

Ossi Martikka

IMPACT OF MINERAL FILLERS ON THE PROPERTIES OF EXTRUDED WOOD-POLYPROPYLENE COMPOSITES

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium 1383 at Lappeenranta University of Technology, Lappeenranta, Finland on the 19th of December, 2013, at noon.

Acta Universitatis
Lappeenrantaensis 563

Supervisor: Professor Timo Kärki
Faculty of Technology
Department of Mechanical Engineering
Lappeenranta University of Technology
Finland

Reviewers: Professor Reijo Lappalainen
BioMater Centre
Department of Applied Physics
University of Eastern Finland
Finland

Dipl.-Ing. Dr. Robert Putz
Division Wood Polymer Composites
Competence Center for Wood Composites and Wood Chemistry
Kompetenzzentrum Holz GmbH
Austria

Opponent: Ph.D. Kalle Nättinen
VTT Technical Research Centre of Finland
Finland

ISBN 978-952-265-542-4
ISBN 978-952-265-543-1 (PDF)

ISSN-L 1456-4491
ISSN 1456-4491

LUT Yliopistopaino 2013

ABSTRACT

Martikka, Ossi

Impact of mineral fillers on the properties of extruded wood-polypropylene composites

Lappeenranta 2013

79 p. + 5 original articles

Acta Universitatis Lappeenrantaensis 563

Diss. Lappeenranta University of Technology

ISBN 978-952-265-542-4, ISBN 978-952-265-543-1 (PDF)

ISSN-L 1456-4491, ISSN 1456-4491

The main aim of this thesis is to study the effect of mineral fillers on the properties of extruded wood-polypropylene composites (WPC). The studied minerals are Talc, Calcite (CaCO_3), two quantities of Wollastonite and Soapstone, and the level of mineral addition is 20 w-%. The study shows that mineral fillers can be used to modify and improve the properties of wood-plastic composites. Especially the moisture-related properties of WPCs were found to be improved significantly by mineral addition. As the WPCs of the studied type are commonly used in outdoor applications, this is of importance in terms of usability. In machining, the addition of two minerals retained the surface roughness at same level throughout the test, indicating a favorable effect on machinability. The use of hard minerals shortened the tool life in machining. In general, a modest increase in density was observed. In many of the studied properties, no apparent influence of mineral addition was found, indicating that the properties were not weakened. An overall result was that talc showed the best overall performance, indicating that it can be used as an active filler improving most of the studied properties, especially moisture resistance. Calcite was found to have nearly similar performance. According to the findings, mineral addition to wood-plastic composites appears to be beneficial; especially moisture resistance can be enhanced without diminishing the other properties or usability in general.

Keywords: wood-polypropylene composite, mineral fillers, WPC

UDC 678.046.3:678.742.3:539.23

AKNOWLEDGEMENTS

The research work presented in this thesis was mainly carried out in various projects during the years 2009 and 2012 at the Fiber Composite Laboratory, Lappeenranta University of Technology.

First of all, I would like to thank my supervisor, Professor Timo Kärki, for presenting me the opportunity to conduct this work, for extensive guidance throughout the work and support.

I also would like to express my gratitude to the reviewers, Professor Reijo Lappalainen, who gave plenty of valuable comments and ideas, and Dipl.-Ing. Dr. Robert Putz for his encouraging comments.

My utmost gratitude goes to doctors Svetlana Butylina and Tiina Huuhilo for their valuable work in joint articles and assistance in conducting the research. Especially I thank Svetlana for her rather altruistic help and guidance.

I address my deepest thanks to all of my colleagues at the Fiber Composite Laboratory for their support. Special thanks go to Rauli Kinnunen for his work in the laboratory, especially with samples and testing

Last but not least I would like to thank Tarja for her affection and long-mindedness; I would not have made it without you.

In Joutseno, 30th of November, 2013.

Ossi Martikka

CONTENTS

LIST OF ORIGINAL PAPERS.....	2
1 INTRODUCTION.....	5
1.1 WOOD PLASTIC COMPOSITES.....	5
1.1.1 <i>Market and production</i>	6
1.1.2 <i>Manufacture</i>	8
1.1.3 <i>Raw materials used in WPC</i>	11
2 PURPOSE OF THE STUDY.....	32
3 MATERIALS AND METHODS.....	33
4 REVIEW OF THE RESULTS AND DISCUSSION.....	34
4.1 EFFECT OF WOOD MATERIAL.....	34
4.2 MECHANICAL PROPERTIES.....	35
4.3 MOISTURE RESISTANCE.....	36
4.4 THERMAL PROPERTIES.....	38
4.5 MACHINABILITY.....	40
5 SYNTHESIS OF THE IMPACT OF MINERAL FILLERS.....	42
5.1 MECHANICAL PROPERTIES.....	42
5.2 MOISTURE RESISTANCE.....	46
5.3 THERMAL PERFORMANCE.....	48
5.4 PHYSICAL PROPERTIES.....	49
5.5 MACHINABILITY.....	51
5.6 SUMMARY OF PROPERTIES AND PERFORMANCE.....	54
6 DISCUSSION.....	56
6.1 MECHANICAL PROPERTIES.....	58
6.2 MOISTURE RESISTANCE – BIOLOGICAL RESISTANCE.....	60
6.3 THERMAL PROPERTIES.....	61
6.4 PHYSICAL PROPERTIES.....	62
6.5 MACHINING.....	63
6.6 ECOLOGICAL AND ECONOMICAL ASPECTS.....	64
7 CONCLUSIONS.....	68
8 REFERENCES.....	70

ORIGINAL PAPERS I-V

LIST OF ORIGINAL PAPERS

This thesis is a summary of the following papers, which are referred to in the text by the Roman numerals I - V.

- I Butylina, S., Martikka, O., Kärki, T. 2011. Properties of Wood Fibre-Polypropylene Composites: Effect of Wood Fibre Source. *Applied Composite Materials*. 2(18): 101-111.
- II Huuhilo, T., Martikka, O., Butylina, S., Kärki, T. 2010. Mineral fillers for wood-plastic composites. *Wood Material Science and Engineering*. 5(1): 34-40.
- III Huuhilo, T., Martikka, O., Butylina, S. and Kärki, T. 2010. Impact of Mineral Fillers to the Moisture Resistance of Wood-Plastic Composites. *Baltic Forestry* 16 (1): 126-131.
- IV Martikka, O., Huuhilo, T., Butylina, S. and Kärki, T. 2012. Impact of mineral fillers on the thermal properties of wood plastic composites. *Wood material science and engineering*. 7(2): 107-114.
- V Martikka, O & Kärki, T. 2013. Machinability of extruded wood-polypropylene composites – comparison with solid wood. In review, *Baltic Forestry*.

NB: These articles should be referred to according to the bibliographic information given above. No reference should be made to the reprint in this thesis.

The author is responsible for the following in the joint papers:

In paper I, the author was responsible for producing the materials studied, had responsibility for planning, sampling, measuring, and analyzing the results, as well as writing the paper.

In papers II and III, the author was responsible for producing the materials studied, had full responsibility for planning and sampling, and was responsible for measuring and analyzing the results, as well as writing the paper.

In paper IV the author had the main responsibility for planning, producing the materials studied, analyzing the results, and writing the paper.

In paper V, the author had the responsibility for producing the materials studied, planning, sampling, measuring, analyzing the results, and writing the paper.

SECTION I

OVERVIEW OF THE THESIS

1 INTRODUCTION

1.1 Wood plastic composites

Improved sophistication in processing technologies and formulations has led to the development of wood-plastic composites (WPC) that exhibit synergistic material properties. Wood-plastic composites consist primarily of wood and thermoplastic polymers. Traditionally, the materials have been viewed as wood fiber or particles reinforcing a continuous thermoplastic matrix. Therefore, the development of WPCs has followed previous work on synthetic fibers and fillers such as glass, carbon, aramid, and various mineral fillers. As with the synthetic counterparts, WPC researchers have sought enhanced strength, stiffness, creep, and thermal stability. However, the commercial success of these emerging materials has depended primarily on the promise of improved moisture performance, utilization of recycled and waste material, and efficiency in product and process design (Wolcott & England 1999).

WPC materials consist primarily of a thermoplastic and a lignocellulosic component, but a variety of additional components are commonly used to improve the processing and properties of the resulting materials. Wood is the most common source of the lignocellulosic component of WPCs. A variety of wood species is used; and even though differences between species may exist, they have not been studied explicitly. Many agricultural fibers have also been used successfully in WPCs. Agricultural fibers often display certain advantages with respect to aspect ratio and specific mechanical properties. For both wood and agricultural fibers, the material is used in the form of fiber, flour, or particle. In general, the particles and flour are formed with hammermills and grinders commonly used in the production of wood-based particleboard. Fibers can also be produced with thermomechanical and chemical pulping methods that are used in pulp and fiberboard manufacture (Wolcott 2007).

The primary criterion in selecting the thermoplastics for WPCs is the processing temperature less than ca. 250°C. Above this threshold, unmodified lignocellulosic materials undergo rapid thermal degradation. This thermal criterion has limited WPCs to polyolefins. The commonly used thermoplastics include poly(propylene) (PP), high and low density poly(ethylene) (HDPE, LDPE), poly(vinyl chloride) (PVC), and poly(styrene) (PS). In addition, impact-modified

versions of PP and PS have been explored. Both recycled and virgin sources of these commodity thermoplastics are commonly employed in powder or pellet form (Wolcott 2007).

Wood plastic composites have become a noticeable group of materials that are used or being introduced to especially non-structural or semi-structural outdoor building applications, such as decking and railing systems, fenestration applications, moldings and exterior covering applications like siding and trim (Pritchard 2004, Stark & Matuana 2004, Smith & Wolcott 2006, Klyosov 2007).

1.1.1 Market and production

The global trend has been towards more ecological materials for decades, and the trend is also evident in the composite market. Bio- and bio-based composites consist of composites made of both natural/biofibers and biodegradable polymers (eg., starch, PLA) or petroleum-derived non-biodegradable polymers (e.g., PP, PE) (Mohanty et al. 2005, John & Thomas 2008), of which wood-polymer composites are a good example. The global markets for bio-based composites grew by 15% per annum from 2005 to 2010 (Figure 1) and are expected to reach \$ 3.8 billion by the year 2016 with a 10% growth per year.

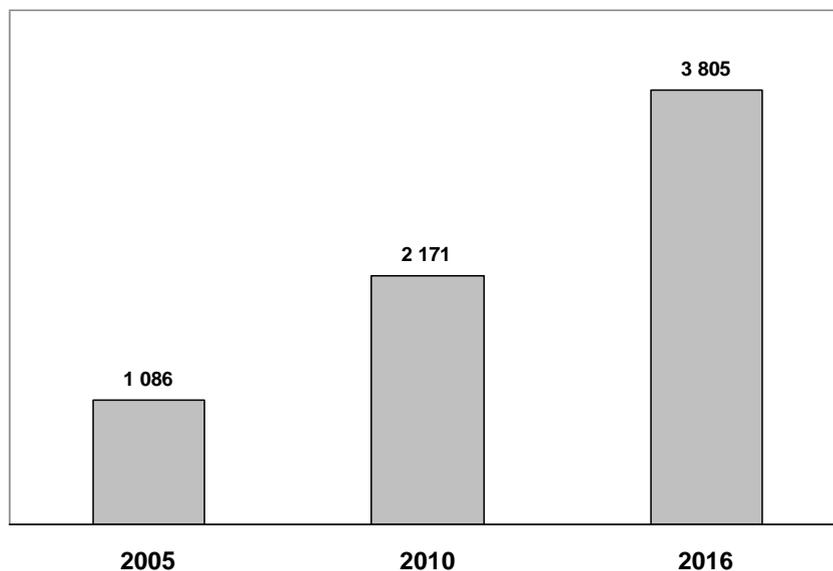


Figure 1. Global markets for bio-based composites in millions of dollars (adapted from Eder 2011).

The growth in WPC production has been noticeable in North America and Europe in the 2000s – in North America the production increased from the annual rate of nearly 150 000 tons in 2000 to 800 000 tons in 2009. During the same interval, the production in Europe increased from nothing to over 100 000 tons a year (Eder et al. 2007). Of the production, WPC deck board alone accounts for about 50 % of the overall WPC volume, in Europe the share is 57% (Eder et al. 2007, Eder 2010). The use of WPC in Europe increases by 10% annually and is expected to advance by more than 10% per year in the United States. The growth in China is at the level of 30% per year and is predicted to increase by up to 5 million tons per year between 2009 and 2015 (Faruk et al. 2011). The trends and current status of the European WPC markets according to AMI consulting (Nash 2011) are presented in Table 1.

Table 1. Volume of WPC in the EU 25* and Norway and Switzerland (adapted from Nash 2011).

	2005	2010	2013	2005-2010	2010-2013
	'000 tonnes			% per annum	
Construction	2	5	9	18%	22%
Building exteriors	23	144	180	44%	8%
Building interiors	7	8	14	4%	21%
Miscellaneous	5	10	11	14%	5%
Total	37	167	214	35%	9%

* EU 25 denotes all member states of the EU excluding Bulgaria, Croatia and Romania.

1.1.2 Manufacture

Generally, wood-polymer composites are processed by either injection molding or extrusion (Kim & Pal 2011). Injection molding requires a polymer with low molecular weight, so as to maintain low viscosity. By contrast, in extrusion a polymer with a higher molecular weight is required for better melt strength (Faruk et al. 2011).

The general processing of WPC is performed in several steps, as illustrated in Figure 2.

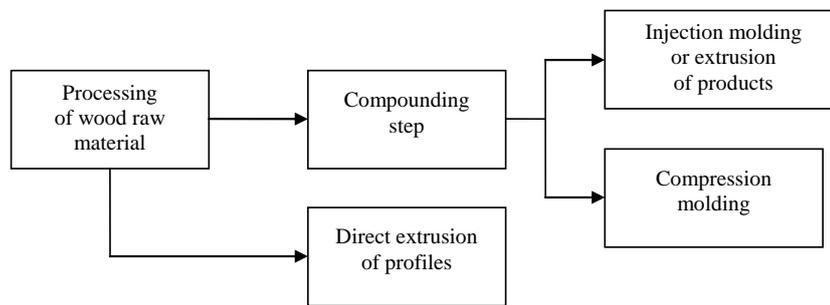


Figure 2. WPC processing (adapted from Oksman & Bengtsson 2007).

The first step in the WPC processing is to increase the value and quality of the wood raw material, which is divided into different sizes or species, and finally dried before the compounding step. The compounding step means blending the reinforcement/filler with the thermoplastic. The compounding is usually made in a twin-screw extruder, and the most common technique today is direct extrusion to profiles, such as decking materials or sheets for compression molding. Another possibility is to produce pellets (granulate), which can be injection-molded or extruded (Oksman & Bengtsson 2007).

The use of twin-screw extruders results in better dispersion compared to single-screw extruders. Better dispersion between the plastic matrix and fibers causes noticeable improvement in the mechanical (tensile) properties of the WPC (Yang, et al. 2006). A majority of WPCs are manufactured by profile extrusion. The types of extruders and processing strategies vary; some processors run compounded pellets through single-screw extruders while others compound and extrude in one step with twin-screw extruders. It is also possible to use two types of extruders in tandem, one for compounding and the other for profiling (Clemons et

al. 2012). Moisture can be removed from the wood component before processing, during a separate compounding step (or in the first extruder in a tandem process), or by using the first part of the extruder as a dryer in an in-line process (Clemons et al. 2012).

The density of biomass materials is much lower than that of inorganic fillers, and feeding the extruder can be a problem. Fibers are usually fed into the extruder in one of two ways. Pellets can be made of the biomass material and fed into the extruder along with the plastic pellets. A side stuffer can be added to the extruder line, and the fiber or flour can be added at that point. If loose fiber or flour is used, there is usually a build-up of static electricity that has to be dealt with (Rowell 2007).

Composites can be produced by different processing strategies, namely injection molding (Figure 3), extrusion (Figure 4), or thermoforming/compression molding (Figure 5), and all three methods produce composites with different properties (Rowell 2007). For example, it was found in moisture absorption tests that compression-molded composites reached the equilibrium fastest and the equilibrium was the highest: 4.1% in about 5 weeks; extruded composites reached the equilibrium (3.6%) in 9 weeks; and injection-molded specimens had a moisture content of less than 2% and had not reached the equilibrium at the end of the 9 week test (Clemons 2002, Rowell 2007).

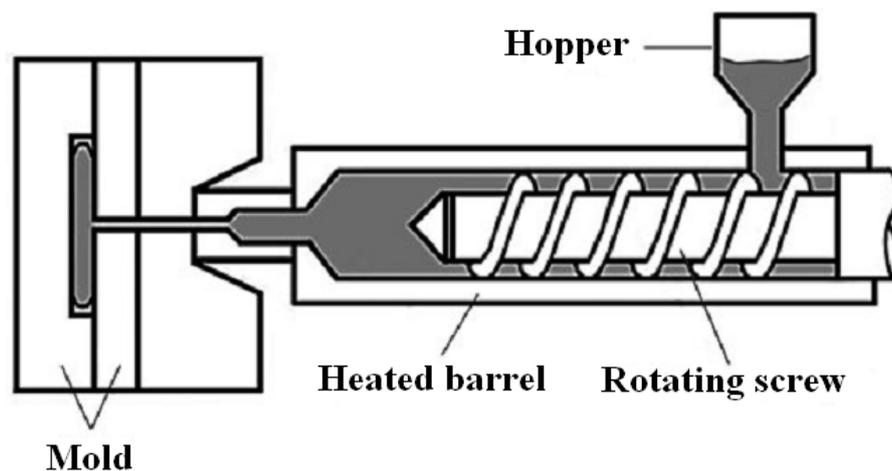


Figure 3. The principle of injection molding. (Zheng et al. 2011)

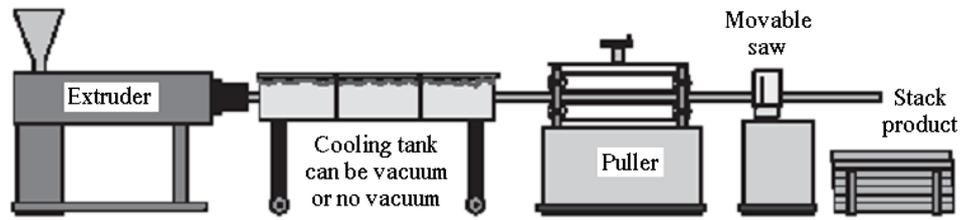


Figure 4. Illustration of a profile extrusion line. (Giles et al. 2005)

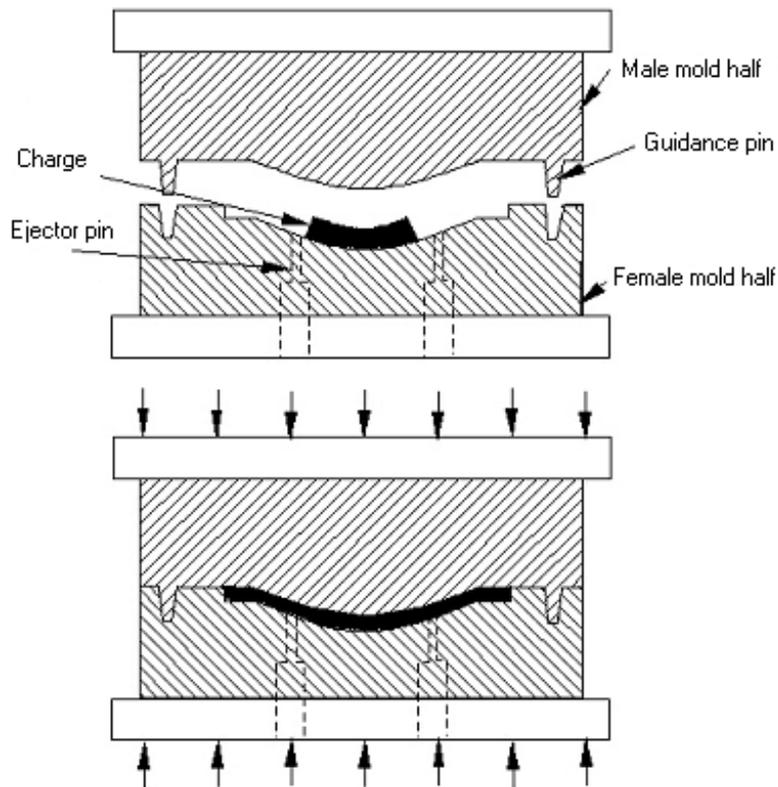


Figure 5. Schematic of the compression molding process. (Mazumdar 2002)

1.1.3 Raw materials used in WPC

Wood-plastic composites usually consist of more than just wooden material and plastic – various additives and fillers are also typically added. These materials are briefly presented in the following chapters.

1.1.3.1 Wood material

The term “wood-plastic composites” (WPCs) refers to wood as a proxy for fibrous materials of plant origin. They can be wood flour or sawdust, agricultural plant residues, typically cut, milled or ground, or other types of natural fiber, such as hemp, jute, and kenaf, commonly a by-product of the respective industrial process (Klyosov 2007).

In fiber-reinforced composites, such as WPCs, the fibers serve as reinforcement by giving adhesive to hold the fibers in place so that suitable structural components can be made. A broad classification of the natural fibers used in WPCs and biocomposites in general is presented in Figure 6. (Mohanty et al. 2005) The term biocomposite is generally used as a proxy for composites consisting of at least one natural/biobased component (Pilla 2011).

