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

KASE VÄÄRLÜLIPUIDU MÕJU PUITPLASTKOMPOSIITIDE FÜÜSIKALISTELE JA MEHAANILISTELE OMADUSTELE

MASTER THESIS

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AUTHOR’S DECLARATION

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Introduction

Wood plastic composites (WPC) are materials comprised of polymers and wood particles. The material has shown adequate properties compared to traditional materials. The materials properties are dependent on the constituents, their ratios, interfacial adhesion and production technology. Thermoplastics are the main matrix material used in WPCs. Research has shown that wood particle size significantly affects the mechanical properties of composites. Proper adhesion between hydrophobic polymers and hydrophilic wood particles is a necessary process in WPC processing for enhanced properties. Using different production technologies various products can be made, such as board via extrusion, complex parts via injection moulding and foams using blowing agents during production.

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. 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.

WPCs find application in decking boards, siding, garden furniture and hidden constructional elements that are not visible. WPCs have adequate mechanical properties at low weight and offer lower prices when compared to virgin materials as WPCs use recycled materials.

Composites made of false heartwood have not been studied to see what kind of properties the false heartwood would impart to the composite. The aim of this thesis 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.

The thesis consists of literature overview where constituents, coupling methods, processing technologies and applications of WPC are described. The second part of the thesis describes the materials used, chemical modification, test specimen preparation and testing methods. The third part presents the results and analysis of the experiments.

1 Literature overview

1.1 Lignocellulosic fibres used in composites

Composite material is a type of material that consists of two or more different materials. Typically, composites are composed of a matrix or a binder and a reinforcing material. Synergy between the matrix and reinforcing material gives the composite enhanced mechanical and physical properties.

The use of renewable materials has been a growing trend for years and lignocellulosic reinforced composites have found a growing number of applications varying from structural applications to outdoor furniture. Lignocellulosic fillers have a number of advantages such as: low price, renewable nature, availability and improved mechanical properties (table 1). The number of different fibre sources is increasing but the most widely used are: Flax (*Linum usitatissimum)*, Jute (*Corchorus olitorius)*, Hemp *(Cannabis sativa)*, Sisal (*Agave sisalana)* etc. (Faruk, et al., 2012)

Table 1. Mechanical properties of lignocellulosic fibres (Pickering, 2008)

Fibre	Tensile strength, MPa	Tensile modulus, GPa	Flexural strength, MPa	Flexural modulus, GPa
Wood	30.5	8.2	55.3	7.5
Bagasse	27	5.4	47.8	5.1
Coconut	25.9	3.6	46.9	3.6
Pineapple	48.1	7.1	77.6	6.1
Flax	36.1	6.1	58.4	5.8
Hemp	33.5	6.1	61.5	6.2
Jute	34.6	7.2	57.8	6.9
Ramie	43.2	5.4	70.2	5.1
Sisal	34.3	7.1	60	6.6

As the used plant parts are in the form of leaves and stems they require further processing to be compounded with polymers. Fibre dimensions are important in strength properties and also in manufacturing. A high aspect ratio (length/width) is very important in composites as it gives strength to the material in a way that the stress is carried over to the fibres. Wood fibres usually have an aspect ratio of 3:1 – 4:1 and orientation along the flow improves the mechanical properties (Klyosov, 2007). When it comes to production, longer fibres may get tangled and the composite will not have even distribution of fibres.

1.1.1 Wood fibres

Over half of the territory of Estonia is covered by forests. The most popular trees found are Scots pine (*Pinus sylvestris)*, Norway spruce (*Picea abies)* and Silver birch *(Betula Pendula)*. Forestry and timber refining are important sections of industry thus waste wood in the form of sawdust and production waste is available. Commercially produced wood flour fibre length is usually 180-840 µm and the diameter 15-45 µm depending on the species and milling rate (Niska & Sain, 2008).

Wood is often categorized as softwoods and hardwoods which differ in anatomical features. Wood is composed of hollow long tracheids in the case of softwoods and fibres in the case of hardwoods. These cells are firmly placed next to each other in the longitudinal axis along the trunk of the tree and make up the structural component of wood tissue (figure 1). The length of wood fibres is typically 1 mm for hardwoods and 3-8 mm for softwoods and the fibre diameter is in the range of 15-45 µm (Niska & Sain, 2008).

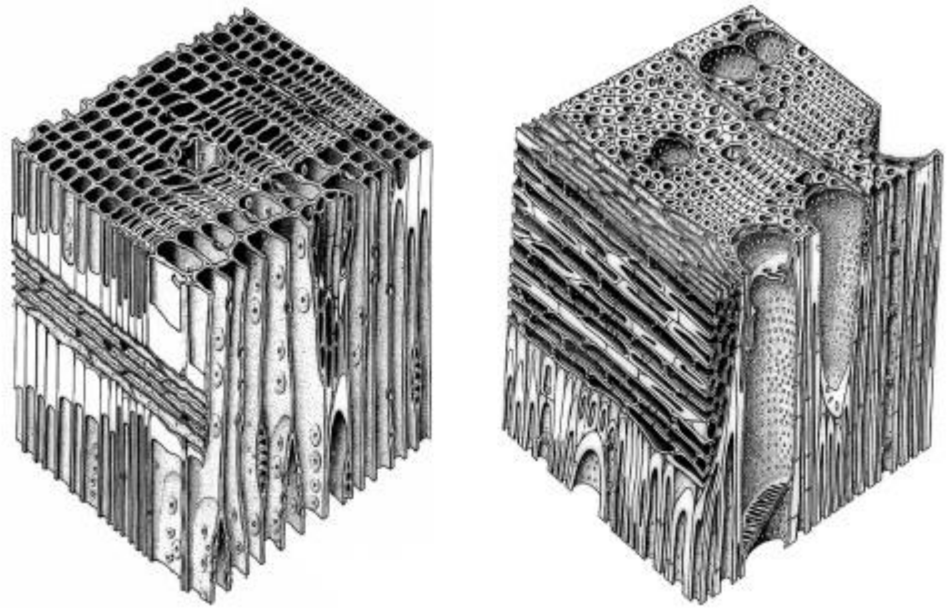

Figure 1. Anatomy of softwood (left) and hardwood (right) (Niska & Sain, 2008)

The three main constituents of woody tissue are cellulose, hemicellulose and lignin but many extractives such as ash, tannins, gums and resins are found in woody tissues (table 2). The composition of wood varies between species but the general difference is that softwoods (29%) contain more lignin than hardwoods (18%) (Klyosov, 2007).

Table 2. Composition of wood (Godavarti, 2005)

Component	**Composition, %**	**Polymeric nature**	**Water affinity**	**Degradation**	**Role**
Cellulose	44 - 50	Linear, crystalline	Hydrophilic	> 200 °C	Strength
Hemicellulose	20 - 25	Branched, amorphous	Hydrophilic	~160 °C	Bind microfibrils, structural reinforcement
Lignin	20 - 30	Amorphous	Hydrophobic	~110 °C	Stiffness
Extractives	0 - 10	Polymeric	Hydrophobic	100 °C - 200 °C	Encrusting

Cellulose (figure 2) is made from thousands of linked 1,4-βanhydroglucose units (Li, 2011). The hydroxyl groups found in 1,4-βanhydroglucose form intramolecular bonds and bonds with other macromolecules. This makes wood fibres hydrophilic. The chemical structure of cellulose is the same in different plant fibres but the degree of polymerization (DP) varies which shows the number of monomers in a macromolecule. Mechanical properties are greatly dependant on the degree of polymerization (DP). (Mohanty, et al., 2005)

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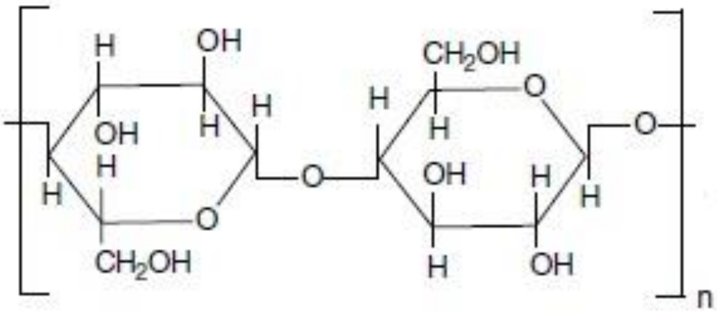

Figure 2. Cellulose structure (Mohanty, et al., 2005)

Hemicellulose has numerous heteropolysaccharide structures and they contain carboxyl, acetyl, and methyl substituted groups (Li, 2011). Hemicellulose is a short polymer which has a DP of only a few hundred and thus it is a low molecular weight polymer. Hemicelluloses contain high numbers of hydroxyl groups thus making them more active in participating in chemical reactions (Hill, 2006). Hemicellulose binds the microfibrils together providing additional structural reinforcement around cellulose regions. It can be relatively unbranched or nonlinear. The type and proportion of hemicellulose is somewhat different in species but tends to follow a similar composition. (Godavarti, 2005) The detailed structure of hemicelluloses have not been specified, rather the ratios of hemicellulose containing sugar have been determined (Li, 2011).

Lignin is an amorphous crosslinked polymer consisting of erratic cluster of differently bonded hydroxy and methoxy substituted aromatic phenyl-propane units. The chemical composition depends on the source. Lignin is biosynthesized from p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (figure 3). Softwood lignin is mainly composed of coniferyl alcohol and hardwood lignin is composed of coniferyl and sinapyl alcohols producing covalent bonds with hemicelluloses acting as an adhesive between cellulose fibres. Lignin is attributed with providing stiffness and durability to wood. Lignin also reduces the accessibility of cellulolytic microbes. (Klyosov, 2007) (Niska & Sain, 2008) (Li, 2011) (Godavarti, 2005)

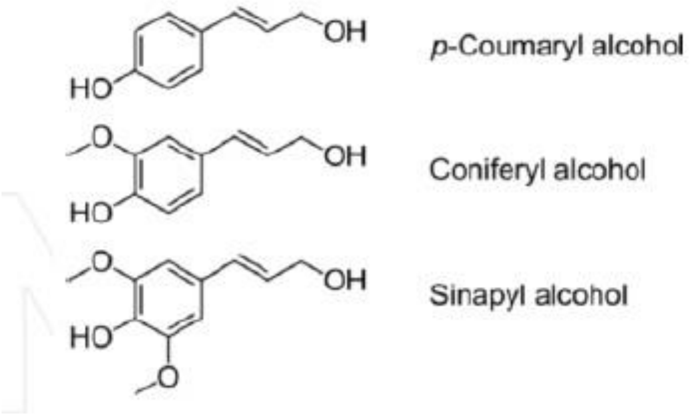

Figure 3. Lignol structures (Li, 2011)

In addition, extractives make up 3-10% of wood which include fats, waxes, proteins and terpens. Most of these substances function in metabolism as energy reserves or as a defence against microbial attack. At small concentrations, extractives can have a big influence on properties such as colour, odor and decay resistance. (Niska & Sain, 2008)

1.2 False heartwood

Heartwood has been defined as the non-living core of the tree free of stored sugars and not containing conducting tracheary elements. Heartwood has also been defined on the basis of colour due to the impregnation of extractives. (Smith, 2015) False heartwood (figure 4 and 5) is a defect that significantly influences the quality of wood. Its formation is caused by the penetration of air into the trunk or wounds on the trunk or broken branches. Oxygen will accelerate the process of parenchyma dying and initiates the formation of heartwood substances. False heartwood reduces the aesthetic property of the wood and it reduces the possibility of applications. False heartwood also reduces the permeability of liquids. It has not been verified if the formation of false heartwood affects the mechanical properties and adhesion ability. (Račko & Cunderlík, 2010)

Figure 4. False heartwood on the right (SW – sapwood, HW – heartwood, DW – discoloured wood) (Smith, 2015) and regular wood cross section on the left

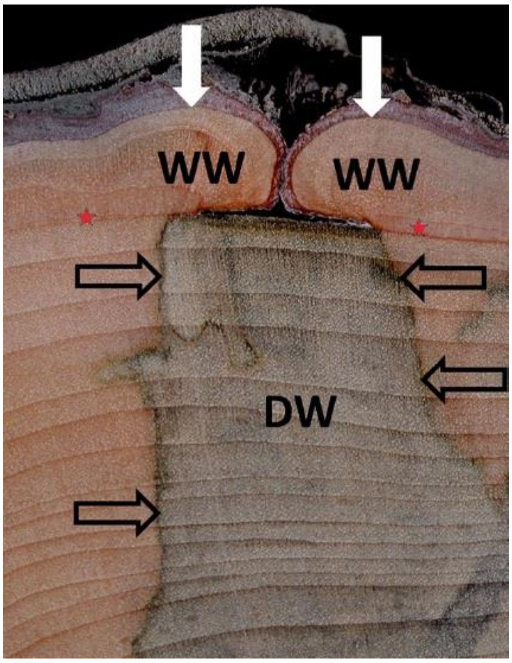

Figure 5. Discoloration due to wounding, vascular cambium (white arrow), woundwood (WW), discoloured wood (DW), reaction zones (black arrows) (Smith, 2015)

There are important differences between normal heartwood that has been formed from internal stimuli associated with aging and the discoloured sapwood induced by wounds or penetration of oxygen into the stem.

Normal heartwood continues to grow in width along with the height of the tree but false heartwood is limited to the dimeter of the tree when it was wounded or the stem was penetrated by oxygen. Regular heartwood has similar colour in the stem cross section and has constant chemical composition. The amount of extractives in false heartwood is higher and it has a darker colour compared to normal heartwood. Normal heartwood and false heartwood differ in water content, ash content, pH and frequency of amorphous deposits. (Pallardy, 2008)

From an economic point of view, it is important that all parts of the tree can be used. In 2001, the region of North Rhine-Westphalia in Germany reported losses of 5,1 M €. Economic return and timber quality could be increased and the number of trees felled would decrease as more quality timber can be used. (Knoke, 2003)

1.2.1 False heartwood formation and properties

There are numerous theories and interpretations when describing discoloration in trees and many of them are hypothetical even today. There are many different names for the phenomenon: affected wood, discoloured wood, stained wood, wetwood, wounded wood, black heart, red heart, black heartwood, false heartwood, pathological heartwood, red heartwood etc. (Johansson & Hjelm, 2013). One of the theories suggests that false heartwood is formed as a reaction of wood cells to the attack of fungi but a later theory suggests that the formation of false heartwood is the effect of a reaction of living wood cells to the penetration of oxygen into the tree trunk. This is a defence mechanism as oxygen acts as a poison to living cells and results in chemical and anatomical changes to prevent further penetration of air into the stem. (Prka, et al., 2009)

The formation of false heartwood favours growth and greater size without the increase of living cells. (Smith, 2015) This may also be attributed to a self defence mechanism. For longer drought periods the tree will increase the heartwood zone to reduce sapwood proportion. The reduced sapwood proportion will require less water.

The reddish-brown discoloration of false heartwood is due to the polymerization and oxidation of phenolic compounds. Broken or dead branches and invasion of microorganisms are common reasons for the presence of discoloration in birch trees (*Betula Pendula*). It can be said that discoloration represents 70% of the total volume of defects found in paper birch. (Belleville, et al., 2011)

There are other factors that affect the formation of false heartwood, for example: natural aging, low temperatures, draught, presence of fungi, genetics, place of growth, altitude, slope, soil quality, mechanical damage, height of crown and air pollution.

In general, false heartwood formation depends on two main factors: dehydrated zones in the tree and penetration of oxygen into the tree by broken branches. The wounds are mainly caused by bark necrosis, wounding of wildlife, breaking of branches caused by wind. Reduction of soil nutrients will cause reduction of wood quality and will increase the occurrence and size of false heartwood. (Račko & Cunderlík, 2012)

1.2.2 False heartwood in wood plastic composites

As compatibility between the wood flour and polymer is a fundamental problem in wood plastic composites it is necessary to chemically modify the wood flour to make it more compatible with the polymer. As false heartwood has many extractives such as fats, waxes, alkaloids, proteins, phenols, sugars, pectin, mucilage, gums, resins, terpenes, starches, glycosides, saponins, and essential oils it is important to purify the wood flour (Pettersen, 1984).

There are many ways to remove extractives from wood. Ether is a nonpolar substance that extracts fats, resins, oils, sterols, and terpenes. Ethanol is more polar and extracts most of the ether-soluble substances and organic materials insoluble in water. Hot water extracts some inorganic salts and low molecular weight polysaccharides including gums and starches. (Pettersen, 1984)

The properties of WPCs made of false heartwood have not been investigated previously. WPCs provide an application for using false heartwood that is rejected in traditional wood industry. It is important to understand the composition and properties of false heartwood to use optimal coupling agents for enhanced adhesion between wood fibres and polymers.

1.3 Polymers used in WPC production

For the production of wood plastic composites synthetic thermoplastics based on crude oil or natural gas are mainly used such as polyethylene (PE) and polypropylene (PP) but also polyvinyl chloride (PVC) and polystyrene (PS). The most widely used thermosets are polyesters, epoxy resins, phenol formaldehyde (PF) and vinyl esters. (Faruk, et al., 2012)

1.3.1 Thermoplastics in WPC production

Thermoplastics are a type of polymer that can soften when heated and solidify when cooled. They retain their properties after multiple melt cycles but the length of the polymer chain and thus its molecular weight decrease (Larson, 2015). In table 3 physical properties of common thermoplastics are shown. Wood particles tend to start degrading at temperatures of 190-200 °C thus polymers with melting temperatures under 200 °C must be used otherwise the degradation of wood fibres may lead to reduction of mechanical properties, odour or discoloration in composites (Poletto, et al., 2012). Lignin and hemicelluloses are more sensitive to temperature as cellulose decomposes at temperatures exceeding 240 °C. (Klyosov, 2007)

Table 3. Physical properties of common thermoplastics (Akdogan & Vanli, 2017)

Polymer	**Melting temperature (T_m °C)**	**Glass transition temperature (T_g °C)**	**Density (g/cm^3)**
PE (low density)	98-115	-125	0,91 – 0,92
PE (high density)	120-137	-130 to -100	0,94 – 0,96
PP	160-173	-20 to 0	0,90 – 0,91
PVC	100-260	80-87	1,16 – 1,38

1.3.2 Biopolymers in WPC production

Environmental thinking has brought up the use of biopolymers in WPC production in the place of polyolefins. Polylactic acid (PLA) which can be made from lactic acid from fermentable sugars and polyhydroxyalkanoate (PHA) which can be attained from vegetable oils and thermoplastic starch (TPS) which can be derived from plants or vegetables (potato, wheat, corn, etc.) are all composed of renewable resources. The comparison of petrolbased and biobased polymers can be seen in table 4.

