	0.93
5	7.96	4.24	0.92
6	7.61	4.18	0.85
Mean	7.78	4.32	0.98
Range	0.47	0.44	0.47
Standard Deviation	0.20	0.18	0.17

Appendix 3- Result of tensile properties of PB

First our test method for plastics bones.

Rate 1	5.00000 mm/min
Humidity (%)	28.00000
Temperature (deg C)	23.00

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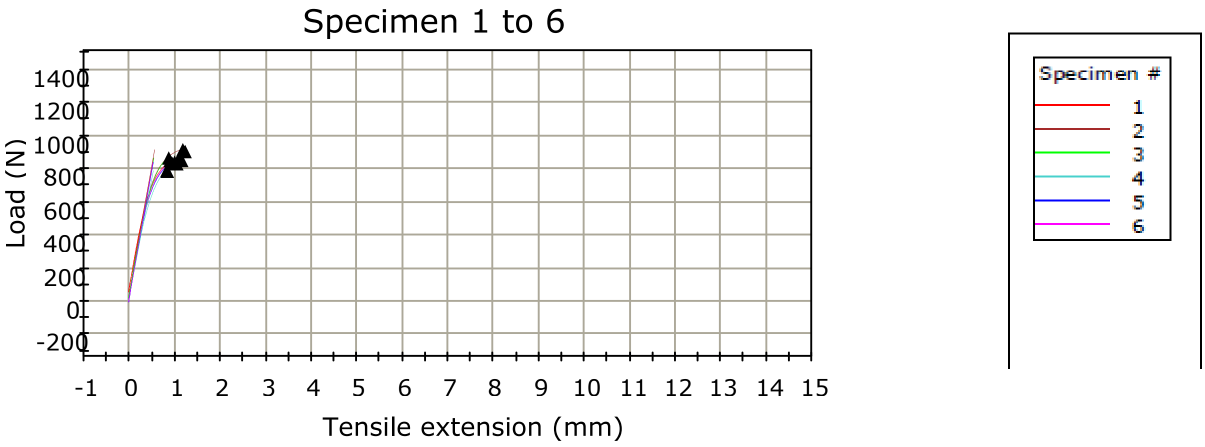

	Specimen label	Thickness (mm)	Load at Break (Standard) (N)	Maximum Load (N)	Tensile stress at Maximum Load (MPa)
1		4.00	851.10	864.42	21.61
2		4.00	903.83	914.34	22.86
3		4.00	849.12	865.49	21.64
4		4.00	786.05	788.30	19.71
5		4.00	831.24	840.68	21.02
6		4.00	831.69	836.10	20.90
Mean		4.00	842.17	851.56	21.29
Range		0.00	117.79	126.04	3.15
Standard Deviation		0.00	38.24	41.62	1.04

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
1	21.28	4158.76	4158.76	1.17	1.22
2	22.60	4450.77	4450.77	1.20	1.25
3	21.23	4330.10	4330.10	0.89	0.92
4	19.65	4125.79	4125.79	0.85	0.87
5	20.78	4434.83	4434.83	1.04	1.09

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
6	20.79	4469.16	4469.16	2.07	2.09
Mean	21.05	4328.24	4328.24	1.20	1.24
Range	2.94	343.38	343.38	1.22	1.22
Standard Deviation	0.96	152.28	152.28	0.45	0.45

	Tensile extension at Maximum Load (mm)	Tensile extension at Break (Standard) (mm)	Nominal Strain at break	Tensile strain at Break (Standard) (%)	Nominal Strain at max Load
1	1.10	1.16	1.01	1.01	1.01
2	1.19	1.24	1.01	1.07	1.01
3	0.87	0.91	1.01	0.79	1.01
4	0.83	0.85	1.01	0.74	1.01
5	1.01	1.06	1.01	0.92	1.01
6	0.93	0.95	1.02	0.83	1.01
Mean	0.99	1.03	1.01	0.89	1.01
Range	0.35	0.39	0.01	0.34	0.00
Standard Deviation	0.14	0.15	0.00	0.13	0.00

	Tensile strain at Maximum Load (%)	Tensile stress at Preset Point (Tensile strain 0.0025 mm/mm) (MPa)	Tensile stress at Preset Point (Tensile strain 0.0005 mm/mm) (MPa)
1	0.96	12.34	4.03
2	1.03	12.04	3.13
3	0.76	11.79	3.13
4	0.72	10.76	2.51
5	0.88	11.46	2.59
6	0.81	11.56	2.62
Mean	0.86	11.66	3.00
Range	0.31	1.58	1.52
Standard Deviation	0.12	0.55	0.57

Appendix 4- Result of tensile properties of MP

First our test method for plastics bones.