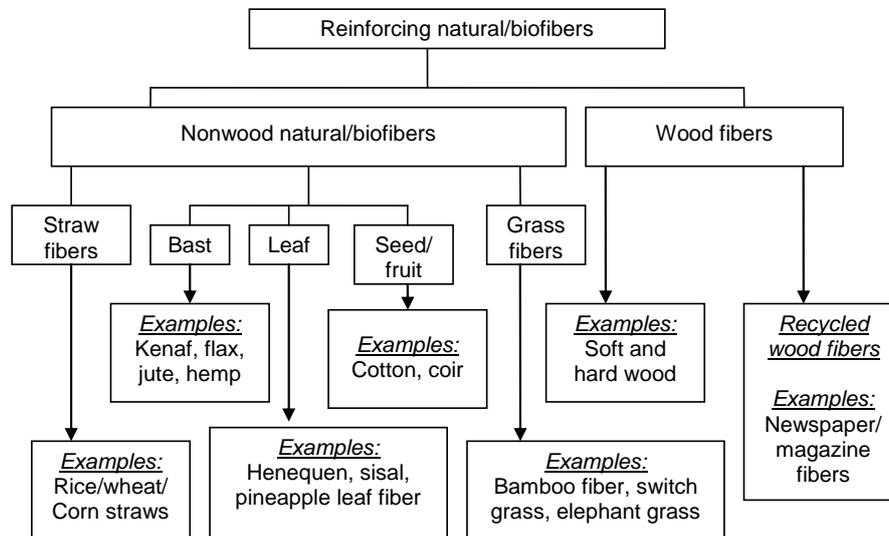


Figure 6. Schematic representation of reinforcing natural/biofiber classification (adapted from Mohanty et al. 2005).

In industry, most producers use wood flour (or “wood fiber”) in WPCs (Klyosov 2007). Fibers are explicitly added to increase the stiffness and strength of the composite. In WPCs, the wood is generally in the form of short fiber, particle, or flour. These small sizes integrate well with the processing techniques utilized in the plastics industry. Many species are used in commercial production - pine, maple, and oak being the most common ones. Currently, the selection of species seems to be influenced more by availability than engineering (Wolcott & Englund 1999).

A European aspect is presented in a study conducted by Wood K Plus (Haider & Eder 2010), where the use of wood fiber material is divided as presented in Figure 7 (per company). The figure shows that hardwood is used in over 50% of the companies and softwood in 80% of the companies. It also appears that in many cases European companies use more than one type of fiber in the WPCs they produce.

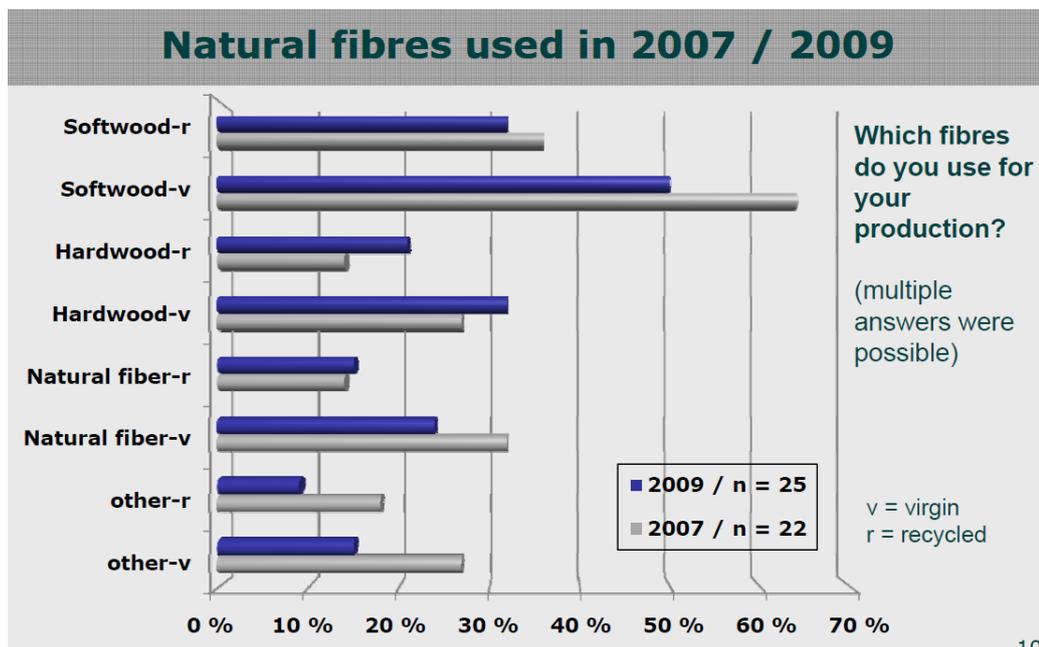


Figure 7. Use of natural fibers by European WPC producers. (Haider & Eder 2010)

1.1.3.1.1 Structure of wood

Wood is produced by a thin zone of dividing cells near the outside of the trunk or branch just beneath the bark. Known as the vascular cambium, its cells are thin-walled and meristematic. The cambium is essential for the continued growth of the tree; more wood is added by the cambium to the trunk and the stem thickens. In temperate climates the cyclic production of new wood cells each spring and summer and the subsequent cessation of cambial divisions each autumn and winter leave a pattern in the wood that we know as annual growth rings; however, drought may cause the growth to restart later in the season, creating a ‘false’ ring. In variable tropical climates trees may produce new growth rings in each rainy period. In such cases the rings are obviously not annual. Growth rings are very distinct in some woods but not well defined in others. This can be due to the differences in the cell types produced in the wood in the case of complex hardwoods, or it may be due to the severity of the winter season where the tree grows. Trees growing in milder climates with warm winters do not produce growth rings that are as sharp and distinct as in trees growing in climates where the winters are more severe and extreme. In softwoods, growth rings show up as a result of differences in density across the year’s growth (Butterfield 2007).

Early in the growing season, the vascular cambium tends to produce tracheids that may have large central cavities or lumens and thin walls. These cells function more for the conduction of water than for supporting the trunk, and the wood is called earlywood or springwood. Towards the end of the growing season, the cambium produces cells that have smaller lumens and much thicker walls in keeping with the transition in function from conduction to primarily that of support. These cells form latewood or summerwood. The tree thus concludes its annual growth with a cylinder of strong thick-walled cells suitable to help the tree overwinter. The transition from earlywood during the growing season can be gradual as in spruce or radiata pine, or quite abrupt as in Douglas fir (Butterfield 2007).

The wood at the center of a trunk or stem is often harder and darker in color than the wood nearer the bark. This darker central region is known as heartwood, and its cells are dead and physiologically inactive. The outside of the trunk is known as sapwood, which is active in water transport and other physiological activities. Sapwood is usually paler in color than heartwood, though the heartwood of some species such as ash, fir, poplar and spruce is also quite pale. The cells of the heartwood are darker in color due to the enrichment of the cells by various extraneous chemicals, known as extractives. These chemicals permeate both the cell wall and the cell lumen. Small quantities of the precursors of extractives may be found in the living cells near the sapwood-heartwood boundary (Butterfield 2007).

Heartwood is formed after several years of growth of the trunk or branch. It forms a cone within the trunk that spreads slowly outwards and upwards as the stem expands with age. Heartwood formation in *Pinus radiata* and the southern pines of North America begins when the tree is about 15 years old: young trees have little or no heartwood, whereas older trees may have a substantive percentage of heartwood in their trunk. The precise cause of heartwood formation is not known, but it is characterized by the accumulation of polyphenolic substances in the cells and a general reduction in the moisture content of the wood. Heartwood is of considerable interest because its color renders it pleasing for furniture, paneling or craftware. In addition to color, it may be more aromatic due to the extractives. The durability of heartwood and its resistance to decay are quite variable. Heartwood is generally more difficult to penetrate with preservatives than sapwood and also more difficult to dry (Butterfield 2007).

In botanical terms, softwoods come from gymnosperms (mostly conifers), and hardwoods come from angiosperms (flowering plants). Softwoods and hardwoods also differ in terms of their component cells. Softwoods have a simpler basic structure than hardwoods: they have only two cell types and relatively little variation in structure within these cell types. Hardwoods have greater structural complexity because they have both a greater number of basic cell types and a far greater degree of variability within the cell types. The single most important distinction between the two general kinds of wood is that hardwoods have a characteristic type of cell called a vessel element (or pore), whereas softwoods lack these. An important cellular similarity between softwoods and hardwoods is that in both kinds of wood, most of the cells are dead at maturity, even in the sapwood. The cells that are alive at maturity are known as parenchyma cells and can be found in both softwoods and hardwoods (Wiedenhoef 2010).

Softwoods are built up primarily of axially-elongated cells termed tracheids. Tracheids have no living cell contents at functional maturity and comprise thick-walled conduits with their tips densely interlaced. Their length varies between species and also with their position in the stem. Tracheids tend to be longer at lower levels in the tree than higher up and also longer nearer the bark than at the stem center. They also tend to be longer in the latewood than in the earlywood of each growth ring. In mature wood, tracheids range from between 2 to 5 mm in length, but longer tracheids can occur in some species. With diameters of about 15-60 μm , tracheids are about 100 times longer than they are wide. Because they are cut off from the dividing cambial cells, they tend to remain in radial files in the wood. As a result, their tangential dimensions remain fairly uniform. The radial width of the tracheids is largest in the earlywood and smallest in the latewood, where the cells appear radially flattened. The tracheids overlap one another along their thinner, wedge-shaped ends, which appear sharply tipped in tangential view but are more rounded in outline in radial view. This cellular arrangement, which is a direct result of the pattern of the fusiform cambial cells in coniferous species, helps give softwoods a high 'along the grain' strength, allowing for maximum sidewall cell contact for the movement of water up the stem or branch (Butterfield 2007). The different structures are illustrated in Figure 8.

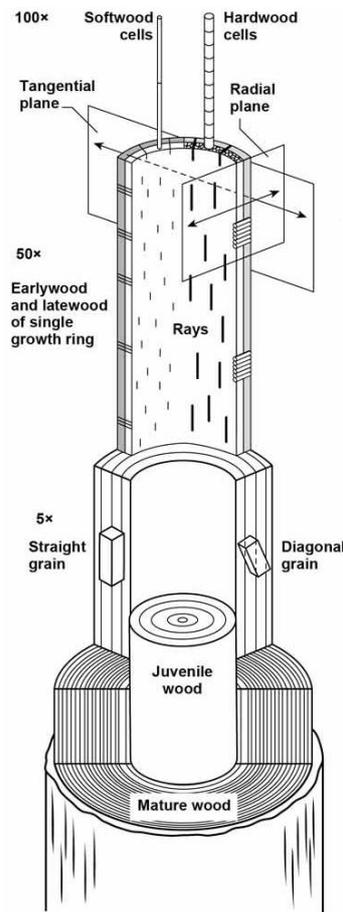


Figure 8. Illustration of a cut-away tree at various magnifications. At the top, at an approximate magnification of 100×, a softwood cell and several hardwood cells are illustrated, to give a sense of scale between the two; one tier lower, at an approximate magnification of 50×, is a single growth ring of a softwood (left) and a hardwood (right), and an indication of the radial and tangential planes; the next tier, at approximately 5× magnification, illustrates many growth rings together and how one might produce a straight-grained rather than a diagonal-grained board; the lowest tier includes an illustration of the relative position of juvenile and mature wood in the tree, at 1× magnification. (Wiedenhoeft 2010)

A living plant cell consists of two primary domains: the protoplast and the cell wall. The protoplast is the sum of the living contents that are bounded by the cell membrane, and the cell wall is a non-living, largely carbohydrate matrix extruded by the protoplast to the exterior of the cell membrane. The plant cell wall protects the protoplast from osmotic lysis and often provides mechanical support to the plant at large (Wiedenhoeft 2010).

For the cells in wood, the situation is somewhat more complicated than the highly generalized case presented above. In many cases, the ultimate function of the cell is borne solely by the cell wall. This means that many mature wood cells not only do not require their protoplasts, but must remove their protoplasts completely prior to achieving functional maturity. For this reason, a common convention in wood literature is to refer to a cell wall without a protoplast as a cell. Although this is technically incorrect from the cell-biological standpoint, the convention is common in the literature and will be observed throughout the remainder of the chapter. In the case of a mature cell in wood in which there is no protoplast, the open portion of the cell where the protoplast would have existed is known as the lumen. Thus, there are two domains in most cells in wood; the cell wall and the lumen. The lumen is a critical component of many cells, whether in the context of the amount of space available for water conduction or in the context of the ratio between the width of the lumen and the thickness of the cell wall. The lumen has no structure per se, as it is a void space in the interior of the cell. Thus, wood is a substance that has two basic domains; air space (mostly in the lumina of the cells) and the cell walls of the component cells (Wiedenhoef 2010). The structure is illustrated in Figure 9.

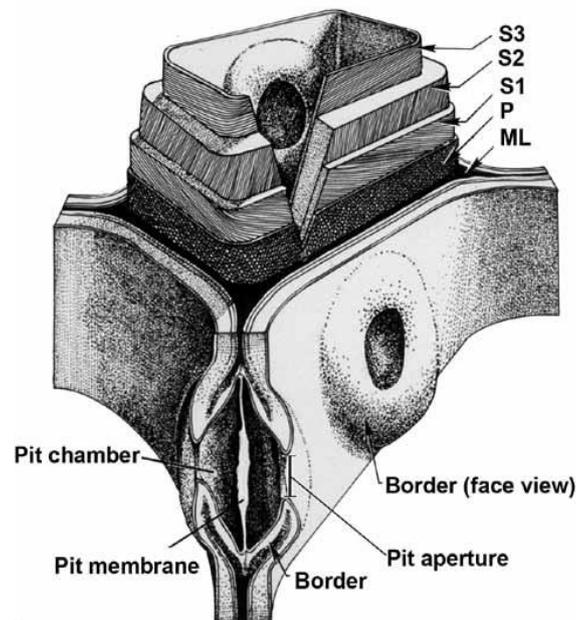


Figure 9. Cut-away drawing of a wood cell: the various layers of the cell wall are detailed at the top of the drawing, beginning with the middle lamella (ML). The next layer is the primary wall (P), and on the surface of this layer the random orientation of the cellulose microfibrils is detailed. Interior to the primary wall is the secondary wall in its three layers: S1, S2, and S3. (Wiedenhoef 2010)

1.1.3.2 Plastics and additives

1.1.3.2.1 Volume plastics

In the manufacture of WPCs, the most commonly used polymer types are polyethylene (PE), polypropylene (PP) and polyvinylchloride (PVC). In North America, the great majority of WPCs have polyethylene as the matrix, though polypropylene, polyvinylchloride, and others are also used. The large use of polyethylene is in part due to the fact that many of the early WPCs were developed as an outlet for recycled film, as well as the low cost and availability of recycled sources of polyethylene. Polypropylene is widely used in Europe (Clemons 2008).

Some of the general properties of the plastics mentioned above are presented in Table 2 below. The properties of the plastics used in WPCs can be modified with various methods, starting from the polymerization process. Also a multitude of modifiers are available (e.g. plasticizers to alter flexibility, thermal stabilizers), and hence the properties listed in Table 2 are of a general nature. The chemical structure of the plastics mentioned above is presented in Figure 10.

Table 2. Properties of plastics commonly used in WPC (adapted from Baker & Mead 2002 and Erhard 2006).

Common name (abbreviation)	Microstructure	Melting temperature [°C]	Density [g/cm ³]	Tensile strength [MPa]	Impact strength [J/m]	Heat deflection temperature [°C]@1.82MPa
HDPE	Semi-crystalline	130-140	0.95	38.2	373	74
LDPE	Semi-crystalline	108-115	0.92	11.6	NB*	43
PP	Semi-crystalline	160-165	0.90	35.8	43	102
PVC (rigid)	Amorphous	N/A*	1.4	44.4	181	68

*NB=No Break, *N/A=Not Applicable

Compared to PVC, the density of polyolefins (PE and PP) is noticeably lower and they have an apparent melting temperature/point unlike amorphous PVC, which softens until its decomposition starts at 148°C. The lowest density of LDPE is due to its branched structure (illustrated in Figure 10).

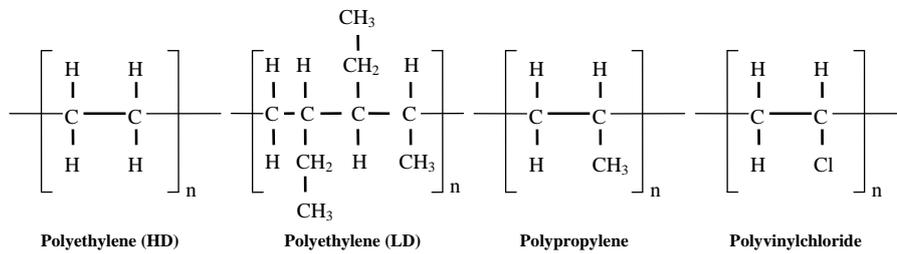


Figure 10. Chemical structure of the common plastics used in WPC.

1.1.3.2.2 Bio-based plastics

The general trend has been towards materials of natural, renewable origin, and the trend is the same with plastics. An overview of bio-plastics and their categorization is given in Figure 11. Bio-based plastics, also applicable to WPCs, include polylactic acid (PLA), thermoplastic starch (TPS), cellulose acetates (CAB and CAP) and polyhydroxyalkanoates (PHA). Biodegradable plastics can be divided into three categories (Khanna & Srivastava 2005): chemically synthesized polymers (e.g. PLA), susceptible to enzymic or microbial attack; starch-based biodegradable plastics (e.g. TPS) that make micro-organisms degrade easily; and polyhydroxyalkanoates (PHAs), which is a family of biopolyesters, the only bioplastics completely synthesized by microorganisms (Chen 2010). Depending on the copolymer composition of the polyhydroxyalkanoate, a range of designer PHAs with desirable properties can be obtained. Some of the most common ones are listed in Table 3 and their properties in Table 4.

Table 3. Physical properties of poly(3-hydroxybutyrate), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and poly(4-hydroxybutyrate) (Adapted from Philip et al. 2007).

Properties	Poly (3HB)	Poly (3HB-3HV)	Poly (4HB)
Melting temperature (°C)	177	150	60
Glass transition temperature (°C)	4	- 7.25	- 50
Tensile strength (MPa)	40	25	104
Elongation at break (%)	6	20	1000

Table 4. Properties of bioplastics.

Properties	PLA	TPS	CAB	PHB (3B)
Melting temperature (°C)	150-162	139	192	168-182
Density (g/cm ³)	1.21-1.25	1.37	1.2	1.18-1.262
Glass transition temperature (°C)	45-60	48	132	5-15
Tensile strength (MPa)	21-60	4	51	40
Elongation at break (%)	2.5-6	78	78	5-8

Data sources: PLA+PHB (3B): Van de Velde & Kiekens 2002, TPS: Schwach et al. 2008, CAB: Wertz, et al. 2010, Phuong & Lazzeri 2012, Xing et al. 2012.

To improve the properties of bio-plastics, they can be blended, remaining fully bio-based. For example, studies show that the brittleness (impact strength and elongation at break properties) of PLA can be remarkably improved through the addition of TPS (Martin & Avérous 2001, Sarazin et al. 2008), and the impact strength is greater if PLA is grafted with maleic anhydride and subsequently blended with thermoplastic starch (Huneault & Li 2007).

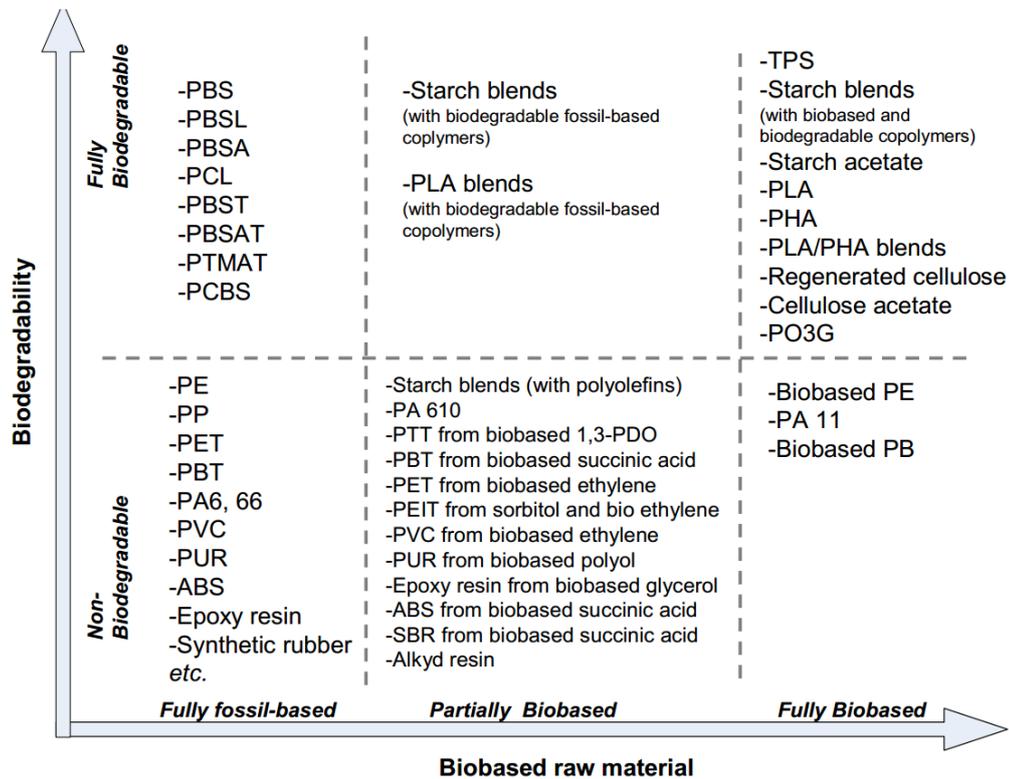


Figure 11. Current and emerging (partially) bio-based plastics and their biodegradability. (Shen et al. 2009)

1.1.3.2.3 Coupling agents/promoters

Strongly polarized wood fibers are inherently incompatible with hydrophobic polymers because of their hydrophilic nature (Faruk et al. 2011). In natural fiber composites, weak adhesion may result from poor dispersion and incompatibility between the fibers and the polymer (Keener et al. 2004). Poor interfacial properties between the fibers and the matrix manifest as poor toughness and poor stress transfer efficiency between the fibers and the matrix, resulting in poor overall mechanical properties. A lack of chemical or physical bonding can result in the development of interfacial gaps from external forces, and these gaps may, in addition to reducing the mechanical properties, reduce biological resistance by means of providing a pathway for fungi. For the reasons mentioned above, various physical and chemical methods have been developed and used to modify the surface properties of fibers as well as the polymer matrices to improve the interaction and dispersion between the fiber and the matrix (Pendleton et al. 2002, Wanjale & Jog 2011).

