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LAPPEENRANNAN TEKNILLINEN YLIOPISTO

Kirsi Immonen

LIGNO-CELLULOSE FIBRE POLY(LACTIC ACID) INTERFACES IN BIOCOMPOSITES

LUT
University

Kirsi Immonen

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Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium of the Student Union House at Lappeenranta University of Technology, Lappeenranta, Finland on the 23rd of November, 2018, at noon.

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Supervisors Professor Tuomas Koiranen
LUT School of Engineering Science
Lappeenranta University of Technology
Finland

Professor Timo Kärki
LUT School of Energy Systems
Lappeenranta University of Technology
Finland

Reviewers Professor Dr. Andreas Krause
Faculty of Mathematics, Informatics and Natural Sciences
Department Biology
Institute of Wood Science
Wood Physics
Universität Hamburg
Germany

Professor Qinglin Wu
Roy O.Martin Sr. Professor, Biocomposites/Nanomaterials
Louisiana Forest Products Development Center
School of Renewable Natural Resources
Louisiana State University
USA

Opponent Professor Mikael Skrifvars
Department of Resource Recovery and Building Technology
University of Borås
Sweden

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Abstract

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Thermoplastic composite materials based on renewable raw materials are promoted globally in various ways. They can be prepared as durable, but biodegradable materials as poly(lactic acid) (PLA) ligno-cellulose composites are. Their advantages are their absence of fossil carbon, material recyclability, conversion to products using normal thermoplastic converting methods, absence of microplastic formation due to their biodegradability and haptic, unplastic-like feeling.

The most important issue in tailoring PLA ligno-cellulosic fibre composites is to control the interfacial connections between fibre and polymer and porosity. The main components affecting the interface are fibre length, fibre aspect ratio, fibre surface roughness and surface chemistry, fibre modification and additives used in composite such as plasticisers and coupling agents. In injection-moulded products and especially with short wood fibres, the fibre length is usually below the critical fibre length needed for fibre reinforcement. This is due to fibre degradation occurring in typical thermoplastic processing at high temperatures. Compounding followed by injection moulding were the main processing methods also used in this study.

The main aims of this research are to prove that regardless of the fibre dimensions of ligno-cellulosic wood fibre PLA composites, there is a need to couple between fibre and polymer to obtain optimal properties for the composite. It is also suggested that especially suitable coupling agents are oils from renewable origin and especially from modified oils such as epoxidised linseed oil (ELO) which can provide coupling between fibre and a polymer matrix.

The conclusions of this research are the following: The fibre-polymer bonding was improved and the porosity of the material reduced in PLA composites with cellulose nanofibres (CNF), high consistency nanocellulose (HefCel), micro-cellulose (MC) and bleached softwood kraft pulp (BSKP) with ELO addition on fibre. The improved fibre dispersion with nanocelluloses, especially with HefCel was found due to ELO addition. The coupling of fibre and polymer was proved by FTIR analysis, by increased melt viscosity and by improved mechanical performance due to ELO addition to compounds.

Keywords: polylactic acid, PLA, cellulose, ligno-cellulosic fibre, epoxidised linseed oil, biocomposite, bleached softwood kraft pulp, fibre composite

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This work was carried out in the School of Engineering Science and Energy Systems at Lappeenranta University of Technology, Finland, between 2017 and 2018. This work is based on the research I have carried out in my work in VTT Technical Research Centre of Finland during 2009 and 2018.

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Kirsi Immonen
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Lappeenranta, Finland

Contents

Publications

List of publications

This thesis is based on the following papers. The rights have been granted by publishers to include the papers in the dissertation.

I. Immonen, K., Wikström, L., and Anttila, U. (2018). Coupling of PLA and bleached softwood kraft pulp for enhanced properties of biocomposites. *Journal of Thermoplastic Composite Materials,* Published on-line March 1st, pp. 1-14; DOI: 10.1177/0892705718759387. url: http://journals.sagepub.com/doi/pdf/10.1177/0892705718759387

II. Immonen, K., Lahtinen, P., and Pere, J. (2017). Effects of Surfactants on the Preparation of Nanocellulose-PLA Composites. *Bioengineering*, 4, 91; doi:10.3390/bioengineering4040091

III. Immonen, K., Lahtinen, P., Isokangas, P., and Torvinen, K. (2017). Potential of Hemp Thermoplastic Biocomposites. Conference article. In: Fangueiro, R., and Rana, S., eds, *Advances in Natural Fibre Composites*, pp. 1-11. Cham: Springer International Publishing; doi:10.1007/978-3-319-64641-1_1

IV. Virtanen, S., Wikström, L., Immonen, K., Anttila, U., and Retulainen, E. (2016). Cellulose kraft pulp reinforced polylactic acid (PLA) composites: effect of fibre moisture content. AIMS Material Science, 3(3), pp. 756-769; doi: 10.3934/matersci.2016.3.756

V. Sippola, M., Immonen, K., Miettinen A., Laukkanen A., Andersson, T., Peltola, H., Harlin, A., and Holmberg, K. (2015, 2016). Predicting stiffness and strength of birch pulp – Polylactic acid composites. *Journal of Composite Materials,* First published, October 14, 2015, Vol. 50, Issue 18, pp. 2549-2563, 2016; doi:10.1177/0021998315608431

Author's contribution

The author Kirsi Immonen, is the principal author and investigator in papers I, II and III. In Paper IV, where Sanna Virtanen was the main writer, Kirsi Immonen contributed to the results and conclusions part of the work. In Paper V, Merja Sippola was the corresponding and main author and Kirsi Immonen conducted the experiments and pre-processed the experimental data.

Nomenclature

In the present work, variables and constants are denoted using *slanted style* and abbreviations are denoted using regular style.

Latin alphabet

A	area	m^2
a	constant	–
d	diameter	m
f	frequency	Hz
h	enthalpy	J/kg
L	characteristic length	m
l	length	m
m	mass	kg
T	temperature	°C
t	time	s
V	volume	m^3

Greek alphabet

β	beta-cellulose
Δ	difference
η	efficiency factor
μ	micron
σ	tensile strength
τ	shear strength

Superscripts

n	porosity efficiency exponent
*	dimensionless

Subscripts

c	composite
f	fibre
i	interfacial
l	length
o	orientation
p	pores
max	maximum
min	minimum

Abbreviations

2D	two-dimensional
3D	three-dimensional
a	amorphous
AA	acrylic acid
AKD	alkyl ketene dimer
AN	acrylonitrile
BC	bacterial cellulose
BP	birch pulp
BSKP	bleached softwood kraft pulp
c	crystalline or composite depending on relation
°C	degree Celsius
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAGR	Compound Annual Growth Rate
CAP	cellulose acetate propionate
CLP	critical length pullout
cm	centimeter
CMC	carboxymethyl cellulose
CNC	cellulose nanocrystal
CNF	cellulose nanofibril
CNFSD	cellulose nanofibrils from softwood dissolving pulp
CO_2	carbon dioxide
d	fibre diameter
DA	dispersion agent
DOP	dioctyl phtalate
DSC	differential scanning chromatography
E	stiffness
e.g.	exempli gratia
ELO	epoxidised linseed oil
ESO	epoxidised soy oil
et al.	et alia
etc.	et cetera
FDM	fused deposition modeling
FFF	fused filament fabrication
FLM	fused layer manufacturing
FTIR	Fourier transfer infrared
g	gram
-g-	grafted
GMA	glycidyl metacrylate
GPa	giga Pascal
GTA	glycerol triacetate
h	hour
HCl	hydrochloride