Rate 1	5.00000 mm/min
Humidity (%)	28.00000
Temperature (deg C)	23.00

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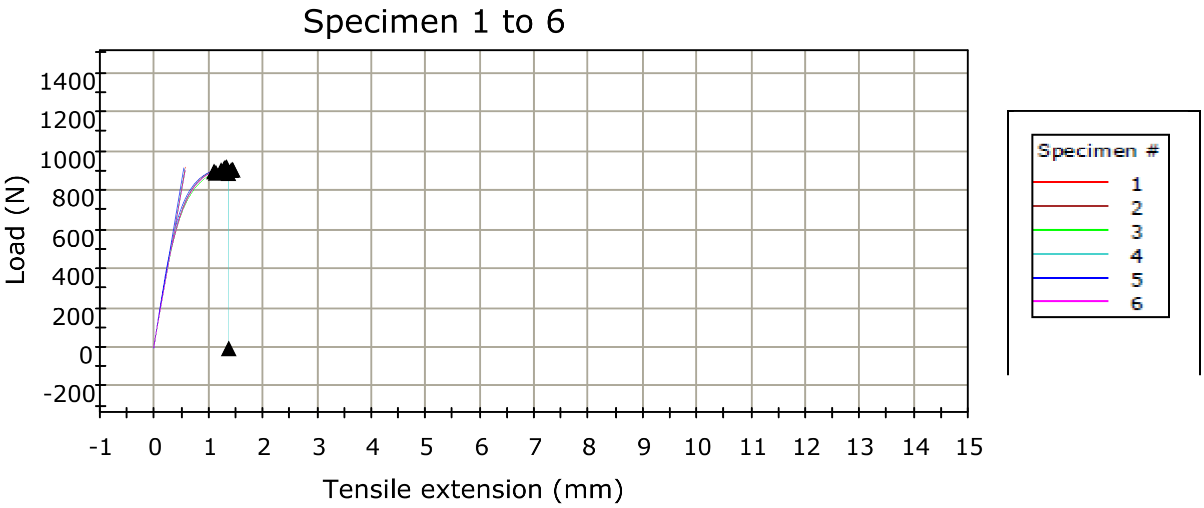

	Specimen label	Thickness (mm)	Load at Break (Standard) (N)	Maximum Load (N)	Tensile stress at Maximum Load (MPa)
1		4.00	907.63	919.05	22.98
2		4.00	891.52	896.83	22.42
3		4.00	887.91	901.20	22.53
4		4.00	-1.80	913.72	22.84
5		4.00	904.03	915.51	22.89
6		4.00	898.36	904.54	22.61
Mean		4.00	747.94	908.47	22.71
Rang e		0.00	909.43	22.21	0.56
Standard Deviation		0.00	367.37	8.86	0.22

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
1	22.69	4494.54	4494.54	1.36	1.47
2	22.29	4415.82	4415.82	1.12	1.16
3	22.20	4421.48	4421.48	1.34	1.40

4	-0.05	4570.98	4570.98	1.34	1.42
5	22.60	4702.63	4702.63	1.35	1.46

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
6	22.46	4428.70	4428.70	1.26	1.31
Mean	18.70	4505.69	4505.69	1.29	1.37
Range	22.74	286.80	286.80	0.24	0.31
Standard Deviation	9.18	113.37	113.37	0.09	0.12

	Tensile extension at Maximum Load (mm)	Tensile extension at Break (Standard) (mm)	Nominal Strain at break	Tensile strain at Break (Standard) (%)	Nominal Strain at max Load
1	1.34	1.45	1.01	1.26	1.01
2	1.11	1.14	1.01	0.99	1.01
3	1.31	1.37	1.01	1.19	1.01
4	1.29	1.38	1.01	1.20	1.01
5	1.31	1.42	1.01	1.24	1.01
6	1.24	1.28	1.01	1.11	1.01
Mean	1.26	1.34	1.01	1.17	1.01
Range	0.23	0.31	0.00	0.27	0.00
Standard Deviation	0.08	0.11	0.00	0.10	0.00

	Tensile strain at Maximum Load (%)	Tensile stress at Preset Point (Tensile strain 0.0025 mm/mm) (MPa)	Tensile stress at Preset Point (Tensile strain 0.0005 mm/mm) (MPa)
1	1.17	11.64	2.65
2	0.96	11.48	2.65
3	1.14	11.37	2.53
4	1.12	11.82	2.68
5	1.14	12.14	2.74
6	1.07	11.50	2.64
Mean	1.10	11.66	2.65
Range	0.20	0.77	0.21
Standard Deviation	0.07	0.28	0.07

Appendix 5- Result of tensile properties of FHW

First our test method for plastics bones.