The physical methods of fiber modification include corona discharge and cold plasma treatments. These treatments change the surface as well as the structural properties of the fiber and thus improve the mechanical bonding between the fiber and the matrix. Cold plasma treatment generally modifies the fiber surface through roughening by the sputtering effect. The roughened surface enhances the contact area between the fiber and the matrix (Wanjale & Jog 2011).

There are various chemical methods to improve the interfacial adhesion (coupling) between the fiber and the matrix by modifying the fiber surface, such as acetylation, benzylation, acrylation, and permanganate and isocyanate treatment. The most common treatments used for fiber modification are alkali treatment and silane treatment. Silanes are coupling agents that are used to improve the adhesion between the fibers and the matrix. In silane treatment, one end group attached to silicon reacts with the hydrophilic fiber and the other with the matrix. Thus, it improves the degree of cross-linking in the interface region and leads to perfect bonding between the matrix and the fiber. It has been shown that alkaline pretreatment of fibers is essential for improving the efficiency of the silane coupling agents (Wanjale & Jog 2011).

The most widely used coupling agents are maleated polyolefins, which contain two functional domains: a polyolefin (e.g. PP, HDPE), which is able to form entanglements with the polymer

matrix to build into the matrix, and maleic anhydride, which is able to interact strongly with cellulose fiber at extrusion temperatures covalently via hydrogen or ionic bounds (Klyosov 2007). It must be noted that the inherent properties of functionalized polyolefins have a significant influence on their effectiveness as coupling agents. For example the chemical structure and molecular weight affect the miscibility and entanglement with the base resin, and the degree of grafting determines the level of functionality present in the coupling agent. Thus the choice of a suitable coupling agent is an important issue in developing polyolefin composites. Maleic anhydride -grafted PP (MA-g-PP) and PE (MA-g-PE) have been widely used for coupling (Wanjale & Jog 2011). Most commercially available coupling agents based on reactive groups are derivatives of maleic anhydride, or siloxanes (Godavarti 2005).

1.1.3.2.4 Lubricants

Lubricant is a generic term used for a variety of different chemicals that affect the rheology of molten thermoplastics, whether or not they contain fibers. Additives intended for other functions may have a rheological effect that can be seen in unfilled thermoplastics and is even more evident in highly filled thermoplastic composites. Lubricants are used to improve the rheology of the total formula so that it can be processed as required. Rheology refers to how the melt behaves in processing. There can be a number of parameters having an effect on where in the process the material melts (or fuses in case of polyvinyl chloride): apparent viscosity, apparent pressure at different process points, anti-stick attributes on the metal part of the equipment, how the melt flows into different zones of the extrusion die or mold, even energy consumption, etc. Other terms for lubricants that are used interchangeably are wax, process aid, anti-stick, slip, release agent, flow modifier, etc. Most of these terms describe a function, while wax refers to the appearance of many lubricant materials regardless of the actual chemistry. Wax products as a group have diverse chemistry. The most fundamental division can be made between oleo- and petroleum-derived products. The oleo-derived materials originate from naturally occurring triglycerides (fats and oils), where the fatty acids and alcohols derived from triglycerides are subsequently saponified, esterified, or otherwise chemically reacted. Petroleum-derived materials are paraffin, microcrystalline wax and polymer waxes. Polymer waxes are chemically similar to many of the thermoplastic polymers commonly used, but with much lower molecular weights, therefore behaving wax-like, not resin-like. The best way to distinguish between them is the melting point range as all waxes are solid. However, though

rarely desirable, many products of similar chemistry are also available as liquids. If the compound blending system is more oriented to liquid additives, it is important to look for the same general chemistry, but select additives with low enough molecular weights and/or a more branched than linear structure, and/or containing hydrocarbon chains that are predominantly unsaturated (Satov 2008).

Common wax lubricants are metal stearates (soaps), amides, and esters. Stearates are cost-effective lubricants that provide external lubricity, and the rheology is often balanced with amide wax for flow attributes (Satov 2008). However, if maleic coupling agents are introduced into the WPC, it has been noticed that their effect often depends significantly on the lubricants employed in the same system. The most striking is a conflicting effect between maleated polyolefins as metal stearate lubricants; it has been found that zinc stearates (ZnSt) invariably decrease both the strength and stiffness of WPC compared to a nonmetal lubricant (Klyosov 2007). Evidence exists that ZnSt interacts chemically with MAPP, and this interaction may impair any potential for bonding between MAPP and wood (Harper & Wolcott 2004).

1.1.3.2.5 Colorants

Colorants are commonly used for both aesthetics and UV protection. For a consistent color matching of the wood materials and the thermoplastic, it may be necessary to add the colorant to both materials separately before extrusion. If the wood fiber is very light in color and the thermoplastic dark, the composite will have light specks throughout the composite (Rowell 2006). Pigments, especially dark ones, are able to reduce the discoloration/bleaching of WPC in weathering. However, even though the addition of darker pigments masks the color change caused by photo-oxidation, similar chemical changes take place both in the lignin of the wood material and in the polyolefin of composites made with and without pigment when the wood load is constant (Butylina et al. 2012a).

1.1.3.2.6 Stabilizers

Stabilizers function by preventing or minimizing the deleterious chemical reactions that are a result of degradation of either the composite matrix or a component of the matrix. The focus is on the stabilization of the main matrix components, polymers and fibers, the subsections being antioxidants, UV stabilizers, heat stabilizers for PVC, and a few miscellaneous types, considering the demands of processing and field performance (Satov 2008). As wood-plastic composites are often used in outdoor applications, stabilizing additives are discussed in detail in the following.

The energy of UV radiation impacting an outdoor end product can initiate chemical reactions. Many possible chemical reactions will utilize the presence of oxygen and water. To counter the potential of UV-initiated degradation, three strategies can be employed: blocking/screening UV energy, absorption of UV energy, and stabilization, which means trapping the radical species generated subsequent to degradation. Blocking/screening is done with high-coverage/opacity materials such as titanium dioxide, carbon black, and many pigments. UV absorption is achieved with the chemistries of benzophenones and benzotriazoles. UV stabilization is traditionally achieved with hindered amine light stabilizers (HALS). HALSs are available in both monomeric and polymeric forms. Blocking/screening is an important concept, and in WPCs the very high level of fiber can be an effective UV blocker, as UV radiation can penetrate only to just below the surface, and thus the bulk of the matrix is protected. Hence many processors achieve satisfactory product attributes without anything further than appropriate pigments used for aesthetics. It should be kept in mind that these chemistries should only be used for the prevention of polymer degradation, as they have no effect on preventing the fade of wood fiber. Utilization of pigment systems also requires separate considerations for UV protection (Satov 2008).

Weathering shows in WPCs as color fading and changes in yellowing. It has been proposed (Muasher & Sain 2006) that WPCs undergo two competing redox reactions upon UV exposure; the first is the oxidation of lignin which leads to the formation of paraquinone chromophoric structures dominant in the first 250 h of exposure, and the second is the reduction of the paraquinone structures to hydroquinones, which leads to photobleaching.

In controlling long-term fading and yellowing changes, high molecular weight diester HALS has been found to be the most effective agent. Furthermore, the addition of a benzotriazole ultraviolet absorber has shown great synergism in controlling fading when added to a diester HALS (Muasher & Sain 2006).

1.1.3.2.7 Biocides

The microbial effects on WPCs can be divided into three stages: first, when mold forms colored spots on the surface without degrading the material, remaining structurally sound. In this case the mold feeds itself by particles. The second is when mold and other fungi consume some ingredients of the composite formulation insignificantly. The third is when fungi (called decay fungi or cellulolytic fungi) specifically and rapidly attack the wood/cellulose fiber in the composites, causing a decrease in the mechanical properties of the materials (Klyosov 2007). In order to prevent the effects listed above, biocides can be added to the WPCs.

Borates are excellent fungicides and insecticides, and zinc borate is especially attractive because it has very low water solubility and does not appear to affect or be affected by the manufacturing process (Morrell et al. 2009). Zinc borate is the most popular additive to wood-fiber composite materials, primarily because of its relatively low cost. Zinc borate can be an effective preservative against microbial degradation of composite materials in amounts of 1% and less. At 3%, it has been reported to protect against surface mold problems and in some cases, 1.8–2.0% of zinc borate has been shown to protect WPC test decks during exposure up to 14 months (Klyosov 2007).

1.1.3.2.8 Fire retardants

Ammonium polyphosphate (APP), melamine phosphate and other phosphorus–nitrogen flame retardants are effective flame retardants for wood, whereas intumescent flame retardants and bromine-containing flame retardants are effective flame retardants for polyolefins (Li & He 2004). The most commonly used flame retardant in PE and PP is ammonium trihydrate (ATH), used almost ten times more than the second group of fire retardants (chlorinated compounds) (Klyosov 2007). In the case of wood-plastic composites, it has been found that magnesium

hydroxide (MH) and ammonium polyphosphate (APP) are functioning fire retardants (Stark et al. 2010). It has also been found that the addition of 5 wt % APP gives results comparable to the addition of 15 wt % zinc borate or 15 wt % MH (Ayrilmis et al. 2011). However, due to the complex nature of flame retardance, it is difficult to generalize the results and draw conclusions regarding the mechanisms of flame retardance for various WPCs (Stark et al. 2010).

1.1.3.2.9 Foaming/Blowing agents

Foaming is a method used to decrease the density of WPCs in decking applications closer to that of common solid wood. Foamed wood composites also accept screws and nails like wood, more so than their non-foamed counterparts (Faruk et al. 2007). Composites with less wood fiber are generally easier to foam than more highly loaded ones, but the wood-fiber type and size play a role. Longer fibers give the composite strength but they also give the foaming gas a pathway to escape. Foaming is easier with amorphous polymers like PVC and PS than with crystalline ones like PP or PE. Amorphous polymers have generally better melt strength, but crystalline resins have lower viscosities and accept higher filler levels. More viscous amorphous polymers make it harder to wet out the wood flour and disperse it evenly, but they hold gas bubbles better (Schut 2001).

In the variety of foamed composites, density reductions range from 5% to 50% and wood filler levels from 3% to 60% (Schut 2001). However, it has been found (Bledzki et al. 2005) that with the increase of a microvoid content (due to foaming) equaling the density reduction of around 20%, a reduction of the flexural strength on wood fiber-PP composite is around 20%, indicating a proportional trend between flexural strength and foaming.

Wood composites are typically foamed with 0.5-1.0% of an endothermic blowing (foaming) agent (Schut 2001). It has also been noticed that the types and forms of the chemical foaming agent (CFA) do not affect the void fractions in HDPE/wood-flour composites, and also the average cell size achieved in the composite foams remains insensitive to the CFA contents, regardless of the foaming agent type used (Li & Matuana 2003).

Azodicarbonamide is the most widely used exothermic chemical foaming agent, decomposing at about 200°C with the blowing gas yield of 220cm³/g (Throne 2004). The decomposition

temperature can be reduced to 155-200°C by means of metal compounds such as lead and zinc stabilizers. It can thus match the temperatures at which the melt viscosity of many polymers is suitable for foaming (Murphy 2001). Reduction in the metric weight of extruded WPCs can naturally also be affected by the design of profiles, e.g. the use of a profile with a hollow cross section.

1.1.3.3 Mineral fillers

Mineral fillers are commonly used in the plastics industry to shorten the cycle time in production (injection molding), improve the properties, especially stiffness, and to lower the amount of plastics used, leading to decreased material costs (Jancar 1999, Klyosov 2007).

The first commercially used fillers for polypropylene were talc and asbestos fibers due to their beneficial effects on stiffness and heat resistance. The need for replacing asbestos fibers due to health issues led to the introduction of calcium carbonate particles and mica flakes to plastics. Mica was found to be more effective than talc for increasing stiffness and heat resistance, while calcium carbonate proved to be less effective in increasing stiffness, but increased the impact resistance of PP homopolymers (Xanthos 2010a).

The surface modification of mica with coupling agents to enhance the adhesion and stearate modification of calcium carbonate in order to assist dispersion have been found to enhance these functions and to introduce other benefits such as improved processability, a means of imparting color, and reduced long-term heat ageing. Other fillers impart entirely different functions. For example, barium sulfate enhances sound absorption, wollastonite enhances scratch resistance, solid glass spheres add dimensional stability and increase hardness, hollow glass spheres lower the density, and combinations of glass fibers with particulate fillers provide unique properties that cannot be attained with single fillers (Xanthos 2010a).

The fillers can be classified according to their specific function, such as their ability to modify mechanical, electrical or thermal properties, flame retardancy, processing characteristics, solvent permeability, or simply formulation costs. It needs to be recognized that fillers are multifunctional and may be characterized by a single, primary function and a surplus of other, additional functions (Xanthos 2010a).

Traditionally, most fillers have been considered as additives, which, because of their unfavorable geometrical features, surface area, or surface chemical composition, can only moderately increase the modulus of the polymer, whereas strength (tensile, flexural) remains unchanged or even decreases. Their major contribution is in lowering the cost of materials by replacing the most expensive polymer; other possible economic advantages are faster molding cycles as a result of increased thermal conductivity, and fewer rejected parts due to warpage. Depending on the type of filler, other polymer properties can be affected; for example, melt viscosity can be significantly increased through the incorporation of fibrous materials. On the other hand, mold shrinkage and thermal expansion would be reduced, a common effect of most inorganic fillers (Xanthos 2010a).

The properties of mineral-filled composites are affected by the type of mineral used, including the surface chemistry, morphology (size and shape) and loading level of the mineral in the system. An increase in the aspect ratio in general increases the flexural modulus of composites (Dombrowski et al. 2005). Examples of the morphology of certain fillers used in polymers are presented in Table 5.

Table 5 Particle morphology of fillers (adapted from Xanthos 2010a).

Shape	Aspect ratio	Examples
Cube	1	Feldspar, calcite
Sphere	1	Glass spheres
Block	1–4	Quartz, calcite, silica, barite
Plate	4–30	Kaolin, talc, hydrous alumina
Flake	50–200++	Mica, graphite, montmorillonite nanoclays
Fiber	20–200++	Wollastonite, glass fibers, carbon nanotubes, wood fibers, asbestos fibers, carbon fibers

Example SEM images of different morphologies of certain minerals are presented in paper II (Figure 2).

The addition of fillers to thermoplastic polymers have usually effects on their appearance. In general, it is regarded to be beneficial if the filler produces a pleasant white appearance or has no effect on the color, while this is not absolutely essential. It is a distinct disadvantage if the

filler produces dark colors and makes the composite harder to pigment (Rothon 1999).

The methods of filler production from mineral sources can be broadly classified into direct and synthetic methods. Direct methods are more inexpensive of the two, but generally result in a less pure product and in less optimal particle size and shape. Filler surface treatments are of considerable use in thermoplastic applications and are often integrated as part of the production process. Various synthetic processing methods are available and two of them are of most relevance; precipitation from an aqueous solution and melt forming (Rothon 1999).

When used as fillers, especially in composites, the cost is of essence and hence directly produced (most often ground) materials are the most common ones. Mineral addition to WPCs has been studied to some extent with talc, calcite, kaolin, wollastonite and mica, among others (Huda et al. 2005, Klyosov 2007, Lee et al. 2008, Godara et al. 2009). The general properties of these minerals are described in the following.

1.1.3.3.1 Mica

Mica is a term for a group of more than 35 phyllosilicate minerals with a layered texture and perfect basal cleavage. This cleavage, results in splitting or delamination of the mica layers into thin sheets due to weak bonding between the layers. Micas compose roughly 4% of the earth's crystal minerals. Micas are a variable group both in chemical composition and in physical and optical properties. They are basically complex potassium aluminosilicates with some aluminum atoms replaced by magnesium and iron and may also contain minor amounts of a variety of other elements. Muscovite and phlogopite, the two most important commercial types, have unique characteristics such as chemical inertness, superior electrical and thermal insulating properties, high thermal stability, and excellent mechanical properties. The Mohs hardness of commonly used micas is between 3-4 for muscovite and 2.5-3.0 for phlogopite, and the densities (g/cm^3) are in the range of 2.7–3.2 and 2.75–2.9, correspondingly (Xanthos 2010b).

1.1.3.3.2 Talc

Talc is a natural mineral found worldwide and is the major constituent of rocks known as soapstone or steatite. The color of talc can be gray, green, blue, pink, and even black, depending on the geographical area of origin. Pure talc is a hydrated magnesium silicate with the chemical formula $Mg_3Si_4O_{10}(OH)_2$ that belongs to the group of phyllosilicates. The center brucite plane is chemically bonded by bridging oxygen atoms to two tetrahedral silica planes. Talc has a plate-like structure, unless heated at above 800°C. , The planar surfaces of the individual platelets are held together by weak van der Waals force, enabling delamination of talc at low shearing forces. This makes the mineral easily dispersible and accounts for its slippery feel. The greasy feel is also due to its very low hardness (Mohs hardness ~1) and density 2.7–2.8 g/cm³ (Flaris 2010).

1.1.3.3.3 Kaolin

The term kaolin covers a group of minerals, the dominant one being kaolinite. In industry, mineral kaolinite is mainly referred to as kaolin, and this term is also used here. The lesser minerals of the kaolin group comprise hydrated aluminosilicates such as dickite, nacrite, and halloysite. Structurally, kaolinite consists of an alumina octahedral sheet bound on one side to a silica tetrahedral sheet, stacked alternately. The two sheets of kaolinite form a tight fit with oxygen atoms forming a link between the two layers. The theoretical composition for the $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ mineral is 46.3% SiO₂, 39.8% Al₂O₃, and 13.9% H₂O. Kaolin is considered to be a phyllosilicate mineral. Unlike talc, kaolin booklets can be delaminated only by significant grinding (Duca 2010).

1.1.3.3.4 Wollastonite

Wollastonite is a naturally occurring acicular (needle-like) silicate mineral, a calcium metasilicate (CaSiO₃), belonging to the family of inosilicates, with chemical similarity to the group of pyroxene minerals. In its pure form wollastonite is brilliant white and contaminants or impurities from associated minerals or element substitutions may change the color to cream, pink, or gray. The theoretical composition of calcium metasilicate is 48.30% CaO and 51.70%

SiO₂. Typical reported compositions (calculated as oxides) are 44.04–47.5% for CaO and 50.05–51.0% for SiO₂. Based on unit cell parameters, the specific gravity is calculated to be 2.96. However, the generally accepted reported value is 2.90. In commercial grades, deviations from the theoretical specific gravity are due to various impurity ions that substitute for calcium in the crystal lattice, or impurity minerals such as calcite, garnet, and diopside. The hardness of wollastonite is in the range of 4.5–5 (Mohs) (Robinson & Xanthos 2010).

1.1.3.3.5 Calcite

Calcite is a form of calcium carbonate (CaCO₃), the most common deposit formed in sedimentary rocks. Natural CaCO₃ used as filler in plastics is produced from chalk, limestone, or marble. Calcium carbonate is an abundant, largely inert, white filler with cubic, block-shaped, or irregular particles of a very low aspect ratio. Calcium carbonate occurs in different crystalline forms. The most widespread is calcite, which has either a trigonal-rhombohedral or a trigonal-scalenohedral crystal lattice. The density of calcite is 2.7 g/cm³ and hardness 3 Mohs. Another form is orthorhombic aragonite, which is less stable and can be converted to calcite by heat. Vaterite, a third form of calcium carbonate is unstable and will transform into the other two forms over time. Aragonite has higher density (2.8–2.9 g/cm³) and somewhat higher Mohs hardness (3.5 – 4) than calcite (Khanna & Xanthos 2010).

There are some studies regarding the impact of mineral fillers on certain properties of WPCs. However, no broader overview is available on how various minerals hybridized with wood fibers simultaneously affect the multiple properties of wood-plastic composites.

2 PURPOSE OF THE STUDY

The main aim of this thesis is to study the impact of mineral fillers on various properties of wood-polypropylene composites and thereby their overall usability. Also the effect of wood fiber source/type on the properties of wood-polypropylene composites is discussed. The effects of minerals have been discussed in four different articles (II-V). The work is divided into five sub-categories, which are the following:

Introduction to WPCs, effect of wood material (Article I),
Mechanical properties (Article II),
Moisture resistance (Article III),
Thermal properties (Article IV), and
Machinability (Article V).

This synthesis is based on these articles. The main idea in the synthesis phase is to determine the impact of mineral addition and its significance on different properties of composites. A flow chart of the structure of the thesis is presented below (Figure 12).

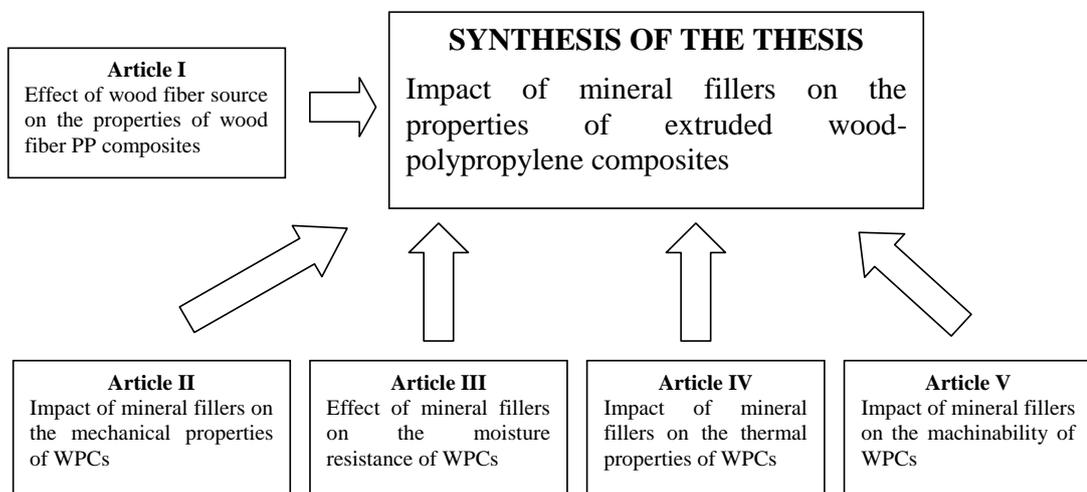


Figure 12. Structure of the thesis.