ΔH	enthalpy
HDT	heat distortion temperature
HDPE	high density polyethylene
HEC	hydroxy ethyl cellulose
HPC	hydropropyl cellulose
i.e.	id est
IFSS	interfacial shear strength
kJ	kilo Joule
$KMnO_4$	potassium permanganate
l	litre
M	molar
m^2	square metre
MAH	maleic anhydride
MAMCC	maleated microcrystalline cellulose
MAPP	maleic anhydride polypropylene
MC	microcellulose
MCC	microcrystalline cellulose
MFC	microfibrillated cellulose
min	minutes
ml	millilitre
mm	millimetre
Mn	number average molecular weight
MnO_3^-	Mangantrioxide-ion
MPa	mega Pascal
Mw	weight average molecular weight
N	nitrogen
NaBr	sodium bromide
NaOH	sodium hydroxide
NC	nanocellulose
nd	net detected
NFC	nanofibrillated cellulose
nm	nanometer
O	oxygen
OH	hydroxyl group
Pa	Pascal
PA	polyamide
PBAT	polybutulene adipate terephtalate
PBS	polybutylene succinate
PBST	polybutyrate succinate terephtalate
PC	polycarbonate
PCL	polycaprolactone
PE	polyethylene
PEF	polyethylene furanoate
PEG	polyethylene glycol

PET	polyethylene terephtalate
pH	pH -value
PHA	polyhydroxy alkanoate
PHB	polyhydroxy butyrate
PHBV	polyhydroxy butyrate valerate
PGA	polyglycolic acid
PLA	polylactide
PDLA	polylactide from D-isomers
PDLLA	polylactide from D-isomers and L-isomers
PLLA	polylactide from L-isomers
PP	polypropylene
PPC	polypropylene carbonate
PTT	Polytrimethylene terephtalate
PUR	polyurethane
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
R^2	probability for the curve fit
R&D	research and development
ROP	ring opening polymerisation
s	second
sb	stereoblock
sc	stereocomplex
s.d.	standard deviation
SEM	scanning electron microscopy
SFF	single-fibre fragmentation
Si	silane
SWP	softwood pulp
T	transmittance
Tc	crystallisation temperature
TEMPO	2,2,6,6-tetramethyl-piperidinyl-1-oxyl
Tg	glass transition temperature
Tm	melting temperature
TMP	thermo-mechanical pulp
TOFA	tall oil fatty acid
UD	unidirectional
USD	United States Dollar
UV	ultra violet
V	volume fraction
VST	Vicat softening temperature
WPC	wood polymer composite
wt-%	weight percentage

1 Introduction

Thermoplastic biocomposites can be defined as materials combining thermoplastic polymers with agro- or wood-based ligno-cellulosic fibres or carbohydrates (for example chitosan) in various size and polymer contents. On the other hand, a bioplastic film containing a few per cent nanocellulose is a biocomposite as well as a paper sheet with a thin layer of bioplastic (for example cellulose acetate) on surface. In between there are many classes of material and products prepared with techniques such as thermoforming, injection moulding, extrusion, compression moulding or 3D-printing.

The origin of the polymer in commercially produced biocomposites is still mostly Petrochemical based. Polymers such as polypropylene (PP), polyethylene (PE) or polyvinyl chloride (PVC) are used to make wood polymer composites (WPC) for decking, fencing, window frames, automotive interior parts, loudspeakers, musical instrument etc. The content of the renewable material in those products, fibre, is typically between 20 and 75 % depending on the processing method. In injection moulding the average fibre content in Europe (2012) was 42%, in extrusion for WPC type profiles 52%. The compression moulding allows higher fibre contents and the average was 72% in Europe in 2012. The total volume for wood plastic composites and natural fibre composites in 2012 was 352000 tonnes, roughly 15 % of total composite production in Europe (Carus et al. 2014).

The path to biobased materials are promoted today globally in various ways. The starting point was the oil crisis in the 1970’s and the dependence of materials on fossil raw materials, which led to an intensive search for their replacements by materials from renewable origin. The first reason was a high oil price, but later the most important arguments were related to the climate change and the increasing amount of carbon dioxide (CO_2) and other greenhouse gases. The next global issue was raised in the last few years, plastics in nature and especially microplastics in aquatic systems, which has sped up the development of biodegradable materials and plastic recycling methods. The increasing production volumes of bio-based materials has decreased the production costs at a comparable level to fossil-based materials. The intensive research and development efforts have created bio-based materials with advanced technical properties suitable for many demanding applications such as in replacement of metals and in glass fibre-reinforced composites. Last but not least, is the high consumer acceptance of renewable-based materials. The visual outlook of many natural fibre-containing materials is familiar to our eyes with the ‘natural wooden appearance’ and the sense of touch in many cases is warmer and softer compared to plastics.

Microplastics originating from oil-based polymers has become one of the main environmental concerns, not only from a visual standpoint, but due to the fact that they accumulate in our food chain. They can either inherently contain hazardous ingredients for animals, fish and humans, but also absorb toxic agents when transferred in aquatic environments or land (Hartmann et al. 2017). The transfer towards renewable-based materials does not necessarily provide and answer to the problem of microplastics, but can give us tools, for example, design biodegradable materials with a low carbon footprint. The utilisation of composite materials instead of pure polymers gives us a way to tailor materials with high stiffness that are also lightweight, enabling a reduction in energy needs (Mohanty 2005, Wright et al. 2017).

Legislators take small but significant steps to combat climate change problems all over the globe. Italy banned all non-biodegradable shopping bags on January 1, 2011. China has banned the production, use and sales of plastic bags with thickness of less than 0.025 mm since 2008. Presidential orders in the U.S. mandate a preference for the use of sustainable materials by the government in the form of the USDA bio-preferred programme. Specific municipal ordinances may have a tiny effect, but due to high publicity they create significant public awareness of the issue. In Japan, the city of Kochi is planning to ban the use of plastic items less than 40 microns in thickness. The PE bags less than 40 microns thick are discarded carelessly, leading to clogged drains in monsoons. The Japanese government has set a goal that 20% of all plastics consumed in Japan will be renewably sourced by 2020. (Chan 2016). As single-use bag ban is already in effect in Bangladesh, China, Kenya, Mexico and South-Africa. A new French law will require all disposable tableware to be made from a minimum of 50% biologically-sourced materials that can be composted at home by January of 2020. That number will rise to 60% by January of 2025 (Eastaugh 2016). The more such bans for oil-based plastics arise, the higher the demand will be for biodegradable materials, single-use materials that in many cases are biocomposites containing, e.g., starch as filler in bio-based plastic. One way to approach this challenge is cellulose-based, thin, paper like materials with high water, oil and grease resistance created with bio-based polymers, i.e., - cellulose composites. In addition to getting the high barrier properties for those materials a proper connection between fibre or filler and biopolymer is needed. There are already some novel commercial materials in that direction such as cellulose based compostable bag from Paptic, BioWare cardboard based take away cups from Huhtamäki and Kotkamills take away cup or cellulose acetate film and even edible composite solutions such as KFC's Scoff-ee cup (Anucyia 2015, Goodnewsfromfinland 2016, European commission 2017, Huhtamäki 2018).

In commonly used glass fibre composites the good mechanical properties are not only a result of a specific length of glass fibre with good mechanical properties, but their good compatibility with polymeric matrix. In glass fibre composites the most essential thing is sizing, which is critical to several key fibre characteristics that determine both how fibres will handle during processing and how they perform as part of a composite. The main components in sizing are the film former and the coupling agent. Glass fibre is abrasive and needs to be protected by film formers, which are designed to protect and lubricate the fibre and hold fibres together prior to moulding, yet also to promote their separation when in contact with resin, ensuring wet out of all the filaments. Coupling agents serve primarily to bond the hydrophilic glass fibre to the hydrophobic matrix resin. Besides these two components the sizing may include additional lubricants and antistatic agents and sizing is typically developed to focus on each polymer type separately (Mason 2006).