Table 4. Comparison of petrolbased and biobased polymers (Lackner, 2015)

	Pros	**Cons**
Conventional plastics	low cost	based on petrochemicals
	good technical properties	difficult to recycle
	easy processability	mostly not biodegradable
	can save energy and resources compared with traditional materials, depending on application	uncontrolled combustion can release toxic substances
	thermal recycling possible	ecotoxicity, particularly microplastics in the marine environment
		partly toxic raw materials and additives
Bioplastics	(partly biodegradable	costly
	(partly) based on natural feedstock, hence reducing the emission of CHG and the dependence on crude oil	(partly) use of genetically modified organisms
	interesting properties	use of land, fertilizer, and pesticides for crops, potential food competition
	generally, standard manufacturing processes and plants can be used for biobased feedstock and standard processing machines can be used for biobased plastics	narrow processing window (lower melting temperature)
		brittleness
		thermal degradation

PLA (figure 6) has considerable advantages - its renewable nature, recyclability, compostability, adequate strength and stiffness. On the other hand, this material possesses some drawback as well. It is quite sensitive to moisture, it ages fast, it has poor impact resistance and it is rather expensive. To overcome these problems numerous processes are used, for example: plasticization, copolymerization, blending or by production of composites. PLA has been named as the most promising commercial biopolymer on the market. It is synthesized by ring-opening polymerization of lactides which are derived from starch fermentation. (Imre, et al., 2014) (Zhu, et al., 2012)

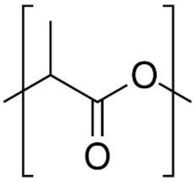

Figure 6. Structure of polylactic acid (PLA) monomer (Biomedicals, 2017)

PHAs (figure 7) are biodegradable polyesters which are produced by bacterial fermentation from glucose. These polymers are made from saturated or unsaturated hydroxyalkanoic acids. Branched or unbranched 3-hydroxyalkanoic acids or substituted 4 or 5-hydroxyalkonoic acids are the main monomers making up PHAs. The diversity of monomers, possibility of chemical and physical modification of the microstructure create numerous biopolymers with different properties. (Endres & Siebert-Raths, 2011)

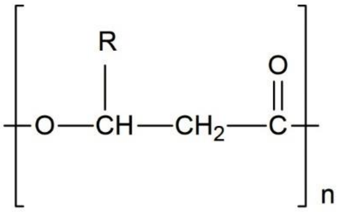

Figure 7. Structure of polyhydroxyalkanoate (PHA) monomer (Endres & Siebert-Raths, 2011)

Polyhydroxy butyric acid (PHB) is a linear isotactic highly crystalline polymer (figure 8). It is quite brittle and has similar melting and degrading temperatures which make production problematic. Secondary crystallisation and loss of plasticizer are to blame for the decrease of mechanical properties of the material. These disadvantages however can be overcome by polymerization with comonomers. (Endres & Siebert-Raths, 2011)

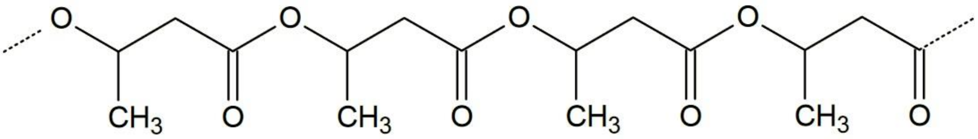

Figure 8. Structure of polyhydroxy butyric acid (PHB) (Endres & Siebert-Raths, 2011)

TPS (figure 9) is made from starch granules which are processed in water and with thermal and mechanical forces with plasticizers that do not evaporate during processing at high temperatures. The main advantages of TPS are: renewability, low cost and availability. On the other hand, starch contains hydroxyl groups which give it hydrophilic properties. Both constituents of starch, amylose and amylopectin react with water as amylose dissolves in water and amylopectin swells in water thus starch loses its structure, integrity and mechanical properties when exposed to aqueous environments. From a processing point of view, starch cannot be manufactured using traditional plastic production machinery due to the fact that starch in its fundamental state is not thermoplastic. During heating pyrolysis occurs before the crystalline melting point of starch is reached. (Nafchi, et al., 2013) Chemical modification and the use of plasticizers can help overcome these problems and starch can be processed by extrusion, injection moulding or other methods. Both stiffness and strength are increased in TPS-wood composites with increasing fibre length and content. Strong interfacial adhesion has been verified with scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and changing glass transition temperature (Müller, et al., 2014)

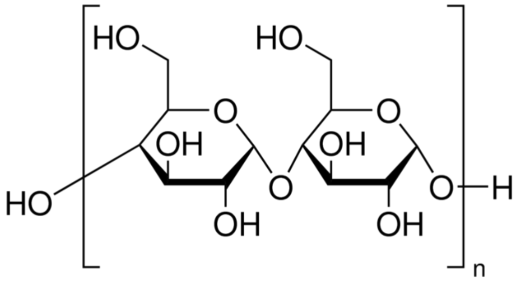

Figure 9. Starch structure (Biomedicals, 2017)

1.4 Coupling agents

Composites reinforced with wood fibres possess a problem in interfacial adhesion as polyolefin based polymers are hydrophobic and wood fibres are hydrophilic. Adhesion forces can be divided into primary and secondary forces. Primary forces are generated from chemical bonding by covalent, ionic of metallic bonds and provide strong adhesion. Secondary forces are physical attraction forces such as hydrogen bonds. The poor adhesion makes for inadequate stress transfer and in turn poor mechanical properties and increased water adsorption. To overcome this handicap coupling agents are used. Coupling agents can be added to the fibre surface or by grafting functional groups to the polymer or high energy surface treatments which impart oxygen donating groups (Kim & Pal, 2011) (John & Anandjiwala, 2008). Coupling agents can be divided into surface active agents and bonding agents. Coupling agents bind polymers and wood fibres by covalent bonding or strong secondary interactions such as hydrogen bonds (Kim

& Pal, 2011). Coupling agents can be divided into chemical, physical and enzymatic by their nature.

1.4.1 Physical modification

Physical methods do not alter the chemical composition of the wood particles but rather the structure properties which influence the mechanical bonding with the polymer. Physical modifications improve oxidation and surface activity. Physical modifications such as thermo-treatment, calendaring, corona, plasma and electron beam irradiation are most common and find practice. (Kim & Pal, 2011)

Corona and plasma modification purify the surface of wood fibres of impurities and increase the surface energy for enhanced adhesion with polymers. Different gas composition used for modification can impart reactive free groups or even surface cross linking. These modifications also make fibres more porous to enhance mechanical interlocking (figure 6). Another benefit of plasma treatment is short processing time as fibres are treated for 1-3 minutes, longer processing results in mechanical fibre degradation. (Kim & Pal, 2011) High energy electron and γ-radiation are an option for generating free radicals.

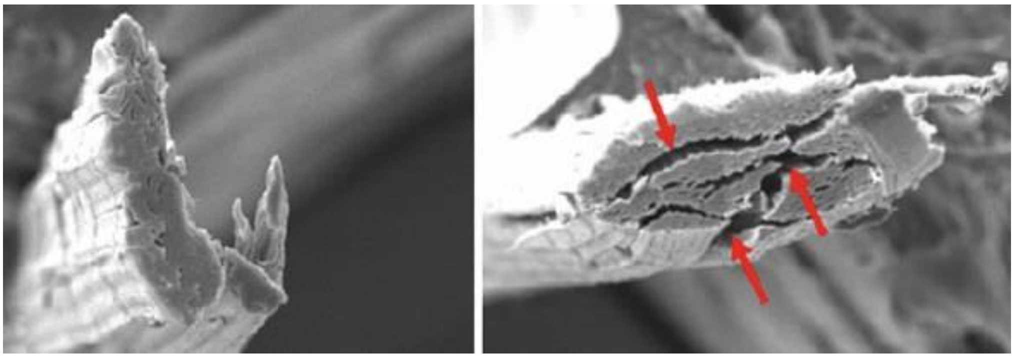

Figure 10. Before (left) and after (right) effect of plasma treatment (Kim & Pal, 2011)

1.4.2 Chemical modification

Chemical modification activates hydroxyl groups or results in the formation of new functional groups on the fibres. Alkaline treatment or mercerization is one of the oldest and most used chemical modifications known. Alkali treatment is very effective and efficient in removing surface impurities, lignin, waxes and oils from the fibre surface. In addition, alkali treatment removes hemicellulose from the fibre surface reducing the density in the interfibrillar region and provides a rougher surface by swelling which enhances mechanical interlocking. (Kim & Pal, 2011) The type of alkali used (KOH, NaOH, LiOH) will influence the degree of swelling.

Sodium ions can expand the smallest of pores and penetrate into them. The hydroxyl groups are converted into ONa groups and the molecules expand (figure 7). (Farsi, 2010) (John & Anandjiwala, 2008)

$$\mathrm{Fiber} - \mathrm{OH} + \mathrm{NaOH} \rightarrow \mathrm{Fiber} - \mathrm{O^{-}Na^{+}} + \mathrm{H_2O}$$

Figure 11. NaOH reaction with wood fibres

Acetylation makes the surface of the fibres more hydrophobic. The hydroxyl groups from the fibres in hemicellulose and lignin react with acetyl groups which will make the fibre more hydrophobic (figure 8). This will make the fibres more resistant to swelling in water. (John & Anandjiwala, 2008)

$$\begin{aligned}&\mathrm{Fiber} - \mathrm{OH} + \mathrm{CH_3CO} - \mathrm{O} - \mathrm{OC} - \mathrm{CH_3}\\ &\qquad \xrightarrow[\mathrm{conc.H_2SO_4}]{\mathrm{CH_3COOH}} \mathrm{Fiber} - \mathrm{O} - \mathrm{CO} - \mathrm{CH_3} + \mathrm{CH_3COOH}\end{aligned}$$

Figure 12. Acetylation of wood fibres

The addition of maleic anhydride in polypropylene based composites has shown increased fibre dispersion and enhanced mechanical properties. The reaction of hydroxyl groups of wood fibres and maleic anhydride is shown in figure 8. (Ndiaye, et al., 2011) Covalent bond formation by esterification and hydrogen bonding takes place across the interface providing adhesion. The molecular weight and amount of maleic anhydride added strongly affects the molecular entanglement and number of bonds formed. (Godavarti, 2005)

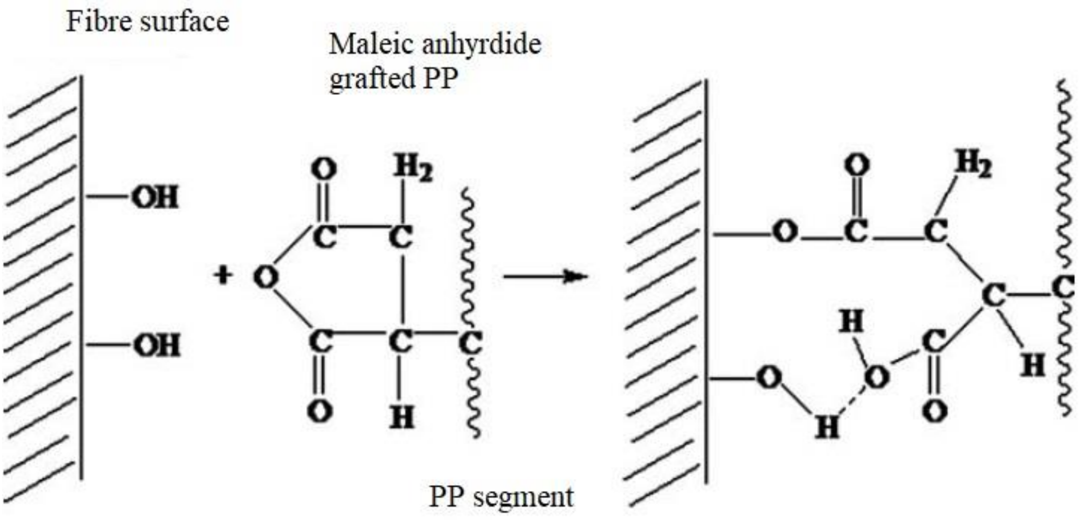

Figure 13. Reaction of MAPP with hydroxyl groups of wood flour (Ndiaye, et al., 2011)

Silanes are hydrophilic compounds with different end groups attached to silicon atom. Silanes create bonds with the matrix on one end and with the wood fibres on the other (figure x). Silane bonding is affected by hydrolysis time, organofunctionality, temperature and pH. (John & Anandjiwala, 2008) There are many functional groups available in silanes but the most commonly used are vinyl silanes, epoxy silanes, amino silanes and alkyl silanes. The wide range of available silanes makes the use of different polymers possible as it is advised to use silanes that can bond with reactive groups of polymers but in the case of thermoplastics this is made more difficult as there are no reactive groups present. (Klyosov, 2007) As a result of fibre drying a condensation reaction takes place between silanol and hydroxyl groups forming a polysiloxane layer on the fibres (Franco & Valadez-González, 2005).

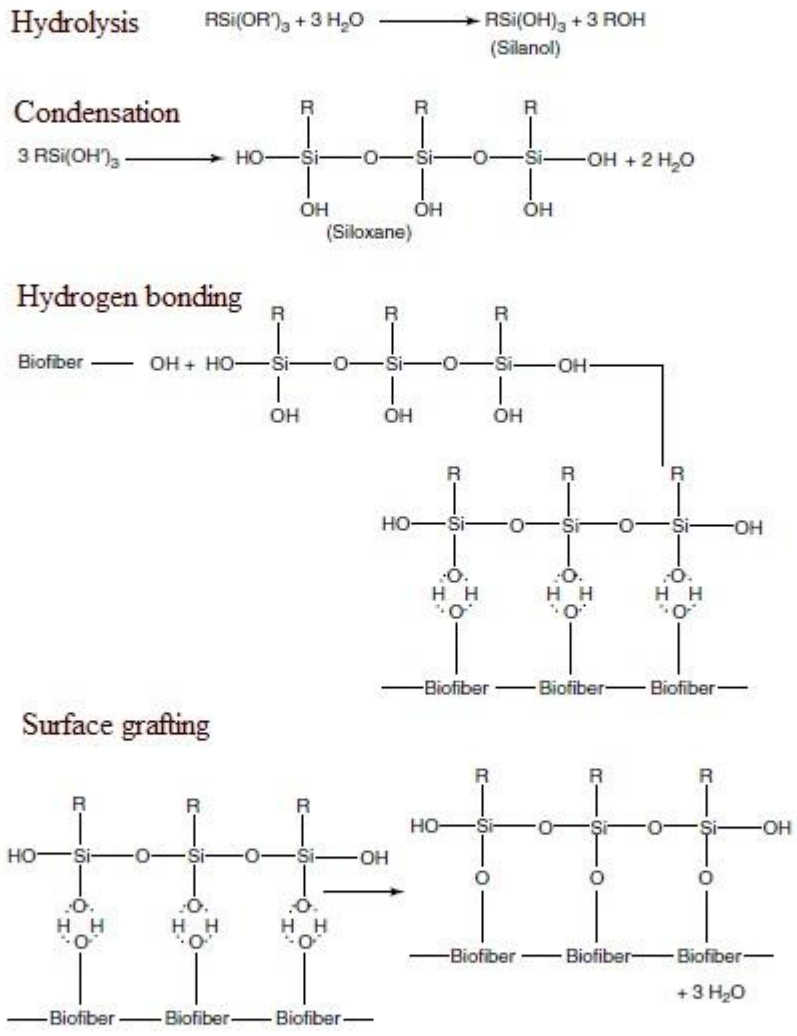

Figure 14. Silane treatment of wood fibres (Franco & Valadez-González, 2005)

The use of glycerine for modification has allowed the production of highly filled composites with fibre loading up to 95% by weight without thermal degradation of fibres. Presently, in commercial applications the amount of filler used is limited to 60%. (Sanadi & Caulfield, 2008) Glycerine, an important by-product of biodiesel production has shown an accelerating role in degradation of lignin and hemicellulose in thermally treated wood. (Shupin, et al., 2014)

1.4.3 Enzymatic modification

In addition to physical and chemical modification, enzymes are used for targeting specific functional groups or components of fibres. Enzymes are biological catalysts that convert the substrates, in this case wood fibres into products, in this case modified fibres. In addition to being very efficient in reactions they are extremely selective (Murray, et al., 2003). Many enzymes have been identified that can react with cellulose, hemicelluloses or lignin without affecting other components. Enzymatic modifications do not cause as much damage to the fibres and are more environmentally friendly than chemical or physical modifications. (Kim & Pal, 2011) Laccase is a well-known enzyme that specifically reacts with lignin in cellulose fibre hydrolysis and hemicellulase (Xylanase) is used for reaction with hemicellulose (Nasir, et al., 2015). The activity of enzymes depends on temperature, pH and concentration of substrate. The disadvantages of enzymatic modification are high cost, long reaction time and possible excessive degradation as the rate of modification is affected by characteristics of wood species, age and region. As a result of excessive degradation, the cell wall of fibres is reduced. (Kim & Pal, 2011)

1.5 Production technologies

In production of WPCs injection moulding, extrusion and compression moulding are used but other technologies like 3D printing are also possible. It is important to distribute and encapsulate the wood fibres evenly in the polymer matrix.

Compounding is needed for the adequate distribution of fibres and ease of further processing. As a result of compounding the wood fibres and polymer are produced into pellets using different configurational and rotational direction screws (figure 15) or by using thermokinetic mixing. The advantages of twin-screw compounders compared to single-screw compounders are high throughput and simplicity but the process can result in the degradation of fibres when processing temperatures are high and fibres stay in the screw for too long thus processing temperature and screw speed need to be monitored. Fibre loading in compounding is also limited because higher concentrations may cause the screw to clog. Thermokinetic mixing provides low processing time as high temperatures are reached in 30 seconds, high dispersion rate of fibres and possibility of high filler loads. This method does not require previous fibre drying as higher moisture content in fibres causes the propagation of cracks in the composite (Bledzki & Gassan, 1999).

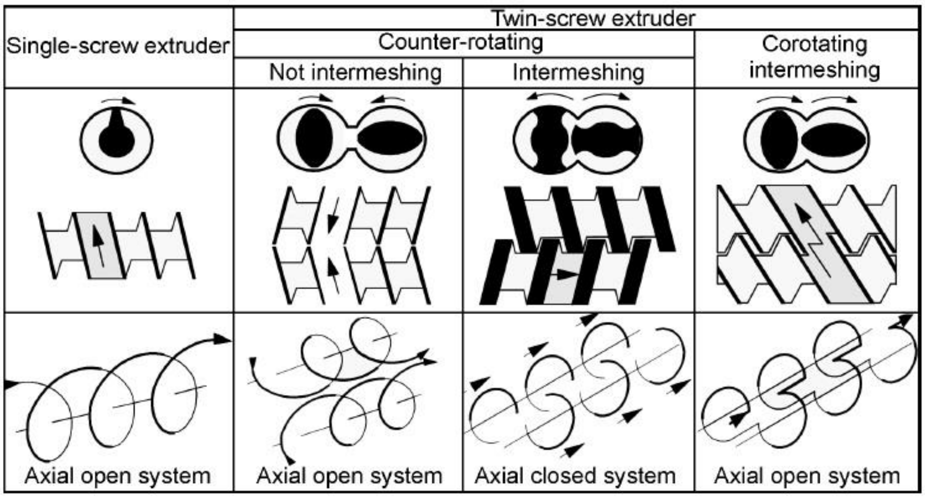

Figure 15. Compounding systems (Niska & Sain, 2008)

Extrusion is mainly used for continuous profile and sheet formation in various designs and they can be classified into hollow and solid profiles. The compounded material is pressed through a die and cooled (figure 16). This method is continuous and requires the cutting and stacking of extruded composite. (Bledzki, et al., 2002) For multilayer materials, conical twin-screw extruders are used where rotors in the extruders form multiple layers. This is useful for producing materials that have different composition in different layers. This enables for higher filler loads in the middle layer and lower filler loads in the outer layer for economic benefit.

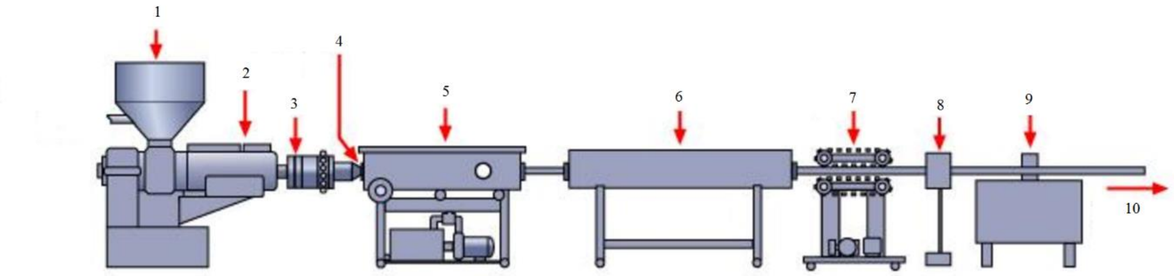

Figure 16. Extrusion process, 1 – Hopper (Pellet Material Supply), 2 – Extruder, 3 – Die, 4 – Sizing Plate or Sleeve, 5 – Vacuum-Sizing Chamber, 6 – Water Cooling Bath, 7 – Pullout Assembly, 8 – Reheat Station, 9 – Cutting Unit, 10 – To Handling Operations (Indibay, 2015)

Injection moulding technique is used for products with complex geometry (figure 17). The advantages of injection moulding are short cycle times thus high production volume and minimal shrinkage and warping and no requirement of finishing. (Faruk, et al., 2012) Injection moulding has numerous parameters. The temperatures of melt zones and mould, injection pressure and cooling time.