3 MATERIALS AND METHODS

The materials and methods of the studies (I–V) are presented in more detail in each article, and therefore the material and methods are outlined only generally in this chapter, and the general information of each article is presented in Table 6.

Table 6. Main materials and methods used in the articles.

Article	Wood materials used	Mineral fillers used	Methods
I	Coniferous pellets, heat-treated birch, spruce wood flour	Not applicable	Determination of water absorption, thickness swelling, tensile, flexural, and impact strength, moisture resistance under cyclic conditions, and micromechanical deformations
II	Coniferous sawdust	Calcium carbonate, wollastonite, talc, soapstone	Determination of density, tensile and bending strengths, impact strength, hardness, moisture resistance under cyclic conditions, and micromechanical structure
III	Coniferous sawdust	Calcium carbonate, wollastonite, talc, soapstone	Determination of density, moisture content, thickness swelling, water absorption, moisture resistance under cyclic conditions, and micromechanical structure
IV	Spruce saw chips	Calcium carbonate, wollastonite, talc, soapstone	Thermogravimetric analysis, differential calorimeter analysis, evaluation of heat built-up, determination of color and gloss
V	Coniferous pellets, heat-treated pine, spruce wood flour	Calcium carbonate, wollastonite, talc, soapstone	Determination of surface roughness and tool wear

The research material consists of eleven different WPCs; 5 having minerals as fillers, 3 made of pellets, 2 made of heat-treated wood material, and one reference made of untreated saw chips, present in all the articles. In this synthesis, composites made with heat-treated wood flour are combined to one material (HT), the mineral-filled composites are treated both as one group of materials (WF+Mineral) and as individual minerals. The plastic used in all the composites is isotactic polypropylene.

4 REVIEW OF THE RESULTS AND DISCUSSION

A brief description of the work and the main findings of the individual articles are presented in the following. The sections are named regarding to the sense and purpose the articles are referred to in this work.

4.1 Effect of wood material

In paper I, the effect of the type of the wood fiber source on the physical and mechanical properties of wood fiber-polypropylene composites was studied by means of determining the density, moisture content, mechanical properties (tensile strength, flexural strength, and Charpy impact strength), water absorption and thickness swelling, moisture resistance, and micromechanical deformations.

It was discovered that the source of the wood fibers used had a noticeable impact on the studied properties. The highest density was found for composites made of heat-treated wood fibers compared to composites made of other types of wood. Scanning electron microscopy (SEM) examination revealed better adhesion between the polypropylene and heat-treated wood fiber in these composites, which led to lower porosity and thus higher density. The lowest moisture content was found in the composite made of heat-treated fibers.

The mechanical properties depended on the source of the fibers. The highest values were recorded for the composite made with heat-treated fibers with a margin compared to the composite reinforced with pellets, and especially compared to the wood flour -reinforced composite.

It was noted that in water absorption and thickness swelling, the density/porosity of the composites was a key factor and a good predictor. As a result, the composite having heat-treated wood fiber as reinforcement was characterized as having the lowest water absorption and the least thickness swelling, compared to the rest of the composites.

For all the materials, the moisture resistance test revealed a decrease in flexural strength and dimensional stability after exposure to freeze-thaw cycling for all the composites, but the severity was dependent on the wood fiber source; the largest decrease in flexural strength of approximately 75% and dimensional stability was found on the composite containing wood flour. The best performance was found on the composite containing heat-treated fibers, followed by the composite made with pelletized wood. The long fibers of wood flour, which in SEM were shown to have poor adhesion with the polypropylene matrix, were inferred as the cause of the rise in water absorption, thus degrading the moisture resistance.

In SEM, random distribution and random orientation of fibers was revealed for all types of composites. Also the phenomenon of aggregation of fibers and presence of voids was noted in the case of composites produced with both pelletized and fibrous wood. This was suggested to have a strong influence on the fracture behavior of the composites, and consequently their mechanical properties.

4.2 Mechanical properties

In paper II, the impact of mineral fillers, added as active fillers, on the mechanical properties (bending strength, tensile strength, Brinell hardness and Charpy impact strength) of the composites was studied, and the microstructure of the composites was examined with scanning electron microscopy (SEM).

The mineral addition had an effect on the mechanical properties of the WPCs; both the tensile strength and hardness of the composites increased compared to the reference composite with no added mineral. The mineral addition had a small, non-significant negative effect on the bending strength. In previous studies, with the introduction of a mineral (talc) to a WPC, both the tensile strength and bending strength improved (Noel & Clark 2005). It has been suggested (Xue et al. 2007) that fiber decrease would improve the tensile strength, which agrees with the achieved results. The impact strength of the composites was improved by mineral addition. However, this cannot always be regarded as a positive effect, as according to the literature (Godara et al. 2009), brittleness increases with increasing impact strength. The Brinell hardness of the composite was improved with the addition of minerals, and along with the increasing hardness

of the used mineral, the hardness of the composite increased. The mechanical properties of the studied composites are presented in Figure 13.

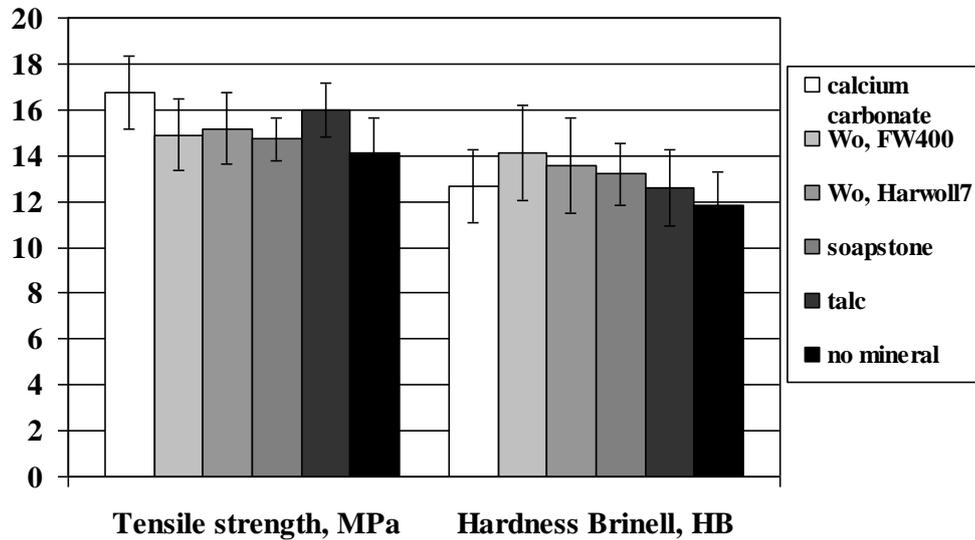


Figure 13. Mechanical properties of WPCs (Wo denotes Wollastonite).

In the SEM analysis it was perceived that the acicular shape of wollastonite was absent, which was presumed to be due to crushing of the mineral during the extrusion process. No fiber orientation along the machining direction was observed.

In conclusion, it is possible to improve some of the mechanical properties (tensile strength, impact strength, hardness) of WPCs with mineral addition. The difference between different minerals is minimal, and it is difficult to draw any conclusions regarding which mineral performs better than others.

4.3 Moisture resistance

The main aim in paper III was to study the impact of mineral fillers on the moisture resistance of wood-plastic composites (WPC). It was found that all the added minerals decreased the swelling and moisture absorption of the wood-plastic composites considerably. Also the density of the wood-plastic composites increased when minerals were added.

Without any added mineral, clear openings could be seen in the composite structure in scanning electron microscope (SEM) pictures. These openings could work as pathways for water into the inner parts of the WPC and increase swelling. It could also be seen in the SEM pictures that when mineral was added, these pathways for moisture were closed.

After three weeks soak/freeze/dry cycles, the bending strength of the reference sample decreased considerably more than the bending strength of the samples with added minerals. Of the studied minerals, talc was the most effective.

In this study, the effect of five different minerals on the moisture-resistance of wood-plastic composites was examined. The studied minerals were calcium carbonate, two different types of wollastonite, soapstone and talc. The mineral adding had a clear effect on the water absorption and thickness swelling of the studied wood-plastic composites. The reference composite with no added mineral absorbed considerably more water, and the swelling took place already during the first week in the water bath. This result was as expected, as according to the literature, 30 % talc adding would cut the moisture absorption to a half (Schut 2004). The wood particles used in the study had a rather rough form, which could affect the quality of the WPC. If the wood had been in smaller chips or even as flour, there could have been more bonding between the wood and grafted maleic anhydride polypropylene (MAPP). Adding a mineral clearly improves the resistance of a wood-plastic composite against moisture by closing the pathways for water in the composite. Mineral adding also diminishes the swelling of the WPC in the manufacturing stage, which would make the manufacturing more accurate. After three weeks of soak/freeze/dry cycles, the bending strength of the reference sample with no mineral weakened a lot more than the bending strength of the samples with added minerals. At the same time, also the density of the WPC increased remarkably. Soapstone and talc are hydrophobic by nature, and the composites having these minerals as fillers were the least swollen in the tests. Both wollastonite and calcium carbonate are hydrophilic by nature, and in the study these composites had the weakest water resistance of the mineral-filled composites. Of the studied minerals, talc was the most effective one. If minerals are added into the process, their abrasive character to the process equipment should be taken into account. On the other hand, the screws in the manufacturing device might crush the mineral particles, and larger and longer mineral particles might lose their intrinsic shape, which could affect the properties of the composite. Fungal growth and weather resistance should be kept down in composites. In many WPC types, the fungus growing caused by the moisture content can be decreased by adding different chemicals, like zinc borate (Morrell et al. 2009). The results of this study showed that with

minerals the moisture content in WPC can be decreased in an environment-friendly way, thus reducing or removing the need of adding extra chemicals. This reduction in the use of chemicals needed to increase the weather resistance of the composite results in a smaller environmental load.

4.4 Thermal properties

The thermal properties of wood-plastic composites were studied in paper IV. The thermal behavior of the samples was studied by using a differential scanning calorimeter (DSC) and a thermogravimetric (TG) analyzer, and by determining the heat build-up. The analyzed properties were compared with a reference sample made without adding any minerals.

Mineral fillers are less expensive than plastics, and they are used to enhance the moisture resistance and mechanical properties of WPCs. Minerals also improve the dimensional stability of WPCs, both in the long term and at the manufacturing stage. Wood-plastic, especially wood-polyolefin composites are used mainly in outdoor applications, where the composites are exposed to weathering, and all phenomena regarding it are significant. This study sheds light to the effect of mineral fillers on the thermal stability of WPCs, as well as the possible role of mineral fillers in the temperature rise in WPC materials caused by absorption of solar energy (i.e., heat build-up).

In both TG and DSC analyses, the measured differences in temperatures between the reference and mineral-filled samples were at the maximum only a few degrees. It was also found that the studied mineral fillers, except for wollastonite Harvoll FW400, had less than a 3% effect on the degree of crystallinity compared to the reference material, which could not be considered statistically significant. All the studied composites, also the reference material, had a higher degree of crystallinity than pure PP. Also the crystallization temperature was higher in all cases. This was probably caused by both the wood and MAPP; other studies have indicated that pure wood can nucleate PP (Borysiak 2007), and when used together with MAPP, the impact is greater (Yin et al. 1999). All the measured changes were of such a magnitude that they could not be considered statistically significant, and thus it appears that mineral addition has only a small or an insignificant effect on the thermal degradation or stability of WPCs. A simple regression test and the created model showed that of the studied color values (L^*a^*b), only the

L* and a* components of the CIE color space had an explanatory value for the magnitude of the heat build-up. It was found that the measured b* color component and surface gloss of the composites had no explanatory value for the heat build-up. This may have been the result of the overall low gloss values of all the studied composites. In addition, the evaluated gloss values were only in the wavelengths of visible light. According to the literature, many minerals (e.g., calcium carbonate, crystalline and amorphous silica, silicate minerals such as talc, kaolin, calcined clay, wollastonite, nepheline syenite, feldspar, mica, attapulgite clay, bentonite and organically modified bentonite, alumina trihydrate, aluminum oxides, barites, and lithoponeare) are known to have considerable infrared reflectivity (Bendiganavale & Malshe 2008). The data concerning the studied minerals available at the USGS Digital Spectral Library (Clark et al. 2007) shows that these minerals have in general a reflectance of 84-93% at wavelengths from 700 to 2500 nm. It also appears in the same data that for talc, wollastonite and calcite, the visible light wavelengths have rather similar reflectivity with the near infrared region (NIR) (e.g. for talc the reflectivity in the visible light area is 86 and in the NIR range 84; the average reflectivity for calcite in both wavelength areas is 93). Unfortunately, data for soapstone was not available. From the data available in the literature (Schimleck et al. 2003, Fackler et al. 2006), it can be approximated that the wood material (spruce) used in the study has the average reflectivity between 0.6 and 0.7 in the NIR. As wood was the main component of the studied composites, it can be concluded that the properties of the wood material were dominant. A further study could be beneficial for understanding the heat built-up phenomena. This study could benefit from including all components affecting heat built-up, i.e. reflectance, absorbance and transmittance.

It can be stated on the basis of all the obtained results that at 20 w-% levels, all the investigated minerals can be used as active fillers for WPCs without the risk of diminishing the thermal stability and thermal properties in general. Only the heat build-up was evidently affected by the soapstone filler, which also had a noticeable effect on the color and shade of the composite. On the basis of these findings, it appears that industrial process residual soapstone powder could be used as an active filler for WPCs, as it has an impact on the thermal stability that is close to that of common, commercially available fillers.

4.5 Machinability

The aim of the study presented in paper V was to determine the possible differences between the machinability of solid wood and wood-polypropylene (plastic) composites. Additionally, factors affecting tool wear and surface roughness in machining of wood-plastic composites were investigated. The machinability of nine different wood-thermoplastic composites and two solid wood species (pine and birch) was determined by measuring surface roughness and tool wear in routing.

In the tests, the smallest mean surface roughness value was measured for composite material made of heat-treated pine fiber, and the highest value was final Ra for the composite material having wollastonite FW400 as the filler. In terms of increase in surface roughness, the smallest absolute change was recorded for two mineral-filled composites, one having CaCO₃ and the other talc as the filler, and for solid wood birch there was no noticeable change. The largest absolute change was found with the wollastonite FW400 -filled composite. The composite materials made of pellets gave similar results to those filled with wollastonite.

When relative surface roughness change was considered, the results changed slightly; the greatest increase was found with the composite with heat-treated wood: 35%, followed by the composite made of pellets, with a 31% increase. At 95% confidence level, there was no statistically significant difference in the surface roughness values between the start and finish for materials made of spruce chips, materials filled with either calcite, wollastonite HarWoll7 or talc, and solid wood specimens. At the start, significantly lower surface roughness values compared to the solid wood specimens were found on the composite made of heat-treated wood, two composites made of pellets and the composite having soapstone as the filler. At the finish, there was a noticeable difference in surface roughness between the solid wood specimens and the composites; when the composites were compared to the solid pinewood specimen, most materials had a lower Ra, except for the composite filled with wollastonite FW400, which had higher roughness.

The composite filled with wollastonite FW400 had the greatest mean tool wear width after routing, more than twice that of pine. The composite with wollastonite HarWOLL7 as the filler also yielded a large mean tool wear width: 1.8 times that of pine. For the other materials studied, the tool wear was relatively similar.

For machinability, a commonly used European wood material, Scots pine (*Pinus sylvestris*), was chosen as the reference. Three machinability values relative to solid pine were calculated: relative surface roughness values at start and finish, and relative tool wear after machining. The relative surface roughness reveals how the performance of certain materials is better at the end of the machining than at the start. Such materials were composites made of spruce chips, those filled with the minerals wollastonite HarWOLL7 or talc, and birch. All the composites caused higher tool wear than the reference. The highest relative tool wear was found on both of the composites where wollastonite was used as the filler; for the material with FW400 it was 213% and for the material filled with HarWOLL7 181% compared to pine. The birch material had the lowest relative tool wear, 92% of that of pine.

The results indicate that for the studied mineral-filled composites, the type of filler has a remarkable impact on tool wear. However, the filler appeared to have only a minor effect on surface roughness. The findings regarding differences in tool wear when machining composites and solid wood would seem to be in broad agreement with recent published work (Saloni, Buehlmann et al. 2011). The results for surface roughness also seem consistent - it was observed that solid wood materials had in many cases higher surface roughness than WPCs. It is interesting to note that the degree of tool wear did not have an obvious relationship with changes in the development of surface roughness.

In general, based on the findings, the machinability of most of the studied wood-polypropylene composites did not remarkably differ from that of the studied solid wood specimens. The addition of hard mineral fillers to WPCs had a noticeable effect on tool wear, and it can be hypothesized that similar effects may also be found on extrusion machinery.

5 SYNTHESIS OF THE IMPACT OF MINERAL FILLERS

It was noticed that using heat-treated wood fiber as raw material yielded in many occasions improved properties compared to WPCs made of other types of fiber material. In article I, composite 1 (HTW Fibers), was made using heat-treated birch as fiber, and in article V, material 1 was heat-treated pine.

Considering the main components of the studied composites, the composites were first divided into groups regarding the main component or components as follows: heat-treated fibers (referred to as HT), pellets (Pellet), wood flour/chips (WF) and wood-flour/chip+mineral filler (WF-Mineral). The latter group (WF-Mineral) represents the mean values of all mineral-containing composites, a combination of all minerals. The values of individual mineral-containing composites are also presented; Calcite denotes a composite containing CaCO_3 , FW400 and HarWOLL7 composites filled with different qualities of wollastonite, SoapS indicates a soapstone-powder -filled composite, and Talc is self-explanatory.

5.1 *Mechanical properties*

Of the mechanical properties of the studied composites, tensile strength, bending strength, un-notched Charpy impact strength, and Brinell hardness were determined. The data presented in Figures 14-17 have been gathered from all the five articles.

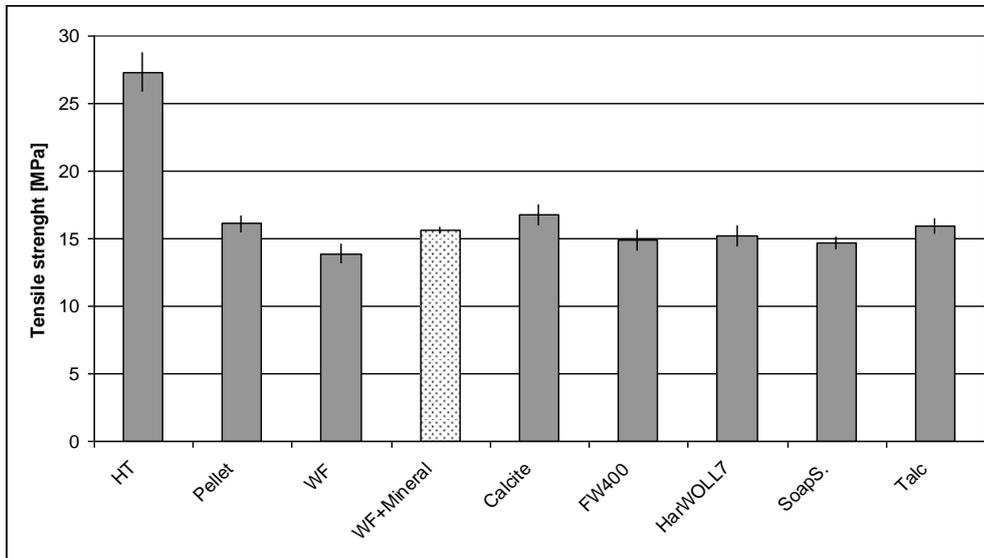


Figure 14. Tensile strengths (with 95% confidence levels).

The determined tensile strengths indicate that mineral addition brings small improvement on the tensile strength compared to the material made of wood flour, and is at the same level with the material made of pellets. The tensile strength of the composites made of heat-treated wood is 1.7 – 2 times higher than that of the others; on average 1.75 times higher than the average mineral-filled (WF+Mineral) material. Compared to the composite made of untreated wood material, both Talc and Calcite -filled composites show a statistically significant increase in tensile strength.

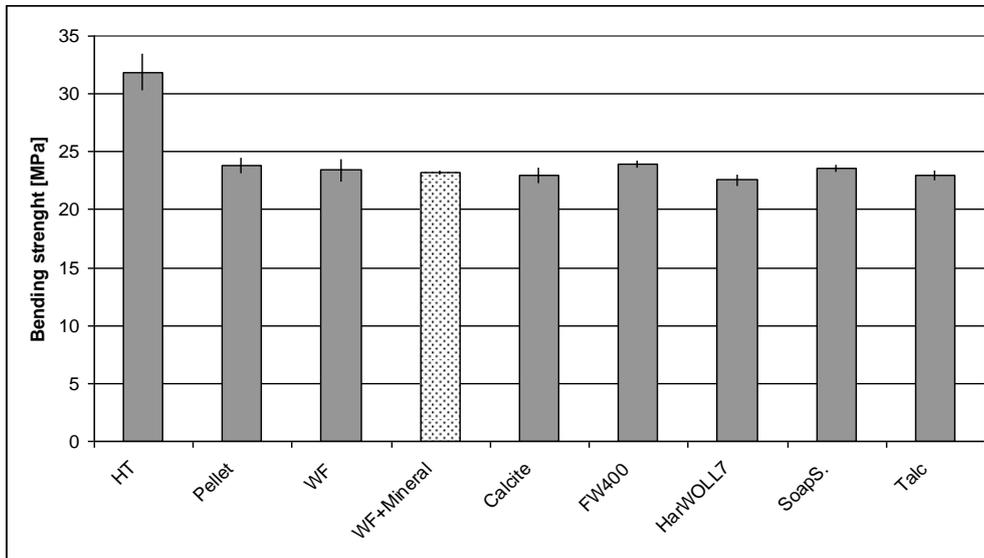


Figure 15. Bending strengths (with 95% confidence levels).