Glass fibre is a hydrophilic material (McDonald 1958, Zisman 1964) and in polymer composites, the fibre-polymer interfaces can to some extent be compared to natural fibre or ligno-cellulosic fibre polymer composites. Strongly polarised cellulose fibres are not inherently compatible with hydrophobic polymers. The compatibility and dispersion ability of fibre and matrix can be improved by creating on a surface of the fibre a hydrophobic coating, which is compatible with a polymer before mixing fibre with a polymer matrix. In addition, the coupling agents facilitate stress transfer at the interface between fibre and matrix. Coupling agents are molecules possessing two functions. The first reaction is with the -OH groups of cellulose, and the second reaction is, for example, with carboxyl of the matrix. The most common coupling agents are silane, isocyanate and titanate-based compounds (George et al. 2001). In natural fibre composites the type of fibre treatment and physical characteristics of the natural fibres significantly influence the mechanical behaviour of composites. The most important step in designing a natural fibre/polymer composite is the interfacial adhesion of the fibre with the matrix (Shalwan & Yousif 2013).

The selection of a coupling agent and/or plasticising agent on the basis of that which is or can be derived from renewable raw materials, can add hydrophobic properties for fibre, provide improved fibre dispersion to polymer and enable coupling properties between fibre and polymer are the aim of this research. Vegetable oils are attractive raw materials for many industrial applications as they are derived from renewable resources, biodegradable, environmental friendly, safe to use in human contact, easily available and produced in large quantities at a competitive cost and they are already used in paints, adhesives and plasticisers for polymers (Buong et al. 2014, Samarth & Mahanwar 2015). By modification they can also be made reactive for the coupling of fibres and polymers. The polymeric material polylactic acid (PLA) was chosen as a matrix for fibre composites. PLA is widely known bio-based polymer among plastic converters. It has good availability in different grades suitable from blow moulding and film extrusion to injection moulding and 3D-printing. It is a biocompatible polymer, biodegradable in industrial composting facilitiesa and can be processed as free from food chain (Jamshidian et al. 2010). One aim of this study was to show that in PLA-fibre composites with fibres below critical fibre length one of the feasible ways to gain overall improved mechanical properties is the coupling of fibres, polymers, and epoxidised vegetable oils that are especially suitable coupling agents, because they can provide coupling and improved fibre dispersion for short fibres in composites.

2 Thermoplastic biocomposites as sustainable materials

2.1 Thermoplastic biocomposites

Composite materials are a class of materials combining two or different materials together in a way that their combination has better performances compared to either of them alone. In thermoplastic composite materials the free shapes and moulding properties that thermoplastic polymers provide are combined with high strength performance reinforcing fibres (e.g. carbon fibres or glass fibres) or functional fillers (e.g., inorganic micro or nano scale particles).

The most common biocomposite material is made by nature - wood. It consists of cellulose fibre, lignin as a binder and hemicellulose as an adhesive material in between those two (Hubbe & Lucia 2007). It is however more thermosetting material than thermoplastic. Some mouldability to the wood can be gained by using hot steam, which is an old method to manufacture artistic shapes of wood, sleigh skids or boats. In steam moulding, the moisture act as a plasticiser for the wood by penetrating in between cellulose, hemicellulose and lignin. (Veritas 2011, Wright et al. 2013). During steam treatment the hemicellulose is partially hydrolysed, lignin is partially degraded and there also occurs relaxation of stresses in stored in microfibrils and matrix. All those phenomena enable the moulding of wood into novel forms (Fang et al. 2012).

There were promising attempts to make biocomposite as early as in 1930s. For example, Henry Ford started the first soy plastic plant in 1936. In the first soy composites the soy mill was mixed with formaldehyde, the two reacted together and mixed with wood flour (filler), clay and stearic acid to promote a smooth layer. Formaldehyde reacted with soy proteins to form a thermoplastic resin. Ford brought out a first car made out of bio-based plastics and composites in 1941. The car body was made of thermosetting composite 70% cellulosic material and 30% soy resin (soy, formaldehyde, phenol or urea) pressed into cloth, the new rust-free, dent-proof plastic was reported to be 30% lighter than steel and could absorb 10 times more knock without denting than steel. The cellulosic material mixture was a combination of wheat straw, flax, hemp, cotton and slashed pine cellulose utilising different properties of fibres in various scales. As early as 1934, Ford remarked that ‘almost all new cars will be soon made of such things as soybean’. Ford’s laboratories also developed renewable-based fibres for felts (soy wool) and reinforcements, and enamel-type coatings during that time. The biocomposite material was used to make car parts and refrigerator cabinets. (Shurtleff & Aoyagi 2011)

The promising soy plastic and many new renewable based materials did not get used in industry due to the discovery of crude-oil and new large-scale industrial synthetic polymers in the 1950s. However the oil crisis in the 1970s brought back the interest in materials originating from other raw materials than oil. This interest has become bigger in the last 30 years and finally led to new commercial bioplastics and increasing development of biocomposite materials. The global concern about environment, climate change and the limited fossil fuel resources has speeded up the development of material based on renewable origin with a low carbon footprint (Shurtleff & Aoyagi 2011, Shan et al. 2009).

The traditional composite materials containing glass, carbon or aramid fibres reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics, are difficult from the perspective of end of life. The components (fibre and polymer) are closely interconnected, relatively stable and therefore difficult to separate and recycle (Mohanty et al. 2000). The environmental laws and guidance such as the United Nations Kyoto protocol to globally reduce greenhouse gases and the European 2020 strategy with the Sustainable Growth Initiative are promoting materials and products that can be easily recycled or converted into new products, are based on sustainable origin and have longer service life (UN Kyoto Protocol, EU Sustainable Development 2008). The biocomposite materials are in line with these new demands for materials.

The term biocomposites can contain several material classes from thermosetting natural fibre mat composites to totally renewable-based thermoplastic short-fibre composites. The classification of biocomposites can be made according to their reinforcement forms as presented in Figure 1 (Ramakrisna et al. 2004).

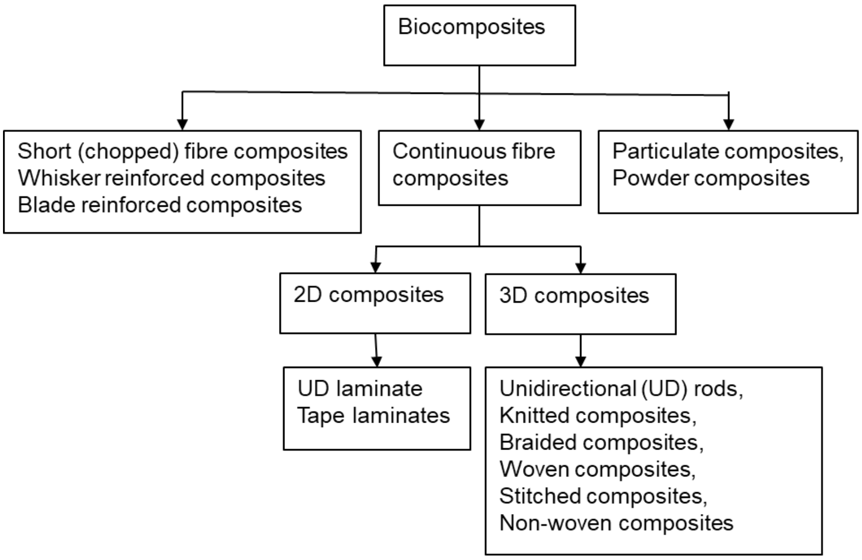

Figure 1: Classification of biocomposites according to architectural structure (Ramakrisna et al. 2004).