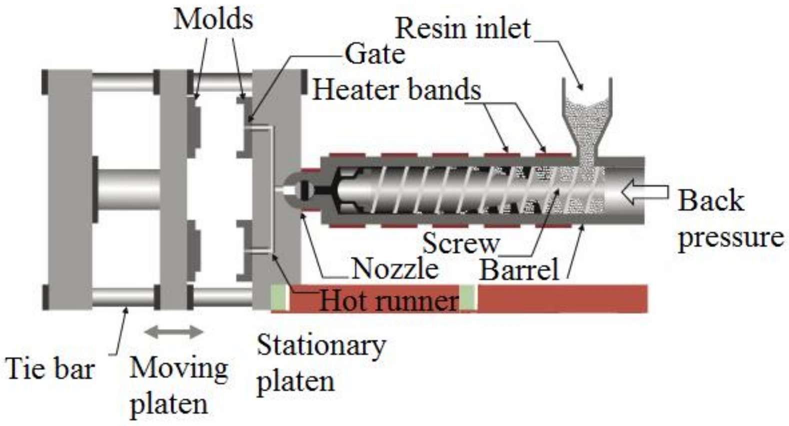

Figure 17. Injection moulding process (Lim, et al., 2008)

Compression moulding is used for products of simple geometry (figure 18). The productivity of this process is rather high due to short cycle time. This method enables the use of long fibres and high filler loads. The disadvantage of compression moulding is that the formed sheets need to be cut into shape. (Bledzki, et al., 2002)

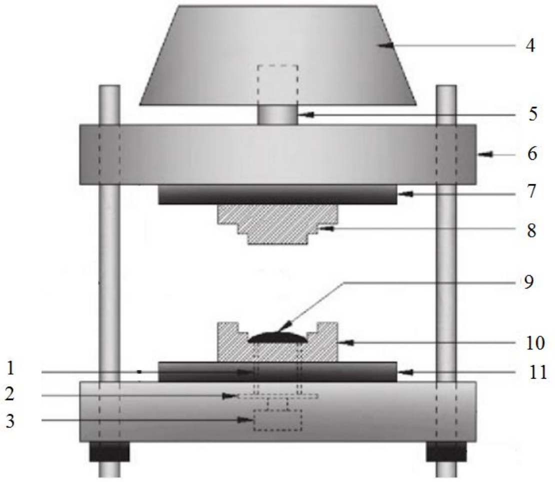

Figure 18. Compression moulding technology, 1 - Ejector pins, 2 - Ejector plate, 3 - Ejector actuator, 4 - Hydraulic unit, 5 - Piston, 6 - Upper moving plate, 7 - Upper heated platen, 8 - Upper mould half, 9 - Charge resin, 10 - Lower mold half, 11 - Lower heated platen (Tatara, 2016)

Polymeric foams are materials where voids consisting of gas are surrounded by a polymer. Blowing agents are substances that decompose at processing temperatures forming CO_2 or N_2 or are injected into the system as a liquid or gas (figure 19). There are many ways to classify foams, one way is to classify foams as reprocessable thermoplastic foams and unprocessable thermosetting foams. Another way to classify foams is by the size of foam cells. They can be divided into macrocellular foams (100 µm), microcellular foams (1-100 µm), ultra microcellular foams (0,1-1 µm) and nanocellular foams (< 0,1 µm). By selecting foaming agents the formation of closed cells or open cells can be controlled. In closed cell foams each cell is surrounded by polymer and cells are separated. In open cell foams cells are connected to each other. (Kim & Pal, 2011)

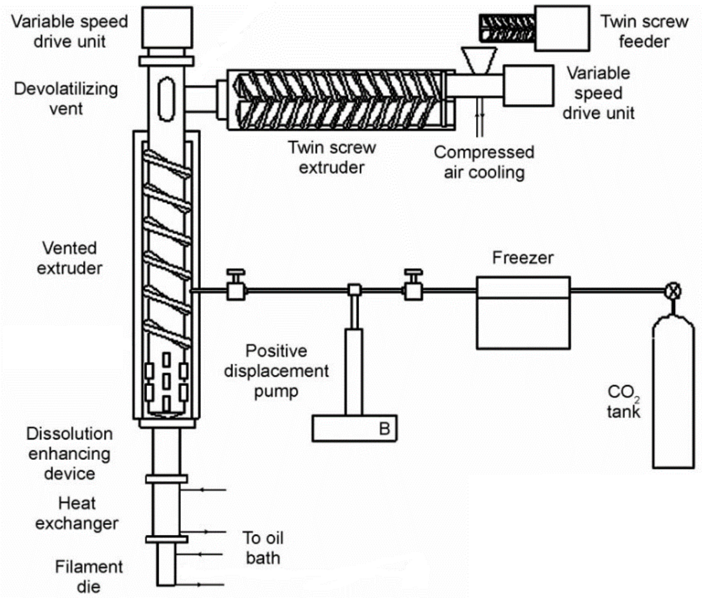

Figure 19. Foam processing (Niska & Sain, 2008)

1.6 Properties and uses

Wood fibres are suitable as a filler material in composites because they offer high strength, stiffness and low density and good biological resistance. Due to the hydrophilic nature of wood fibres, moisture adsorption in composites may be an issue. Coupling agents and adequate fibre coverage however can overcome this issue. The properties of WPCs have been compared with an ideal material in figure 11. WPCs offer adequate mechanical properties at low density, relatively easy processability, low cost, environmental friendliness, good resistance to biological attack and decent resistance to ultraviolet light (UV). The main disadvantages are poor resistance to moisture, and large-scale modification of wood fibres is complex. The main uses of WPCs are outdoor applications as decking boards, siding boards, fences, constructional elements, garden furniture, musical instruments, and different hidden interior elements.

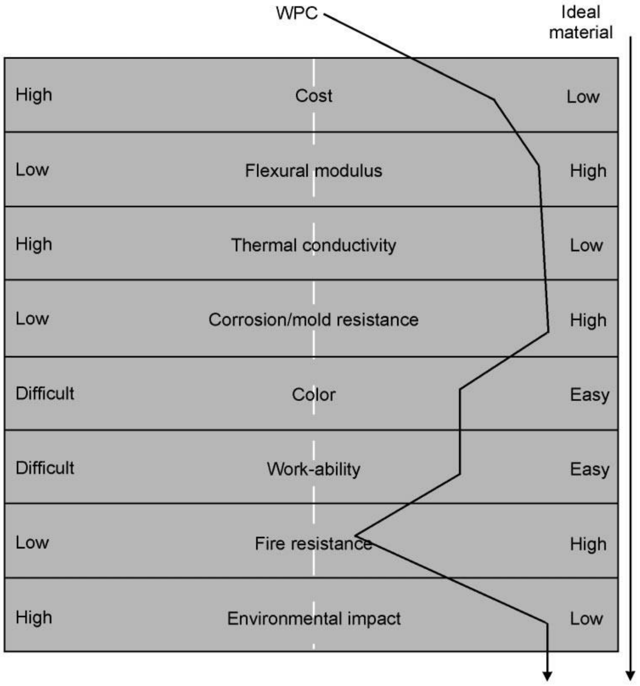

Figure 20. Properties of WPC (Niska & Sain, 2008)

2 Materials and methods

2.1 Materials

2.1.1 Polymer

Borealis polypropylene (PP) heterophasic copolymer BC245MO by Borealis Polymer Oy was used as a matrix material for the production of composites. This polymer is quite rigid with high impact strength characteristics even at low temperatures and resistance to creep. It exhibits great thermal stability and good process ability and it is mainly used in injection moulding processing. The mechanical and physical properties of the PP are shown in table 5.

Table 5. Mechanical and physical properties of Borealis PP BC245MO

Property	**Conditions**	**Value**	**Unit**	**Test method**
Melt flow index	230℃/ 2,16 kg	3,5	g/10 min	ISO 1133
Density	-	905	kg/m^3	ISO 1183
Impact strength	+23 ℃ / - 20 ℃	15 / 6,5	kJ/m^2	ISO 179
Flexural modulus	-	1250	MPa	ISO 178
Tensile modulus	50 mm/min	1350	MPa	ISO 527-2
Tensile strain at yield	50 mm/min	6	%	ISO 527-2

2.1.2 Filler material

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. As the false heartwood veneers had to be milled the veneer sheets had to be cut into smaller pieces and then milled. The false heartwood veneers were milled in the Tallinn University of Technology, Department of Mechanical and Industrial Engineering. The false heartwood was milled using disintegrator DSL-115 and DSA3 (figure 21). DS series disintegrator mills are used for agricultural applications for milling of different materials and processing, such as: beets, grains, potatoes, limestone, branches, etc. The processing of the material is accomplished by collision, unrestricted impact at certain velocity. Material refining takes place as a result of fracturing the treated material (Tümanok & P, 1999). In addition to mechanical disintegration steam explosion is also used as the material is treated with saturated steam at pressure up to 40 atmospheres. Within a few minutes the material is decompressed in less than a second to atmospheric pressure. (Kukle, et al., 2011) Besides the reduction in particle seize steam explosion removes some amount of lignin, waxes and oils (Kim & Pal, 2011).

Three different fractions are used, 0,04 mm, up to 1 mm, and 1-2 mm to see if this will affect the properties of the material. The smaller fraction size will not wear the machinery compared to larger fraction sizes. Smaller fraction sizes will also be less likely to be tangled together (Migneault, et al., 2008).

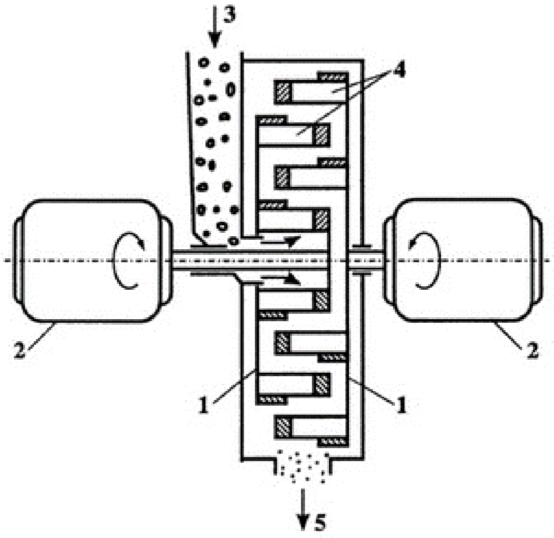

Figure 21. Disintegrator system: 1 – rotors; 2 – electric drives; 3 – material supply; 4 – grinding elements; 5 - output (Tümanok & P, 1999)

Data gathered from the milling (figures 22 and 23) shows that false heartwood needs more energy to be milled down to smaller fractions when comparing to normal birch. This can be attributed to the extractives found in the false heartwood. Sieve analysis (table 6, figure 23) show how much of the wood particles flow through the sieves at what percentage of weight. Feed is the fraction size of the material before milling. The results of the sieve analysis are in accordance with the desired average particle size.

Table 6. Results of sieve analysis

Sieves, mm	11,2	5,6	2,8	1,4	0,71	0,35	0,18	0,09	0,045	0,02
FHW 2,4kWh/t (% mass)	0.0	6,7	23,2	38.0	18,6	7,7	3,7	1,1	0,7	0,3
FHW 4,8kWh/t (%mass)	0.0	0,4	7,5	32,1	25,9	17.0	10,8	3,7	1,8	0,8
FHW 7,2kWh/t (% mass)	0.0	0.0	3.0	21,7	28,7	23,5	15,2	4,4	2,2	1,3

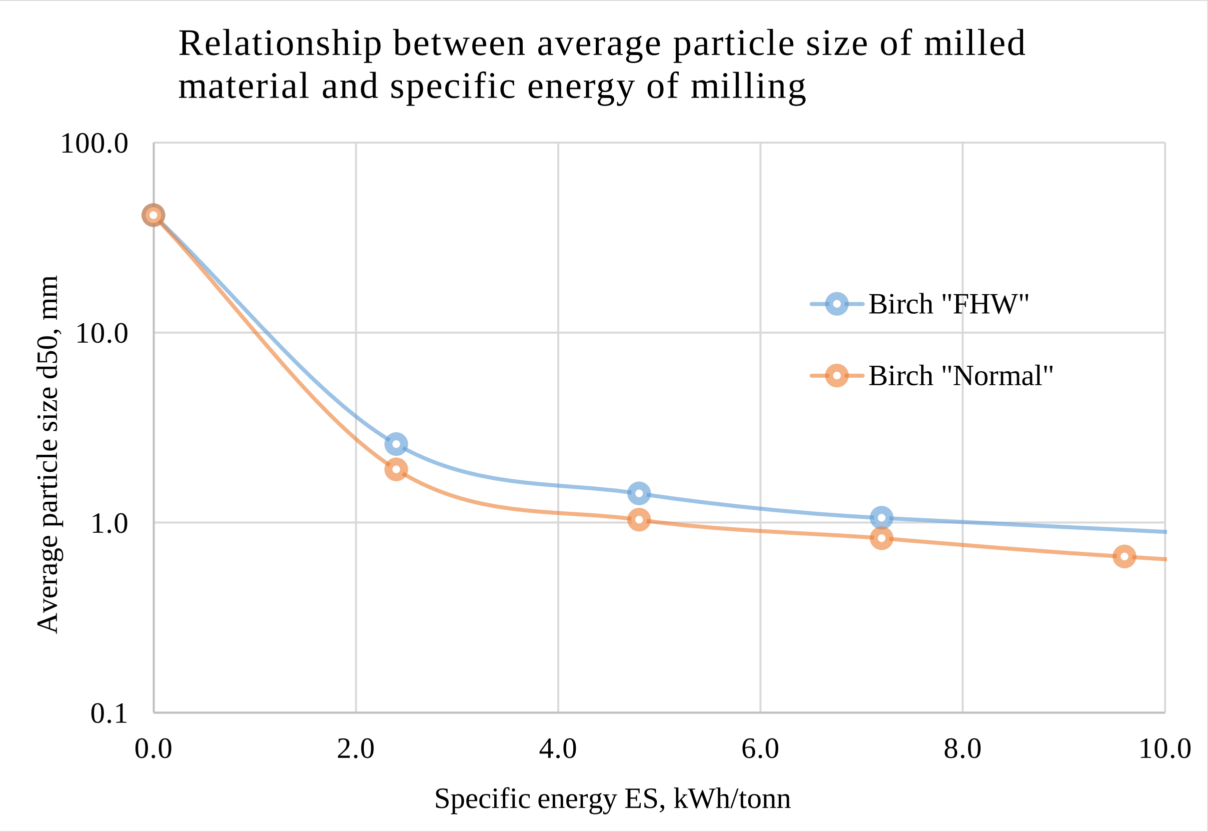

Figure 22. Relationship between average particle size of milled material and specific energy of milling

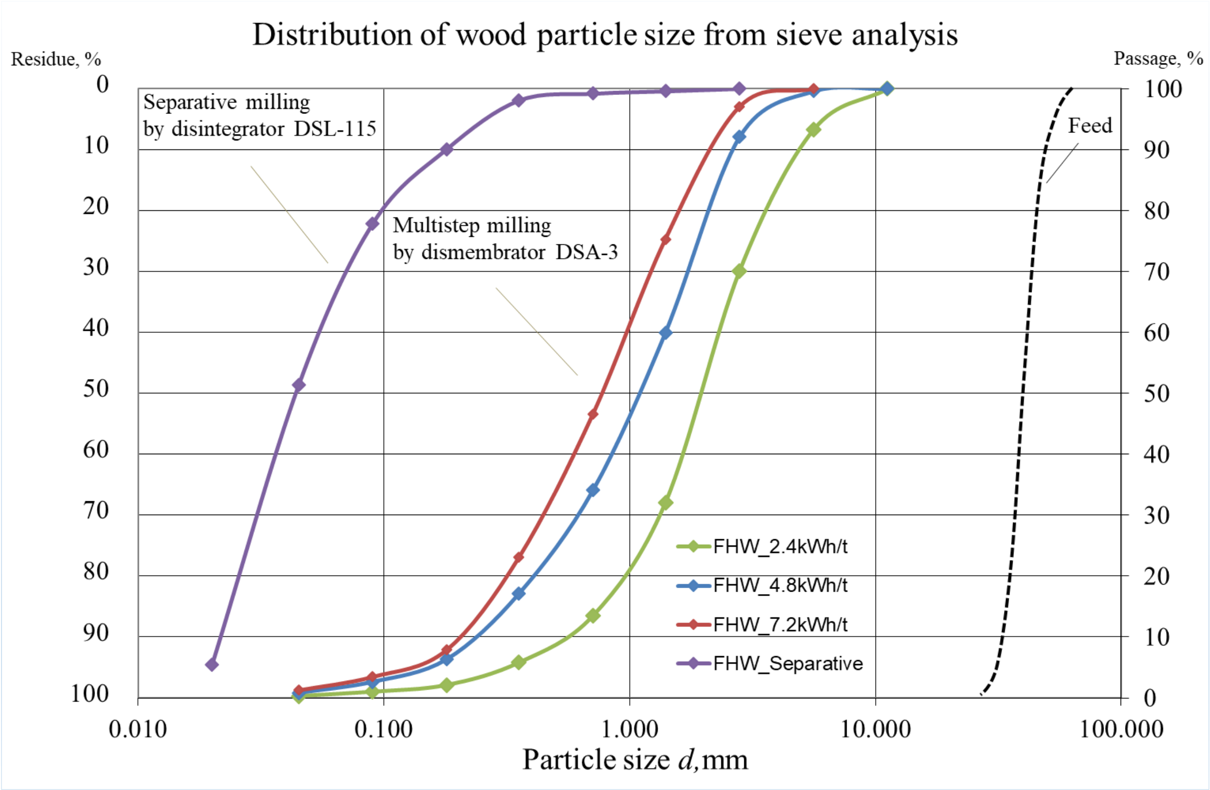

Figure 23. Distribution of wood particle size from sieve analysis

2.2 Manufacturing of wood plastic composites

Production of wood plastic composite boards were prepared in the Department of Materials and Environmental Technology, Laboratory of Polymers and Textile Technology in TTÜ. The material will vary in composition as can be seen in table 7.

For the purification of wood flour a strong base, technical grade (95% pure) Sigma-Aldrich NaOH (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 silane (3-aminopropyl-triethoxysilane) APTES (CAS number 919-30-2) was used. The molecular weight of the substance is M_w= 221,37 g/mol and the boiling point at atmospheric pressure is 217 °C. The modification of wood fibres was carried out based on previous research (Gwon, et al., 2010) (Kim, et al., 2010) (Farsi, 2010) (Ichazo, et al., 2001).

Table 7. 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

2.2.1 Requirements for test specimens

The composite boards need to be solid boards with a thickness of 4 mm so that test specimens with dimensions of 150x20x4 mm can be easily procured from larger solid boards. It is also important that the test specimens are dimensionally and visually even. According to EN ISO 527-2 all the surfaces of the test specimens need to perpendicular, test specimens cannot be bent or twisted and surfaces must be free of flaws, scratches and impurities.

2.2.2 Preparation of wood-polymer composites

As the production process of the composite has potential losses the exact amount of raw material is theoretical. In table 8 the calculations for material requirements is shown. In every mixture, the amount of wood flour is 100 g so the amount of wood flour with each fraction size is 300 g. The total amount of polypropylene is 1665 g, the amount of NaOH required is 60 g and APTES is 15 g. Added to these materials ethanol and water is also used in processing. The amount of ethanol and water is directly related to how wet the process able mix is required to be. The needed amount of ethanol is 3 litres and acetic acid is required for the pH of the wood flour to be 4-5 pH. Hydrolysis and condensation is dependent on the pH and the rate of hydrolysis needs to be greater than the rate of condensation (Arkles, 2014).

Table 8. Material requirements for composites

Mixture nr.	Wood particle size, mm	Wood particle content, g	NaOH content, g	APTES content, g	Polypropylene content, g
Mixture 1	0.04	100	-	-	185
Mixture 2	1	100	-	-	185
Mixture 3	1 - 2	100	-	-	185
Mixture 4	0.04	100	10	-	185
Mixture 5	1	100	10	-	185
Mixture 6	1-2	100	10	-	185
Mixture 7	0.04	100	10	5	185
Mixture 8	1	100	10	5	185
Mixture 9	1-2	100	10	5	185

The preparation of the composites starts with the modification of wood flour. Wood flour is weighed and NaOH aqueous solution is made. NaOH is taken 5% of the weight of wood flour. After the NaOH aqueous solution is mixed with the wood flour and washed with water the blend is placed into a kiln at 40 °C for drying.

For adding silane as a coupling agent a solution of ethanol and water is made with volume ratio of 6:4. Silane is taken 5% of the weight of the wood flour. After the silane, water and ethanol mixture is made the pH of the solution is measured with pH indicator paper. Acetic acid is added until the pH of the solution is 4-5 as desired. (Kim, 2010) After the wood flour is mixed with the silane solution it is placed into a kiln for drying at 40 °C.

The dry wood flour and PP were compounded with a twin co-rotating Brabender Plast-Corder PLE651 compounder seen in figure 24. The mixtures were processed at temperatures 190℃, 190℃, 190℃ and 190℃ and screw speed was 60-70 RPM (rotations per minute). The compounded composite was collected in small batches and milled using Retsch SM 100.

Figure 24. Brabender Plast-Corder PLE651 (left) Hot pressing machine (right)

The boards were pressed using a manual hydraulic hot press (figure 24). The granulated material (100 g) was weighed and placed into the mould as can be seen in figure 6. The mould consisted of two steel sheets and a 4 mm thick steel frame with a 150x150 mm cutout. The 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. For aiding in the removal of the composite boards from the mould a silicone free release agent OKS 1511 was used. It was evenly applied from a distance of 20 – 30 cm on to the surface of steel plates that come into contact with the composite and the mould itself as it makes it easy to remove the composite boards without leaving behind residues. After pressing the weight of the boards was determined. The average weight of the boards was 80 g thus the processing waste is approximately 20%.

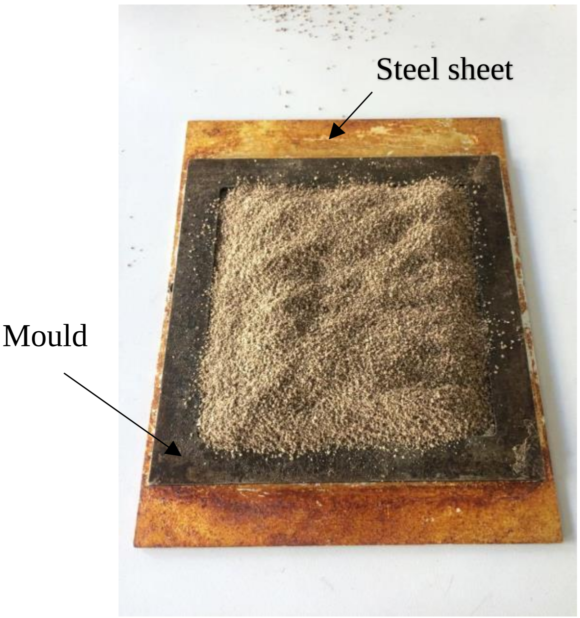

Figure 25. Composite board mould

2.2.3 Preparation of test specimen

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. The tensile test specimen was created using AutoCAD (figure 27) and the program for the milling was created in WoodWOP. The test specimens were milled with a WEEKE Optimat BHC 280 three-axis CNC machining centre with ball screw movement in Y and Z axes and rack & pinion movement in X axis. For milling the tensile test specimens, a Rinaldi HW P1A-04-015 milling bit was used (figure 26). The milling bit is used for cutting hard plastics such as plexiglass. The cutter has a 4 mm cutter diameter and has a single cutter face for better chip ejection. When using traditional cutter bits, the plastic chips may cluster and start melting by friction forces. In order to keep the composite board from shifting a jig had to be made (figure 28). The board was set on a 19 mm thick medium density fibreboard (MDF) base plate and it was secured with double sided adhesive tape and plywood slats with screws.