In bending strength, the trend in the values between different materials is similar to that with tensile strengths; the material made of heat-treated fibers has 1.34 to 1.38 times higher values than the rest of the studied materials. There is no statistically significant difference between the other materials. The mineral fillers have no apparent impact on the bending strength compared to the Pellet or WF material.

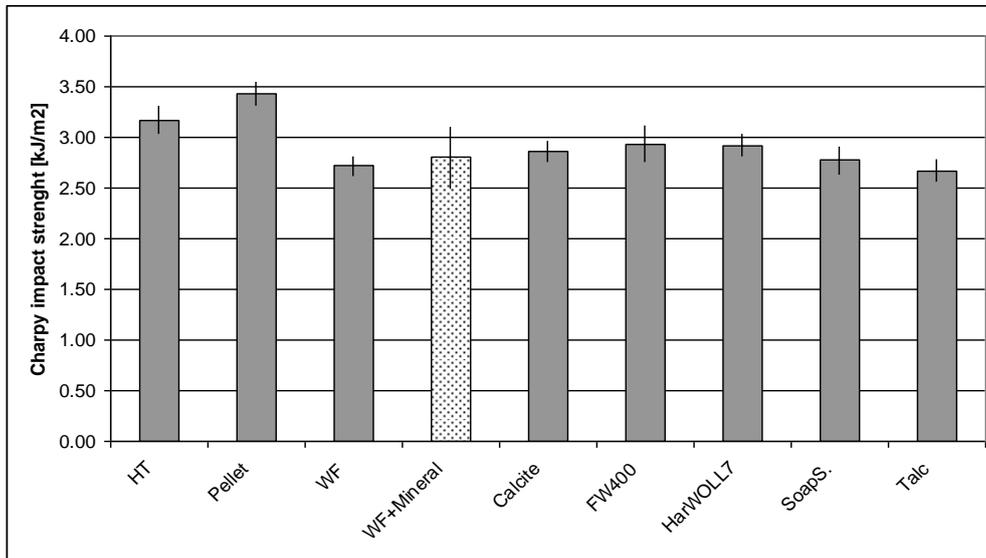


Figure 16. Charpy impact strengths (with 95% confidence levels).

The composite made of pellets has the highest Charpy impact strength by an 8% margin to the material HT. Both WF and WF+Mineral have an impact strength 23% to 26% lower than the material HT. There is no statistically significant difference between the strength of WF and the average WF+mineral or any individual mineral-filled materials.

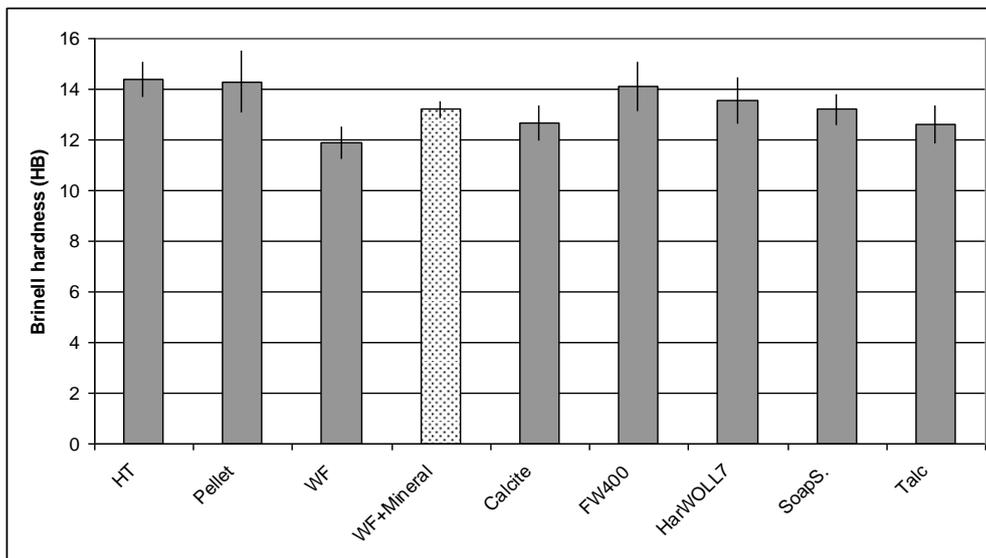


Figure 17. Brinell hardness values (with 95% confidence levels).

The highest mean Brinell hardness value was found for the material made of HT, 14.4. The second highest mean value was recorded for the material Pellet, being less than 1% lower, and the composite made with wollastonite FW400 had the third highest value. The lowest value was found in the material WF, which was 11% lower than that of the average WF+Mineral. A statistically significant difference was found, indicating that WF has a significantly lower HB value than the rest of the materials which were found to reside at the same level of hardness. In general, mineral addition brings a moderate improvement on the Brinell hardness compared to material WF. Between the mineral-containing composites, Fisher's least significant difference (LSD) procedure implies that at 95% confidence level, there is a statistically significant difference between FW400 and both Calcite and Talc, FW400 having higher hardness.

5.2 Moisture resistance

To evaluate the moisture resistance of WPCs, water absorption and thickness swelling were determined according to EN 317, and the decrease in bending strength after exposure to cyclic treatments was determined according to standard EN 321:2001. The results have been combined from articles I and III and are presented in Figures 18-20 below.

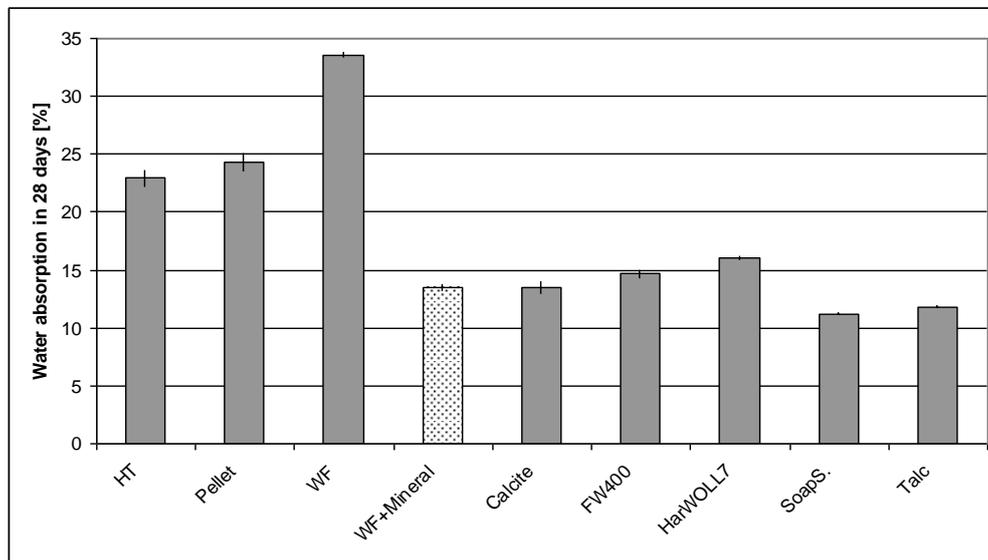


Figure 18. Water absorption of composites after 28 days of immersion (with 95% confidence levels).

Remarkable differences in water absorption were found between different composites. Water absorption of 13.5% was found for the average WF+Mineral. Compared to that, HT had 1.5,

Pellet 2.1 and WF 2.5 times higher water absorption after 28 days of immersion. All mineral-filled composites had significantly lower water absorption compared to the unfilled ones.

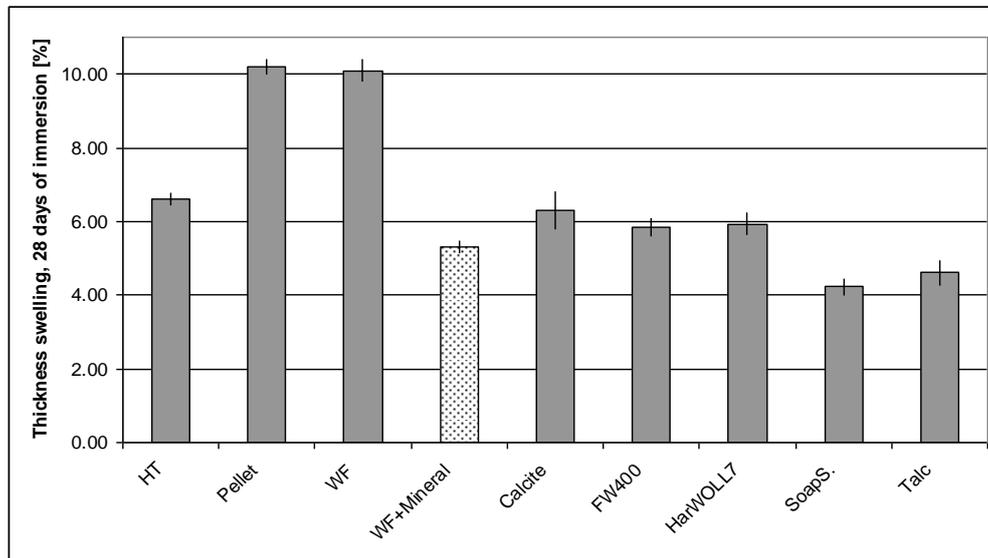


Figure 19. Thickness swelling of composites after 28 days of immersion (with 95% confidence levels).

In thickness swelling, the average mineral material (WF+mineral) had the value of 5.3% of swelling, followed by HT having a 25% higher value. Both Pellet and WF had swelling of over 90% higher than the average WF+Mineral. No statistically significant difference was found between the materials Pellet and WF. Of the mineral-filled composites, the lowest values were recorded for materials filled with Soapstone and Talc: 4.2% and 4.6%.

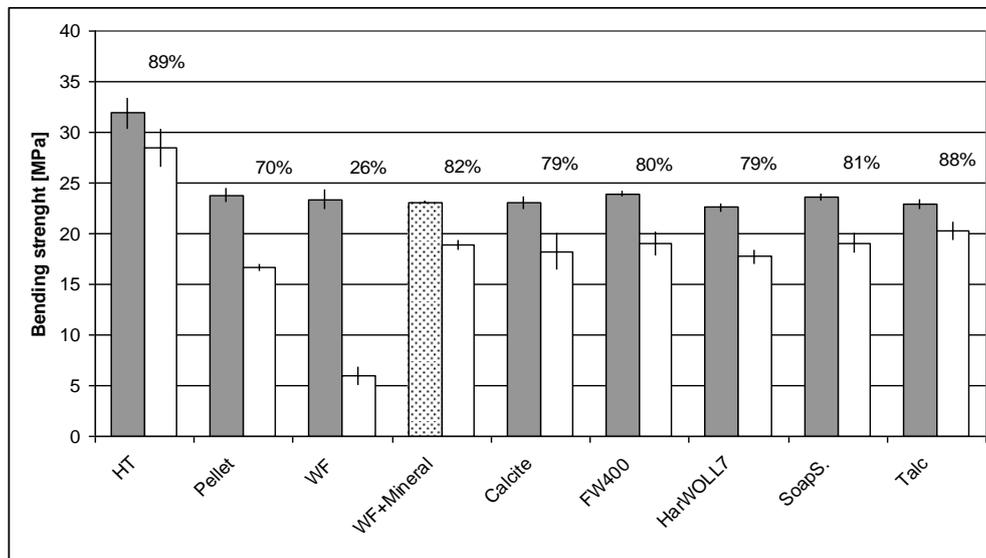


Figure 20. Initial and retained bending strength after cyclic resistance testing (with 95% confidence levels).

The impact of cyclic treatment was the lowest on the material HT, a loss of 11% of bending strength. The average WF+mineral lost 18% of strength, and Pellet had a 30% reduction. The greatest decrease was observed in the case of WF, only 26% of the initial bending strength remained after the test. The performance of mineral-filled materials was rather similar; the loss of bending strength was less than 20%. The best performance in the filled materials was found with the composite filled with talc - a decrease of 12% in bending strength.

5.3 Thermal performance

Thermal performance was determined by the degree of crystallinity of the composite, the melting temperature, and by temperature differences recorded in heat build-up testing. These are shown in Table 7. The properties were studied only in article IV, and therefore the results are limited. The materials are WF, average mineral (WF+Mineral) and individual minerals.

Table 7. Thermal properties.

<i>Material</i>	T_m [$^{\circ}\text{C}$]	X_c [%]	ΔT_{max}
WF	161.4	50.4	37.4
WF+Mineral	163.4	51.2	38.5
Calcite	163.1	50.4	37.1
FW400	163.0	54.8	37.3
HarWOLL7	163.4	48.9	38.7
Soapstone	163.7	50.7	41.8
Talc	163.8	51.7	37.4

As can be seen in the table, it appears that mineral addition results in slightly higher values of melting temperature, degree of crystallinity and temperature difference in heat build-up. The performed Mann-Whitney W –test indicates that there is a statistically significant difference at a 95% confidence level between the melting temperatures, but not between the degree of crystallinity or the maximum temperature differences in heat build-up in the comparison of WF and the average mineral containing material (WF+Mineral).

5.4 Physical properties

The physical properties taken into consideration here are the residing moisture content after manufacture and the density of the composites.

The property values presented in Figures 21 and 22 have been gathered from articles I, III and IV.

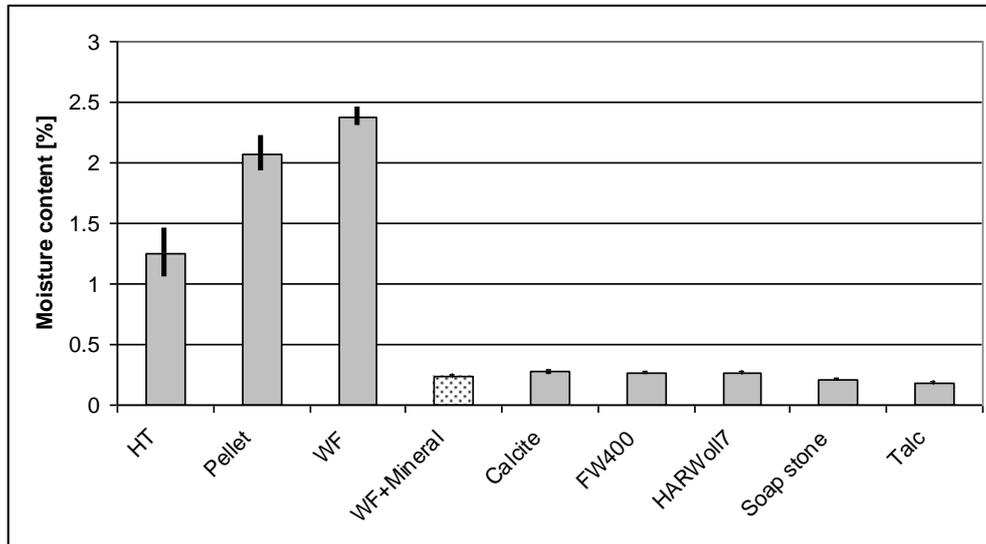


Figure 21. Residual moisture content of composites.

The moisture content of the HT material was 5 times higher than that of WF+Mineral, and both the pellet and WF materials had over 8 times higher values, with the moisture content of 2.1% for pellet and 2.4% for WF. Of individual minerals, the lowest moisture content was measured for talc, 0.19% and the highest for calcite, 0.27%. The mean moisture content of 0.25% was found for the average mineral-containing composite (WF+Mineral).

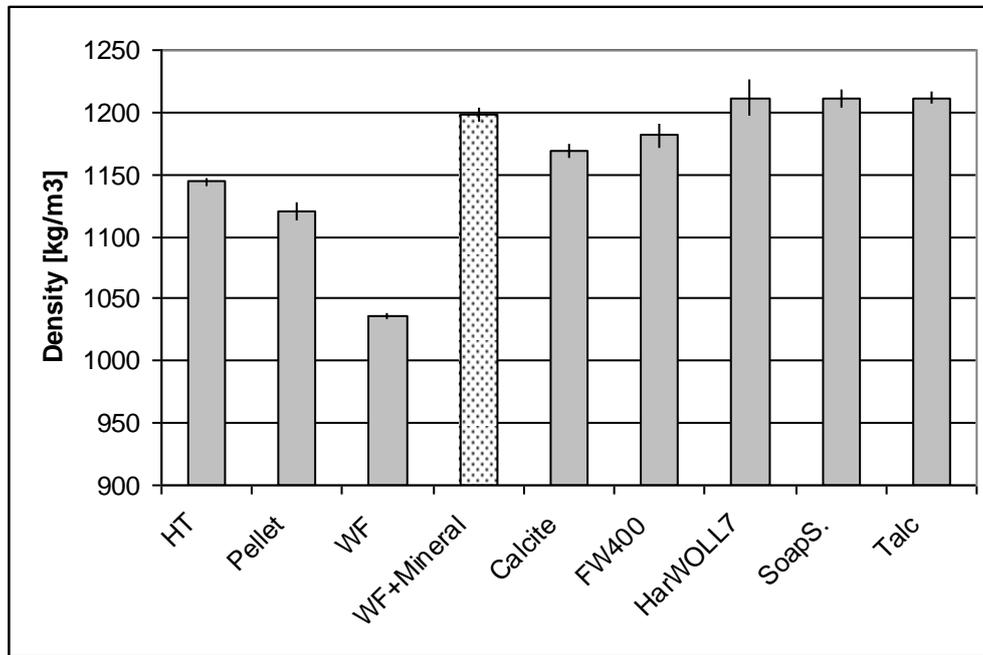


Figure 22. Densities of the composites.

A statistically significant difference (Tukey HSD@95% confidence level) in densities was found between the composites containing minerals and those without minerals. The materials with mineral addition had the mean density of 1.2 g/cm^3 , which was less than 10% higher than with the materials HT and Pellet and 16% higher than with WF. Interestingly, the density of the mineral used did not appear to define the density of the composite, e.g. talc has the density of 2.75 g/cm^3 and FW400 2.94 g/cm^3 , and the corresponding composites have densities of 1.212 g/cm^3 and 1.181 g/cm^3 .

5.5 Machinability

The performance of the materials in machining was determined by evaluating the changes in surface roughness and determining tool wear. The results presented in Figures 23 and 24 and Table 8 below have been gathered from article V.

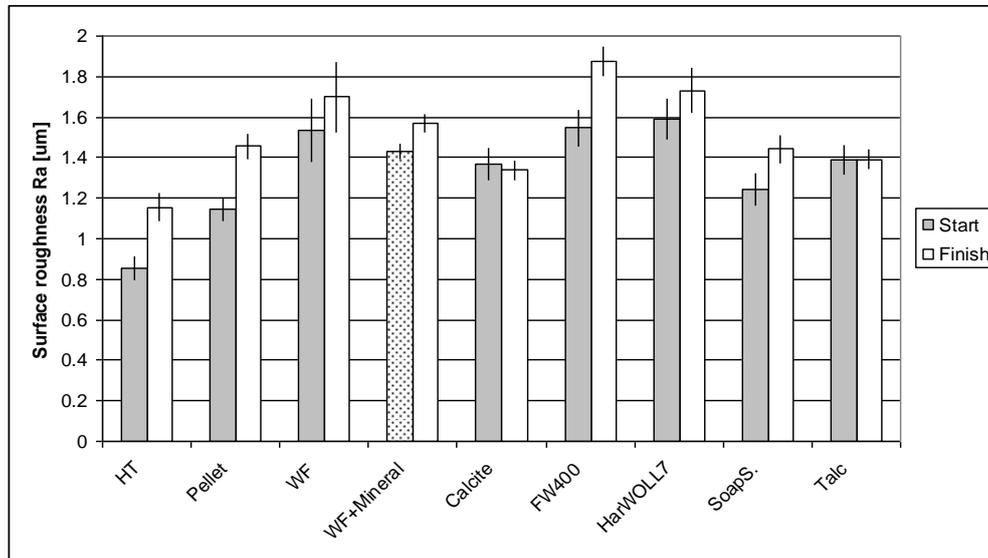


Figure 23. Surface roughness values at start and finish.

At the start, the lowest surface roughness Ra value of 0.86µm was found on the composite HT and the highest Ra value of 1.58µm on the composite HarWOLL7, followed closely by the other wollastonite FW400 with the Ra value of 1.55µm. Also at the start, a statistically significant difference (Tukey HSD@95% confidence level) in surface roughness was found between the materials HT and every other material, between pellet and talc, WF and soapstone, calcite and HarWoll7, FW400 and soapstone, and Harwoll7 and soapstone.

At the finish, the lowest surface roughness Ra value was recorded for the composite HT, 1.15µm, and the highest for the composite FW400, 1.87µm, followed by the other wollastonite-containing composite HarWOLL7 having the Ra value 1.73µm. Statistically significant differences in Ra at the finish was found between HT and all other materials except for calcite, between pellet and WF, pellet and FW400, pellet and HarWOLL7, WF and calcite, soapstone and talc, and calcite and both FW400 and HarWOLL7.

Another aspect concerning machinability is the absolute and relative change in surface roughness during machining, which table 8 below illustrates. The statistical significance (Tukey HSD@95% confidence level) between the surface roughness values at start and finish is expressed with S in the case of significant and NS in the case of not significant.

Table 8. Development of surface roughness.

Material	Ra Start [μm]	Ra Finish [μm]	Absolute difference [μm]	Increase relative to start	Statistically significant
HT	0.856	1.154	0.298	34.8 %	S
Pellet	1.145	1.456	0.311	27.2 %	S
WF	1.535	1.698	0.163	10.6 %	NS
<i>WF+Mineral</i>	<i>1.431</i>	<i>1.571</i>	<i>0.14</i>	<i>9.8 %</i>	<i>S</i>
Calcite	1.3698	1.338	0.0318	-2.3 %	NS
FW400	1.547	1.873	0.326	21.1 %	S
HarWOLL7	1.588	1.731	0.143	9.0 %	NS
SoapS.	1.243	1.441	0.198	15.9 %	S
Talc	1.388	1.392	0.004	0.3 %	NS

Regarding consistency in machining, materials containing the softest minerals in terms of MOHs hardness (calcite and talc) performed best with practically no increase in surface roughness over the tested machining distance. By the same terms, the HT material had the largest increase in Ra of a third, but the Ra value at the finish was still the lowest among the studied materials. There was a notable difference in the surface roughness values between the composites containing different minerals, namely between the two grades of wollastonite and the rest of the studied minerals.