Rate 1	5.00000 mm/min
Humidity (%)	28.00000
Temperature (deg C)	23.00

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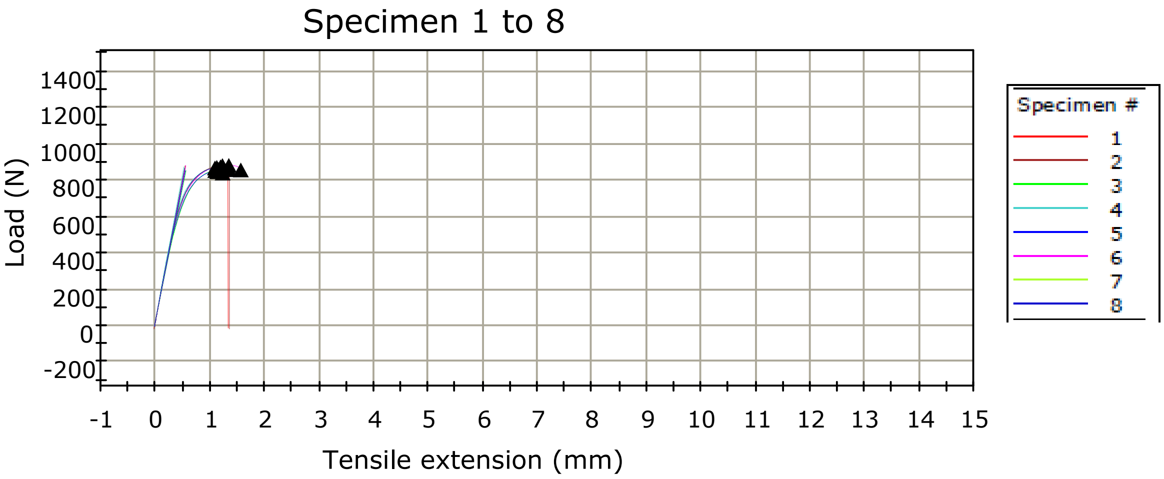

	Specimen label	Thickness (mm)	Load at Break (Standard) (N)	Maximum Load (N)	Tensile stress at Maximum Load (MPa)
1		4.00	863.01	878.68	21.97
2		4.00	858.21	880.13	22.00
3		4.00	847.61	854.48	21.36
4		4.00	860.94	873.76	21.84
5		4.00	840.67	853.64	21.34
6		4.00	857.59	882.65	22.07
7		4.00	861.28	871.05	21.78
8		4.00	859.78	867.60	21.69
Mean		4.00	856.14	870.25	21.76
Rang e		0.00	22.33	29.01	0.73
Standard Deviation		0.00	7.82	11.13	0.28

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
1	21.58	4434.10	4434.10	1.28	1.38
2	21.46	4519.01	4519.01	1.29	1.42

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
3	21.19	4228.07	4228.07	1.15	1.19
4	21.52	4643.21	4643.21	1.24	1.36
5	21.02	4335.53	4335.53	1.21	1.30
6	21.44	4436.93	4436.93	1.40	1.62
7	21.53	4481.81	4481.81	1.19	1.27
8	21.49	4499.82	4499.82	1.14	1.20
Mean	21.40	4447.31	4447.31	1.24	1.34
Range	0.56	415.14	415.14	0.26	0.43
Standard Deviation	0.20	124.39	124.39	0.09	0.14

	Tensile extension at Maximum Load (mm)	Tensile extension at Break (Standard) (mm)	Nominal Strain at break	Tensile strain at Break (Standard) (%)	Nominal Strain at max Load
1	1.24	1.34	1.01	1.16	1.01
2	1.24	1.36	1.01	1.18	1.01
3	1.11	1.14	1.01	0.99	1.01
4	1.20	1.32	1.01	1.15	1.01
5	1.14	1.24	1.01	1.08	1.01
6	1.35	1.57	1.01	1.37	1.01
7	1.14	1.22	1.01	1.06	1.01
8	1.10	1.16	1.01	1.01	1.01
Mean	1.19	1.29	1.01	1.12	1.01
Range	0.25	0.43	0.00	0.37	0.00
Standard Deviation	0.09	0.14	0.00	0.12	0.00