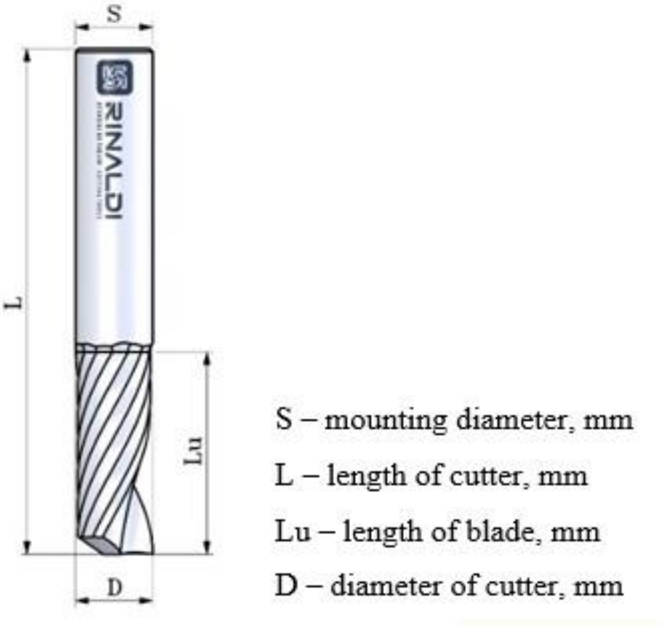

Figure 26. Cutter bit for milling of composites

Figure 27. Test specimen visualisation

Figure 28. Jig for tensile specimen milling

2.3 Experiments

For understanding the properties of the composite different physical and mechanical experiments were chosen. The experiments are conducted in the Tallinn University of Technology, Department of Materials and Environmental Technology. Mechanical properties were analysed using bending strength, impact strength and tensile strength test. Physical properties were analysed using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and density measurement by immersion. In table 9 the amount of test specimen needed is shown. There are 9 different mixtures of composites. The needed amount of test specimens per mixture is 16.

Table 9. Experiments and quantities of test specimen needed

Experiment	Standard	Quantity of test specimens required from each composite mix
Bending strength	EN ISO 178	5
Impact strength	EN ISO 179-1	5
Tensile strength	EN ISO 527-2	5
FTIR	Laboratory method	1
DSC	Laboratory method	1
Density measurement by immersion	EN ISO 1183-1	1

2.3.1 Bending strength test

The bending strength was conducted at room temperature (23º C) according to EN ISO 178 using Instron 5866 tensile tester. Before testing the thickness and width of the test specimens are measured. The span length is 60 mm and testing speed is set at 20 mm/min (figure 29). The test specimens are placed between the supports so that the pressure is applied to the centre of the test specimen. Five samples from each mixture are tested. Bending strength is calculated using formula 1 and the module of elasticity is calculated using formulas 2 and 3.

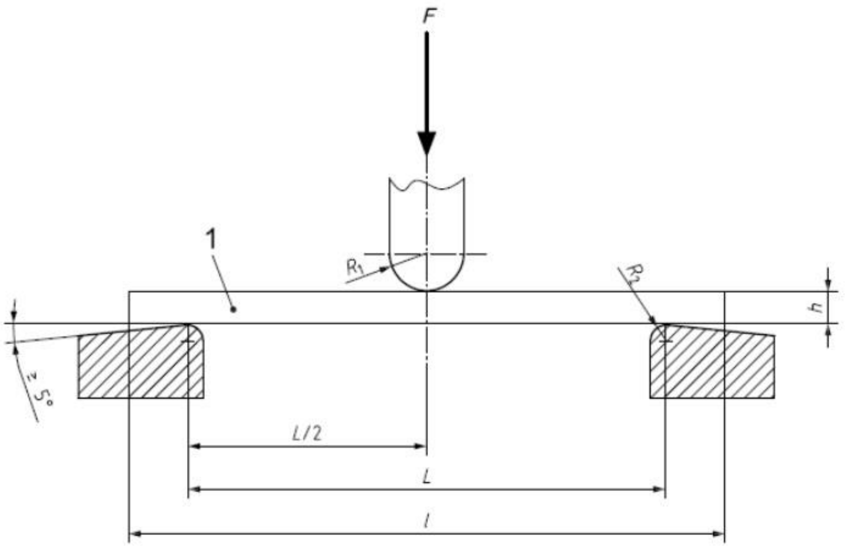

Figure 29. Three point bending test

$$\sigma_f=\frac{3FL}{2bh^2}, \tag{1}$$

where σ_f – flexural stress, MPa
F – applied force, N
L – span, mm
b – width of the specimens, mm
h – thickness of the specimens, mm

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

where S_i – deflection, mm
ε_{fi} – corresponding flexural strain ε_{f1}=0,0005 ja ε_{f2} = 0,0025

$$E_f=\frac{\sigma_{f2}-\sigma_{f1}}{\varepsilon_{f2}-\varepsilon_{f1}}, \tag{3}$$

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

2.3.2 Impact strength

Impact strength is tested at room temperature (23º C) according to EN ISO 179-1 using Zwick Charpy 5102 pendulum impact tester. The energy of the pendulum is 4 J. Small 2 mm deep notches are cut into the test specimens (figure 30). Thickness and width of the test specimens is measured and they are placed in a way that the notched side would be on the opposite side of the trajectory and the impact would happen in the centre of the test specimen. The impact energy is measured, the type of break was noted (C – complete break, H – hinge break, P – partial break, NB – non-break) and impact strength calculated using formula 4. The test requires 10 samples from each composite mixture.

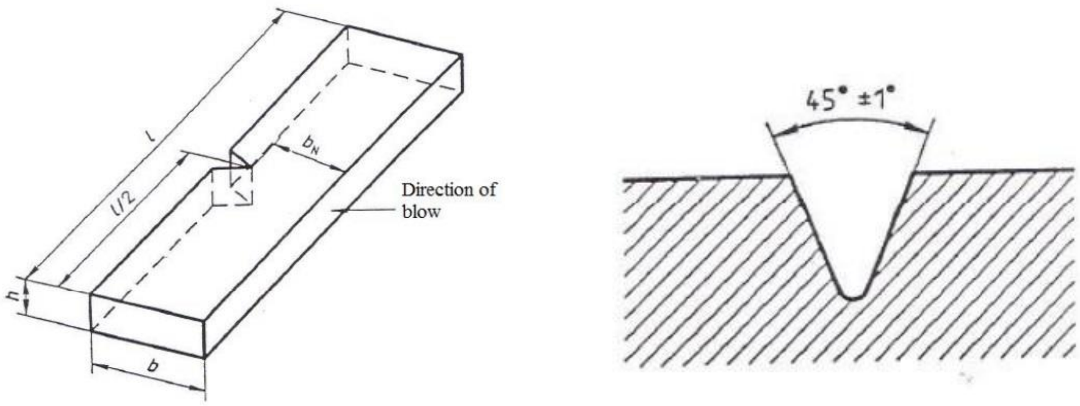

Figure 30. Impact test specimen, notch on the right

$a_{cN} = \frac{W}{hb_n} \times 10^3$, (4)

where, a_{cN} – impact strength, kJ/m^2
W – enegry absorbed by the test specimen, J
h – thickness of the test specimen, mm
b_N – width of the test specimen from the notch, mm

2.3.3 Tensile Strength

Tensile strength is tested at room temperature using Instron 5866 tensile tester according to EN ISO 527-2. The dimensions of the test specimen are 150x20x4 mm and the radius is 25 mm (figure 31). The test speed is set to 20 mm/min and the tensile modulus is calculated using formula 5.

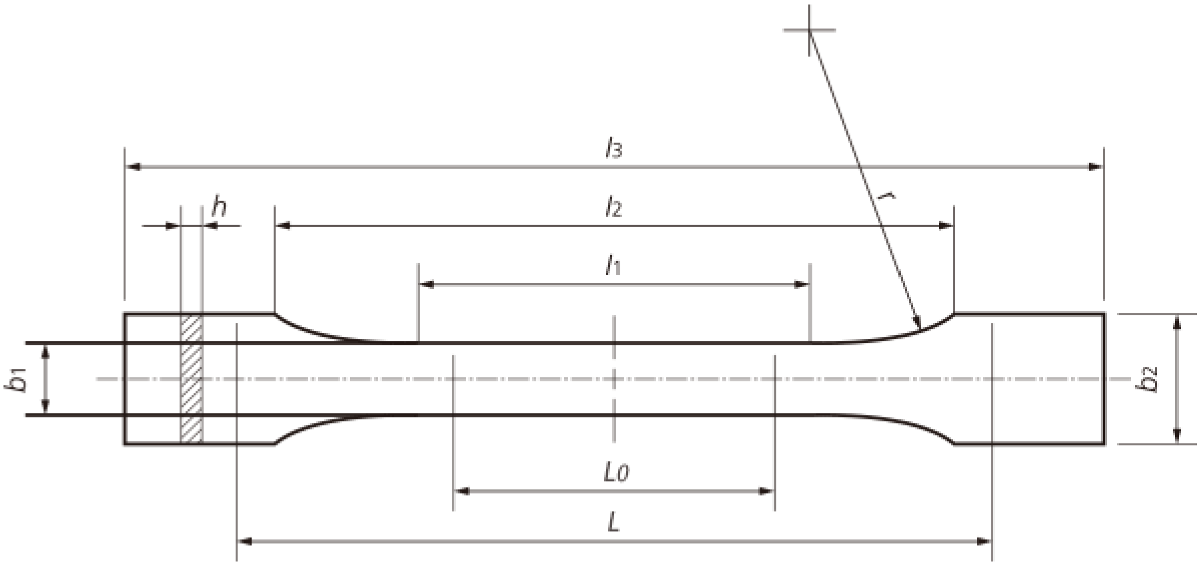

Figure 31. Tensile strength test specimen

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

$E_t = \frac{\sigma_{t2} - \sigma_{t1}}{\varepsilon_{t2} - \varepsilon_{t1}}$, (5)

where E_t – tensile modulus, Mpa
σ_{t1} – tensile stress at deflection, s_1, MPa
σ_{t2} – flexular stress at deflection, s_2, MPa
ε_{ti} – corresponding flexular strain ε_{t1}=0,0005 ja ε_{t2} = 0,0025

2.3.4 Fourier transform infrared spectroscopy (FTIR)

The efficiency of the chemical modification is verified using Fourier transform infrared spectroscopy (FTIR) with a 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 are cut from the previously produced test specimens using a scalpel. The thin wafers are placed under a clamp and the spectra is measured and peaks are marked.

2.3.5 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a thermos-analytical technique. A calorimeter measures the heat going into or the heat removed from the sample. This technique measures the heat of the sample in comparison to the reference sample which is typically empty. The sample is heated with a linear temperature ramp. The amount of heat required to increase the temperature of the sample and reference are measured as a function of temperature. Both the sample and the reference are maintained at the same temperature throughout the experiment. Only a few mg of the sample material is needed. When a sample is undergoing physical transformation such as phase transition more or less heat will need to flow through it compared to the reference. When a solid melts to a liquid it will require more heat to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it goes through endothermic phase shift from a solid to a liquid and exothermic crystallisation process.

For DSC testing a Perkin Elmer DSC 7 was used. Thin wafers of the material were cut using a scalpel, 3 mg of each mixture was needed. The wafers were put into a capsule and it was closed with a crimper press. For a reference, PP Borealis BC 245MO was used to compare the results of the pure PP to composites. The program parameters were set to record the heat flow starting from 50 °C up to 200 °C and to hold the temperature for 1 minute and to cool it back to 50 °C. Both heating and cooling were set at 20 °C/min.

2.3.6 Density measurement by immersion

The density measurement is done in accordance to EN ISO 1183-1. Firstly, the test specimen is weighed in air using Kern KE-PLJ2000-3A scale. If the test specimen weighs less or equal to 10 g the specimens mass is 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 is weighed in freshly deionized water with not more than 0,1% of a wetting agent to help in removing air bubbles. The temperature of the immersion liquid shall be 23 °C ± 2 °C and all air bubbles need to be removed with a fine wire. Density can be calculated using formula 6.

$$\rho_S = \frac{m_{S,A} \times \rho_{IL}}{m_{S,A} - m_{S,IL}} \tag{6}$$

where ρ_S- density, g / cm^3
$m_{S,A}$ – apparent mass of the test specimen in air, g
$m_{S,IL}$ – apparent mass of the test specimen in the immersion liquid, g
ρ_{IL} – density of the immersion liquid at 23 °C g / cm^3

3 Results and analysis

3.1 Flexural strength

Flexural strength shows the stress applied perpendicular to the longitudinal axis in the outer layer of the material before yielding. Flexural strength greatly depends on the adhesion between the two materials for the stress to be carried over from the polymer to the fibres. The flexural strength results are shown in figure 30. 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. Birch, alder and thermally treated alder were produced by injection moulding and may have better distribution as the composite boards made of false heartwood exhibited voids in the material which may reduce the mechanical properties. Using higher pressure during processing may help to eliminate the voids. 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. 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. (Gwon, et al., 2010)

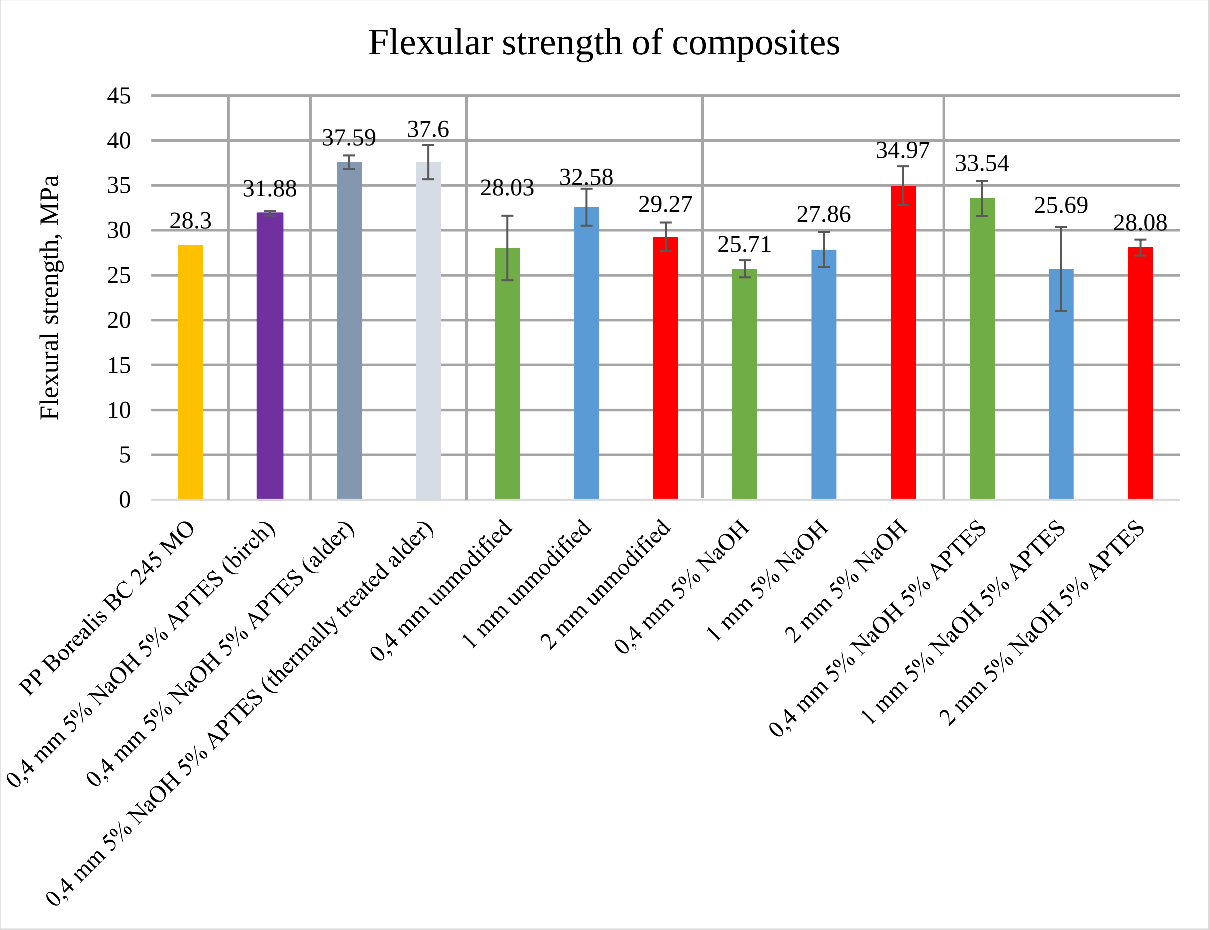

Figure 32. Flexural strength of composite materials

Modulus of elasticity shows the materials stiffness. The force is applied and deformation of the material takes place. The deformation can be stored elastically or distributed plastically. Figure 33 shows the values of the elastic modulus of composites. Wood fibres increase the modulus of elasticity when comparing to pure PP. The modulus of elasticity shows a similar trend to flexural strength as the highest value is recorded from 2 mm false heartwood with alkaline modification. The increasing fraction size has decreased the modulus of elasticity as alkaline treated 0,4 mm fraction shows an 51% decrease when comparing to unmodified composite and a 20% decrease when comparing to silane modified composite. The same trend is shown in other fraction sizes. Silane treated pure birch composite show a 45% increase in modulus of elasticity when comparing to silane treated false heartwood composite. Untreated composites show similar elastic properties but chemically modified composites show an increasing trend with alkaline treated composites and a slight decrease in silane treated composites. The decrease in elastic modulus can be attributed to the fact that excessive alkaline treatment has corroded the wood fibres and weakened the interfacial adhesion between wood fibres and PP (Kallakas, et al., 2016).

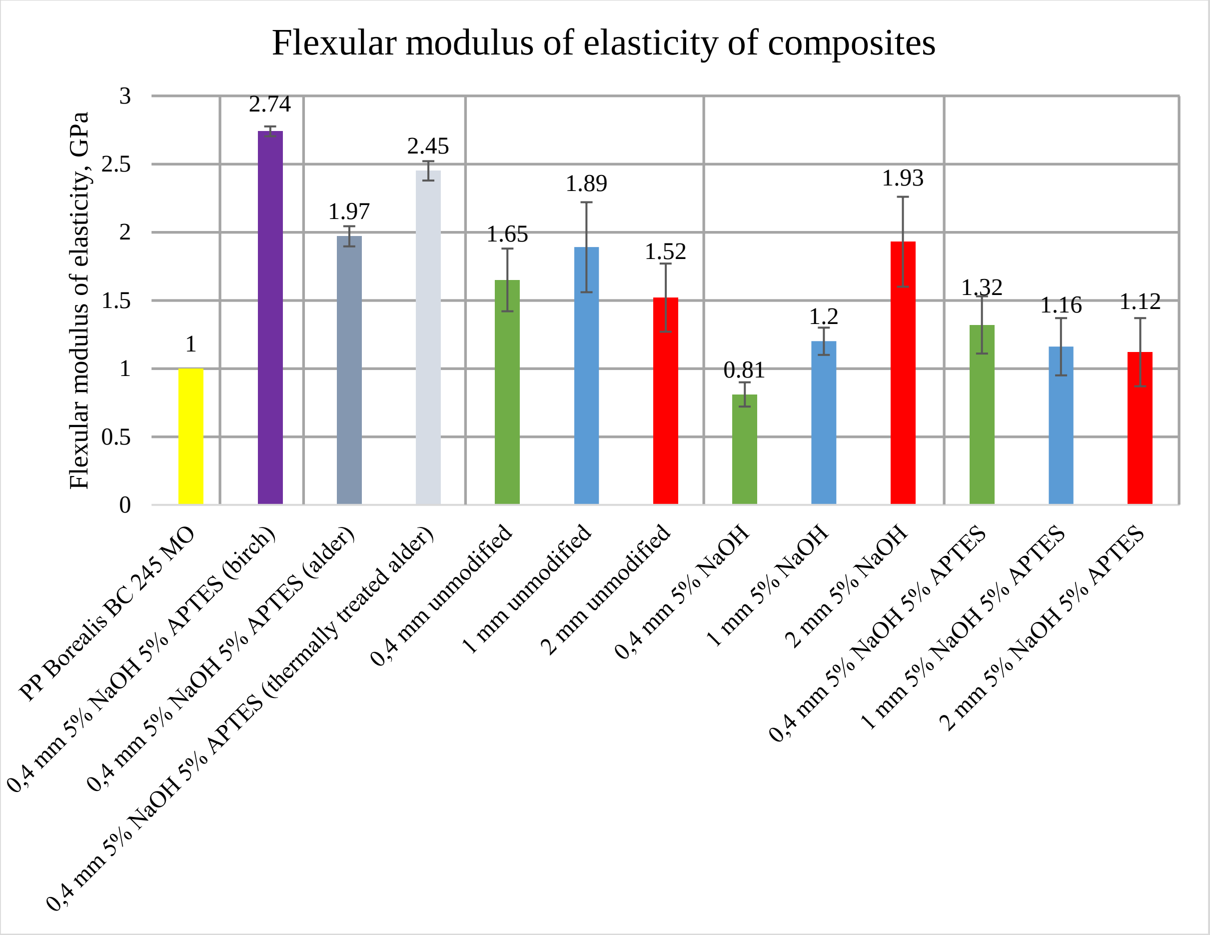

Figure 33. Flexural modulus of elasticity of composite materials

3.2 Impact strength

Impact strength shows the materials ability to withstand force without breaking. 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). Figure 34 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.