All the biocomposites mentioned above can be prepared with thermoplastic polymers to thermally formable materials. Biocomposite materials can be classified according to origin of monomers used to prepare polymer and biodegradation properties. The term ‘biocomposites’ covers composite materials where at least one constituent is bio-based.

Figure 2 shows one classification of biocomposites (Mitra 2014). One class of biocomposites is so called Green composites, where all constituents are from renewable sources.

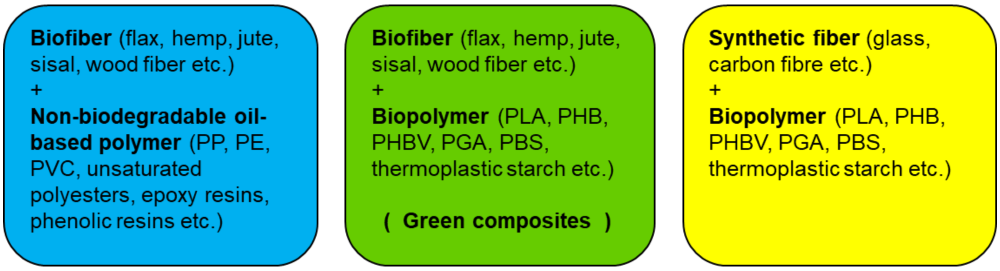

Figure 2: Classification of biocomposites according to constituents (Mitra 2014).

Biocomposite materials are suitable for many application areas from biodegradable to durable materials. There are, however, some issues that retards their adaptation to some areas e.g. in connection with water, high temperature use and some very high strength dependent applications. Those limitations are in many cases linked to a fibre-polymer matrix interface, polymer properties or temperature limitation of ligno-cellulosic fibre. A sufficient degree of adhesion between the surface of hydrophilic ligno-cellulosic natural fibres and the typically hydrophobic polymer matrix resin is usually needed to achieve optimum performance of the biocomposite. Due to the presence of hydroxyl and other polar groups in various constituents of natural fibres, the moisture absorption in biocomposites tends to be high, which leads to weak interfacial bonding between fibres and matrix polymer (Mohanty et al. 2001). The temperature stress on natural fibres during processing also has an effect on biocomposite strength properties and limits their maximum service temperature (Herrmann et al. 1998). The interrelationship between the biocomposite development and applications is presented schematically in Figure 3. The challenge in replacing conventional glass-fibre reinforced plastics with biocomposites is to design materials that exhibit structural functional stability during both storage and use, yet are susceptible to microbial and environmental degradation. (Mohanty 2005)

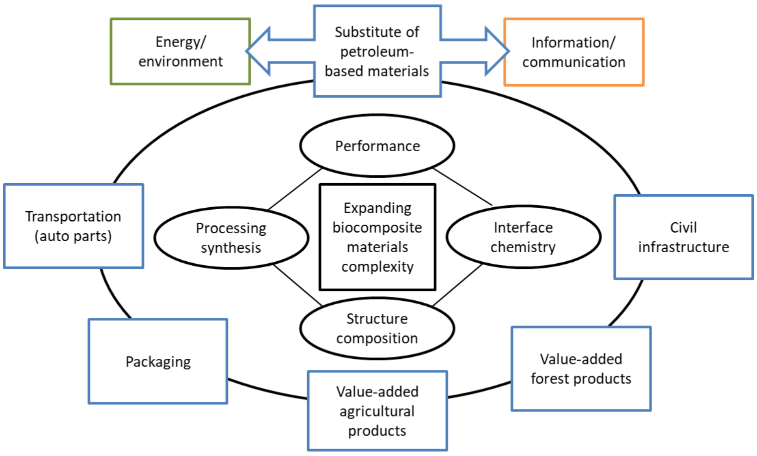

Figure 3: Biocomposite limits are to be governed through their uses via value-added products for various applications from energy and environmentally beneficial perspectives and through industrial interactions, thus creating effective communication that would enable real-world use of biocomposite materials (Mohanty 2005).

2.2 Markets

The global natural fibre composite market size was over USD 3.50 billion in 2015 and the global wood plastic composite market was USD 4.06 billion. Superior properties as compared to more traditional fibres (e.g. carbon and glass fibre) is expected to speed up growth. Natural fibre and wood plastic composites offer, better recyclability, excellent mechanical properties, high durability, low weight, and low cost. Growing consumer awareness regarding energy efficiency and the use of renewable sources is expected to have a positive impact on demand over the next eight years. In Europe, natural fibre composites market revenue is expected to be 1.1 billion (USD) in 2020 and 1.6 billion in 2024 (Grandview Research 2016).

The most important market sectors for biocomposites (wood plastic composites and natural fibre composites) are decking, automotive, siding and fencing followed by technical parts, furniture and consumer goods. The total volume for wood plastic composites and natural fibre composites in 2012 was 352000 tonnes, making up roughly 15 % of total composite production in Europe (Carus et al. 2014).

In 2015, construction segments were the biggest with over 50% volume share and products for siding and fencing are likely to increase. The trend for energy efficient building and novel materials for renovation is also increasing the demand for fibre composites. There, the wood-based composites dominate. The automotive industry has increasing demand for lighter materials to cut down fuel consumption, but also safer materials and materials with reduced carbon footprint, which increases the demand for natural fibre composites. The natural fibre including wood fibre containing composites are becoming more popular in electronics (e.g. loudspeakers and covers for electric appliances), but also furniture and consumer goods (e.g. toys, pencils, cups). The use of inorganic compounds including clay, lime, and cement are increasingly used in natural fibre composites to provide insulation and fire performance (Grandview research 2016).

The global bioplastics market in 2015 was 1,632,119 tons with estimated growth of 30% (CAGR) making up under 2% of total plastic production. The global bioplastic market is boosted by global brand owners such as Coca-Cola, Pepsi, H.J. Heinz, Ford, AT&T and Toyota. The volumes of material used in those applications is vast. At the same time, governments around the world are looking for ways to reduce carbon dioxide emissions and their dependence on oil-based products. Bioplastics are seen as one way to accomplish these goals. Another important factor is the Chinese government's growing support for agricultural development in areas such as bioplastics as a way to prop up the standard of living in the country's rural regions. Major indigenous producers of starch plastics and other types of bioplastics are emerging rapidly, hence changing the shape of the marketplace. Thailand and Brazil are also emerging as bioplastic-producing powerhouses (Chen 2016).