	Tensile strain at Maximum Load (%)	Tensile stress at Preset Point (Tensile strain 0.0025 mm/mm) (MPa)	Tensile stress at Preset Point (Tensile strain 0.0005 mm/mm) (MPa)
1	1.08	11.34	2.47
2	1.07	11.56	2.52
3	0.96	10.88	2.42
4	1.05	11.91	2.63
5	0.99	11.13	2.45
6	1.18	11.35	2.47
7	0.99	11.53	2.57
8	0.96	11.57	2.57
Mean	1.03	11.41	2.51
Range	0.22	1.03	0.20
Standard Deviation	0.07	0.31	0.07

Appendix 6- Result of tensile properties of MFHW

First our test method for plastics bones.

Rate 1	5.00000 mm/min
Humidity (%)	28.00000
Temperature (deg C)	23.00

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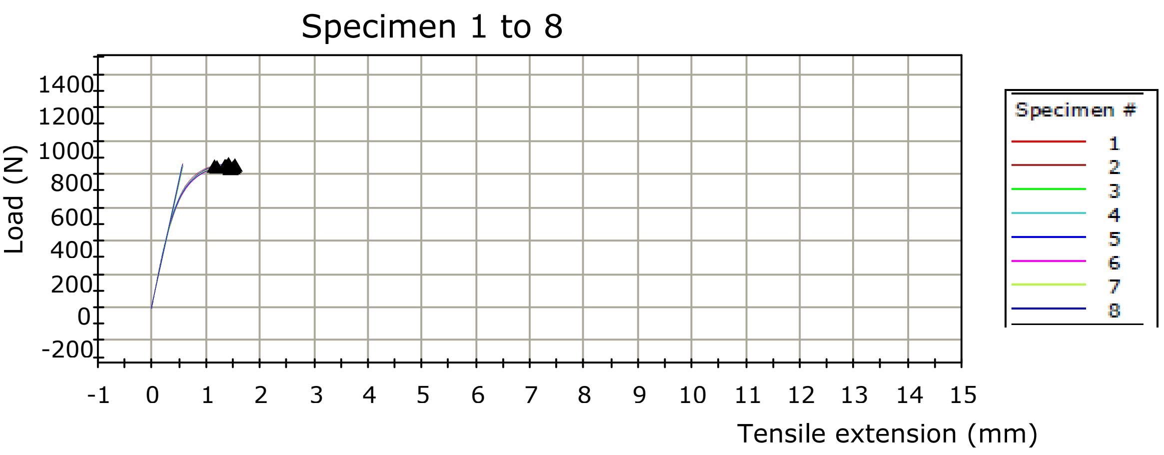

	Specimen label	Thickness (mm)	Load at Break (Standard) (N)	Maximum Load (N)	Tensile stress at Maximum Load (MPa)
1		4.00	849.29	859.26	21.48
2		4.00	845.72	850.78	21.27
3		4.00	845.79	852.26	21.31
4		4.00	836.48	852.10	21.30
5		4.00	856.91	864.99	21.62
6		4.00	842.17	851.68	21.29
7		4.00	841.91	851.60	21.29
8		4.00	836.66	845.84	21.15
Mean		4.00	844.37	853.56	21.34
Range		0.00	20.43	19.15	0.48
Standard Deviation		0.00	6.74	5.88	0.15

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
1	21.23	4317.51	4317.51	1.48	1.58
2	21.14	4290.94	4290.94	1.19	1.23

3	21.14	4153.81	4153.81	1.41	1.48

Page 1 of 2

	Tensile stress at Break (Standard) (MPa)	Modulus of Elasticity	Modulus (Chord 0.0005 mm/mm - 0.0025 mm/mm) (MPa)	Extension at Maximum Load (mm)	Extension at Break (Standard) (mm)
4	20.91	4354.36	4354.36	1.41	1.52
5	21.42	4240.49	4240.49	1.48	1.60
6	21.05	4214.03	4214.03	1.47	1.56
7	21.05	4292.74	4292.74	1.40	1.51
8	20.92	4294.66	4294.66	1.46	1.55
Mean	21.11	4269.82	4269.82	1.41	1.50
Range	0.51	200.55	200.55	0.29	0.37
Standard Deviation	0.17	63.74	63.74	0.10	0.12