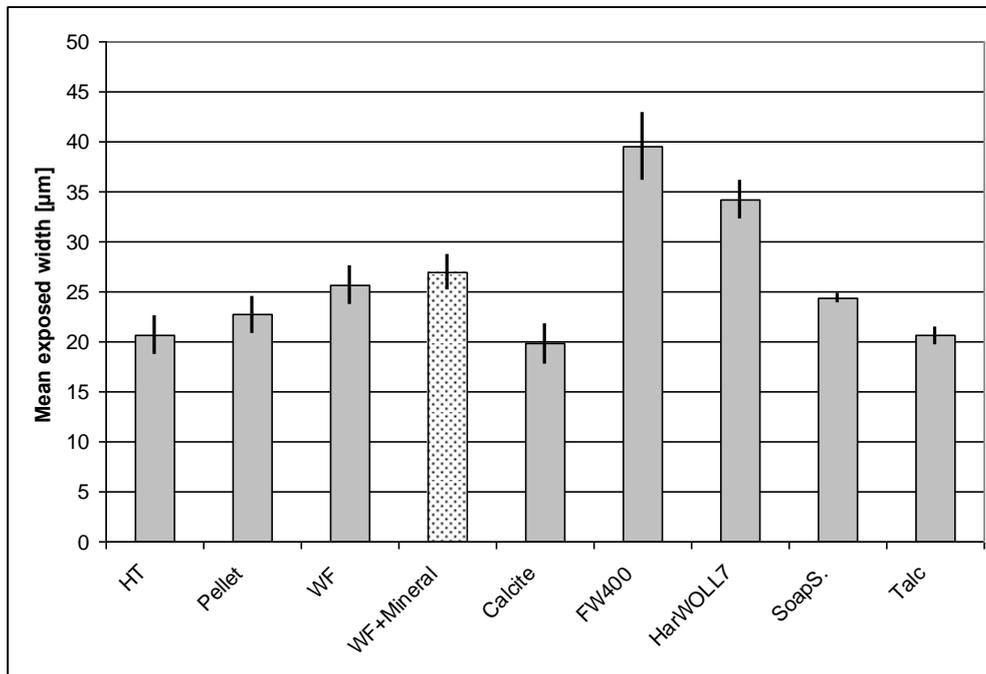


Figure 24. Tool wear in machining.

In the case of tool wear, the use of different minerals resulted in remarkable differences between the materials. The highest mean tool wear was recorded for the composite containing wollastonite FW400, exposed width of 39.6µm. The lowest tool wear was found for the composite containing calcite, 19.8µm. Also the composites HT and talc resulted in low mean tool wear, being at the same level with calcite.

5.6 Summary of properties and performance

The impact of the studied mineral fillers and wood materials on the different properties of wood-plastic composites is exemplified in Table 9, in which the influence is marked with + and – -signs. In some cases the influence was modest and is marked with 0, as is the reference material, WF.

Table 9. Impact of materials and minerals on composites, N/A=not available.

Property Material	Mechanical	Moisture resistance	Thermal	Machining	Physical
HT	++	+	N/A	+	+
Pellet	+	0	N/A	0	0
WF	0	0	0	0	0
WF+Mineral	0	+++	0	+/-	+
Calcite	0	+++	0	++	+
FW400	0	+++	0	--	+
HarWOLL7	0	+++	0	--	+
Soapstone	0	+++	-	+	+
Talc	0	+++	0	++	+

In brief, the effect of mineral fillers is notable in the case of moisture resistance. In the case of machinability, the impact of mineral addition can be positive or negative, depending on the hardness of the mineral. In the case of physical properties, the mineral addition brings increase in density and noticeable reduction in residing the moisture content. When the mechanical and thermal properties are taken into consideration, mineral addition seems to have no remarkable impact.

6 DISCUSSION

As wood was the main component in the studied composites, its influence on the properties of WPCs deserves further attention. Various aspects of the wood material used in producing WPCs influence many of their properties.

Stark and Rowlands (2003) found that in the case of wood flour, the composites made of it showed increase in tensile and flexural strength and modulus, corresponding with increases in the aspect ratio. The notched impact strength was found to increase with increasing particle size, whereas the un-notched impact energy decreased with increasing particle size. Wood fiber, compared to flour, was found to result in higher strengths at both filler levels and higher moduli. The higher aspect ratio of the wood fiber had little effect on impact energy. Similar results have been presented by Bouafif et al. (2009), indicating that higher fiber size produces higher strength and elasticity but lower energy for break and elongation. An increasing fiber load improves the strength and stiffness of the composite but decreases elongation and the energy to break. It was also found by Bouafif et al. (ibid.) that water absorption increases with the increasing fiber content, but the effect of fiber size is minimal. A similar trend was found by Migneault et al. (2009). Data indicating that the wood species used in WPC manufacture can affect the properties as well has been presented in the literature (Kim et al. 2009, Fabiyi & McDonald 2010). It appears that flexural properties are not dependent on whether the wood is of the coniferous or non-coniferous type, and the wood species also affect the tensile strength. It has been suggested (Ashori & Nourbakhsh 2010) that the differences in mechanical properties can be explained by differences in the fiber length and aspect ratio between hardwood and softwood species.

The analysis of thermal properties indicated that the thermal stability of WPC is also species-dependent, which may be caused by the fact that the final decomposition of hemicelluloses in hardwood occurs at higher temperatures compared to softwood (Fabiyi & McDonald 2010). Different wood species also have different nucleation density, and the dynamic mechanical properties of WPCs appear to be related to the crystallization behavior of the wood flour, which depends on the surface roughness (Kim et al. 2009). The weathering tests of WPCs presented in the literature show that the degree of color change and lightness increased with exposure time is dependent on the wood species (Fabiyi & McDonald 2010).

The wood material used in this study with mineral addition and as a generic reference was made to represent saw chips that are formed as a by-product of wood/timber processing. Both the particle size distribution and the used wood species (spruce) were considered to be comparable to the chips produced in Finnish sawmills.

Based on the findings, untreated wood flour/chips which come directly from the processing of sawn goods, appear to be inferior compared to pre-treated wood material, in terms of the properties the WPCs made of them possess. Especially the performance in water absorption, thickness swelling and in cyclic testing are remarkably weaker. It has to be noted that heat treatment in this paper means treating wood in high (above 180°C) temperatures according to the Finnish ThermoWood Association (2003), in contradiction to heat treatment of lumber and wood packaging material defined in ISPM 15 (International Standards for Phytosanitary Measures 2009). In the ISPM 15, heat treatment is defined so that the core temperature of the treated wood material must achieve a minimum of 56°C for the minimum of 30 minutes.

In bending and tensile strength, the composites made of heat-treated wood fibers have clearly the highest strength values. This finding is in contradiction with the fact that the strength properties of wood material decrease in heat-treatment up to 50% (Rowell et al. 2012), indicating that the improving factor is probably related to fiber-matrix interactions in the WPC. In heat-treatment, the moisture content of wood fibers is reduced and the equilibrium moisture content decreases because of the loss of hygroscopic hemicellulose polymers (Finnish ThermoWood Association 2003, Rowell et al. 2009). It has been found that the exposure of wood material to a high temperature also changes its chemistry and affects the surface energy. An increase in surface energy has been reported in the case of both softwood (pine) and hardwood (beech) species (Gérardin et al. 2007), and a decrease in the oxygen-to-carbon (O/C) –ratio (Inari et al. 2006, Gérardin et al. 2007). The change in surface energy inducted by heat-treatment shows clearly in the contact angle value, which changes suddenly from close to 0° to reach 90° for a treatment temperature between 120 and 160 °C and for treatment temperatures up to 240 °C; the contact angle remains constant and equal to 90°, indicating a change from naturally hydrophilic to rather hydrophobic (Hakkou et al. 2005, Follrich et al. 2006). It is also believed that heat-treatment would result in the production of by-products with a lower oxygen content caused either by dehydration of polymers initially present in the wood, or in the formation of new components resulting from the degraded by-products (Inari et al. 2006). The

hydroxyl content has been found to reduce by 20-40% due to a loss of hygroscopic hemicellulose polymers in heat treatment (Rowell et al. 2012), and the concentration of non-polar wood components on the wood surface have been found to increase after drying at 103 °C (Inari et al. 2006). These changes in the properties of wood material appear to improve the compatibility between wood material and polymer matrix notably in the presence of MAPP and also without coupling agents (Follrich et al. 2006), thus explaining the elevated mechanical and moisture properties found in composites made with heat-treated material.

Unfortunately, the availability of heat-treated wood material is scarce; e.g. the sales production of ThermoWood was 109 757 m³ in 2011 (International Thermowood Association 2012). When these numbers are compared to the total global sawn wood production in 2011, 406 186 839 m³, or wood chips and particle production of 246 898 111 m³ (FAOSTAT 2012), it is safe to claim that heat-treated wood, and thus inexpensive heat-treated wood fibers available for WPC manufacturing are a rarity in the global scale. Therefore an environmentally friendly and economically feasible method, such as mineral addition, for improving the properties of WPCs made with inexpensive, un-treated wood material would be beneficial.

6.1 Mechanical properties

In mechanical tests, mineral addition in general did not have notable influence on the properties of WPCs. In tensile strength some improvement was found in the cases of calcite and talc addition, but no significant change was found in bending strength and Charpy impact strength. An increase in Brinell hardness was found with the addition of wollastonites and soapstone. Not a multitude of publications regarding polyolefin-wood/mineral –hybrid composites exists, but it has been found that the addition of calcium carbonate improves the flexural strength of high-density polyethylene/wood flour composites, and the impact strength is decreased with the increase of mineral filler loading (Kord 2011). This differs slightly from the results obtained in this study, and especially interestingly, in our case the impact strength was not affected even at the 20% filler rate. This can be due to the different plastic used or differences in particle size and shape both in the mineral and wood material used. The addition of only 3% of talc to a wood-plastic composite has been found to increase its tensile strength by approximately 29% (Gwon et al. 2010), but the water absorption increased from 3.9% to 5.7%. In this study the increase in tensile strength by mineral addition was minor and no increase in water absorption

was recorded with the addition of any of the minerals. It must be noted that the effect of particle size of the filler in polymeric composites appears to have notable influence on the properties. In a study by Cho et al. (2006) the effect of particle size on the mechanical properties of composites reinforced with spherical particles (size varying from macro (0.5 mm) to nano (15 nm) scale) was investigated. The studied composites consisted of vinyl ester resin as the matrix material and two types of particles: glass beads and spherical alumina (Al_2O_3). The findings indicated that micro scale -sized particles had a minor influence on the stiffness of composites while the stiffness increased as the particle size decreased at nano scale. It was also observed in the study that the tensile strength of the composite is considerably dependent on particle size. A study conducted by Dubnikova et al. (1997) reveals that in the case of a PP- $\text{Al}(\text{OH})_3$ composite (filler sizes $d=1, 2.5, 8$ and $25 \mu\text{m}$), the ultimate elongation decreases in tensile testing with an increase in filler size, and the ultimate strains increase with filler size. Takayama et al. (2013) studied 15 w-% hydroxyapatite (HA)/75 w-% polylactic acid (PLA) composites. It was found that with $1\mu\text{m}$ sized filler the flexural strength decreased dramatically compared to composites filled with a $5\mu\text{m}$ sized filler and a composite filled with a mixture of $1\mu\text{m}$ and $5\mu\text{m}$ filler. It was noted that in mechanical properties the composite filled with both particle sizes ($1\mu\text{m}$ and $5\mu\text{m}$) exhibited the best performance. These findings suggest that the differences in the performance of the studied minerals, and also between the results obtained in this study and the results presented in the literature, may be caused also by differences in particle sizes to some extent.

Processing the biomass component without a loss of fiber properties is a major issue, as for example a loss of fiber length, width and aspect ratio has been reported in processing oil palm fiber in an extruder with polypropylene at 180°C . No matter what fiber length or width is used before processing, the fiber loses length and width during the processing (Rowell 2007). In this study, a similar impact of processing was found with the high-aspect ratio wollastonite HarWOLL7 - in the SEM analysis it was perceived that the acicular shape of wollastonite was absent, which was presumed to be due to crushing of the mineral during the extrusion process. No excessive changes in the wood material were noticed due to processing, possibly because the wood material was chips and fiber bundles rather than in the form of single fibers.

For pure polypropylene, it has been concluded that a mixture of minerals used as filler shows improved performance compared to a single filler (a synergistic hybridization effect); the flexural strength and impact strength were highest among the hybrids when the PP/talc/ CaCO_3

weight ratio was 70:15:15 (Leong et al. 2004). The hybridization of different mineral fillers may also improve the performance of mineral-filled WPCs.

6.2 Moisture resistance – biological resistance

The addition of minerals was found to enhance all the studied moisture-related properties of the WPCs. The results suggest that water absorption and thickness swelling are not efficient in forecasting the performance of WPC in cyclic resistance testing.

It has been noted that when the fiber content in WPCs is above the level of about 50%, the fiber-to-fiber interfaces increase, enabling the moisture gain to go deeper into the composite. (Rowell et al. 2002). This indicates the importance of the fiber used and its properties, but it also suggests that mineral addition may limit the conduction of moisture in the composites by interacting with the fiber-to-fiber interfaces. The results in this thesis show that with minerals the moisture content in WPC can be decreased in an environmental way without a need of adding extra chemicals. The use of minerals takes the environmental issue into account; when extra chemicals like zinc borate are no longer needed to increase the weather resistance, the composite has a smaller environmental load.

It is assumed, based on many observations, that cellulose having the moisture content of 19% or lower will generally not support the growth of mold. Generally, there is a clear correlation between the overall moisture content in WPC and its susceptibility to microbial degradation (Klyosov 2007). The results presented in this thesis clearly indicate that the residing moisture content, water absorption and therefore actual moisture content in WPCs exposed to weathering is reduced by the introduction of mineral fillers compared to unfilled composites. It has also been noticed that minerals used as fillers in a relatively high amount (20-60%) can slow down, or even eliminate, some microbial growth in WPC. Also a slightly alkaline pH (7.5–9) of WPC material, which can be a result of e.g. calcium carbonate used as a filler, can provide the same positive effect (Klyosov 2007). On the other hand, it has been noted that talc has an ability to increase the susceptibility of WPC to weight loss in fungal decay; even though fungi cannot directly attack this inorganic substance, the role of talc in decreasing decay resistance may be accomplished through its influence on the composite structure (Pendleton et al. 2002). This

result strongly suggests that the addition of selected minerals has a positive effect on the biological resistance of WPCs.

It has also been reported that the method used to produce WPC affects the properties; it has been found (Migneault et al. 2009) that injection moulding results in better mechanical properties and lower water absorption and swelling than extrusion. When comparing the properties of WPCs, the method of manufacture must always be kept in mind.

6.3 Thermal properties

The effect of minerals on the studied thermal properties was found to be modest. Small improvement in thermal stability could be achieved by mineral addition but of such magnitude that the change is not likely to affect the usability of WPC. In heat built-up, small increase in temperature was measured with some minerals - the color, especially darkness, of the mineral used was found to have influence on the phenomenon. The composite with the addition of soapstone had a distinguished shade of color compared to all other materials, suggestive of the possibility of using colored minerals either as pigments or to amplify the effect of an added colorant.

The thermal conductivity of WPCs was not studied in this thesis, but it is probable that thermal conductivity is increased by mineral addition, e.g. it has been reported (Weidenfeller et al. 2004) that the thermal conductivity of pure polypropylene is increased by over 9 times (from 0.27 up to 2.5 (W/mK)) with 30 vol% talc in the polypropylene matrix. However, the thermal conductivity of fillers cannot be solely used to evaluate the thermal properties of composites; for example 30 vol% addition of copper particles to polypropylene results in thermal conductivity of only half of that measured with talc addition, even though copper has much higher thermal conductivity (≈ 400 W/mK) than talc (≈ 10.6 W/mK) (Weidenfeller et al. 2004). A study of how individual minerals affect the thermal conductivity of WPCs would be required before making broad generalizations.

Heat reversion (according to standard EN 479) establishes the percentage of linear shrinkage of a profile at an elevated temperature. It has been reported to have a negative correlation with the density of the composite (Butylina et al. 2011). As mineral addition clearly increases the

density of WPC, it can be speculated that the heat reversion behavior would also be improved with added minerals.

It has been found (Farhadinejad et al. 2012) that the introduction of nano wollastonite into WPC increases thermal stability as well as crystallinity in the composite due to the high specific surface area of the nano inorganic fiber filler, and also the flammability resistance and the required oxygen content to burn the composite are enhanced when wollastonite is added to the wood plastic composite. In the study of Farhadinejad et al. (ibid.) it was also noticed that wollastonite increased the oxidation of the samples, which poses a threat to the long-term stability of the composites.

6.4 Physical properties

With mineral addition, the moisture content of the composites after processing was reduced and the density increased, compared to the reference material. Both these effects can be explained to some extent by the replacement of wood material with minerals. The moisture content was decreased notably with mineral addition. In the studied composites, 30% of wood material was replaced by minerals, which, assuming that the minerals contained no water, may have decreased the overall moisture content in the raw materials of the composite by approximately 41%. However, the moisture content of the composites made with pellet and wood-flour was over 8 times higher than that with mineral addition. This could be the result of the higher thermal conductivity of the minerals compared to wood – the better thermal conductivity of the composite mass in the extruder may have promoted vaporization and thus removal of moisture in the processing.

An increase in the density of the composites caused by mineral addition was evident. The density of wood substance (softwood) is approximately 1.5 g/cm^3 (Stamm 1928), but the actual density of the wood material within the composite is lower; for example it has been reported that in the injection-molded HDPE composite the density of wood material is 1.40 g/cm^3 and in extruded WPC 1.26 g/cm^3 , due to much higher processing pressures during injection molding than those during extrusion, resulting in higher density values of injection-molded samples than those of extruded samples (Stark et al. 2004). The densities of the minerals used in the present study varied from 2.7 to 3 g/cm^3 , and it can be presumed that the processing had a negligible

effect on the density of the minerals unlike with wood material. It has been reported that during processing, wood cells can be either compressed or filled (Stark et al. 2004), suggesting that, depending on the shape and size, the minerals itself could fill wood cells and protect them from compressing. This phenomenon can explain the difference in density between the composites made with the two qualities of wollastonites.

The increase of density with mineral addition might be avoided by using nano-sized particles, as they can be used in smaller quantities; for example, improvements in the mechanical properties of polymers comparable with those obtained using 25 to 35% of conventional mineral fillers have been reported (Pritchard 2005) to have been achieved with as little as 3 to 6% of nanofiller. The effectiveness of a filler can be characterized by the ratio of its surface area to its volume, which needs to be as high as possible for effective reinforcement (Xanthos 2010). This is the case with nanomaterials; one of the main reasons why they tend to be more reactive than their corresponding bulk counterparts is that, per unit mass, they have a much higher surface area (Stone et al. 2009).

6.5 Machining

Extruded composites are always machined; they must be at least cut to length at the production stage, as extrusion produces a continuous profile. In this study, it was found that the addition of calcite and talc maintained the same level of surface roughness throughout testing, even though these two minerals are rather different; talc belongs to the phyllosilicate minerals group and has a sheet-like structure, while calcite is a member of carbonate minerals having a rhombohedral structure (Dombrowski et al. 2005). This may be a factor in the good spreading of these minerals in the composite, filling the possible gaps between the fibers and the matrix, thus appearing as a smooth surface in measurements. The same phenomenon is also expected to contribute to improving the moisture resistance of WPCs with mineral addition.

The calcite and talc -filled composites also showed low tool wear, lower than without mineral addition. This implies that the MOHs hardness of the minerals used (3 for calcite and 1 for talc) cannot solely predict tool wear in machining, and also the two wollastonite (MOHs hardness 4.5) -filled materials showed different tool wear with each other. Also the mineral shape, size and chemistry should be taken into consideration when trying to predict the machinability of

mineral-filled WPCs. It can also be speculated that the results of machinability testing can be used to some extent in predicting the wear of the WPC processing equipment. However, this would benefit from further study, as it has been noticed (in the paper industry) that the wear in processing equipment is minimal with talc, unlike with calcium carbonate, which is over 3 times higher (Klyosov 2007).

6.6 Ecological and economical aspects

Nowadays not only the economical but also the ecological aspects of products should and must be considered. As some of the raw materials used in this study showed, ecological and economical factors do not have to be mutually excluding - for example the raw materials for the composites can be recyclable or recycled materials like waste wood or saw dust. Also soapstone, a mineral used in this study, was a by-product, waste dust from an industrial process line. Good performance of a WPC filled with by-products from mineral production has been reported as well (Koikkalainen 2012); the performance in moisture resistance and bending strength was found to be at the same level or even better than with the minerals used in this study. By utilizing recycled and recyclable thermoplastics and by-products, both the economical and ecological value of the WPC can be increased. The end of life of a product, as well as the whole life cycle, must be considered prior production – the material should be optimized in such a manner that it has low consumption of resources in manufacture, a long and safe lifespan in use, and after that it can be efficiently and safely reused.

The WPCs of the studied kind (wood-thermoplastic) have an advantage in their recyclability compared to many other composites; the used thermoplastic polymer matrices soften and melt with the application of heat. Although this ability of melting can limit the application of such composites due to comparatively low maximum in-service temperatures, it means that the end-of-life thermoplastic composite components can be shredded/ground and readily re-processed via heating (Reynolds & Pharaoh 2009). In the case of thermosetting systems, e.g. epoxy and phenol -based composites, which undergo a permanent cross-linking reaction when curing, resulting in a stiffer (and more brittle) matrix material, this reaction cannot be reversed with the application of heat. The application of heat after curing only degrades the cross-linked polymer matrix and will not melt it. This means that the practical end-of-life recycling options are limited, and could more properly be defined as ‘reuse’, such as in the case of incineration with

energy recovery, and also the reuse of a thermosetting composite (via regrinding) as a low value filler material (Reynolds & Pharaoh 2009). The reuse of thermosetting composites as fillers in WPCs might improve both the properties of the WPCs and the ecological performance of the thermosets.