2.3 Thermoplastic biopolymers

Thermoplastic biopolymers are a class of polymers which are derived from renewable sources and converted to different products using heat and pressure. Biopolymer according to European Bioplastics is a plastic material if it is either biobased, biodegradable or features both properties. Since the 19th century, natural raw materials such as casein, shellac, gum, natural rubber, and cellulose have been chemically modified to convert them into useful macromolecular materials with new property profiles. The first industrially processable plastic material was galalith, produced by reacting casein from milk (Greek *gala*) with formaldehyde to produce a stiff thermoset resin resembling stone (Greek *lithos*). Although the biodegradable and water-insoluble galalith was not mouldable, sheets could be produced, thus enabling dyeing and machining. The latex of Brazilian rubber trees is collected, coagulated, dried, and vulcanised with sulfur to produce industrial rubber for making tires. Today, around 40% of rubber raw materials are supplied by rubber tree plantations. When the highly flammable and explosive nitrocellulose, obtained via nitration of cellulose and used as smokeless gunpowder, was plasticised with camphor, it was rendered thermoplastic. In fact, plasticised nitrocellulose was the first thermoplastic material marketed as Parkesine™ and Celluloid™. Even if it was rather explosive material, it became a successful substitute for ivory and was used for making billiard balls, thus saving the lives of thousands of elephants. As a flexible carrier, Celluloid™ enabled the manufacturing of photographic films (Mülhaupt 2013). Next on the market in the early stages of the 20th century were other thermoplastic celluloses such as cellulose acetate (CA), cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP) and hydroxyethyl cellulose (HEC), which have found their market beside oil based polymers (Klemm et al. 2005). In the 1920s and 1930s, DuPont began the manufacturing of a variety of thermoplastic polymers based on polycondensation such as polyesters and polyamides, hence launching the era of synthetic polymers, which finally led to oil-based low cost plastics in the 1950s.

Environmental concerns have again sped up the development of bio-based polymers for the last 30 years. The first-generation bio-based polymers such as polylactide (PLA) and polyhydroxyalkanoates (PHA) are based on carbohydrate-rich raw materials such as starches or sugars derived from food chain (corn, cereal, sugar beet, sugar cane, etc.), so they are not concidered to be very sustainable materials. Not only regarding the competition of food, there has also been discussion concerning other issues related to the use of bio-based feedstocks. The main issues or concerns are presented in Table 1 (Mülhaupt 2013). This study does not commit to the other issues than the land use and competition to food production, however they are important and should also be taken into consideration in a separate discussion.

Table 1: Prospects and problems of bio-based feedstock (Mülhaupt 2013).

PRO BIO	CONTRA BIO
Renewable resources conserve non-renewable fossil raw materials	Competition with food production
Lowering CO_2 emissions by switching from fossil fuels to biofuels	Intensified farming, extensive use of fertilisers, deforestation and grassland conversion cause a drastic increase in greenhouse gas emissions
Domestic energy supply and less dependence on oil imports	Energy crop monocultures threaten biodiversity
Plant cells and bacteria serve as solar microreactors for producing chemicals	Use of transgenic plants and genetically modified bacteria
Energy crops as nonfood incentives for farmers in industrial countries with surplus food production	Raising the cost of food because farmers abandon food production in developing countries that are unable to feed their rapidly increasing population
Use of agricultural and forestry wastes	A portion of the biomass must remain on agricultural land to secure soil quality and natural habitants for animals
Biodegradation	No biodegradation in the absence of water and oxygen. Disintegration may cause nanoparticles
No toxicity and no health hazards	Spongy degrading biopolymer particles are food sources and breeding grounds for bacteria and spores, which could be inhaled

The concern regarding food crops and global land use has sped up the development of biopolymers based on raw materials such as agricultural side streams not used for food production, food waste, waste grease, wood or other biomass containing cellulose. These are so-called second-generation biopolymers. European bioplastics and the Institute for Bioplastics and Biocomposites have estimated the need for global agricultural land use for bioplastics to be 0.01% (1.4 million hectares) in 2019 even with the estimated growth (European bioplastics 2015).

The synthesis routes from biomass to products is under intensive development by many research organisations globally. One aim of those studied is to replace oil based polymers with renewable-based ones. It is estimated that 9% of the total polymers consumed can be replaced by biopolymers even if their production is currently only 2% of oil-based polymers (Shan et al. 2009). Appendix A show one schematic approach for a renewable chemical platform, biobased chemicals and raw materials (Werpy & Petersen 2004). Besides biomass-based polymers, there are methods to make bio-based polymers from CO_2. The current routes are to make polycarbonates (PC), CO_2-polyols, polyurethanes (PUR) and finally epoxides through novel catalyst systems (Liu & Wang 2017). Biopolymers can also be categorised in the manner presented in Figure 4, which shows the status of existing commercial and pilot/laboratory scale biopolymes. Yet there are more to come in a few years as shown in Appendix A.

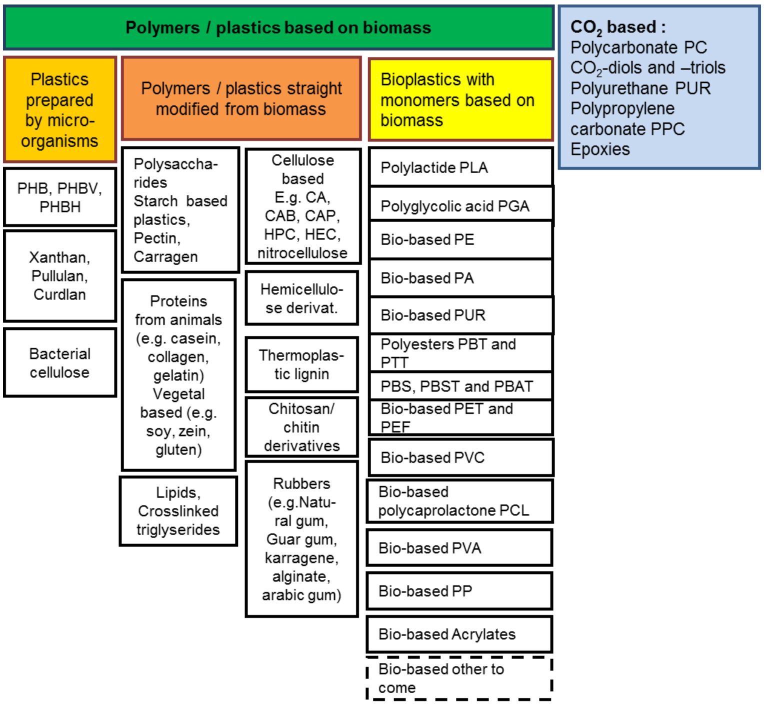

Figure 4: Current biopolymers categorised according to their origin (Reproduced from Weber 2000).

The global bioplastics production capacity in 2016 was 4156 kton with polyurethanes (PUR) share of 41.2%. Bio-based PUR are a fast growing group of polymers with a well-established market and a wide range of application sectors (e.g. in automotives). If PUR is left out, the global production capacity of bioplastics in 2017 was 2054 kton of which 880 kton was biodegradable polymers. The production estimation in 2022 is 2440 kton (European Bioplastics 2017).

Biopolymers such as PLA (polylactic acid) and PHAs (polyhydroxyalkanoates) are the main drivers of the growth in the field of bio-based, biodegradable plastics. PHAs are an important polymer family that has been in development for a while and that now finally enters the market at commercial scale, with production capacities estimated to triple in the next five years. These PHA polyesters are 100 percent bio-based, biodegradable, and feature in a wide array of physical and mechanical properties depending on their chemical composition. The production capacity of PLA is predicted to increase by 50 percent by 2022 over the capacity of 2017. The current share of PLA is 10.3% (212 kton) and is presented in Figure 5.

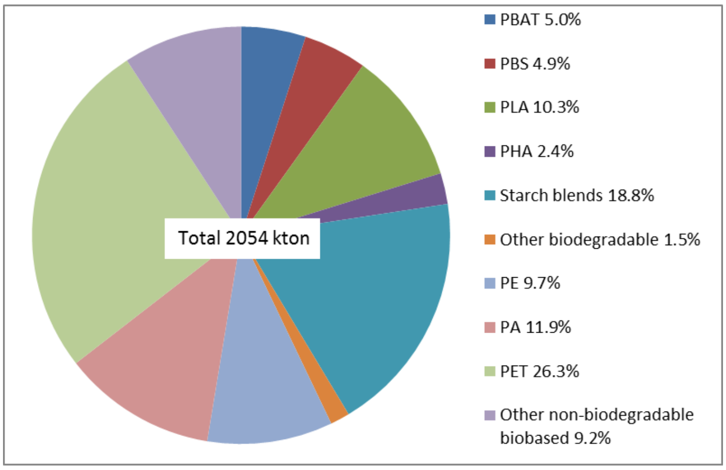

Figure 5: Global production capacities of bioplastics in 2017 by material type (without PUR; reproduced data from European Bioplastics 2018).