	Tensile extension at Maximum Load (mm)	Tensile extension at Break (Standard) (mm)	Nominal Strain at break	Tensile strain at Break (Standard) (%)	Nominal Strain at max Load
1	1.42	1.52	1.01	1.32	1.01
2	1.16	1.21	1.01	1.05	1.01
3	1.38	1.45	1.01	1.26	1.01
4	1.35	1.46	1.01	1.27	1.01
5	1.42	1.54	1.01	1.34	1.01
6	1.41	1.50	1.01	1.30	1.01
7	1.35	1.46	1.01	1.27	1.01
8	1.37	1.47	1.01	1.28	1.01
Mean	1.36	1.45	1.01	1.26	1.01
Range	0.26	0.33	0.00	0.29	0.00
Standard Deviation	0.08	0.10	0.00	0.09	0.00

	Tensile strain at Maximum Load (%)	Tensile stress at Preset Point (Tensile strain 0.0025 mm/mm) (MPa)	Tensile stress at Preset Point (Tensile strain 0.0005 mm/mm) (MPa)
1	1.23	11.09	2.45
2	1.01	11.12	2.54
3	1.20	10.75	2.44
4	1.18	11.21	2.50
5	1.23	10.98	2.50
6	1.22	10.84	2.41
7	1.18	11.09	2.51
8	1.19	11.04	2.45
Mean	1.18	11.02	2.48
Range	0.22	0.47	0.12
Standard Deviation	0.07	0.15	0.04

Page 2 of 2

Appendix 7- Publication

EFFECT OF BIRCH FALSE HEARTWOOD ON THE PHYSICAL AND MECHANICAL PROPERTIES OF WOOD-PLASTIC COMPOSITES

Kallakas, H.[1]; Martin, M.[2]; Ayansola, G.[3]; Poltimäe, T.[4]; Krumme, A.[5]; Kers, J.[6]

ABSTRACT

False heartwood is a phenomenon where penetration of oxygen discolors the wood. It is an undesirable defect which influences the applications of the wood. The properties and formation of false heartwood have been investigated but false heartwood as a filler material in composites has not been previously used. The aim of this research was to investigate the false heartwood fraction size and chemical modification effect on the physical and mechanical properties of wood-plastic composites. The effect of chemical treatment with NaOH and 3-aminopropyltriethoxyslane (APTES) was investigated to see if the modification will provide better interfacial adhesion. Wood-plastic composite boards were produced from three different false heartwood fraction sizes of 0.4 mm, 1 mm and 2 mm. The composites were chemically modified and compounded using a twin-screw compounder and the test specimens were produced via hot pressing and CNC milling. The composites physical properties were investigated using Fourier transform infrared spectroscopy (FTIR) and density measurement by immersion. The mechanical

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properties were investigated using three-point bend test, tensile test and Charpy impact test. The effect of fraction size and chemical modification was compared. The different fraction size of false heartwood does shows substantial differences in results. The density of the material reduced with increasing fiber size and with chemical modification using NaOH and APTES.

Key words: wood-plastic composite, birch, false heartwood, modification.

INTRODUCTION

Wood plastic composites (WPC) are materials comprised of polymers and wood particles. The materials properties are dependent on the constituents, their ratios, interfacial adhesion and production technology. False heartwood (FHW) has been studied for a long time but many theories exist on the formation and the properties it carries over. False heartwood formation discolours the wood by penetration of oxygen into the stem and gives it unique properties. As false heartwood contains various extractives that may inhibit the interfacial adhesion the properties of the material may be diminished (Smith, 2015). Normal heartwood and false heartwood differ in water content, ash content, pH and frequency of amorphous deposits (Pallardy, 2008). False heartwood is a waste material in traditional wood industry and the opportunity of using it as filler material in composites is an attractive possibility. The aim of this study was to investigate how different fraction size of false heartwood particles and chemical modification affect the physical and mechanical properties of WPCs. The tasks were chemical modification of wood flour, hot-pressing of composite boards, CNC milling of test specimens and physical and mechanical testing.