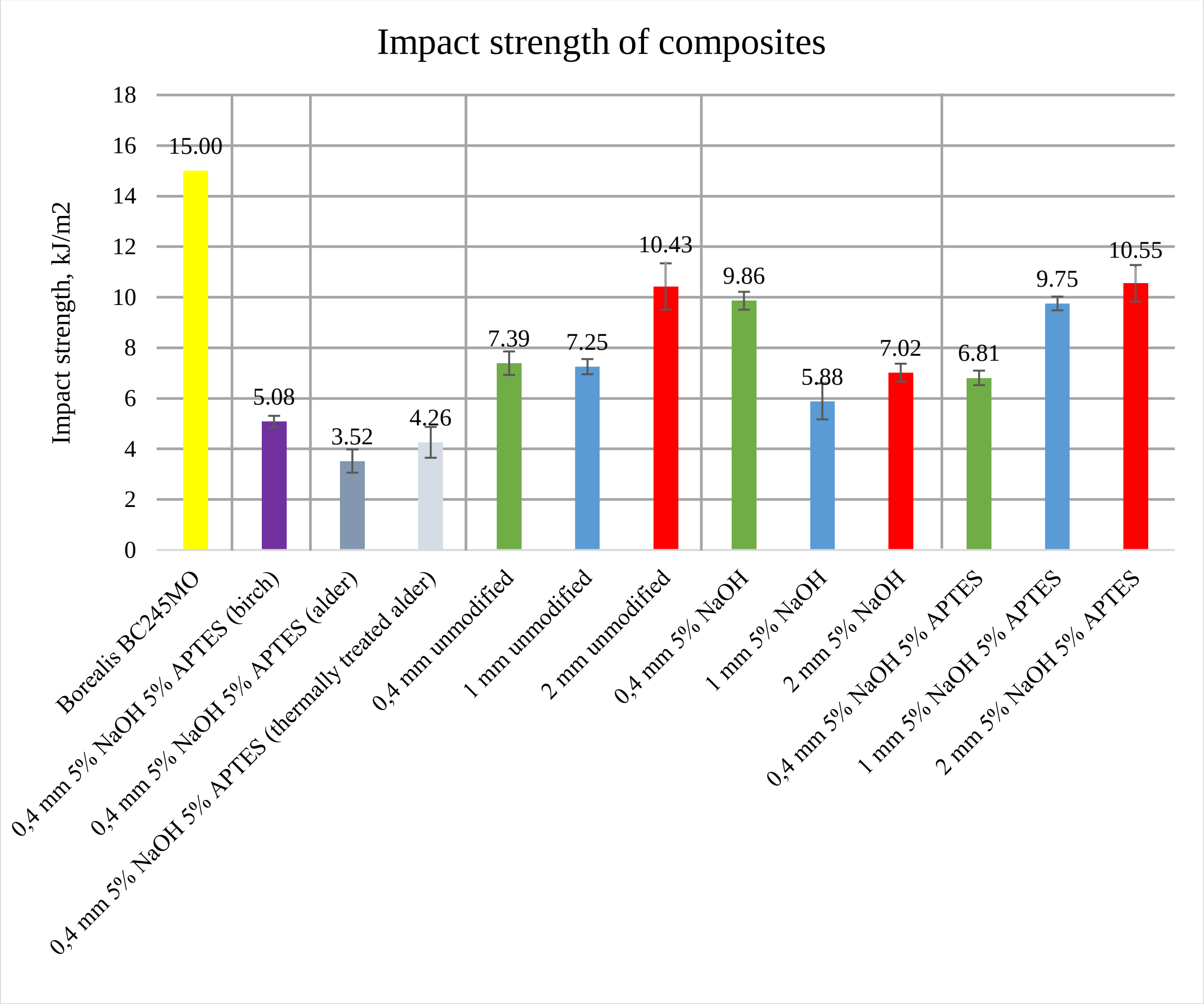

Figure 34. Impact strength of composites

3.3 Tensile strength

Tensile strength measures the force necessary to pull the material until it breaks. Wood fibre reinforced composites show a decrease in tensile strength when comparing to pure PP. The results of the tests are presented in figure 35-36. Increase in fraction size has also 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. Figure 36 shows the extension of test specimens at maximum load and at break. The extension at maximum load of 0,4 mm alkaline treated composite is 40% higher than 0,4 mm untreated composite and extension at break is 48% higher. Alkaline treated 1 mm composite show a decrease in extension at break and maximum load of 33% and 44% respectively. When using the Instron testing device the results of 2 mm alkaline treated and all silane treated composites tensile strength and modulus results cannot be used in this thesis. The previously named composites could not be broken using 5 kN dynamo and a 10 kN dynamo was needed. The 10 kN dynamo was not calibrated and the faulty results are given in appendix 3.

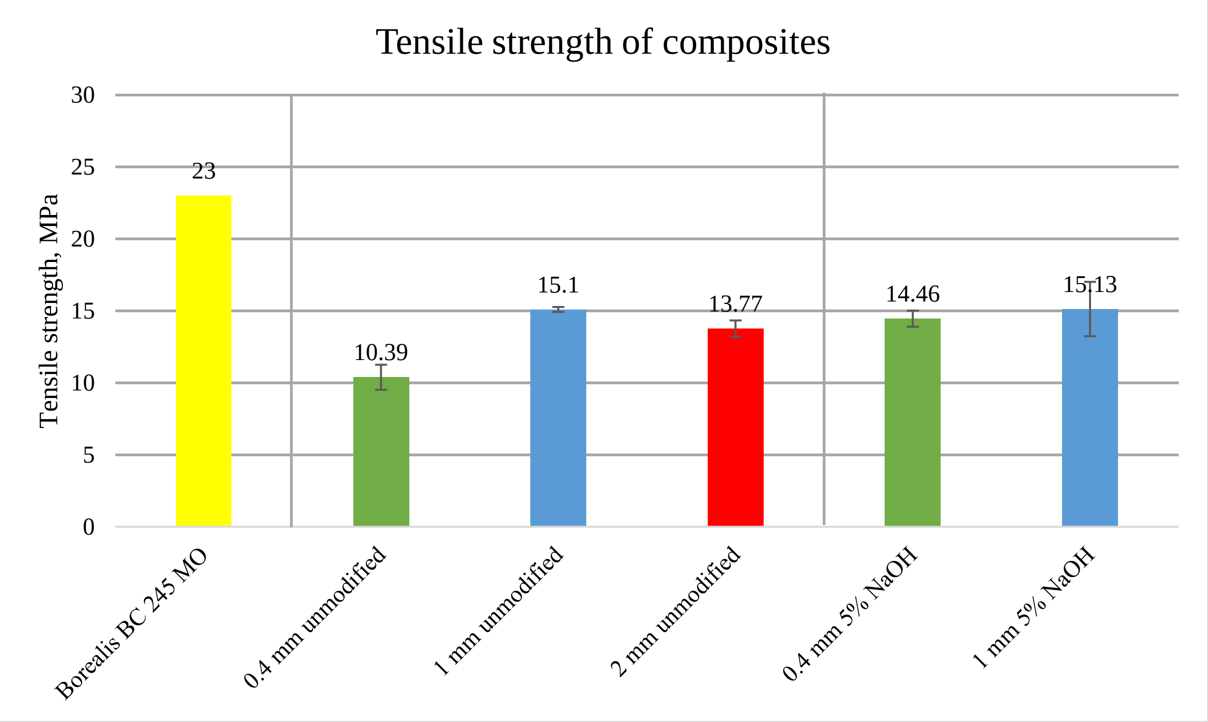

Figure 34. Tensile strength of composites

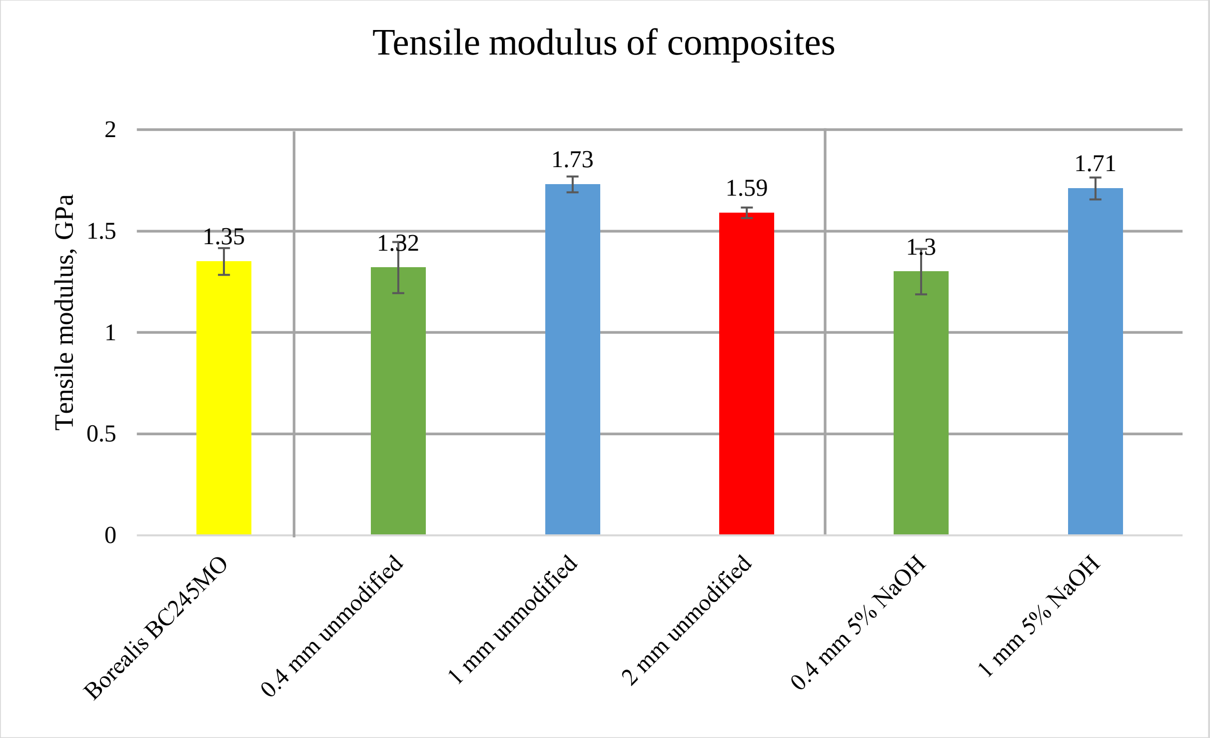

Figure 35. Tensile modulus of composite materials

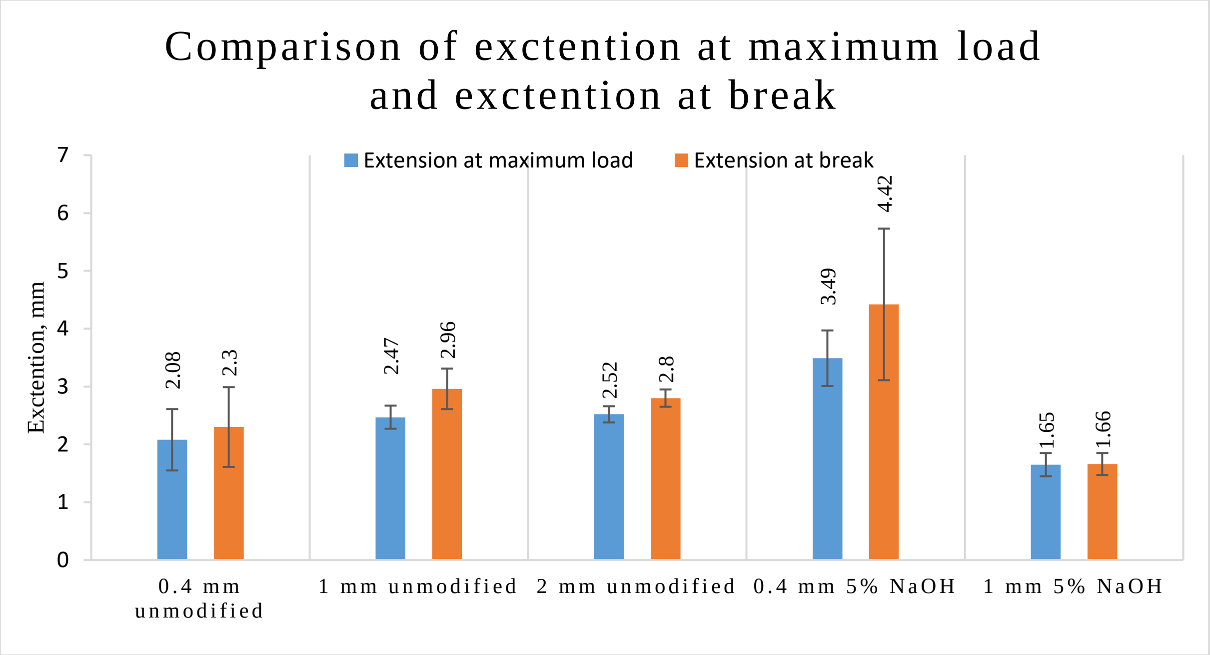

Figure36. Extension of tensile strength test specimens are maximum load and break

3.4 Fourier transform infrared spectroscopy (FTIR)

The wavenumber values can be compared to various tables and specific software for determining the bonds in the material. Table 10 shows the marked wavenumber peaks on the FTIR graphs and the structure and class of the corresponding wavenumbers. Peaks at 1028 cm^{-1} and 1104 cm^{-1} indicate the siloxane chains in the composite. Figures 37 and 38 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). Figures 37 and 38 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).

Table 10. FTIR peaks and respective structures

wavenumber, cm^{-1}	**Structure**	**Class**
809	R2C=CHR	Alkene
842	1,2,3,5 tetra substituted aromatic	Aromatic
899	S-OR	Ether
974	R2C=CHR	Alkane
998	P-OR	Ester
1028	Si-OR	Silyl ether
1104	Si-O-C	Silyl ether
1166	RCOOR	Ester
1245	Si-CH3	Silyl
1376	CH2CH3	Alkane
1453	CH2CH3	Alkane
1593	C-C in ring	Aromatic
2838	RCOOH	Carboxylic acid
2868	CH3	Alkane
2917	CH3CH3	Alkane
2951	CH2CH3	Alkane

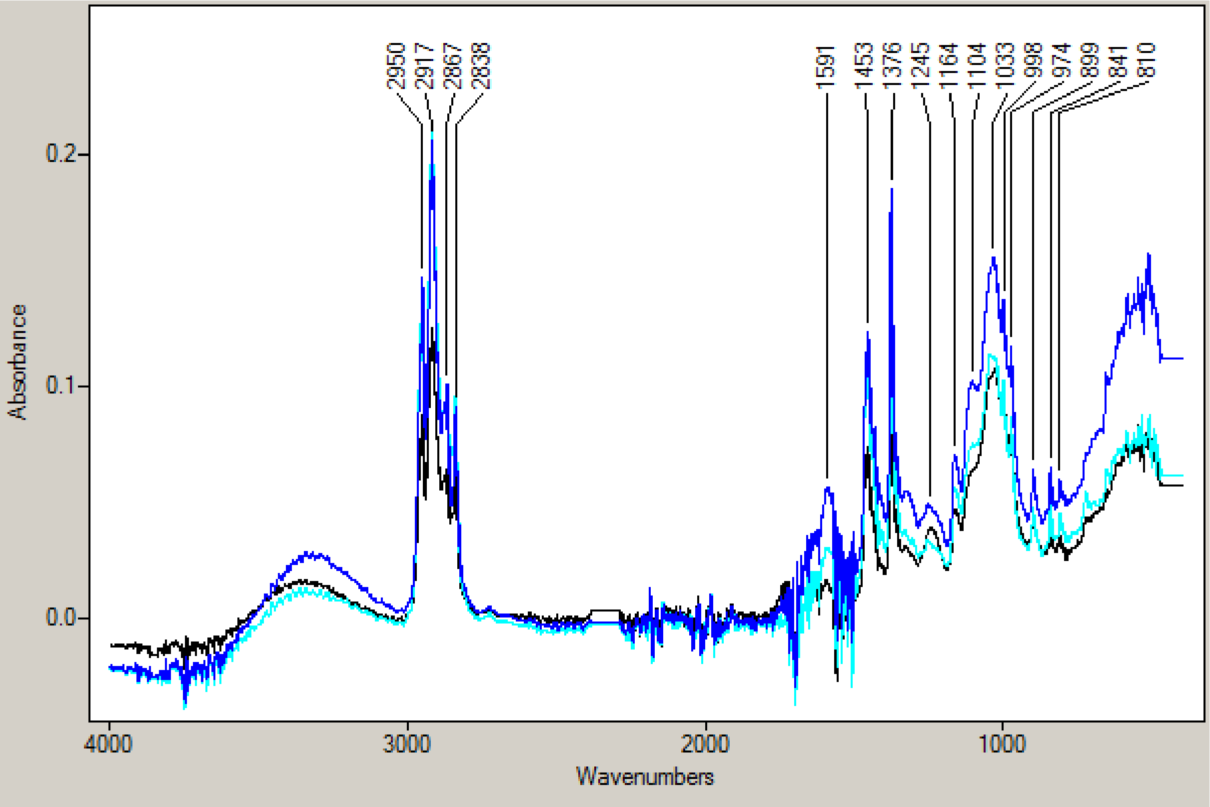

Figure37. FTIR graph of composites fraction size of 1 mm

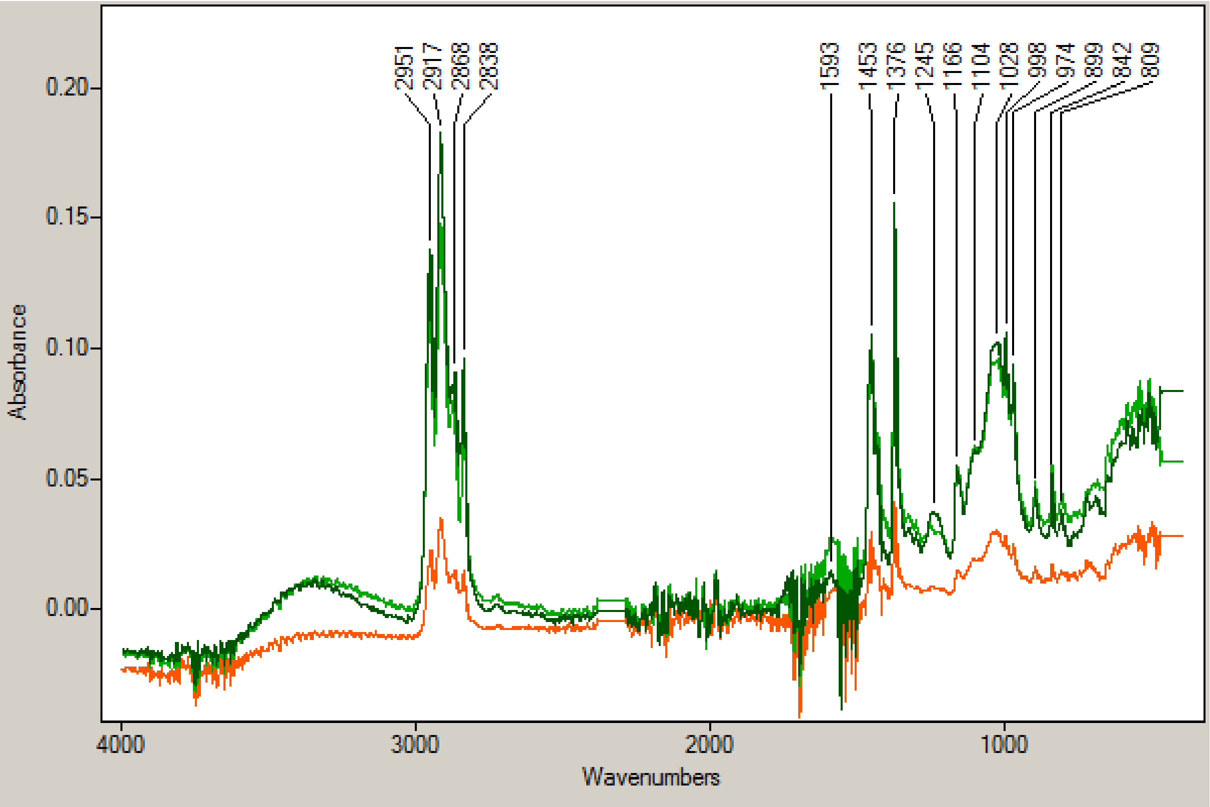

Figure38. FTIR graph of composites fraction size of 2 mm

3.5 Differential scanning calorimetry (DSC)

Thermal properties of the composite materials are shown in 36. The melting temperature varied only 4,01°C and glass transition temperature varied 2,62°C. This shows that fibre size does not affect the thermal properties of composites. The PP product sheet advises to processing temperatures of 230-260°C. The results (figure 39) show that pure PP has a melting temperature of 163,67°C. Somewhat opposite to these results larger wood fibres restrict the flow of polymer macromolecules (Cui, et al., 2010). Chemical modification does not affect the melting temperatures of composites. Similar results were gathered from previous research that shows that chemical modification changes the melting temperature 3,4°C (Kallakas, et al., 2015). The DSC curves can be seen in appendix 2.