Two new interesting bio-based polymers entering the market soon are PEF (polyethylene furanoate) and bio-based polypropylene (PP). PEF is a new polymer that is expected to enter the market in 2020. PEF is comparable to PET (polyethylene terephthalate), but is 100 percent bio-based and is said to feature superior barrier and thermal properties, making it an ideal material for the packaging of drinks, food and non-food products. Bio-based PP is expected to enter the market on a commercial scale in 2022 with a strong growth potential due to the widespread application of PP in a wide range of sectors. (European Bioplastics 2018)

2.3.1 **Poly(lactic acid) (PLA)**

Poly(lactic acid) was first synthesised as early as 1845 by Théophile-Jules Pelouze using polycondensation of lactic acid. The industrial method for PLA production developed by Wallace Hume Carrothers et al. in 1932 and patented by DuPont in 1954. PLA and its copolymers were at first used mainly as biomedical materials due to their bioabsorbable and biocompatible nature in materials such as drug delivery, protein encapsulation, scaffold materials and prostheses. In the 1990s, Cargill Inc. succeeded in ring-opening polymerisation (ROP) for L-lactide on an industrial scale and together with Dow Chemical Company they commercialised the PLLA polymer, which showed high mechanical properties and was biodegradable (Masutani & Kimura 2015, Gruber & O'Brien 2004).

Lactic acid or 2-hydroxypropanoic acid, the monomer for PLA is derived by fermentation from sugar or starch rich biomass such as sugar cane, sugar beet, cassava and maize related to food chain. The second generation PLA originating from non-food biomasses (e.g. lignocellulose) is under development (Harmsen & Hackmann 2013). The fermentation results in L-lactide and D-lactide depending on the bacteria used for fermentation. PLA can be processed by direct condensation of lactic acid or ROP using cyclic lactide dimers. The condensation reaction leads to equilibrium of a low polymerisation degree due to water formed in the reaction and difficulties removing the water from the reactor. So the preparation of high molecular weight PLA combines both synthesis, at first making the low molecular weight PLA by condensation followed by preparation of lactides from prepolymer and finally using tin-catalysed ROP for lactide to form final polymer (Gruber & O'Brien 2004). Yet the researchers of Mitsui Chemical Co. have succeeded in developing high molecular weight PLLA using a special solution polycondensation technique and a bi-catalyst system. Both enantiomer forms PLLA and PDLA are crystalline polymers with melting temperature T_m around 180ºC and glass transition temperature in the range of 50-60º. Instead the mixture of those two PDLLA, is an amorphous polymer having an atactic sequence of ^{D} and ^{L} units. This so called stereocomplex (sc)- or stereoblock (sb)-PLA melting temperature of over 210 ºC and heat deformation temperature (HDT) over 180ºC, which opens a range of new application possibilities for PLA (Kimura 2009). PLA with PLLA content higher than 90% tends to be crystalline, while the materials with lower PLLA content, optically pure form, is amorphous. The melting temperature (Tm), and the glass transition temperature (Tg) of PLA decreases with decreasing amounts of PLLA (Farah et al. 2016). Further, the density of PLLA is dependent on the degree of crystallinity. The density of amorphous PLA is reported to be 1.248 g/ml, while that of crystalline is 1.290 g/ml. High molecular weight polylactides are either amorphous or semicrystalline at room temperature, depending on the amounts of L, D and meso-lactide in the structure (Figure 6). PLA are produced in totally amorphous or up to 40% crystalline forms (Auras et al. 2004).

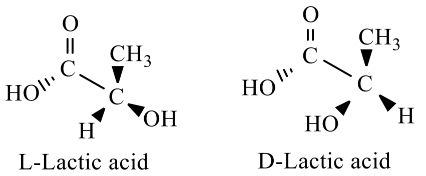
L-Lactic acid D-Lactic acid

Figure 6: Enantiomers of lactic acid: L-lactic acid (left) and D-lactic acid (right).

In terms of feedstock efficiency, PLA is one of the most efficient biopolymers if produced from carbohydrate-rich feedstock. For the production of 1 kg PLA is needed 1.6 kg fermentable sugars. By comparison to production 1 kg of bio-based polyethylene, 4 kg of sugar containing feedstock is needed. The alternative non-food feedstocks for PLA production are biomass crops and agricultural by-products (e.g. wheat straw, bagasse, corn stover, wood chips) and waste streams. Yet intensive R&D efforts are needed to extract C5 and C6 sugars from those before commercialisation (Lovett & de Bie 2016).

PLA properties are dependent on its isomers, processing temperature, molecular weight (Mw), annealing time, crystallinity and thermal history. PLA is quite brittle polymer with low impact strength and elongation, but high modulus leading to easy crazing of the polymer. Among biopolymers PLA is one of the most versatile polymers due to its suitability for all existing melt processing techniques. It is a biopolymer, which currently has the widest selection of grades for different applications. Table 2 shows typical properties of amorphous and crystalline PLA and some comparison to other biopolymers currently in use. For example polyhydroxyalkanoates (PHA, e.g. polyhydroxybutyrate, PHB) are a class of biopolymers under intensive research and development due to their easy biodegradation e.g. in nature. In PLA modifications with other biopolymers such as PHB, polybutylene succinate (PBS) and polycaprolactones (PCL) have been studied to get improved properties in polymers blends in combination with natural fibres (Farah et al. 2016, Nagarajan et al., 2016, Krishnan 2016).

Table 2. General characteristic PLA and some commercial biopolymers (Farah et al. 2016).

Property	PLLA	PLA Ingeo 3052D* Natureworks	PHB P226** Biomer	Bio-HDPE SHA7260 Braskem	Bio-PBS FZ71PM Mitsubishi Chemical Co.
Density kg/m^3	1.24-1.3	1.24	1.18-1.262	0.955	1.26
Tensile strength, MPa	15.5-150	62	40 (24-27**)	29	30
Modulus, GPa	2.4-4.14	3.6	3.5-4 (>1.14**)	1.35	0.63
Elongation at break, %	3.0-10.0	3.5	5.0-8.0	7.2	170
Charpy impact strength (notched, kJ/m^2		0.3	2.7**	25	7 (Izod)
HDT, ºC		55	59** (HDT-A)	74	95 (HDT-A)
Tg, ºC	55-65	55-60	-15.0- (-5.0)	-110.0***	
Tm, ºC	170-200	145-160	168-182	120-140	115

(*) NatureWorks, (2018), (**) Biomer P226, (***) Omnexus, 2018

PLA has the potential to be one of the main polymers to replace oil based plastics. It does possess, however, some degree of limitation. Toughness improvement is a crucial necessity for many consumer applications, while the improvements in hydrophilicity and introduction of reactive groups are beneficial for biomedical applications. Improvements in degradation rate could also be important in both consumer and biomedical applications (Rasal et al., 2010). The low heat resistance of commercial PLA grades has also been an issue restricting its use in many applications. Heat resistance is quantified by the detection of a softening point under a certain load. The two most commonly adopted techniques measured are heat deflection or distortion temperature (HDT) and Vicat softening temperature (VST). A typical value for HDT is roughly 55 °C and VST 65 °C. Various techniques and methods have been explored to improve the crystallinity and heat resistance of PLA. The HDT of PLA can be improved by (i) addition of nucleating agents and stereocomplex PLA for improved nucleation; (ii) adopting different processing strategies such as increased mould temperature in combination with nucleation agents; (iii) blending with heat-resistant polymers; and (iv) fabrication of biocomposites with natural fibres and nano-reinforcements. By using nucleating agents and PDLA, HDT values from 120-150ºC are obtained. (Nagarajan et al. 2016).