MATERIAL AND METHODS

Composites preparation

Polypropylene (PP) heterophasic copolymer BC245MO (density of 0.905 g/cm^3, the melting flow index of 3.5 g/10 min at 230°C/ 2,16 kg) by Borealis Polymer Oy was used as a matrix material for the production of composites. Birch false heartwood (*Betula Pendula*) was used as a filler material in the composites at different fraction sizes. The false heartwood veneers sheets were provided by Kohila Vineer OÜ. The false heartwood veneers were milled using disintegrator DSL-115 and DSA3 to three different fractions (0.04 mm, up to 1 mm, and 1-2 mm) to see if this will affect the properties of the material. The composites will vary in composition as can be seen in Table 1. For the purification of wood flour Sigma-Aldrich NaOH (95% pure, CAS number 1310-73-2) was used to remove lignin and to enhance the coupling with the polymer. For binding agent between the wood flour and polymer, Sigma-Aldrich 3-aminopropyl-triethoxysilane (APTES, ≥98% pure, M_w= 221.37 g/mol, CAS number 919-30-2) was used. The modification of wood fibres was carried out based on previous researches (Gwon, et al., 2010) (Kim, et al., 2010). NaOH was taken 5 wt% of wood flour. Then, the NaOH aqueous solution was mixed with the wood flour and washed with water and then placed into a kiln for drying at 40 °C, 24h. 5 wt% (of WF) of silane was added to the solution of ethanol and water (volume ratio of 6:4). Acetic acid was added until the pH of the solution was 4-5 as desired (Kim, 2010). After the wood flour was mixed with the silane solution it was placed into a kiln for drying at 40 °C, 24h. The dry wood flour and PP were compounded with a twin co-rotating Brabender Plasti-Corder PLE651 compounder. The mixtures were processed at the following zone temperatures from zone 1 to 4: 180°C, 185°C, 190°C and 190°C and screw speed was 60-70 rpm. Then, the boards (150x150 mm) were pressed using a manual hydraulic hot press. Press temperature was set to 190 °C and the boards were prepressed at 1 MPa for 10 minutes and then final pressure of 5 MPa was applied for 10 minutes. The mould was then removed from the press and it was cooled with cold water. Computer numerical control (CNC) milling was chosen as the best method for procurement of the tensile test specimens from the previously hot pressed composite boards.

Table 1. Composition of composites

Mixture nr.	**Polymer, % wt**	**Filler, % wt**	**Filler average fraction size, mm**	**Modification, % wt**
Mixture 1	65%	35%	0,4	-
Mixture 2	65%	35%	1	-
Mixture 3	65%	35%	2	-
Mixture 4	65%	35%	0,4	5% NaOH
Mixture 5	65%	35%	1	5% NaOH
Mixture 6	65%	35%	2	5% NaOH
Mixture 7	65%	35%	0,4	5% NaOH, 5% APTES
Mixture 8	65%	35%	1	5% NaOH, 5% APTES
Mixture 9	65%	35%	2	5% NaOH, 5% APTES

Mechanical property tests

Tensile tests were conducted according to EN ISO 527-2. The test speed was set to 20 mm/min and the tensile strength and modulus was calculated. Flexural (three point bending) strength was conducted according to EN ISO 178. Testing speed was set at 20 mm/min. Flexural strength and the modules of elasticity was calculated. Both tests were done with Instron 5866 test machine and five samples from each mixture were tested. Charpy impact strength was tested according to EN ISO 179-1 using Zwick Charpy 5102 pendulum impact tester. Notched impact strengths were measured. 10 samples from each composite mixture were tested.

Physical property tests

The efficiency of the chemical modification was verified using Fourier transform infrared spectroscopy (FTIR) with an Interspectrum FTIR spectrometer (Interspec 200-X) with Specac Attenuated Total Reflection (ATR) unit using KBr disc method. The spectra are recorded in the range of 4000-800 cm^{-1} with a resolution of 4 cm^{-1}. Thin wafers were cut from the previously produced test specimens using a scalpel. The thin wafers were placed under a clamp and the spectra was measured and peaks were marked. The density measurement was done in accordance to EN ISO 1183-1. Firstly, the test specimen was weighed in air using Kern KE-PLJ2000-3A scale with a precision of 0,001 g. If the test specimen weighed less or equal to 10 g the specimens mass was measured to the nearest 0,1 mg and test specimens with a mass greater than 10 g to the nearest 1 mg. Then the test specimen was weighed in freshly deionized water with not more than 0,1% of a wetting agent to help in removing air bubbles and then the density was calculated. The temperature of the immersion liquid was 23 °C ± 2 °C.