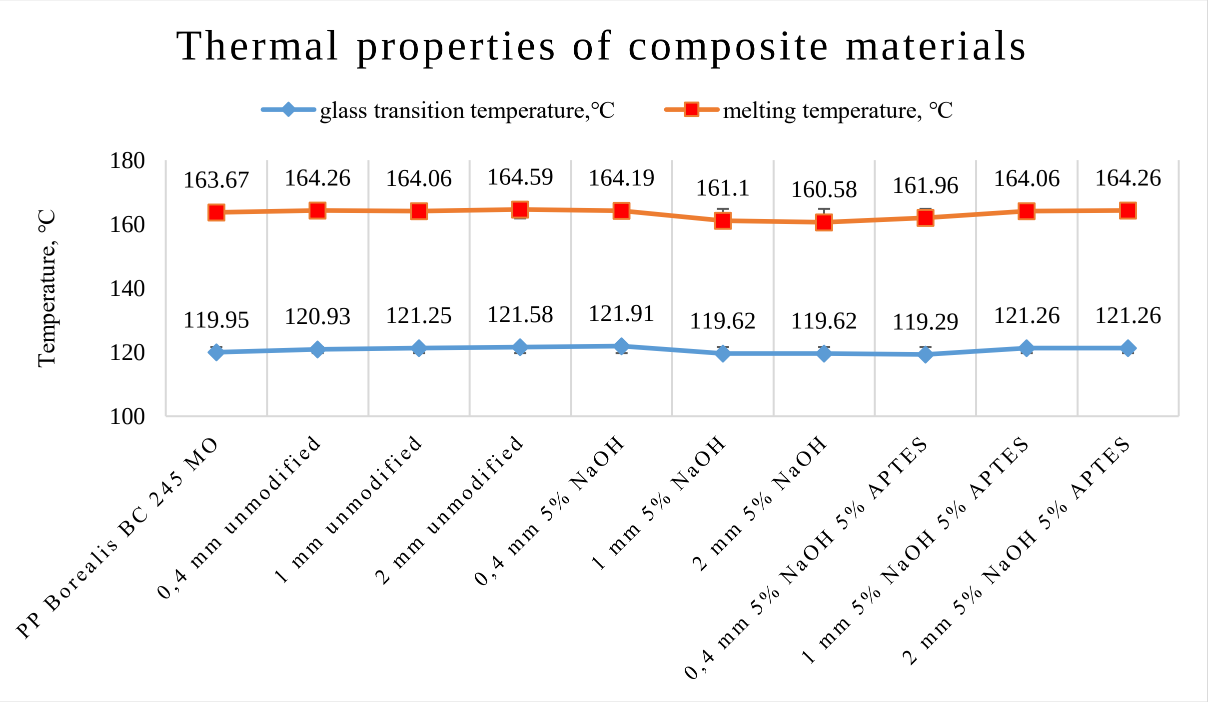

Figure 39. Thermal properties of composite materials

3.6 Density measurement by immersion

The density of composites is shown in figure 40. 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).

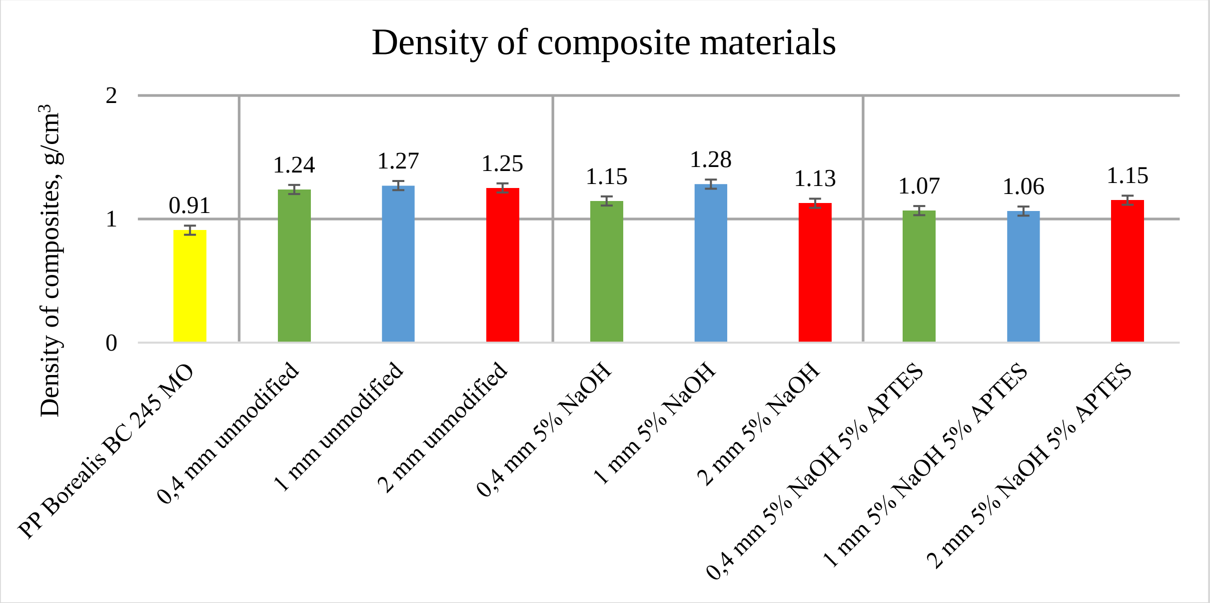

Figure 40. Density of composite materials

Summary

The aim of this thesis was to investigate the false heartwood fraction size and chemical modification effect on the physical and mechanical properties.

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 purification of false heartwood should be investigated to see if this can affect the properties of the composite.

The different fraction size of false heartwood does shows substantial differences in results. Larger particles on average show the best properties and as the results from the milling show less energy is needed for disintegration of wood particles.

Board pressing needs development as voids are present in the material. Higher pressure may be needed or better mould should be used. The microcracks in the material influence the properties of the material.

DSC shows that chemical modification and different particle size do not affect the thermal properties of the composites. Results from DSC show that lower processing temperature could be used as the melting temperature of the materials was 160,58℃ - 164,59℃ compared to the 190℃ used for compounding and board pressing. The temperature used is quite near to the thermal degradation temperature of wood fibres which is ~200℃.

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 purification of fibres may be necessary for enhanced properties. Wood particles have changed the properties of the polymer. Depending on the desired application the filler rate and chemical modification can be applied.

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Abstract

False heartwood is a phenomenon where penetration of oxygen discolours 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 adhesion between polymers and wood fibres is weak because polymers are hydrophobic and wood fibres are hydrophilic. The effect of chemical treatment with NaOH and 3-aminopropyltriethoxyslane (APTES) was investigated to see if the modification will provide better interfacial adhesion. 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), differential scanning calorimetry (DSC) and density measurement by immersion. The mechanical properties were investigated using three-point bend test, tensile test and Charpy impact test. The effect of fraction size and chemical modification was compared. Results show that wood fibres increase the stiffness and rigidity when comparing to PP. The FTIR test showed that chemical modification of APTES had occurred with peaks at 1028 cm^{-1} and 1104 cm^{-1} present. The peaks of the material were identical, only the absorption was somewhat different. DSC showed that fraction size and chemical modification do not alter the melting temperature or glass transition temperature of the material. The density of the material reduced with increasing fibre size and with chemical modification using NaOH and APTES.

Resümee

Väärlülipuit tekib hapniku sisenemisel tüve sisemusse ning mõjutab puidu kvaliteedi, mehaaniliste ning füüsikalisi omadusi. Väärlülipuidu kasutamist puitplastkomposiitides ei ole varem uuritud ning nende omadused on teadmata. Polümeeri ja puiduosakeste vaheline adhesioon on tavalises olukorras nõrk, sest polümeer on hüdrofoobne ning puidu kiud hüdrofiilsed. Keemiliste modifikatsioonide abil saab puiduosakeste keemilist kokkusobivust paremaks muuta. Antud töös uuriti Naatriumhüdroksiidi ning 3-aminopropüültrietoksüsilaani (APTES) modfikatsiooni ning erineva puiduosakese fraktsiooni mõju materjali füüsikalistele ja mehaanilistele omadustele. Komposiitplaadid valmistati kuuumpressimise toimel ning kasutati kolme erinevat puiduosakeste fraktiooni (0,4 mm, 1 mm, 2 mm). Puidujahu modifitseeriti aluse ning APTES-iga, kompaunditi kaheteolise teoga kompaunderiga ja katsekehad valmistati survevormise ning CNC töötluse abil. Komposiitide füüsikalisi omadusi uuriti Fourier transform infrapuna kiirguse (FTIR), differentsaal skanneeriva kalorimeetria (DSC) ning tiheduse määramist uputamise meetodiga. Mehaanilisi omadusi uuriti kolme punkti paindekatse, tõmbekatse ning Charpy löögikatsega. Hinnati modifikatsiooni ning osakeste suuruse mõju komposiidile. Väärlülipuidu osakesed tõstavad materjali sitkust ning jäikust võrreldes puhta polümeeriga. FTIR analüüs näitas, et reaktsioon silaani ja puidujahu vahel on toimunud (1028 cm^{-1} and 1104 cm^{-1}). Materjalide vahel ei olnud piikide erinevust, vaid kiirguse absorptsioon erines mõnevõrra. DSC analüüs näitas, et modifikatsioon ning osakeste suurus ei ole mõjutanud materjali sulamis- ja klaasistumistemperatuuri. Materjali tihedus vähenes puiduosakeste suuruse ning aluselise ning silaaniga töötlemise toimel.

Appendix 1

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Mechanical and physical properties of thermally modified wood flour reinforced polypropylene composites

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Abstract. Heat treatment of wood helps to lower the hydrophilicity and polarity of wood fibres used in wood-plastic composites. By means of heat treatment it is possible to reduce the access to wood hydroxyl (OH) group, which causes hydrophilic and polarity of wood fibres. Therefore improving compatibility between the wood and polymer matrix. In this research, the effect of wood flour (WF) heat treatment and chemical modification with 3-aminopropyltriethoxysilane (APTES) were investigated. WPC test samples were prepared using alder (*Alnus incana*) WF with mesh size of 0.05mm as a filler material and polypropylene (PP) as the matrix material. WF was chemically modified with NaOH and APTES to increase the adhesion and compatibility of WF to polymer matrix. The composites were manufactured using a twin-screw extruder and the test samples were made by injection molding. The composites mechanical properties were tested using three-point flexural test and Charpy impact test. The composite physical properties were investigated with Fourier transform infrared spectroscopy (FTIR). The effect of silane (APTES) and NaOH modification on thermally treated and untreated WF was examined with contact angle measurement. Comparisons were made between the untreated WF and thermally treated WF. Also the effect of NaOH and silane (APTES) modification on the properties of thermally modified and unmodified WF composite were investigated. Using WF as a filler material increased flexural strength, while impact strength decreased thus making the material more rigid and brittle. The test results revealed that there was no significant difference in the mechanical properties between thermally treated and untreated composites. However, chemical modification improved the mechanical properties of the composites.

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

INTRODUCTION

The use of lignocellulosic fillers has received considerable interest from academics and industry for its environmental and economic benefits. Natural fillers have many advantages over inorganic fillers such as: renewable nature, availability, low cost and density, high specific strength and moduli etc. Despite many advantages they have a big disadvantage – they are incompatible with the polymer matrix due to the polarity of the natural fillers and non-polarity of the polymer matrix. Many solutions have been proposed to overcome this problem for instance adding a coupling agent has been a successful way of aiding compatibility (Krzysik & Youngquist, 1991; Gatenholm et al., 1993; Kazayawoko et al., 1999; Lu et al., 2000; Kaboorani et al., 2008). Presently, the use of coupling agents such as silane, maleic anhydride grafted polypropylene, alkali treatment, acetylation have been the most common ways to increase the compatibility of the hydrophilic natural fibers and the hydrophobic polymers (Luo et al, 2013).

Heat treatment is a relatively simple method for modifying wood. This method improves hydrophobicity, dimensional stability and biological resistance. During heat treatment, significant changes take place in the chemical composition of the wood filler including decomposition of hemicellulose which is hydrophilic. Heat treatment also has some drawbacks including the reduction of mechanical properties and unwanted color and odor (Adyembir et al., 2015). With heat treatment the adsorption of water into wood decreases which results in lowered swelling or shrinkage behavior compared to untreated wood. It is noted that moisture is absorbed by the hydrophilic wood fibers into the composite which leads to degradation of the interfacial adhesion quality and therefore decreases the strength of the composite. Thermal modification reduces the polarity of wood fibers and thereby improves their compatibility with hydrophobic thermoplastics and increases interfacial strength. Therefore, these materials provide the needed properties for such uses as decking, railing, cladding and under the hood applications in the automotive industry (Follrich et al., 2010).

Thermal treatments use no chemicals thus making it an environmentally friendly process (Eslam et al., 2011). Wood can be degraded and finally burn at high temperatures. The initial degradation can start at temperatures as low as 117°C depending on the heating period, atmosphere and wood species. Thermal stability is a critical factor in the processing time and temperature (Kaboorani & Faezipour, 2009). In theory, adding heat treated wood in which some components have been decomposed should lead to an improvement in thermal stability (Kaboorani & Faezipour, 2009).

The aim of this research was to explore the use of thermally modified wood as a filler material for wood plastic composites as thermal treatment potentially reduces the polarity of wood and makes it more compatible with thermoplastic polymers. The task of this project is to investigate the effect of chemically treated, thermally treated and untreated wood on the mechanical and physical properties.

MATERIALS AND METHODS

Materials

In this research, PP was used as the matrix material for making WPCs. The PP (BC245MO) obtained from the Borealis Polymers OY company is a heterophasic copolymer (block copolymer) with a density of 0.905 g/cm^3, and melt flow index (MFI) of 3.5 g/10 min. Thermally treated (170°C) hardwood (alder (*Alnus incana*)) boards were supplied by HA SERV OÜ. Thermally modified boards were then comminuted into a fine flour with mesh size of 0.05 mm using a disintegrator device DS-A. As a coupling agent 3-aminopropyl-triethoxysilane (APTES) from Sigma-Aldrich was used. The molecular weight of the substance is M_w= 221.37 g/mol and the boiling point at atmospheric pressure is 217°C. A reagent grade sodium hydroxide (NaOH), 98% was also used and glycerine in some samples.

Wood flour modification

Preparation of the composites started with modification of wood flour (WF). Firstly, WF was weighed in a stainless steel vessel. According to the previous research (Gwon et al., 2010), optimum concentration of alkali for the treatment is 10 wt% and above, so that the mechanical properties may slightly decrease. Therefore, in this study a 10 wt% (based on WF mass) aqueous solution of NaOH was prepared in the laboratory by dissolving NaOH granules in water. WF was immersed in 10 wt% NaOH solution at room temperature (25°C) for 90 min. The WF was then rinsed with distilled water to neutralise the excess NaOH and dried in the oven at 60°C for 24 h.

WF silane modification according to a previous research (Kim et al., 2011) was used. For silane modification, 5 wt% (based on WF) APTES was taken. APTES was immersed in a solution of ethanol/distilled water (6:4 ratio) for 1 h in order for it to be hydrolized and the pH of the solution was adjusted to the value of 4-5 with acetic acid. Then silane solution was poured on the WF was left at room temperature (25°C) for 2 h. After the silane treatment the WF was dried in the oven at 60°C for 24 h.

The usage of glycerine in WPC-s was similar to a previous research (Sanadi & Caulfield, 2008) which showed that adding 2% glycerine resulted in the best properties. Glycerine was used as a processing aid and added to the modified WF in the amount of 2% of the mass of WF. Glycerine was weighed and 500 ml of water was added to it so that the mixing process would be easier. Table 1 illustrates the composition of the composites.

Composite processing

The test specimens were prepared in Tallinn University of Technology, Department of Polymer Materials. The first operation was the modification of WF and then the compounding and granulation of the obtained mixtures. The last step was to produce test specimens by injection molding method.

After the modification, the WF was weighed and mixed with polymer granules maintaining the ratio of 65% polymer and 35% WF for all the samples. The composition of the mixtures are shown in Table 1. The mixtures were compounded using twin-screw extruder Brabender Plast-Corder PLE651. The barrel had four heating zones. The melting zone temperatures were set at 180°C, 185°C and 190°C, and 185°C for die zone. The rotation speed of the twin-screw was 60 rpm. The extruded material was cooled with ventilators and granulated with a Brabender granulator. The test samples were made by injection moulding (Battenfeld BA 230 E) according to standard ISO 178:2010. Depending on the material the temperature and pressure was suitably adjusted. Conditions for injection moulding were: temperature: 170-185°C from the feed zone to the die zone, injection pressure: 7 MPa, screw speed 40 rpm, cooling time 15 s. The mixture was injection moulded into bar shape specimens for flexural and impact tests. Dimensions of the specimens were 63x10x4 mm.

Table 1. Composition of the composites

Sample	PP (wt%)	WF (wt%)	NaOH (wt%)	APTES (wt%)	Glycerine (wt%)
1	100	–	–	–	–
2	65	35	–	–	–
3	65	35	10	5	–
4	65	35	10	5	2
5	65	35*	–	–	–
6	65	35*	10	5	–
7	65	35*	10	5	2

* - thermally treated WF

Mechanical properties

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

Fourier transform infrared spectroscopy (FTIR)

The efficiency of the chemical modification was verified using Fourier transform infrared spectroscopy (FTIR). FTIR spectroscopy measurements were performed using Interspectrum FTIR spectrometer (model Interspec 200-X) with KBr disc method. The spectral resolution was 4 cm^{-1} and the spectra were recorded in the range of 1,800-800 cm^{-1} using. Thin wafers were cut from the previously produced flexural test specimens using a scalpel. The thin wafers were placed under a clamp and the spectra were measured under ambient conditions.

RESULTS AND DISCUSSION

Flexural properties

The flexural strength of WPCs with thermally treated and untreated, silane modified and unmodified WF is presented in Fig.1 The addition of WF has increased the flexural strength by 9-21% (from 32.76 MPa to 41.47 MPa), thus making the composites more rigid and brittle. The results show very slight differences in flexural strength between different composites. In order to achieve better mechanical properties, chemical modification of WF was used to gain better adhesion and better dispersion of the filler in the composite but unfortunately the results show little difference between modified and unmodified WF based composites. Chemical modification of WF slightly decreased the flexural strength (about 10%) compared to unmodified WF based composites. The decrease of flexural strength of modified WF based composites may be due to the excessive alkali that weakens the surface of WF and causes the effect of corrosive interactions between wood fibers in the composites (John et al., 2008; Gwon et al., 2010).

However, there were no significant differences between thermally treated and untreated WF based composites. This can be explained by the fact that WF was ground to very fine flour with mesh size of 0.05 mm and therefore modifications have no effect on the composite properties anymore. WF with mesh size of 0.05 mm acts just as a filler in the PP matrix and not as a reinforcing fiber. WF with mesh size 0.05 mm was chosen to be similar with wood dust in sawmill and furniture industries and to find usage for this wood dust in WPCs. As can be seen from Fig. 1, there is almost no difference between modified, thermally treated or untreated WF used in WPCs. The differences of the results between all the composite remain fit within the boundaries of measurement uncertainty. However, previous researches have shown increase in flexural properties with APTES modified WF/PP composites (Kim et al., 2011; Kallakas et al., 2015). For some WPC samples, glycerine was used as processing aid. The results show (see Fig. 1) that there was no effect of using glycerine on the flexural properties.

Modulus of elasticity (MOE) shows the materials ability to withstand deformation. The results derived from the flexural test show the stiffness of the composite (see Fig. 2). Comparing the results to the MOE of pure PP (1.01 GPa) the stiffness of the composite is significantly higher (over 200%). The increased stiffness can be explained by the stress transfer from the polymer matrix to the filler (Ndiaye & Tidjani, 2012). The results show that chemically unmodified composites have slightly, about 10% higher MOE values than modified composites. When comparing thermally treated and untreated WF composite, it can be seen from the results (see Fig. 2) that there is no difference. The results show a slight effect on MOE values when glycerine was used. MOE decreased by 50% with untreated WF composites where glycerine was used as a processing aid since it is likely that the small molecules of glycerine could act as a plasticizer/lubricant.

Therefore, from the flexural properties, it can be concluded that chemical or thermal modification has minimal or no effect on the flexural properties of WPCs when fine WF with mesh size of 0.05 mm is used.

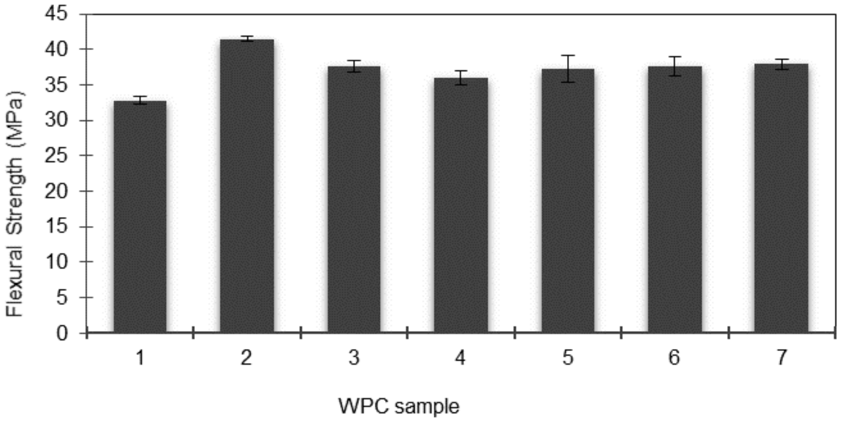

Figure 1. Flexural strength of chemically and thermally modified and unmodified WF/PP composites.