Data indicating good horizontal recyclability of WPCs has been presented in the literature (Balatinecz & Sain 1998, Tajvidi & Ebrahimi 2003). Studies show enhanced water resistance and dimensional stability after recycling, which is believed to be due to better fiber distribution, higher density, lower amounts of voids, better interface quality, and increased hydrophobicity in the recycled formulations (Tajvidi & Ebrahimi 2003), and the results obtained (Balatinecz & Sain 1998) indicate that reprocessing has only a minor deleterious effect on the mechanical properties (tensile and flexural). Unfortunately these studies are based on WPC material that has been kept in laboratory conditions only, not exposed to weathering. The performance of recycled, disused real-life WPC material has not been thoroughly studied – since WPCs are often used in outdoor applications, environmental exposure degrades the performance of the material, reducing the recycling potential (Winandy et al. 2004). Weathering causes deterioration of the polymer surface layer in composites, exposing wood fibers, and thus leaving them susceptible to degradation (Butylina et al. 2012b). However, mineral addition may enhance the weathering properties of WPC; it has been found that a composite containing talc is efficient in retaining the Charpy impact strength in weathering, possibly due to the hydrophobic nature of talc, which facilitates its compatibility with the hydrophobic polypropylene matrix (Butylina et al. 2012b).

The mineral fillers used in this study are considered as chemically non-toxic, and as they have low content of value-added products, they can be considered as fairly environmental. However, other factors such as the size and shape of particles may cause hazards; e.g. some negative changes in the respiratory systems of workers at a wollastonite quarry have been reported (National Toxicology Program 2012) and in the case of animals, in a study (National Toxicology Program 1993), there was some evidence of carcinogenic activity of talc in male rats, and clear evidence of carcinogenic activity of talc in female rats. The possibility of such hazards must be taken into consideration in the manufacturing stage of minerals, the manufacture of composites and also at the end-of-life of WPCs containing such minerals. Especially if nanofillers have been utilized in the manufacture of WPCs, the safety issues should be thoroughly considered throughout the whole lifespan of the composite. The small

size and high relative surface area of nanoparticles introduce properties that are beneficial in terms of material performance but may pose a threat to health and environment. While the small size offers certain distinct advantages for drug delivery, e.g. nanoparticles can penetrate deep into tissues through fine capillaries, cross the epithelial lining and are generally taken up efficiently by living cells (Panyam & Labhasetwar 2012), there may be a risk of unintended particle delivery into a system. Also similarities between high aspect ratio nanoparticles (HARN) and asbestos in terms of their physico-chemical properties and toxicological effects have been reported, and Tran et al. (2008) note that sufficient evidence exists of HARN having the same characteristics (diameter, length and biopersistence) as pathogenic fibers and are likely to have similar pathology.

A favorable effect of mineral addition to other natural fiber composites has also been reported in the literature. In a PLA/recycled newspaper cellulose fiber (RNCF) composite, both the flexural and impact properties were improved with the addition of 10 wt% talc (Huda et al. 2007). In an extruded wood flour-HDPE composite, incorporation of talc into the formulation was found to increase moisture resistance, static strength and stiffness (Rangaraj & Smith 2000). Calcite addition has also been reported (Kord 2011) to improve the tensile properties of a wood-flour-HDPE composite. Both the tensile and flexural properties of bamboo-recycled polypropylene/polyethylene composites have also been reported to improve with the increase of precipitated calcium carbonate content (Kim et al. 2012). It can be assumed that the findings regarding the impact of minerals in this study can to some extent be used to estimate the influence of mineral addition also on other natural fiber-polyolefin and bioplastic composites.

In the plastics industry, mineral addition has been traditionally used to improve the properties of plastics and also to reduce the material costs by replacing expensive plastics with more inexpensive minerals. In WPCs, the amount of plastics in the composite is often relatively low, as wood material is the main component, thus limiting the possibility of replacing plastics with inexpensive minerals.

The use of minerals in WPCs may bring improvement in production capacity; partial replacement of wood flour with talc, or the addition of talc to WPC, has been reported to result in a decrease of the melt viscosity of WPC and to increase of the volumetric output through the die. The substitution of 10% of wood flour with talc increased the output by 15%, and replacing 50% of wood flour with talc increased the output by 36%. It was proposed that talc minimized

the fluidization of the low bulk-density feed and thus enhanced the solid conveying (Klyosov 2007).

It is possible to produce WPCs that are completely biodegradable and/or consist of bio-materials, but the difference between bio-based and biodegradable should be kept in mind when designing such materials. Bioplastics can be obtained from by-products or waste; it has been reported (Thompson et al. 2010) that biopolymers (polyhydroxyalkanoates, PHA) can be successfully produced from the waste streams of wood pulping and that viable wood fiber - reinforced thermoplastic composite products can be produced from these materials; and also that microbial polyester (PHB) can be extruded together with wastewater-derived cell mass and wood flour into deck products having performance properties comparable to the existing commercial HDPE/WF composite products.

To improve the ecology of mineral production, and thus mineral-filled WPCs, the fillers can also be obtained from an unconventional source that may promote both ecological sustainability and economics. Chicken egg shell material (containing 95% of CaCO_3) can be used as a filler with plastics, resulting in even better tensile properties than traditional CaCO_3 (Toro et al. 2007).

7 CONCLUSIONS

The aim of this study was to determine the effect of mineral fillers on the properties of wood-polypropylene composites made by extrusion. The study revealed that the addition of mineral fillers can modify and improve the properties of wood-plastic composites. Especially the moisture-related properties of WPCs were significantly improved by mineral addition. As WPCs of the studied type are commonly used in outdoor applications, this is of great importance in terms of usability. In machining, the addition of two of the minerals retained the surface roughness at same level throughout the test, indicating a favorable effect on machinability. A negative influence of minerals was found in two of the studied properties. In general, a modest increase in density was observed, and the performance in machinability was weakened by the addition of hard minerals. In many of the studied properties, no apparent influence of the mineral fillers was found. An overall result was that in WPCs of the studied kind, talc can be used as an active filler, improving most of the studied properties, especially moisture resistance. Of the studied minerals, nearly similar performance was also found with calcite, suggesting a possibility of using it as an active filler as well. Based on the findings, it can be suggested that a certain amount of minerals can be added to wood-plastic composites to improve the moisture resistance, as this can be done without diminishing the other properties or usability.

Various aspects regarding the use of mineral fillers deserve further study. As the the WPCs studied are often utilized outdoors, the properties related to weathering are of importance, in addition to the mechanical properties. Also thermal properties influence, and possibly limit, the potential areas of utilization, and deeper understanding in this area would be beneficial.

To optimize the performance of WPCs with mineral addition, the optimal level of filling per mineral may vary and should be determined in order to maximize the benefit of mineral use. In this study, the mineral filler level was set to 20%, which may not be the optimal amount.

The knowledge of how the shape and size of mineral particles and their distribution influences the properties of filled WPCs can help in optimizing the composition of the filler. The reduction of particle size of known minerals to nano scale may introduce previously unknown performance of properties when added to WPCs, and this opportunity, also a possible negative influence, should be studied further. The possible safety and health issues of the utilization of

nanomaterials in WPCs should be thoroughly evaluated prior to introducing nanomaterials to broader use.

The mineral fillers could also be mixtures of minerals of different types and sizes. The hybridization of fillers may impel the good properties promoted by individual minerals and modify the properties of filled WPCs further. The minerals to be used as fillers may be found from such sources that reduce energy consumption and the overall environmental impact. These sources include various streams of by-products and wastes from conventional mineral production to combustion power plants using renewable energy sources. In order to understand the total ecological aspects of WPCs fully, a comprehensive life-cycle study would be required. Only comprehensive analysis can reveal how to utilize the possibilities of WPCs in the environmentally best manner.

The optimal machining parameters for both filled and unfilled WPCs have not been determined. It has been shown that WPCs can in general be machined using tools designed for wood processing. However, to optimize tool life, surface quality and the overall consumption of energy and material, an additional study would be beneficial.

In the study it was found that heat-treated wood material performed well in the composites. The performance of a composite containing both heat-treated wood and minerals could be excellent. The effect of wood species was not tested with mineral addition. The results with non-coniferous species having large tracheids (e.g. oak) might be different. It is possible that minerals could fill the tracheids of wood particles, thus reducing the number of cavities open for water, and also promoting the rigidity of the composite.

In conclusion, the addition of minerals to wood-plastic composites had a generally positive effect on the studied properties. The overall performance of the mineral-filled composite was better than that of the unfilled one. Especially moisture resistance and weathering performance were improved with mineral addition. The improved properties and knowledge promote broadening the applications of WPCs beyond the most common ones (e.g. decking) today. As the minerals used with WPCs can be by-products, the mineral addition may also have a positive environmental influence.

8 REFERENCES

- ASHORI, A. & NOURBAKHS, A., 2010. Reinforced polypropylene composites: Effects of chemical compositions and particle size. *Bioresource technology*, 101(7), pp. 2515-2519.
- AYRILMIS, N., BENTHIEN, J.T., THOEMEN, H. & WHITE, R.H., 2011. Properties of flat-pressed wood plastic composites containing fire retardants. *Journal of Applied Polymer Science*, 122(5), pp. 3201-3210.
- BAKER, A.M. & MEAD, J., 2002. Thermoplastics. In: C.A. HARPER, ed, *Handbook of Plastics, Elastomers & Composites*. 4. edn. New York City, USA.: McGraw-Hill, pp. 1-108.
- BALATINECZ, J.J. & SAIN, M.M., 1998. The influence of recycling on the properties of wood fibre-Plastic composites. *Macromolecular Symposia*, 135(1), pp. 167-173.
- BENDIGANAVALA, A.K. & MALSHE, V.C., 2008. Infrared reflective inorganic pigments. *Recent Patents on Chemical Engineering*, 1, pp. 67-79.
- BLEDZKI, A., ZHANG, W. & FARUK, O., 2005. Microfoaming of flax and wood fibre reinforced polypropylene composites. *Holz als Roh- und Werkstoff*, 63(1), pp. 30-37.
- BORYSIK, S., 2007. Determination of nucleating ability of wood for non-isothermal crystallisation of polypropylene. *Journal of thermal analysis and calorimetry*, 88(2), pp. 455-462.
- BOUAFIF, H., KOUBAA, A., PERRÉ, P. & CLOUTIER, A., 2009. Effects of fiber characteristics on the physical and mechanical properties of wood plastic composites *Composites Part A: Applied Science and Manufacturing*, 40(12), pp. 1975-1981.
- BUTTERFIELD, B., 2007. The structure of wood: Form and function. In: J.C.F. WALKER, ed, *Primary wood processing: principles and practice*. 2. edn. Dordrecht, The Netherlands.: Springer, pp. 1-22.
- BUTYLINA, S., MARTIKKA, O. & KÄRKI, T., 2011. Thermal performance and optical properties of wood-polymer composites. *Journal of Thermoplastic Composite Materials*, .
- BUTYLINA, S., HYVÄRINEN, M. & KÄRKI, T., 2012a. A study of surface changes of wood-polypropylene composites as the result of exterior weathering. *Polymer Degradation and Stability*, 97(3), pp. 337-345.
- BUTYLINA, S., HYVÄRINEN, M. & KÄRKI, T., 2012b. Accelerated weathering of wood-polypropylene composites containing minerals *Composites Part A: Applied Science and Manufacturing*, 43(11), pp. 2087-2094.
- CHEN, G.Q., 2010. Plastics Completely Synthesized by Bacteria: Polyhydroxyalkanoates. *Plastics from Bacteria*, pp. 17-37.

- CHO, J., JOSHI, M.S. & SUN, C.T., 2006. Effect of inclusion size on mechanical properties of polymeric composites with micro and nano particles. *Composites Science and Technology*, 66(13), pp. 1941-1952.
- CLARK, R.N., SWAYZE, G.A., WISE, R., LIVO, E., HOEFEN, T., KOKALY, R. & SUTLEY, S.J., 2007. *USGS digital spectral library splib06a: U.S. Geological Survey*. Digital Data Series 231. U.S. Geological Survey.
- CLEMONS, C., 2008. Raw materials for wood-polymer composites. In: K. OKSMAN NISKA and M. SAIN, eds, *Wood-Polymer Composites*. Cambridge, England: Woodhead Publishing Limited, pp. 1-22.
- CLEMONS, C., 2002. Wood-plastic composites in the United States: The interfacing of two industries. *Forest Products Journal*, 52(6), pp. 10-18.
- CLEMONS, C.M., ROWELL, R.M., PLACKETT, D. & SEGERHOLM, B.K., 2012. Wood/Nonwood Thermoplastic Composites. In: R.M. ROWELL, ed, *Handbook of Wood Chemistry and Wood Composites*. 2. edn. Boca Raton, FL, USA.: CRC Press, pp. 473-510.
- DOMBROWSKI, T., MUELLER, S.M.I.W., GARDNER, D. & O'NEILL, S., 2005. Effect of different mineral types upon the performance characteristics of WPC decking boards. *The Global Outlook for Natural Fiber & Wood Composites 2005*, pp. 14-16.
- DUBNIKOVA, I.L., OSHMYAN, V.G. & GORENBERG, A.Y., 1997. Mechanisms of particulate filled polypropylene finite plastic deformation and fracture. *Journal of Materials Science*, 32(6), pp. 1613-1622.
- DUCA, J., 2010. Kaolin. In: M. XANTHOS, ed, *Functional Fillers for Plastics*. 2 edn. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 241-258.
- EDER, A., 2010-last update, Wood-Plastic Composite Markets in Europe. Available: http://www.wpc-consulting.eu/Presentation_eder_2010.ppt.pdf [11/13/2012, 2012].
- EDER, A., STROBL, S. & SCHWARZBAUER, P., 2007. *Worldwide Market Report on "Wood-Plastic Composites"*. Revised Edition 2007. Linz, Austria: Wood K plus. 221 p.
- EDER, A., 2011. Responding to Asian Imports, *Wood-Plastic Composites 2011*, 8-10 November 2011. 2011, AMI, 21 p.
- ERHARD, G., 2006. Thermoplastics. In: G. ERHARD, ed, *Designing with Plastics*. Munich, Germany: Carl Hanser Verlag, pp. 71-99.
- FABIYI, J.S. & MCDONALD, A.G., 2010. Effect of wood species on property and weathering performance of wood plastic composites *Composites Part A: Applied Science and Manufacturing*, 41(10), pp. 1434-1440.
- FACKLER, K., SCHWANNINGER, M., GRADINGER, C., HINTERSTOISSER, B. & MESSNER, K., 2006. Assessing fungal decay of spruce and beech wood using near infrared spectroscopy techniques. *Lenzinger Berichte*, 86, pp. 9-13.

- FAOSTAT, 2012-last update, FAOSTAT [Homepage of FAO Statistics Division], [Online]. Available: <http://faostat.fao.org/site/626/DesktopDefault.aspx?PageID=626#ancor> [11/13, 2012].
- FARHADINEJAD, Z., EHSANI, M., KHOSRAVIAN, B. & EBRAHIMI, G., 2012. Study of thermal properties of wood plastic composite reinforced with cellulose micro fibril and nano inorganic fiber filler. *European Journal of Wood and Wood Products*, 70(6), pp. 823-828.
- FARUK, O., BLEDZKI, A.K. & MATUANA, L.M., 2007. Microcellular Foamed Wood-Plastic Composites by Different Processes: a Review. *Macromolecular Materials and Engineering*, 292(2), pp. 113-127.
- FARUK, O., BLEDZKI, A.K. & NICOLAIS, L., 2011. Wood Plastic Composite: Present and Future. *Wiley Encyclopedia of Composites*. 2. edn. John Wiley & Sons, Inc., pp. 3212-3232.
- FINNISH THERMOWOOD ASSOCIATION, 2003. *ThermoWood® Handbook*. Helsinki, Finland: Finnish Thermowood Association. 66 p.
- FLARIS, V., 2010. Talc. In: M. XANTHOS, ed, *Functional Fillers for Plastics*. 2. edn. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 225-239.
- FOLLRICH, J., MÜLLER, U. & GINDL, W., 2006. Effects of thermal modification on the adhesion between spruce wood (*Picea abies* Karst.) and a thermoplastic polymer. *European Journal of Wood and Wood Products*, 64(5), pp. 373-376.
- GÉRARDIN, P., PETRIČ, M., PETRISSANS, M., LAMBERT, J. & EHRHRARDT, J.J., 2007. Evolution of wood surface free energy after heat treatment. *Polymer Degradation and Stability*, 92(4), pp. 653-657.
- GILES, H.F.J., WAGNER, J.R.J. & MOUNT, ELDRIDGE, M.I., II, 2005. Profile Extrusion. In: H.F.J. GILES, J.R.J. WAGNER and MOUNT, ELDRIDGE, M.I., II, eds, *Extrusion - The Definitive Processing Guide and Handbook*. Norwich, NY, USA.: William Andrew Publishing/Plastics Design Library, pp. 475-485.
- GODARA, A., RAABE, D., BERGMANN, I., PUTZ, R. & MÜLLER, U., 2009. Influence of additives on the global mechanical behavior and the microscopic strain localization in wood reinforced polypropylene composites during tensile deformation investigated using digital image correlation. *Composites Science and Technology*, 69(2), pp. 139-146.
- GODAVARTI, S., 2005. Thermoplastic wood fiber composites. In: A.K. MOHANTY, M. MISRA and L.T. DRZAL, eds, *Natural fibers, biopolymers, and biocomposites*. Boca Raton, FL, USA: Taylor & Francis, pp. 347-389.
- GWON, J.G., LEE, S.Y., CHUN, S.J., DOH, G.H. & KIM, J.H., 2010. Effects of chemical treatments of hybrid fillers on the physical and thermal properties of wood plastic composites. *Composites Part A: Applied Science and Manufacturing*, 41(10), pp. 1491-1497.
- HAIDER, A. & EDER, A., 2010. Markets, Applications, and Processes for Wood Polymer Composites (WPC) in Europe. *Processing Technologies for the Forest and Biobased Products Industries*, pp. 146.

- HAKKOU, M., PÉTRISSANS, M., ZOULALIAN, A. & GÉRARDIN, P., 2005. Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. *Polymer Degradation and Stability*, 89(1), pp. 1-5.
- HARPER, D. & WOLCOTT, M., 2004. Interaction between coupling agent and lubricants in wood–polypropylene composites. *Composites Part A: Applied Science and Manufacturing*, 35(3), pp. 385-394.
- HUDA, M.S., DRZAL, L.T., MOHANTY, A.K. & MISRA, M., 2007. The effect of silane treated- and untreated-talc on the mechanical and physico-mechanical properties of poly(lactic acid)/newspaper fibers/talc hybrid composites. *Composites Part B: Engineering*, 38(3), pp. 367-379.
- HUDA, M.S., DRZAL, L.T., MISRA, M., MOHANTY, A.K., WILLIAMS, K. & MIELEWSKI, D.F., 2005. A Study on Biocomposites from Recycled Newspaper Fiber and Poly(lactic acid). *Industrial & Engineering Chemistry Research*, 44(15), pp. 5593-5601.
- HUNEAULT, M.A. & LI, H., 2007. Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer*, 48(1), pp. 270-280.
- INARI, G.N., PETRISSANS, M., LAMBERT, J., EHRHARDT, J.J. & GÉRARDIN, P., 2006. XPS characterization of wood chemical composition after heat-treatment. *Surface and Interface Analysis*, 38(10), pp. 1336-1342.
- INTERNATIONAL STANDARDS FOR PHYTOSANITARY MEASURES, 2009. *ISPM 15 - Regulation of wood packaging material in international trade*. FAO. 261 p.
- INTERNATIONAL THERMOWOOD ASSOCIATION, 2012. *Thermowood production statistics 2011*. Helsinki, Finland: International ThermoWood Association. 9 p.
- JANCAR, J., 1999. Structure-Property Relationships in Thermoplastic Matrices. In: J. JANCAR, E. FEKETE, P.R. HORNSBY, J. JANCAR, B. PUKÁNSZKY and R.N. ROTHON, eds, *Mineral Fillers in Thermoplastics I*. Berlin Heidelberg, Germany: Springer, pp. 1-65.
- JOHN, M.J. & THOMAS, S., 2008. Biofibres and biocomposites. *Carbohydrate Polymers*, 71(3), pp. 343-364.
- KEENER, T., STUART, R. & BROWN, T., 2004. Maleated coupling agents for natural fibre composites. *Composites Part A: applied science and manufacturing*, 35(3), pp. 357-362.
- KHANNA, S. & SRIVASTAVA, A.K., 2005. Recent advances in microbial polyhydroxyalkanoates. *Process Biochemistry*, 40(2), pp. 607-619.
- KHANNA, Y.P. & XANTHOS, M., 2010. Calcium Carbonate. In: M. XANTHOS, ed, *Functional Fillers for Plastics*. 2. edn. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 291-306.
- KIM, J.W., HARPER, D.P. & TAYLOR, A.M., 2009. Effect of wood species on the mechanical and thermal properties of wood–plastic composites. *Journal of Applied Polymer Science*, 112(3), pp. 1378-1385.