RESULTS AND DISCUSSION

Mechanical properties

The flexural strength results are shown in Fig. 1. The highest flexural strength was recorded by 2 mm false heartwood fibres with alkaline modification as it had 19% higher flexural strength than pure PP. Higher concentration of extractives found in false heartwood may also affect the coupling and mechanical properties. The fact that unmodified composite mixtures show similar flexural properties to mixtures with alkaline and silane modification indicate that false heartwood may need further purification for better adhesion with polymers. Previous research has shown that 30% by weight of untreated Norway Spruce wood flour reinforced PP composites have flexural strength of 48 MPa (Kim, 2010). The composites with 0.4 mm wood fibres show a slight decrease between unmodified and alkaline treated materials but silane treated material shows an increase which has been determined by previous research (Kim, 2010). When comparing fraction sizes, it can be concluded that smaller fraction sizes show increased flexural strength. The reaction between molecules is enhanced due to smaller particles which in turn affect the interfacial bonding although larger particles exhibit greater aspect ratio which should increase the stress distribution (Gwon, et al., 2010). Alkaline treatment increases fibre surface roughness and fibre swelling which increases mechanical interlocking but alkaline treatment can cause fibre burning and loss of mechanical properties.

The results of the tensile tests are presented in Fig. 2. Increase in fraction size has greatly reduced the tensile strength of the material. Alkaline treated 0.4 mm composite show an increase of 28% when comparing to unmodified wood flour reinforced composite and a 61% increase in tensile strength when comparing to silane treated composite. Alkaline treatment shows a small effect to composites of 1 and 2 mm fraction size but a significant decrease when comparing to silane treatment.

The substantial decrease of impact strength when comparing pure PP and composites may be attributed to the fact that the wood fibres limit the deformation of macromolecules thus making the material more brittle. Voids and microcracks in the material also attribute to the decrease of impact strength (Khalil, et al., 2006). Fig. 3 presents the impact strength of the composite materials. Impact strength of unmodified composites increased with fraction size. Composites with alkaline treatment showed the smallest impact strength which may be attributed to the fact that alkaline treatment may have burned the fibres and larger wood fibre fractions did not have effective reaction. Silane treatment increases the impact strength with the increase in fibre size. When comparing false heartwood composite results with the results of composites with birch, alder and thermally treated alder the impact strength is substantially increased. Alkaline treated 0,4 mm composite show the highest impact strength as it is 25% higher than untreated and 31% higher than silane treated composites. False heartwood composites show an increase in impact strength when comparing to pure birch, alder and thermally treated alder at all fraction sizes and modifications.