PLA is biologically degradable polymers, the degradation rate of which is determined by its particle size and shape, temperature, moisture, crystallinity, % isomer, residual lactic acid concentration, Mw, water diffusion and metal impurities from the catalyst. It degrades primarily by hydrolysis, after several months of exposure to moisture. PLA degradation occurs in two stages. First, random non-enzymatic chain scission of ester groups leads to a reduction in Mw. In the second stage, Mw is reduced until lactic and low Mw oligomers are naturally degraded by microorganisms to carbon dioxide and water. The fast degradation of PLA typically needs enough moisture and high temperature (50 to 60ºC) (Auras et al. 2004). The slow environmental degradation in many cases restrict the PLA use in applications where fast degradation, e.g., in nature is needed. There are ways to speed up the PLA degradation, for example, blending with biodegradable polymers with faster degradation speed, introduction of additives (e.g., polyethylene glycol) and mixing with hydrophilic materials, e.g., starch and cellulosic fibres (Zhang & Thomas 2011, Stloukal et al. 2016, Kumar et al. 2010).

Toughness improvements for PLA includes wide variation of methods from polymer grafting to blending with non-biodegradable and biodegradable polymers as well as grafting with different carbohydrates (e.g. soy protein, wheat gluten, konjacglucomannan, chitin, chitosan, starch and cellulose) with or without plasticisers is presented (Krishnan et al. 2016). Some vegetable-based oils are found to be suitable plasticisers for PLA and their epoxidised modifications such as epoxidised soy oil and palm oil are potential toughness-increasing ingredients when blended in low amounts with PLA (Tee et al. 2016). Compared to neat PLA, PLA/epoxidised palm oil (EPO) blends showed good thermal stability. In addition, the PLA/1 wt% EPO blend exhibited improvement in the tensile, flexural, and impact properties (Silverajah et al. 2012).

The main manufacturers for PLA are NatureWorks LLC (Ingeo™) with a wide range of PLA for different processing methods, Total Corbion (Luminy®) with high heat grades and stereoblock PDLA, Toray Industries (ECODEAR®) with flame-retardant and high impact grades, Teijin (BIOFRONT®), Futerro (LOOPLA®) use Galactic Technology lactides to produce PLA (NatureWorks 2018, Total 2018, Toray 2018, Galactic 2018). Some important manufacturers in PLA field are also additive manufacturers for PLA, e.g., DOW (PARALOID™), Arkema (Biostrength®), BASF (Joncryl®), Wacker Chemie (VINNEX®) and RheinChemie (BioAdimide®) (Dow 2018, Arkema 2018, RheinChemie 2018, Frenz & Sherzer 2008, Wacker Chemie 2018). Some of the commercial grades of PLA are presented in Table 3 to show the wide variation of PLA and suitability for different manufacturing methods.

Table 3: Some commercial PLA grades and their properties (NatureWorks 2018, Total-Corbion 2018).

PLA grade	Manufacturer	MFI, g/10 min (210°C, 2.6 kg)	Tensile strength at yield, MPa	Tensile modulus, GPa	Notched impact strength, J/m (Izod)	HDT/(Tg) °C	Tm, °C	Processing
Ingeo™ Biopolymer 2003D	Nature-Works	6	60	3500	16	55	nd	Exrusion/ Thermoform
Ingeo™ Biopolymer 3052D	Nature-Works	14	62	3500	16	55	145-160	Injection moulding
Ingeo™ Biopolymer 4032D	Nature-Works	7	60	3500	16	nd	155-170	Biaxially oriented films
Ingeo™ Biopolymer 6100D	Nature-Works	24	nd	nd	nd	(55-60)	165-180	Fibre Melt Spinning
Ingeo™ Biopolymer 6362D	Nature-Works	70-85	nd	nd	nd	(55-60)	125-135	Specialised Fibres amorphous
Ingeo™ Biopolymer 7001D	Nature-Works	6	nd	nd	nd	(55-60)	145-160	Blow moulding
Ingeo™ Biopolymer 8052D	Nature-Works	14	62	3500	16	(55-60)	145-160	Foaming
Ingeo™ Biopolymer 3D850	Nature-Works	7-9	51	2315	118	80-90 (55-60)	165-180	3DPrinting Monofilament
Luminy L105	Total-Corbion	65	50	3500	$\leq$5 kJ/m^2 (Charpy)	55-60 a 100-110c (55-60)	175	Thin wall injection moulding
Luminy L130	Total-Corbion	24	50	3500	$\leq$5 kJ/m^2 (Charpy)	55-60 a 100-110c (55-60)	175	Injection moulding

Luminy L175	Total-Corbion	8	50	3500	≤5 kJ/m^2 (Charpy)	55-60 a 100-110c (55-60)	175	Extrusion, Thermof., fibres
Luminy LX930U	Total-Corbion	17	40	3500	≤5 kJ/m^2 (Charpy)	55-60 a (55-60)	125-135	Fibres
Luminy D120	Total-Corbion	10	40	3500	≤5 kJ/m^2 (Charpy)	55-60	175	D-isomer for stereo-complex
Compound A	Total-Corbion	12	60	3600	3 kJ/m^2 (Charpy)	90	nd	Injection moulding
Compound E	Total-Corbion	5	60	5400	2 kJ/m^2 (Charpy)	120	nd	Extrusion, Thermof.
Compound K	Total-Corbion	8	50	3600	8 kJ/m^2 (Charpy)	80	nd	Industrially compostable

a amorphous, c crystalline

Natural fibres are usually added to PLA to reduce the cost of material or to modify the physical (mainly stiffness), rheological, optical, acoustic or biodegradation properties of the polymeric compounds (Murariu et al. 2016).

2.4 Fibres

Natural fibres as reinforcements in composites have already found their place in several commercial applications such as transportation, construction and consumer goods. The interest over synthetic fibre, e.g., glass fibre and aramid is increasing mainly due to their low environmental impact and low cost. The availability of different fibre materials also provide alternatives for tailoring of properties when linked with fibre modification techniques. The classification of natural fibres is presented in Figure 7 (Nazim & Ansari 2017).

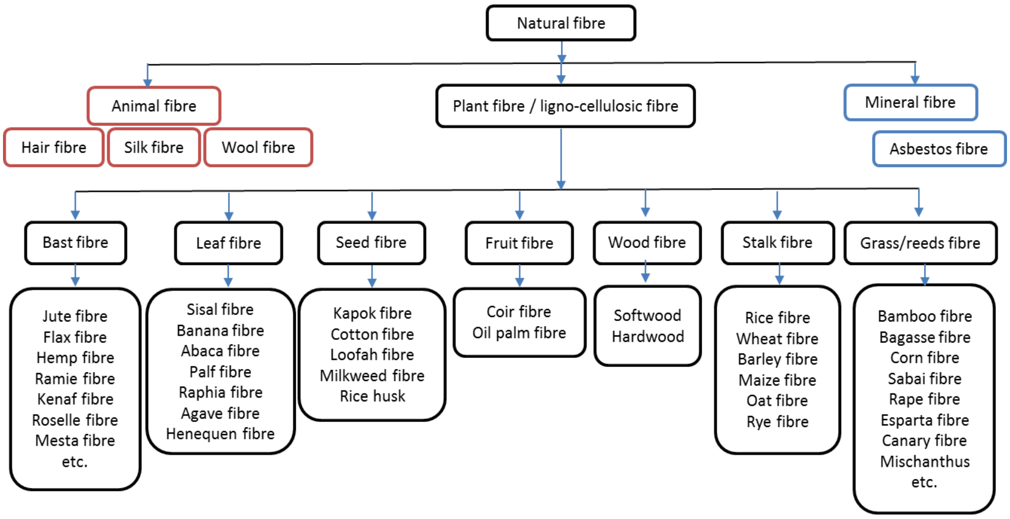

Figure 7: Classification of natural fibres (reproduced from Nazim and Ansari, 2017).