- KIM, B., YAO, F., HAN, G. & WU, Q., 2012. Performance of bamboo plastic composites with hybrid bamboo and precipitated calcium carbonate fillers. *Polymer Composites*, 33(1), pp. 68-78.
- KIM, J.K. & PAL, K., 2011. Process and Machinery Used for WPC. *Recent Advances in the Processing of Wood-Plastic Composites*. Berlin Heidelberg, Germany: Springer, pp. 59-75.
- KLYOSOV, A.A., 2007. *Wood-plastic composites*. Hoboken, N.J. USA: Wiley-Interscience. 698 p.
- KOIKKALAINEN, A., 2012. Mineraaliäyteenä komposiiteissa [Mineral fillers in composites], *Kuidun uudet muodot -teemaseminaari*, 5/21/2012. 2012, Imatran Seudun Kehitysyhtiö Oy, 27 p.
- KORD, B., 2011. Effect of Calcium Carbonate as Mineral Filler on the Physical and Mechanical Properties of Wood Based Composites. *World Applied Sciences Journal*, 13, pp. 129-132.
- LEE, S., KANG, I., DOH, G., YOON, H., PARK, B. & WU, Q., 2008. Thermal and mechanical properties of wood flour/talc-filled polylactic acid composites: Effect of filler content and coupling treatment. *Journal of Thermoplastic Composite Materials*, 21(3), pp. 209-223.
- LEONG, Y.W., ISHAK, Z.A.M. & ARIFFIN, A., 2004. Mechanical and thermal properties of talc and calcium carbonate filled polypropylene hybrid composites. *Journal of Applied Polymer Science*, 91(5), pp. 3327-3336.
- LI, B. & HE, J., 2004. Investigation of mechanical property, flame retardancy and thermal degradation of LLDPE-wood-fibre composites. *Polymer Degradation and Stability*, 83(2), pp. 241-246.
- LI, Q. & MATUANA, L.M., 2003. Foam extrusion of high density polyethylene/wood-flour composites using chemical foaming agents. *Journal of Applied Polymer Science*, 88(14), pp. 3139-3150.
- MARTIN, O. & AVÉROUS, L., 2001. Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. *Polymer*, 42(14), pp. 6209-6219.
- MAZUMDAR, S.K., 2002. *Composites Manufacturing: Materials, Product, and Process Engineering*. Boca Raton, Florida, USA: CRC Press INC. 416 p.
- MIGNEAULT, S., KOUBAA, A., ERCHIQUI, F., CHAALA, A., ENGLUND, K. & WOLCOTT, M.P., 2009. Effects of processing method and fiber size on the structure and properties of wood-plastic composites *Composites Part A: Applied Science and Manufacturing*, 40(1), pp. 80-85.
- MOHANTY, A.K., MISRA, M., DRZAL, L.T., SELKE, S.E., HARTE, B.R. & HINRICHSEN, G., 2005. Natural fibers, biopolymers, and biocomposites: An introduction. In: A.K. MOHANTY, M. MISRA and L.T. DRZAL, eds, *Natural fibers, biopolymers, and biocomposites*. Boca Raton, FL. USA: Taylor & Francis, pp. 1-36.

- MORRELL, J.J., STARK, N.M., PENDLETON, D.E. & MCDONALD, A.G., 2009. Durability of wood-plastic composites, *10th International Conference on Wood & Biofiber Plastic Composites and Cellulose Nanocomposites Symposium*, May 11-13, 2009. Forest Products Society, pp. 71-75.
- MUASHER, M. & SAIN, M., 2006. The efficacy of photostabilizers on the color change of wood filled plastic composites. *Polymer Degradation and Stability*, 91(5), pp. 1156-1165.
- MURPHY, J., 2001. Modifying Processing Characteristics: Blowing Agents. In: J. MURPHY, ed, *Additives for Plastics Handbook*. 2. edn. Oxford, UK: Elsevier Advanced Technology, pp. 177-187.
- NASH, J., 2011. Market outlook for WPC, *Wood-Plastic Composites 2011*, 8-10 November 2011. 2011, AMI. 19 p.
- NATIONAL TOXICOLOGY PROGRAM, 12/12/2012, 2012-last update, Testing Status of Agents at NTP: 13983-17-0 Toxicity [Homepage of National Toxicity Program], [Online]. Available: <http://ntp.niehs.nih.gov/index.cfm?objectid=E87DA78A-BDB5-82F8-FD8A5A9C5472A8BF> [28/10, 2013].
- NATIONAL TOXICOLOGY PROGRAM, 1993. NTP Toxicology and Carcinogenesis Studies of Talc (CAS No. 14807-96-6)(Non-Asbestiform) in F344/N Rats and B6C3F1 Mice (Inhalation Studies). *National toxicology program technical report series*, 421, pp. 1-287.
- NOEL, O. & CLARK, R., 2005. Recent advances in talc-reinforced wood-plastic composites, *8th International Conference on Woodfibre-Plastic Composites (and other natural fibres)*, 23-25 May, 2005. 2005, Forest Products Society. 39 p.
- OKSMAN, K. & BENGTSSON, M., 2007. Wood Fiber Thermoplastic Composites: Processing, Properties, and Future Development. In: S. FAKIROV and D. BHATTACHARYA, eds, *Handbook of Engineering Biopolymers: Homopolymers, Blends and Composites*. Munich, Germany: Carl Hanser GmbH, pp. 655-672.
- PANYAM, J. & LABHASETWAR, V., 2012. Biodegradable nanoparticles for drug and gene delivery to cells and tissue. *Advanced Drug Delivery Reviews*, 64, pp. 61-71.
- PENDLETON, D.E., HOFFARD, T.A., ADCOCK, T., WOODWARD, B. & WOLCOTT, M.P., 2002. Durability of an Extruded Hdpe/wood Composite. *Forest Products Journal*, 52(6), pp. 21-27.
- PHILIP, S., KESHAVARZ, T. & ROY, I., 2007. Polyhydroxyalkanoates: biodegradable polymers with a range of applications. *Journal of Chemical Technology & Biotechnology*, 82(3), pp. 233-247.
- PHUONG, V.T. & LAZZERI, A., 2012. "Green" Biocomposites Based on Cellulose Diacetate and Regenerated Cellulose Microfibers: Effect of Plasticizer Content on Morphology and Mechanical Properties. *Composites Part A: Applied Science and Manufacturing*, 43(12), pp. 2256-2268.

- PILLA, S., 2011. Engineering Applications of Bioplastics and Biocomposites - An Overview. In: S. PILLA, ed, *Handbook of Bioplastics and Biocomposites Engineering Applications*. Hoboken, USA: John Wiley & Sons, pp. 1-15.
- PRITCHARD, G., 2005. Technology. In: G. PRITCHARD, ed, *Plastics Additives*. Shawbury, UK: Rapra Technology, pp. 23-82.
- PRITCHARD, G., 2004. Two technologies merge: wood plastic composites. *Plastics, Additives and Compounding*, 6(4), pp. 18-21.
- RANGARAJ, S.V. & SMITH, L.V., 2000. Effects of Moisture on the Durability of a Wood/Thermoplastic Composite. *Journal of Thermoplastic Composite Materials*, 13(2), pp. 140-161.
- REYNOLDS, N. & PHARAOH, M., 2009. An introduction to composites recycling. In: V. GOODSHIP, ed, *Management, recycling and reuse of waste composites*. Cambridge, UK: Woodhead Publishing Limited, pp. 3-19.
- ROBINSON, S.M. & XANTHOS, M., 2010. Wollastonite. In: M. XANTHOS, ed, *Functional Fillers for Plastics*. 2. edn. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 259-268.
- ROTHON, R.N., 1999. Mineral Fillers in Thermoplastics: Filler Manufacture and Characterisation. In: J. JANCAR, E. FEKETE, P.R. HORNSBY, J. JANCAR, B. PUKÁNSZKY and R.N. ROTHON, eds, *Mineral Fillers in Thermoplastics I*. Berlin Heidelberg, Germany: Springer Berlin Heidelberg, pp. 67-107.
- ROWELL, R.M., 2006. Advances and challenges of wood polymer composites, *Proceedings of the 8th Pacific Rim Bio-Based Composites Symposium 2006*, pp. 20-23.
- ROWELL, R.M., LANGE, S.E. & JACOBSON, R.E., 2002. Effects of moisture on aspen-fiber/polypropylene composites, *Progress in Woodfibre-Plastic Composites Conference Proceedings, Toronto, Canada 2002*. 9 p.
- ROWELL, R.M., ANDERSON, I. & ANDERSONS, B., 2012. Heat Treatment. In: R.M. ROWELL, ed, *Handbook of Wood Chemistry and Wood Composites*. 2. edn. Boca Raton, USA: CRC Press INC, pp. 511-536.
- ROWELL, R., 2007. Challenges in Biomass-Thermoplastic Composites. *Journal of Polymers and the Environment*, 15(4), pp. 229-235.
- ROWELL, R.M., IBACH, R.E., MCSWEENEY, J. & NILSSON, T., 2009. Understanding decay resistance, dimensional stability and strength changes in heat-treated and acetylated wood. *Wood Material Science & Engineering*, 4(1-2), pp. 14-22.
- SALONI, D., BUEHLMANN, U. & LEMASTER, R.L., 2011. Tool Wear When Cutting Wood Fiber-Plastic Composite Materials. *Forest Products Journal*, 61(2), pp. 149-154.
- SARAZIN, P., LI, G., ORTS, W.J. & FAVIS, B.D., 2008. Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer*, 49(2), pp. 599-609.

- SATOV, D.,V., 2008. Additives for wood-polymer composites. In: K. OKSMAN NISKA and M. SAIN, eds, *Wood-Polymer Composites*. Cambridge, England: Woodhead Publishing Limited, pp. 23-40.
- SCHIMLECK, L., MORA, C. & DANIELS, R., 2003. Estimation of the physical wood properties of green Pinus taeda radial samples by near infrared spectroscopy. *Canadian Journal of Forest Research*, 33(12), pp. 2297-2305.
- SCHUT, J.H., 2004. Beyond decking: Wood composites branch out. *Plastics Technology*, 50(8), pp. 50-55.
- SCHUT, J.H., 2001. Foaming expands possibilities for wood-fiber composites. *PLASTICS TECHNOLOGY-NEW YORK*, 47(7), pp. 58-65.
- SCHWACH, E., SIX, J. & AVÉROUS, L., 2008. Biodegradable Blends Based on Starch and Poly(Lactic Acid): Comparison of Different Strategies and Estimate of Compatibilization. *Journal of Polymers and the Environment*, 16(4), pp. 286-297.
- SHEN, L., HAUFE, J. & PATEL, M.K., 2009. Product overview and market projection of emerging bio-based plastics PRO-BIP 2009. *Report for European Polysaccharide Network of Excellence (EPNOE) and European Bioplastics*. Utrecht, the Netherlands: Universiteit Utrecht. 227 p.
- SMITH, P.M. & WOLCOTT, M.P., 2006. Opportunities for wood/natural fiber-plastic composites in residential and industrial applications. *Forest Products Journal*, 56(3), pp. 4-11.
- STAMM, A.J., 1928. Density of Wood Substance, Adsorption by Wood, and Permeability of Wood. *The Journal of physical chemistry*, 33(3), pp. 398-414.
- STARK, N.M. & MATUANA, L.M., 2004. Surface chemistry and mechanical property changes of wood-flour/high-density-polyethylene composites after accelerated weathering. *Journal of Applied Polymer Science*, 94(6), pp. 2263-2273.
- STARK, N.M. & ROWLANDS, R.E., 2003. Effects of wood fiber characteristics on mechanical properties of wood/polypropylene composites. *Wood and Fiber Science*, 35(2), pp. 167-174.
- STARK, N.M., MATUANA, L.M. & CLEMONS, C.M., 2004. Effect of processing method on surface and weathering characteristics of wood/flour/HDPE composites. *Journal of Applied Polymer Science*, 93(3), pp. 1021-1030.
- STARK, N.M., WHITE, R.H., MUELLER, S.A. & OSSWALD, T.A., 2010. Evaluation of various fire retardants for use in wood flour-polyethylene composites. *Polymer Degradation and Stability*, 95(9), pp. 1903-1910.
- TAJVIDI, M. & EBRAHIMI, G., 2003. Water uptake and mechanical characteristics of natural filler-polypropylene composites. *Journal of Applied Polymer Science*, 88(4), pp. 941-946.

TAKAYAMA, T., UCHIUMI, K., ITO, H., KAWAI, T. & TODO, M., 2013. Particle size distribution effects on physical properties of injection molded HA/PLA composites. *Advanced Composite Materials*, 22(5), pp. 327-337.

THOMPSON, D.,N., EMERICK, R.W., ENGLAND, A.,B., FLANDERS, J.,P., LOGE,F.,J., WIEDEMAN,K.,A. & WOLCOTT, M.,P., 2010. *Final Report: Development of Renewable Microbial Polyesters for Cost Effective and Energy- Efficient Wood-Plastic Composites*. INL/EXT-10-18133. Idaho Falls, USA: U.S. Department of Energy, Idaho National Laboratory. 154 p.

THRONE, J.L., 2004. Foam materials. In: J.L. THRONE, ed, *Thermoplastic Foam Extrusion: An Introduction*. Munich, Germany: Hanser Publishers, pp. 9-28.

TORO, P., QUIJADA, R., YAZDANI-PEDRAM, M. & ARIAS, J.L., 2007. Eggshell, a new bio-filler for polypropylene composites. *Materials Letters*, 61(22), pp. 4347-4350.

TRAN, C., HANKIN, S., ROSS, B., AITKEN, R., JONES, A., DONALDSON, K., STONE, V. & TANTRA, R., 2008. An outline scoping study to determine whether high aspect ratio nanoparticles (HARN) should raise the same concerns as do asbestos fibres. *IOM Report on Project CB0406, Edinburgh, UK*, 60 p.

VAN DE VELDE, K. & KIEKENS, P., 2002. Biopolymers: overview of several properties and consequences on their applications. *Polymer Testing*, 21(4), pp. 433-442.

WANJALE, S.,D. & JOG, J.,P., 2011. Polyolefin-Based Natural Fiber Composites. In: S. KALIA, B.S. KAITH and I. KAUR, eds, *Cellulose Fibers: Bio- and Nano-Polymer Composites*. Berlin Heidelberg: Springer-Verlag, pp. 377-398.

WEIDENFELLER, B., HÖFER, M. & SCHILLING, F.R., 2004. Thermal conductivity, thermal diffusivity, and specific heat capacity of particle filled polypropylene. *Composites Part A: Applied Science and Manufacturing*, 35(4), pp. 423-429.

WERTZ, J.L., BÉDUÉ, O. & MERCIER, J.P., 2010. Cellulose derivatives. *Cellulose Science and Technology*. Boca Raton, Florida, USA: CRC Press INC., pp. 275-301.

WIEDENHOEFT, A., 2010. Structure and function of wood. In: R. BERGMAN, Z. CAI, C.G. CARLL, C.A. CLAUSEN, M.A. DIETENBERGER, R.H. FALK, C.R. FRIHART, S.V. GLASS, C.G. HUNT, R.E. IBACH, D.E. KRETSCHMANN, D.R. RAMMER, R.J. ROSS and N.M. STARK, eds, *Wood handbook : wood as an engineering material*. Madison, WI: U.S.: Department of Agriculture, Forest Service, Forest Products Laboratory, pp. 3.1-3.18.

WINANDY, J., STARK, N. & CLEMONS, C., 2004. Considerations in recycling of wood-plastic composites, *Proc. 5th Global Wood and Natural Fibre Composites Symposium*, April 27-28, 2004. Forest Products Laboratory. 9 p.

WOLCOTT, M.P., 2007. Wood-Plastic Composites. In: A. MORTENSEN, ed, *Concise encyclopedia of composite materials*. 2. edn. Amsterdam, The Netherlands: Elsevier, pp. 932-936.

- WOLCOTT, M.P. & ENGLUND, K., 1999. A technology review of wood-plastic composites, *Proceeding 33th Int. Particleboard Composites Material Symposium 1999*, pp. 13-15.
- XANTHOS, M., 2010a. Polymers and Polymer Composites. In: M. XANTHOS, ed, *Functional Fillers for Plastics*. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 1-18.
- XANTHOS, M., 2010b. Mica flakes. In: M. XANTHOS, ed, *Functional Fillers for Plastics*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, pp. 163-176.
- XING, C., WANG, H., HU, Q., XU, F., CAO, X., YOU, J. & LI, Y., 2013. Mechanical and Thermal Properties of Eco-friendly Poly(propylene carbonate)/Cellulose Acetate Butyrate Blends. *Carbohydrate Polymers*, 92(2), pp. 1921-1927.
- XUE, Y., VEAZIE, D., GLINSEY, C., HORSTEMEYER, M. & ROWELL, R., 2007. Environmental effects on the mechanical and thermomechanical properties of aspen fiber-polypropylene composites. *Composites Part B: Engineering*, 38(2), pp. 152-158.
- YANG, H., WOLCOTT, M.P., KIM, H., KIM, S. & KIM, H., 2006. Properties of lignocellulosic material filled polypropylene bio-composites made with different manufacturing processes. *Polymer Testing*, 25(5), pp. 668-676.
- YIN, S., RIALS, T.G. & WOLCOTT, M.P., 1999. Crystallization behavior of polypropylene and its effect on woodfiber composite properties, *Fifth international conference on woodfiber-plastic composites*, 1999 May 26-27; Madison, WI. Madison, WI: Forest Products Society: pp. 139-146.
- ZHENG, R., TANNER, R. & FAN, X., 2011. Introduction. *Injection Molding: Integration of Theory and Modeling Methods*. Berlin Heidelberg, Germany: Springer, pp. 1-9.

SECTION II

PUBLICATIONS

ACTA UNIVERSITATIS LAPPEENRANTAENSIS

522. KURONEN, JUHANI. Jatkuvan äänitehojakautuman algoritmi pitkien käytävien äänikenttien mallintamiseen. 2013. Diss.
523. HÄMÄLÄINEN, HENRY. Identification of some additional loss components in high-power low-voltage permanent magnet generators. 2013. Diss.
524. SÄRKKÄ, HEIKKI. Electro-oxidation treatment of pulp and paper mill circulating waters and wastewaters. 2013. Diss.
525. HEIKKINEN, JANI. Virtual technology and haptic interface solutions for design and control of mobile working machines. 2013. Diss.
526. SOININEN, JUHA. Entrepreneurial orientation in small and medium-sized enterprises during economic crisis. 2013. Diss.
527. JÄPPINEN, EERO. The effects of location, feedstock availability, and supply-chain logistics on the greenhouse gas emissions of forest-biomass energy utilization in Finland. 2013. Diss.
528. SÖDERHOLM, KRISTIINA. Licensing model development for small modular reactors (SMRs) – focusing on the Finnish regulatory framework. 2013. Diss.
529. LAISI, MILLA. Deregulation's impact on the railway freight transport sector's future in the Baltic Sea region. 2013. Diss.
530. VORONIN, SERGEY. Price spike forecasting in a competitive day-ahead energy market. 2013. Diss.
531. PONOMAREV, PAVEL. Tooth-coil permanent magnet synchronous machine design for special applications. 2013. Diss.
532. HIETANEN, TOMI. Magnesium hydroxide-based peroxide bleaching of high-brightness mechanical pulps. 2013. Diss.
533. TYKKÄLÄ, TOMMI M. Real-time image-based RGB-D camera motion tracking and environment mapping. 2013. Diss.
534. PEKKOLA, SANNA. Performance measurement and management in a collaborative network. 2013. Diss.
535. PANOREL, IRIS CHERRY. Pulsed corona discharge as an advanced oxidation process for the degradation of organic compounds in water. 2013. Diss.
536. TORKKELI, LASSE. The influence of network competence of internationalization of SMEs. 2013. Diss.
537. MOLANDER, SOLE. Productivity and services – safety telephone services for the elderly. 2013. Diss.
538. SITARZ, ROBERT. Identification of research trends in the field of separation processes. Application of epidemiological model, citation analysis, text mining, and technical analysis of the financial markets. 2013. Diss.
539. KATTEDEN, KAMIEV. Design and testing of an armature-reaction-compensated permanent magnet synchronous generator for island operation. 2013. Diss.
540. HÄMÄLÄINEN, HARRI. Integration of learning supportive applications to development of e-portfolio construction process. 2013. Diss.

541. RATCHANANUSORN, WARIN. Development of a process for the direct synthesis of hydrogen peroxide in a novel microstructured reactor. 2013. Diss.
542. PERFILEV, DANIIL. Methodology for wind turbine blade geometry optimization. 2013. Diss.
543. STROKINA, NATALIYA. Machine vision methods for process measurements in pulping. 2013. Diss.
544. MARTTONEN, SALLA. Modelling flexible asset management in industrial maintenance companies and networks. 2013. Diss.
545. HAKKARAINEN, JANNE. On state and parameter estimation in chaotic systems. 2013. Diss.
546. HYYPIÄ, MIRVA. Roles of leadership in complex environments
Enhancing knowledge flows in organisational constellations through practice-based innovation processes. 2013. Diss.
547. HAAKANA, JUHA. Impact of reliability of supply on long-term development approaches to electricity distribution networks. 2013. Diss.
548. TUOMINEN, TERHI. Accumulation of financial and social capital as means to achieve a sustained competitive advantage of consumer co-operatives. 2013. Diss.
549. VOLCHEK, DARIA. Internationalization of small and medium-sized enterprises and impact of institutions on international entrepreneurship in emerging economies: the case of Russia. 2013. Diss.
550. PEKKARINEN, OLLI. Industrial solution business – transition from product to solution offering. 2013. Diss.
551. KINNUNEN, JYRI. Risk-return trade-off and autocorrelation. 2013. Diss.
552. YLÄTALO, JAAKKO. Model based analysis of the post-combustion calcium looping process for carbon dioxide capture. 2013. Diss.
553. LEHTOVAARA, MATTI. Commercialization of modern renewable energy. 2013. Diss.
554. VIROLAINEN, SAMI. Hydrometallurgical recovery of valuable metals from secondary raw materials. 2013. Diss.
555. HEINONEN, JARI. Chromatographic recovery of chemicals from acidic biomass hydrolysates. 2013. Diss.
556. HELLSTÉN, SANNA. Recovery of biomass-derived valuable compounds using chromatographic and membrane separations. 2013. Diss.
557. PINOMAA, ANTTI. Power-line-communication-based data transmission concept for an LVDC electricity distribution network – analysis and implementation. 2013. Diss.
558. TAMMINEN, JUSSI. Variable speed drive in fan system monitoring. 2013. Diss.
559. GRÖNMAN, KAISA. Importance of considering food waste in the development of sustainable food packaging systems. 2013. Diss.
560. HOLOPAINEN, SANNA. Ion mobility spectrometry in liquid analysis. 2013. Diss.
561. NISULA, ANNA-MAIJA. Building organizational creativity – a multitheory and multilevel approach for understanding and stimulating organizational creativity. 2013. Diss.
562. HAMAGUCHI, MARCELO. Additional revenue opportunities in pulp mills and their impacts on the kraft process. 2013. Diss.