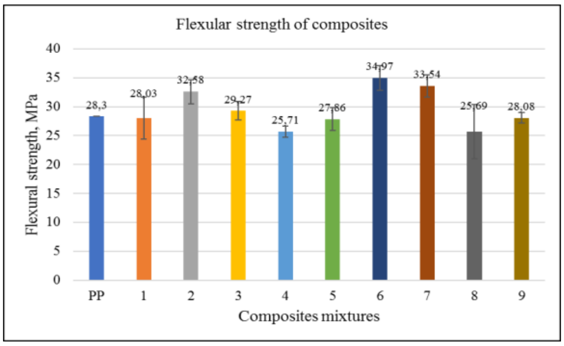

Figure 1. Flexural strength of composite

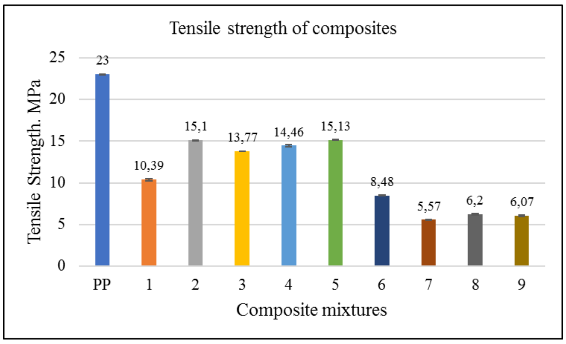

Figure 2. Tensile strength of composite

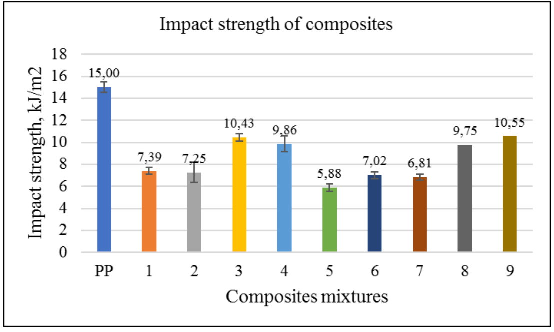

Figure 3. Impact strength of composites

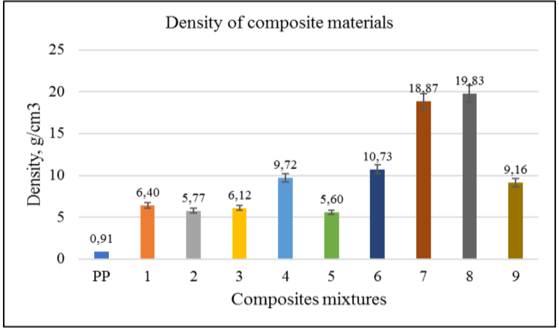

Figure 4. Density of composites

Fourier transform infrared spectroscopy results

The wavenumber values can be compared to various tables and specific software for determining the bonds in the material. Peaks at 1028 cm^{-1} and 1104 cm^{-1} indicate the siloxane chains in the composite. Fig. 5 and 6 show the FTIR graphs of the material. The peaks are identical only the absorbance varies at some points. The peaks between 1100 cm^{-1} and 1800 cm^{-1} are assigned to the main components of wood, cellulose, hemicellulose and lignin (Bodirlau, et al., 2008). Fig. 5 and 6 show slight peaks between 3000 cm^{-1} and 4000 cm^{-1} which are typical wood structures and peaks between 2800 cm^{-1} and 3000 cm^{-1} show hydroxyl group and C-H stretching (Kallakas, et al., 2016). The peaks at 899 cm^{-1} and 998 cm^{-1} represent isotactic polypropylene bands (Jordi, 2017).

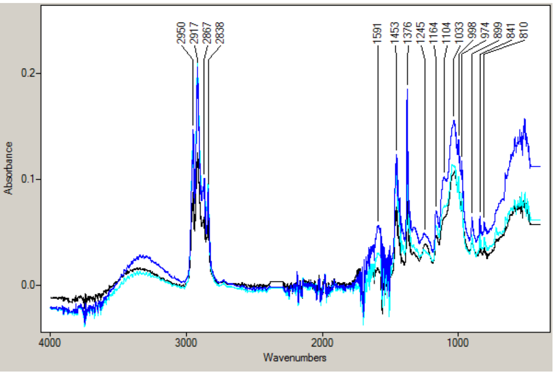

Figure 5. FTIR graph of composites fraction size of 2 mm

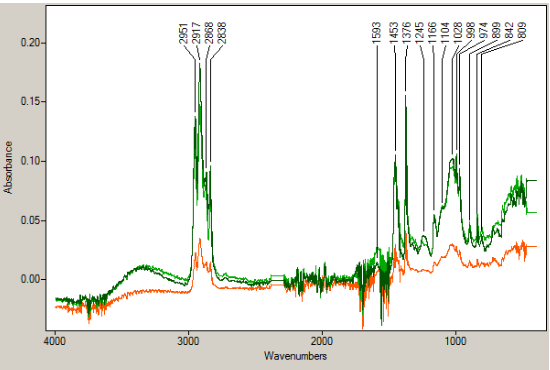

Figure 6. FTIR graph of composites fraction size of 1 mm

Density measurement by immersion

The density of composites is shown in Fig. 4. The results show that density of composites is higher compared to pure PP. The fraction size does not greatly affect the density of the material. Unmodified composites show the greatest density values. This may be attributed to the fact that high molecule weight substances and extractives are present in the material. Alkaline treatment has not changed the density of the material significantly, 0,4 mm fraction has 7% and 14% increase in density when comparing to alkaline treatment and silane treatment respectively. MAPP grafted PP composites show density of values of 1 – 1,02 g/cm^3 so the extractives and chemical modification increase the density of composites (Ayrilmis, et al., 2015).

CONCLUSIONS

The results show that false heartwood is a suitable filler material in WPC but the increase in mechanical properties is low. Despite the low increase of mechanical properties, the potential of false heartwood as a reinforcing material is promising. The chemical modification has not had a significant effect on the mechanical properties as unmodified composites show similar results to chemically modified composites. The different fraction size of false heartwood does show substantial differences in results. Larger particles on average show the best properties. Board pressing needs development as voids are present in the material. The micro cracks in the material influence the properties of the material. FTIR shows that chemical modification or particle size does not affect the chemical bonds present in the material. Peaks at 1028 cm-1 and 1104 cm-1 indicate the siloxane chains in the composite are formed. The use of wood industry wastes in the form of false heartwood is possible but the purification of fibres may be necessary for enhanced properties.

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