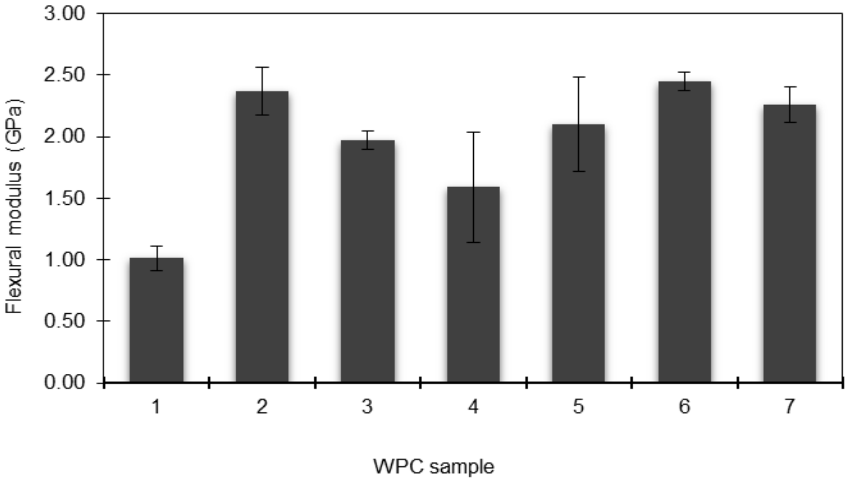

Figure 2. Flexural modulus of chemically and thermally modified and unmodified WF/PP composites.

Impact strength

Impact strength was measured by Charpy impact test of single notched specimens of unmodified and modified WPC samples. Single notched impact test was chosen because the pendulum impact tester machine did not provide sufficient energy to break un-notched PP – because PP matrix has high elasticity which is also shown by previous researches (Bledzki & Frauk, 2004; Bledzki et al., 2009).

The results of the impact test are shown in Fig. 3. From the results it can be seen that using fine WF in the PP matrix lowered the impact properties significantly (about three times) compared to pure PP (11 kJ/m^2) which is also shown in previous researches (Bledzki & Frauk, 2004; Bledzki et al., 2009). Using fine WF in the PP matrix reduces the impact strength because composite is more heterogenic than PP and it creates stress concentration regions in the WPC. These regions require less energy for breaking the composite under impact. Also, small WF particles are difficult to disperse due to their tendency to agglomerate which results in low impact energy therefore making the composite more brittle. The results show lower (50-100%) impact strength on chemically unmodified WF composites. The increased impact strength with chemically modified WF based composites can be explained by the fact that that alkaline treatment removes hemicelluloses, lignin and waxes which produces a rougher surface which in turn increases the length to diameter ratio or aspect ratio (L/D) thus enlarging the surface area of contact with the polymer matrix which increases the surface area of interaction at the interface (Ichazo et al., 2001). Higher impact strength on APTES modified WPC samples is also due to silanol groups in these composites that have strong bonds with hydroxyl groups of WF. These strong bonds increase interfacial adhesion between WF and the polymer matrix. It is supposed that the increased interfacial adhesion between WF and the polymer matrix is supported by the formation of siloxane by condensation reaction. (Kim et al., 2011). Therefore this impact test clearly shows the influence of chemical modification on the mechanical properties of WPC materials.

The results show (see Fig. 3) the highest impact values for WPC samples with APTES modified WF composites based on an addition of 2% glycerine (6 kJ/m^2). The addition of glycerine has increased impact strength by 70% due to a plasticization effect. This plasticization effect is caused by glycerine that plasticizes the amorphous components such as lignin and hemicellulose in wood by breaking some of the H-bonds present (Sanadi & Caulfield, 2008). However, there were no significant differences between thermally treated and untreated WF composite samples. Though, the impact values for thermally treated WF composites were slightly higher than those for untreated WF composites.

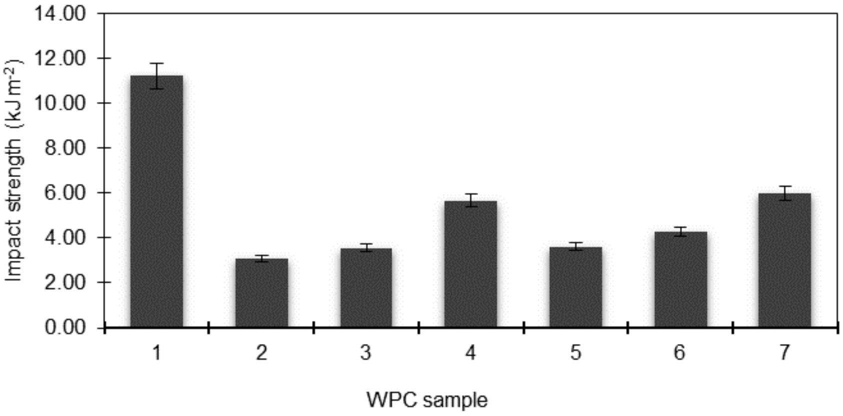

Figure 3. Impact strength of chemically and thermally modified and unmodified WF/PP composites.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra shows the changes of molecular interactions which lead to wave number shifts. The wavenumber values can be compared to multiple tables or specific software designed to give different chemical bond value range. Previous researches (Emandi et al., 2011; Bodirlau et al., 2008) show that typical wood structure has peaks 3,300-4,000 cm^{-1} indicating strong broad OH stretching and C-H stretching (2,800-3,000 cm^{-1}) in methyl and methylene groups. Specific, fingerprint area absorption in the region from 600-1,800 cm^{-1} are assigned to major cell wall components such as cellulose, hemicelluloses and lignin. (Rana et al., 2010).

In this study, FTIR spectra were collected by co-adding 32 scans at a resolution of 4 cm^{-1} in the range from 1600-600 cm^{-1} at room temperature. It is the range of typical PP FTIR spectra which was compared to WPC samples to see any differences. FTIR spectra changes in WPC samples are demonstrated on Fig. 4 and 5. There is no difference in FTIR spectra peaks between thermally modified and unmodified WF based composites. WPC samples had similar peaks to pure PP. However, there were changes in peak intensity in the range of 1164 cm^{-1} to 1025 cm^{-1} which are only present in WPC samples. In this region (1164 cm^{-1} – 1025 cm^{-1}) chemical modification of WF leads to changes of characteristic peaks and peaks changes for APTES treated samples are shown in Fig 5. Modification with APTES showed peak changes at 1,025 cm^{-1} and 1,104 cm^{-1} assigned to Si-O-C band indicating that the coupling reaction between WF and APTES has occurred thanks to the NaOH treatment. The signal intensity of the composite mixtures in comparison to pure PP (blue) in the range of 600-800 cm^{-1} are mostly aromatic structures example lignin molecules (Fig. 4 and 5). Bands specific to PP used as the polymer matrix in WPCs are also present as shown in Table 2 and Figures 4 and 5. Peaks at 1,456 cm^{-1} represent CH_2 deformation; 1,376 cm^{-1} represent symmetric CH_3 deformation; peaks at 1,164, 998 and 974 cm^{-1} represent isotactic polypropylene band (Jordi).

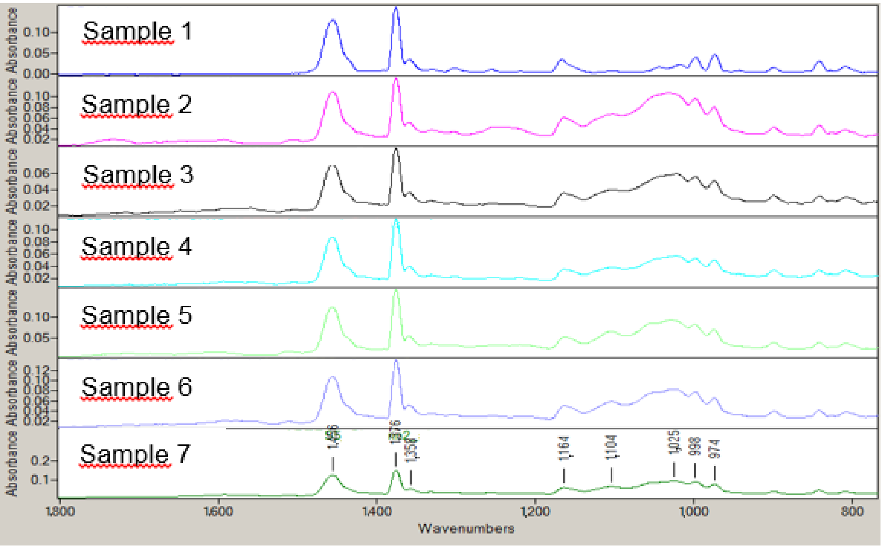

Figure 4. FTIR spectra of chemically and thermally modified and unmodified WF/PP composites.

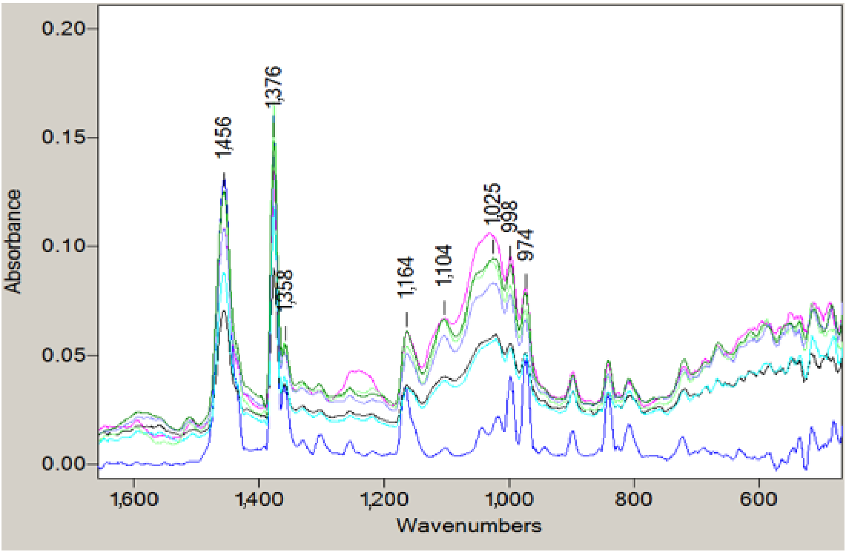

Figure 5. FTIR spectra peaks of chemically and thermally modified and unmodified WF/PP composites.

Table 2. FTIR peaks and identifications of WPC samples

Wavenumber (cm^{-1})	Frequency (cm^{-1})	Bond	Functional group
1,456	1,450–1,470	CH2 and CH3	Alkanes
1,376	1,375–1,380	CH3	Alkanes
1,358	1,350–1,370	C–H	Alkanes
1,164	1,000–1,320	RCOOR	Ester
1,104	1,000–1,100	Si–OR	Silyl ether
1,025	1,000–1,100	Si–OR	Silyl ether
998	900–1,050	P–OR	Ester
974	965–975	cis RCH=HCR	Alkene

CONCLUSIONS

This research focuses on exploring the use of thermally treated wood as a filler in thermoplastic composites. The objective was to investigate the different effects of chemically treated, thermally treated and untreated WF on the mechanical and physical properties of the obtained composites. It was found that thermally treated composite mixtures showed slightly higher MOE and flexural strength values than untreated wood mixtures thus suggesting that thermal treatment can increase the mechanical properties of the composite. However, there were no significant differences between chemically treated and thermally treated WF based composites. An addition of WF made the material more brittle as the impact strength results were lower than for pure PP. Thermally treated composite mixtures showed greater impact strength values than untreated composite mixtures. The addition of coupling agents helped to decrease the brittleness to some extent. FTIR showed that the coupling agent had reacted with the WF with the emergence of silyl ether groups (Si-OR). The addition of glycerine did not show any significant difference in the properties of the composites and may need further research. The use of thermally treated WF shows better mechanical properties than untreated WF composites. Waste materials from the timber industry can be easily used but perhaps the use of thermally treated wood may increase the price of the products.

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Appendix 2

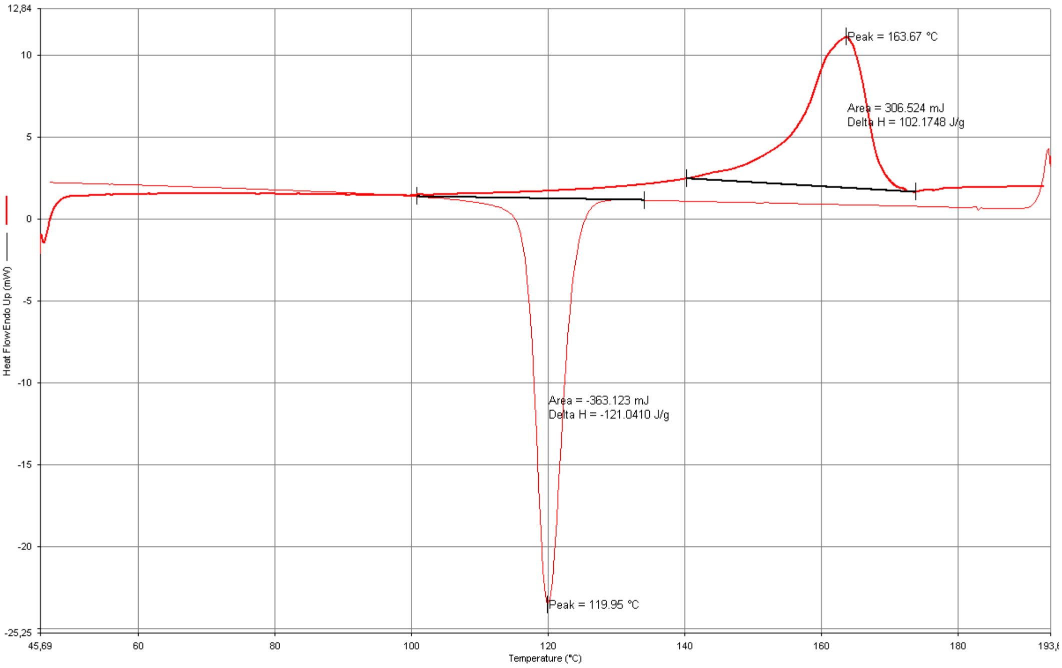


Figure 30. Pure PP DSC curve

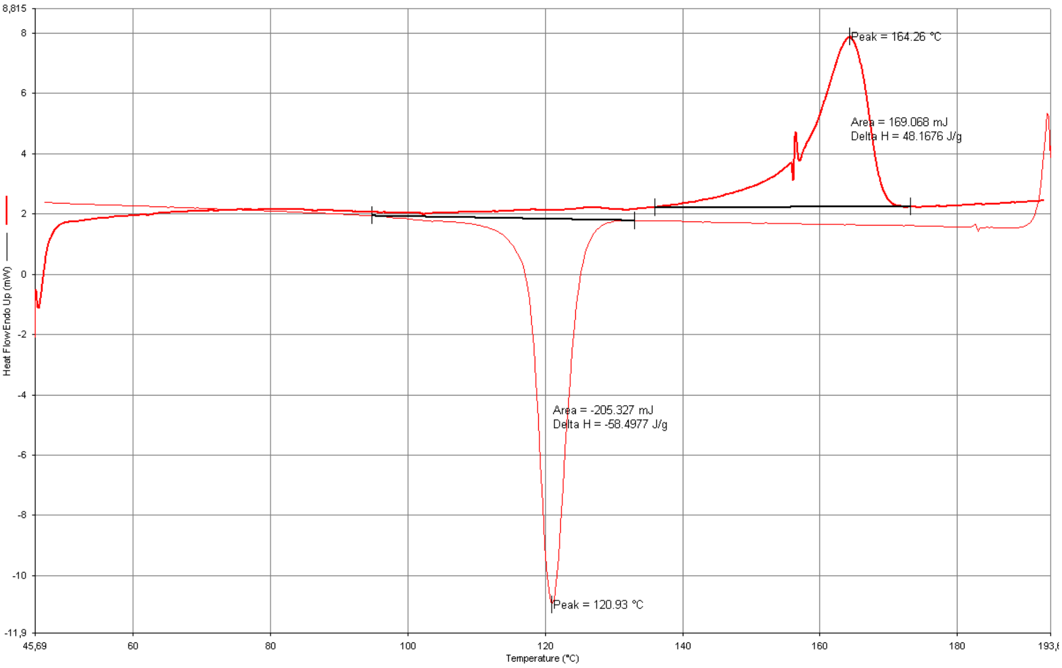


Figure 31. 0,4 mm unmodified DSC curve

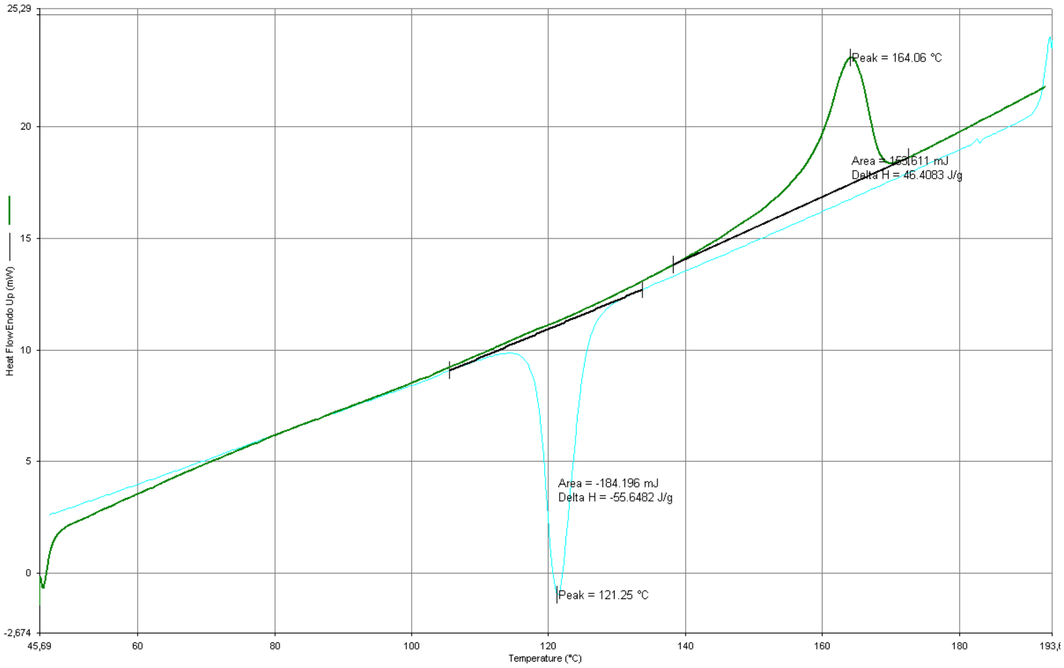


Figure 32. 1 mm unmodified DSC curve

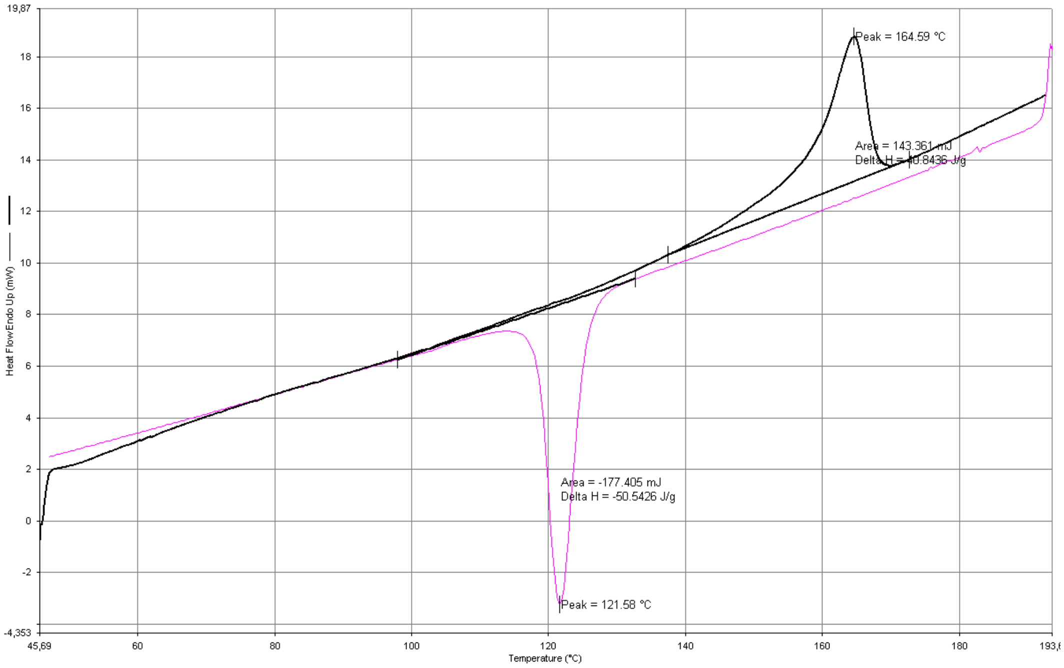


Figure 33. 2 mm unmodified DSC curve

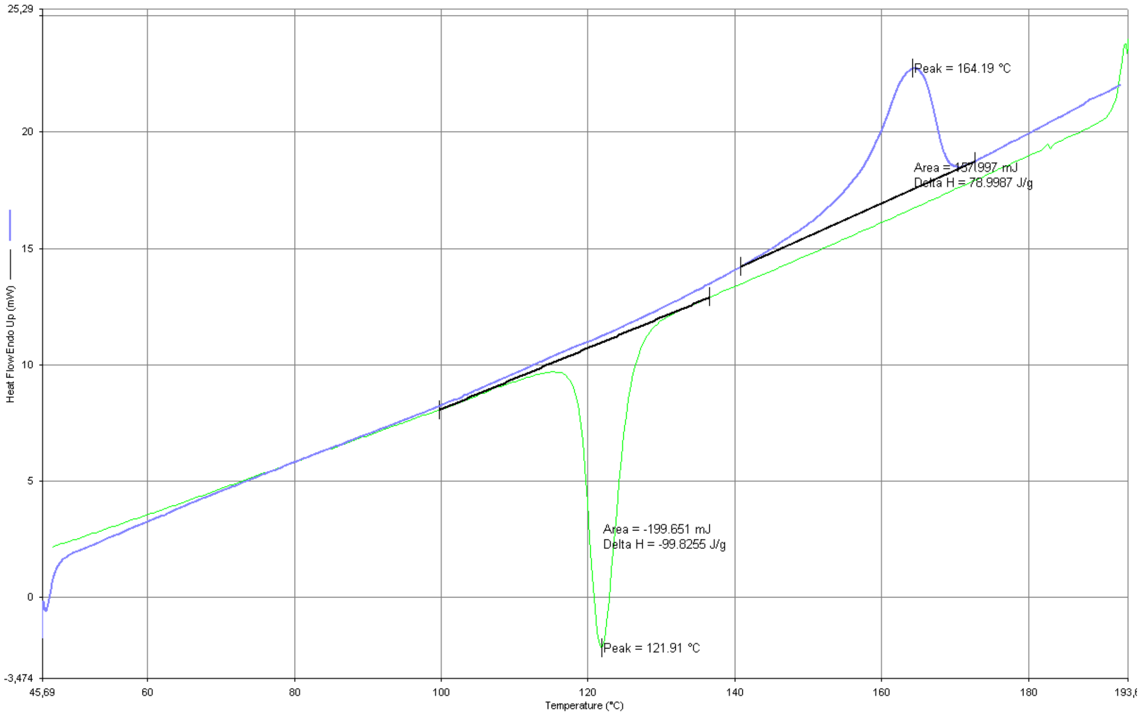


Figure 34. 0,4 mm 5% NaOH DSC curve

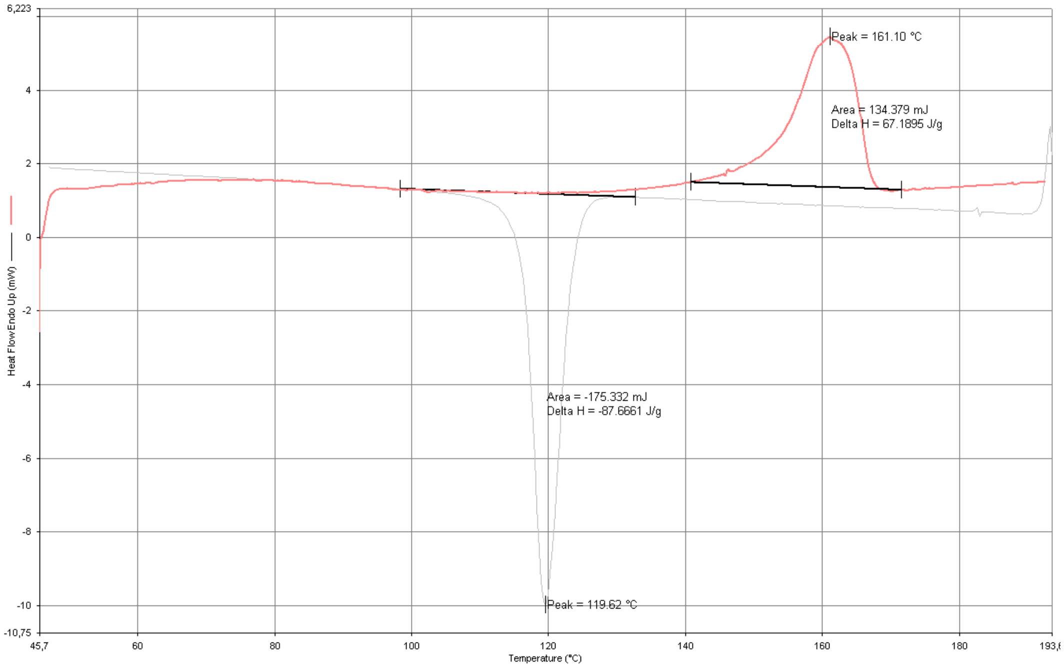


Figure 35. 1 mm 5% NaOH DSC curve

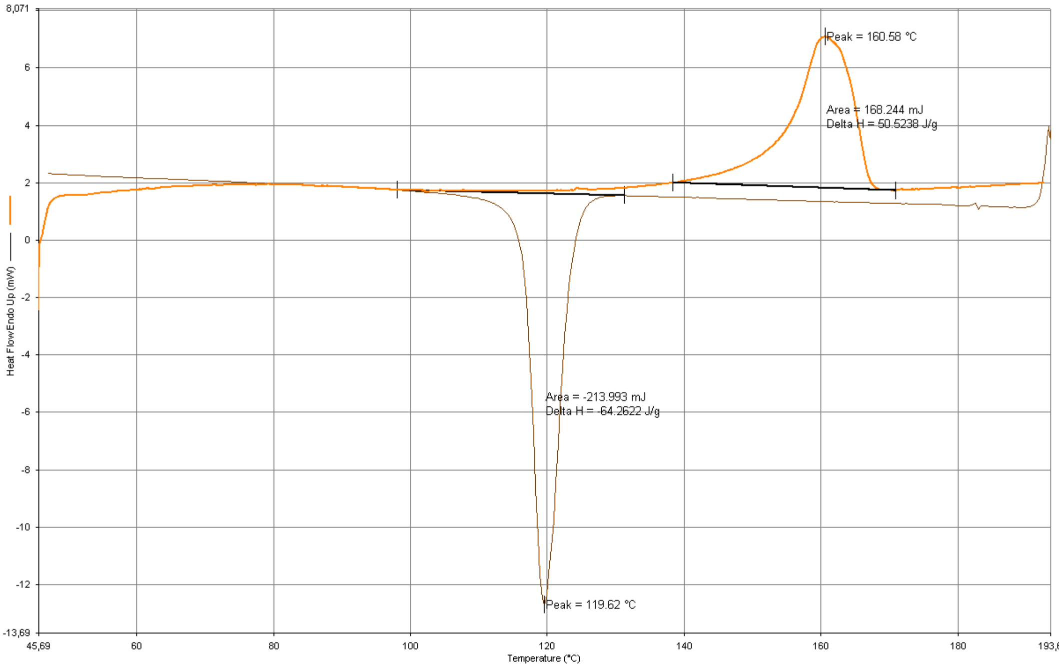


Figure 36. 2 mm 5% NaOH DSC curve

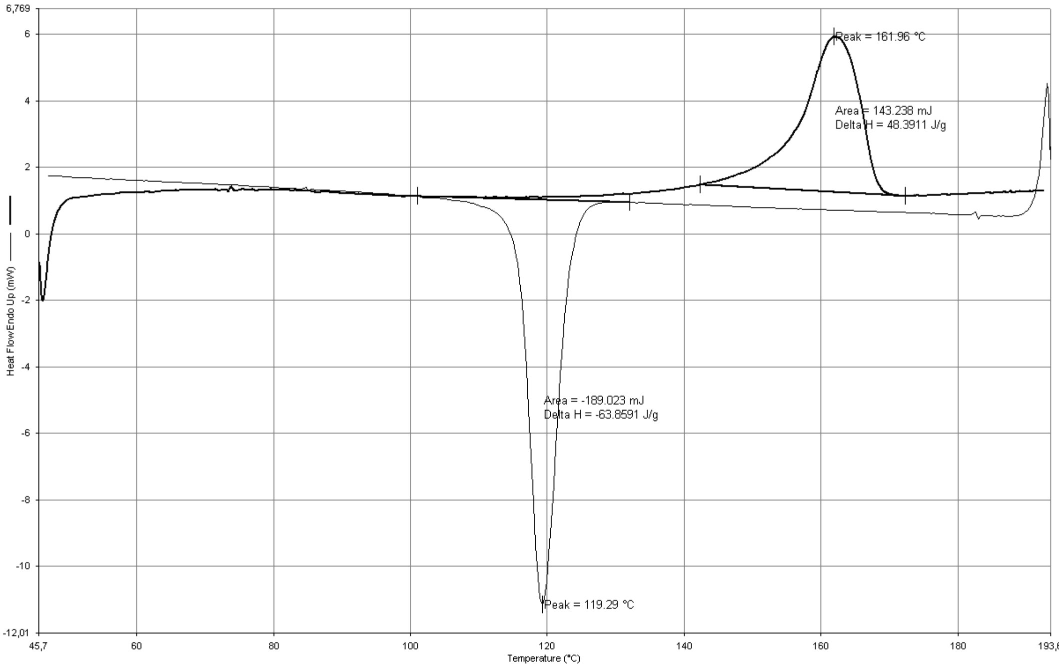


Figure 37. 0,4 5% NaOH 5% APTES DSC curve

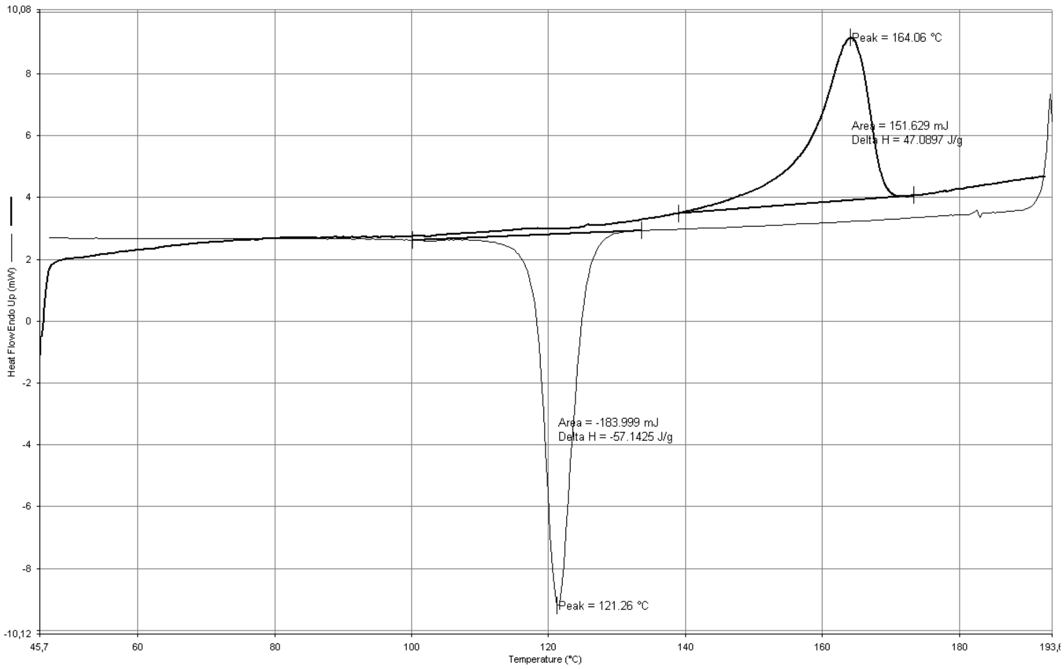


Figure 38. 1 mm 5% NaOH 5% APTES DSC curve

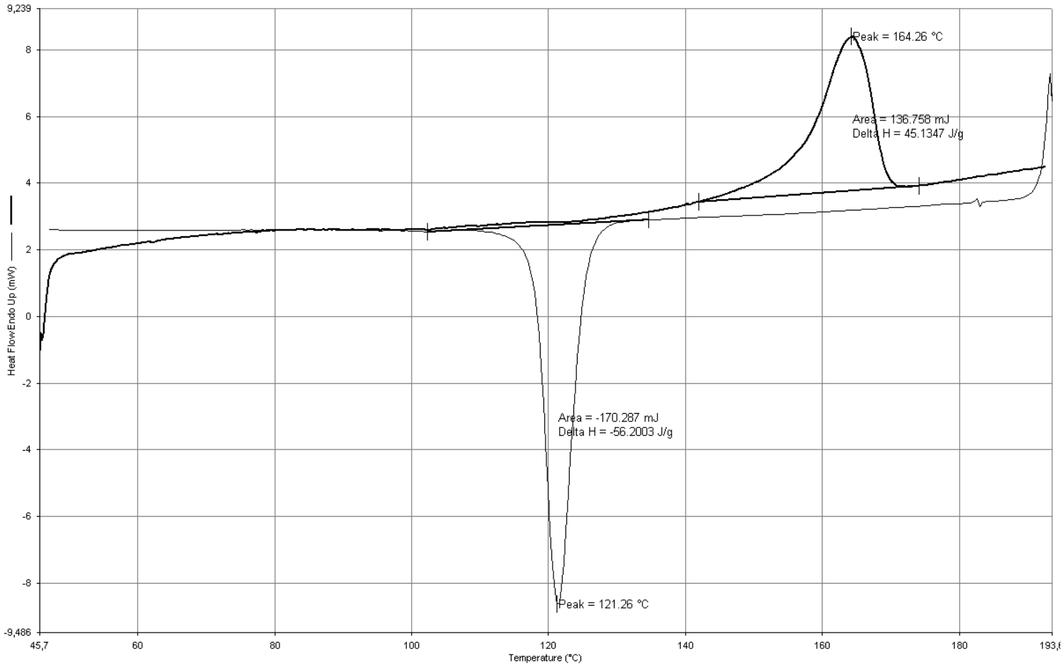


Figure 39. 2 mm 5% NaOH 5% APTES DSC curve

Appendix 3

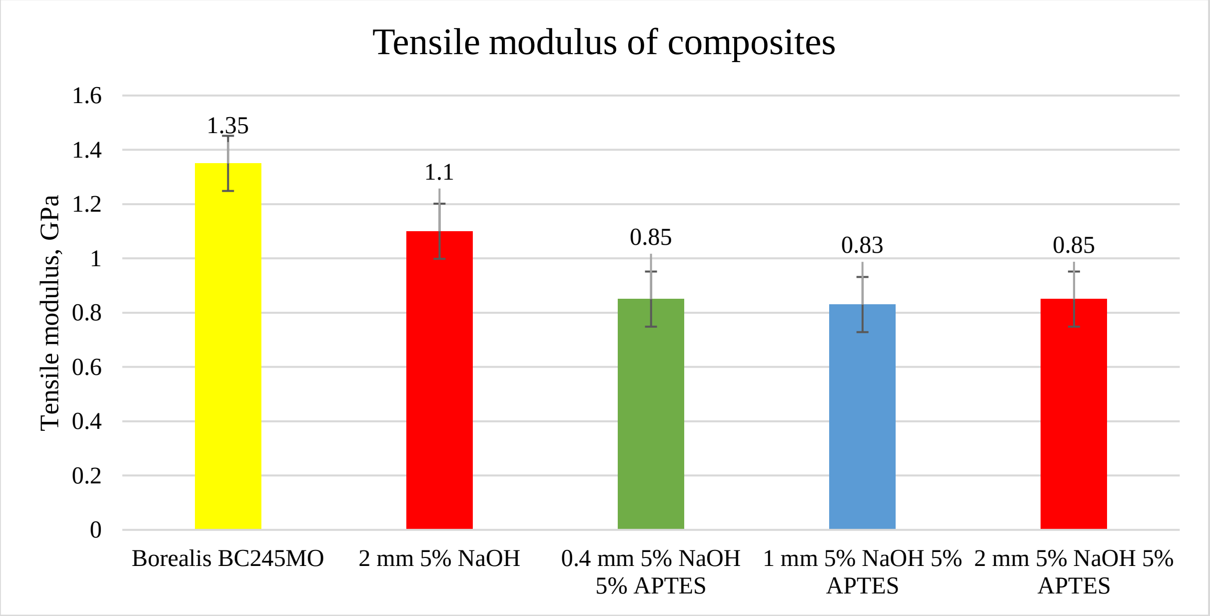


Figure 40. Tensile modulus of composites

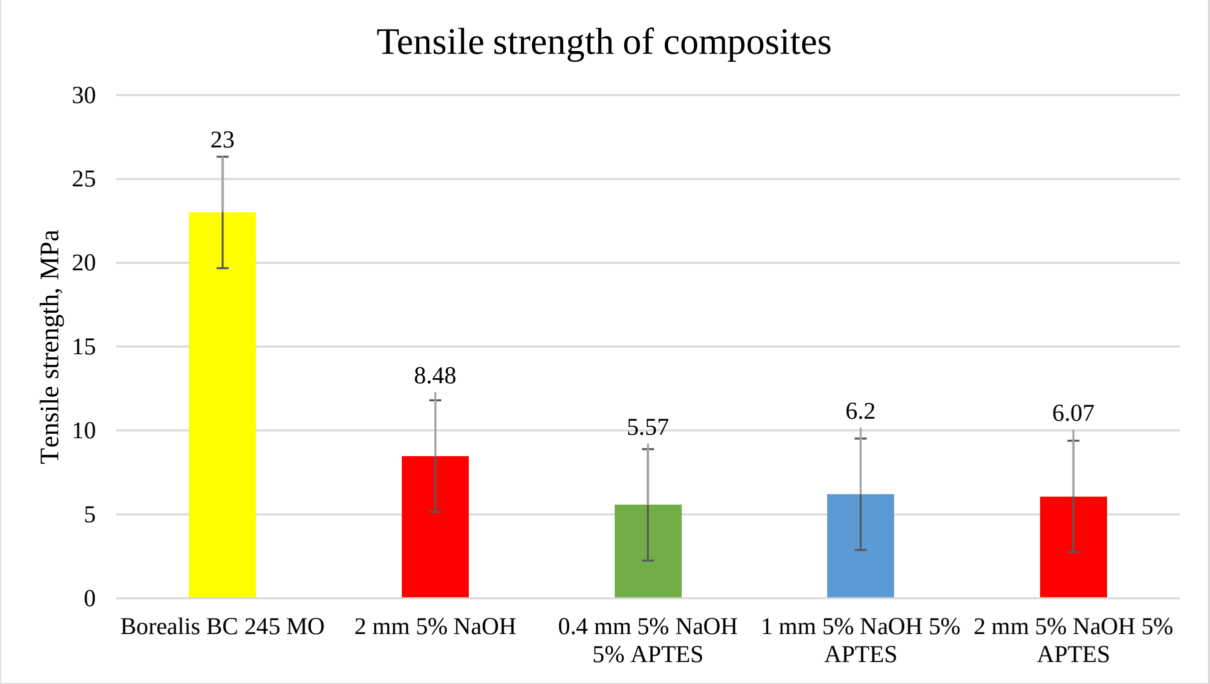
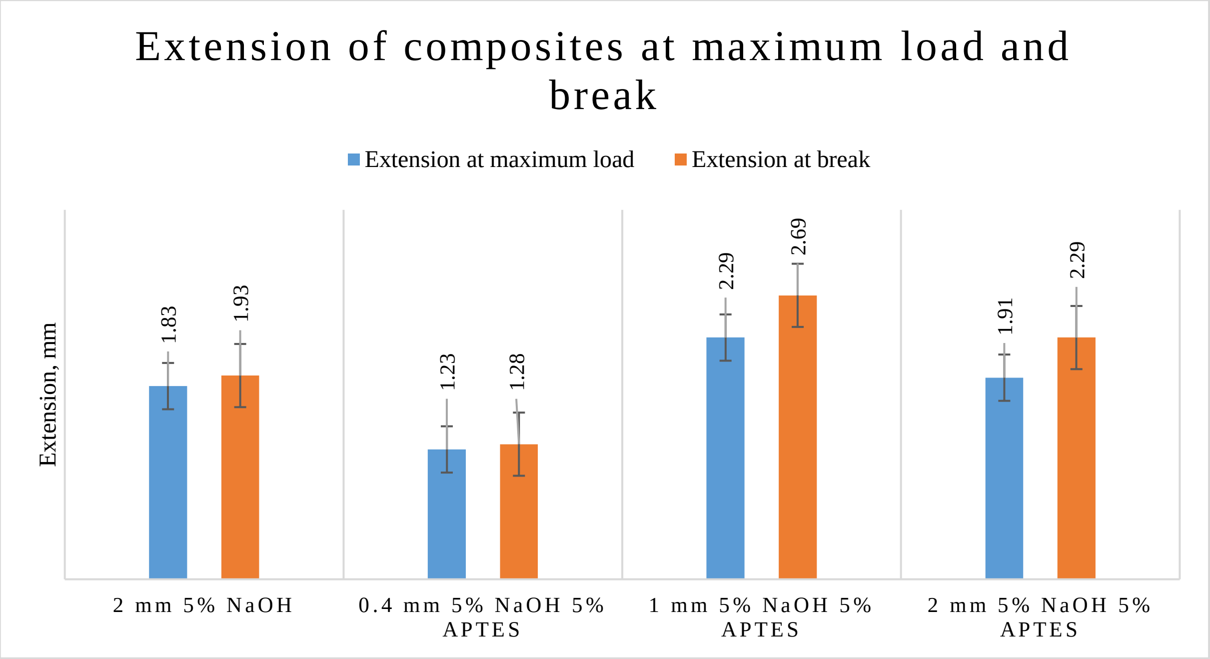


Figure 41. Tensile strength of composites


Extension of composites at maximum load and break
Extension at maximum load
Extension at break
Extension, mm
1.83
1.93
1.23
1.28
2.29
2.69
1.91
2.29
2 mm 5% NaOH
0.4 mm 5% NaOH 5% APTES
1 mm 5% NaOH 5% APTES
2 mm 5% NaOH 5% APTES