Natural fibres have several advantages over synthetic fibre, but also weaknesses related to the performance of fibres in natural fibre composites (NFC). The advantages and disadvantages are presented in Table 3 (Pickering et al. 2016).

Table 4: Advantages and disadvantages of NFCs (Pickering et al. 2016)

Advantages	Disadvantages
Low density and high specific strength and stiffness	Lower durability than for synthetic fibre composite, but can be improved considerably with fibre treatment
Fibres are a renewable resource, for which production needs little energy, involves CO_2 absorption, whilst returning oxygen to the environment	Lower strength, in particular impact strength compared to synthetic fibre composites
Fibres can be produced at lower cost than synthetic fibre	High moisture absorption, which results in swelling
Low emission of toxic fumes when subjected to heat and during incineration at the end of life	Lower processing temperatures limiting matrix options
Less abrasive damage to processing equipment compared with that for synthetic fibre composites	Greater variability of fibre properties related to fibre type, harvest time, extraction method, aspect ratio and fibre treatment method
Low hazard manufacturing processes	Porosity in fibres and often in composites

Due to the high variation of fibre properties originating from grade, harvest quality, processing method, etc., only natural fibres with high technical quality guarantee sufficient reproducibility of mechanical characteristics. For example, cellulose-based ‘man-made’ fibres such as Viscose or Rayon are being considered an option for polymer reinforcement; firstly, due to the sustainability of the fibre source, and secondly because of the high reproducibility of the fibre characteristics (e.g., diameter, stiffness, tenacity etc., Bledzki & Jaskiewicz 2010). The fibre selection for composites in many cases is related to the geographical availability of fibre. For example in Europe the common fibres used in composites are flax, hemp and wood cellulose, while forms of jute, kenaf, sisal and rice are more common in Asia. Generally high performance is achieved with varieties having higher cellulose content and with cellulose microfibrils aligned more in the fibre direction which tends to occur in bast fibres (e.g., flax, hemp, kenaf, jute and ramie) that have higher structural requirements in providing support for the stalk of the plant. When comparing the natural fibres to glass fibres the strength and stiffness of natural fibres are generally lower. However, as the specific properties of fibres are compared, the specific Young’s modulus can be higher for natural fibres and specific tensile strength can compare well with E-glass fibre. (Pickering et al. 2016). The mechanical properties of natural and synthetic fibres are presented in Table 4.

Table 5: Mechanical properties of natural and synthetic fibre (McIntosh & Uhrig 1968, Mohanty et al. 2000, Mathis 2002, Bos 2004, Fao 2009, Zhao et al. 2010, Jajcinovic et al. 2016, Pickering et al. 2016, Thomason et al. 2016, Zoltek 2018)

Fibre	Density, kg/m^3	Length, mm	Dia-meter, µm	Strain, %	Tensile strength, MPa	Young’s modulus, GPa	Specific tensile strength, -	Specific Stiffness, -
Bamboo	1.5	1.5-2	7-20	-	290	12	193	8
Coir	1.15	20-150	100-450	15-30	131-220	4-6	110-180	3.3-5
Cotton	1.5-1.6	10-60	11-22	7-8	287-800	5.5-13	190-530	3.7-8.4
Flax	1.4-1.5	5-900	10-80	1.2-3.2	345-1830	27-80	230-1220	18-53
Hemp	1.5	5-55	16-50	1.6-2.3	550-1110	58-70	370-740	39-47
Jute	1.3-1.5	1.5-120	25-200	1.5-1.8	393-800	10-55	300-610	7.1-39
Ramie	1.5	900-1200	25-30	2.0-3.8	400-938	44-128	270-620	29-85
Sisal	1.3-1.5	900	50-200	2-2.5	507-855	9.4-28	362-610	6.7-20
Wool	1.3	38-152	19-34	13.2-35	50-315	2.3-5	38-242	1.8-3.8
Softwood	1.5	2.2-3.8	25-75	5.5-9.4	370-900	5.9-17		
Hardwood	1.6	0.7-1.7	14-29		523-1105			
E-glass	2.5	Conti-nuous	Variable > 6	2.5	2000-3000	70	800-1400	29
Carbon	1.7	Conti-nuous	5-10	1.4-1.8	4000	230-240	2353	135-141

The chemical composition and complex chemical and physical structure of fibres have an effect on fibre properties, which is also reflected in the composite properties. Natural fibres are ligno-cellulosic fibres composed of cellulose, hemicellulose and lignin. The chemical composition of natural fibres varie considerably not only between fibres, but also due to the fibre origin, age, retting or due to separation process. The main component of cellulose is a hydrophilic anhydroglucose, which contains three alcoholic hydroxyl groups. These hydroxyl groups form intramolecular hydrogen bonds inside the molecule itself and intermolecular hydrogen bonds among other cellulose macromolecules as well as with hydroxyl groups from the air. Therefore, all of the natural fibres are hydrophilic in nature and their balance moisture content reaches 8–12.6% (Bledzki et al. 1996). The chemical composition of some selected fibres are presented in Table 5.

Table 6: Chemical composition of fibres (Fengel & Grosser 1975, Faruk et al. 2012)

Fibre	Cellulose, wt-%	Hemicellulose, wt-%	Lignin, wt-%	Waxes, wt-%
Bamboo	26 - 43	16.8	25.3	
Flax	71	18.6 - 20.6	2.2	1.5
Hemp	68	15	10	0.8
Jute	61-71	14-20	12-13	0.5
Wheat straw	38-45	15-31	12-20	
Softwood	40-45	25-30	25-35	
Hardwood	40-50	25-35	20-25	

The next components of fibre are hemicelluloses, which are short-chained, often branched polysaccharides that coexist with cellulose and other polymers in the plant cell walls. The main classes of hemicellulose are xylans, mannans, and xyloglucans. The structures of hemicelluloses depend on the plant or even the cell wall layer in which they were biosynthesised. They are important load-bearing molecules in cell walls that cross-link cellulose microfibrils (Kontturi 2015).

The third main component of fibre is lignin, which is a phenolic polymeric material that functions as a structural support material in plants. During synthesis of plant cell walls, cellulose and hemicellulose are laid down first, and lignin fills the spaces between the polysaccharide fibres, cementing them together. This lignification process causes stiffening of cell walls, and the carbohydrate is protected from chemical and physical damage. Lignin is believed to be linked with the carbohydrates (cellulose and hemicelluloses) through two types of linkages, one alkali-sensitive and the other alkali resistant. The alkali-sensitive linkage forms an ester-type combination between lignin hydroxyls and carboxyls of hemicellulose uronic acid. The ether type linkage occurs through the lignin hydroxyls combining with the hydroxyls of cellulose. The lignin, being polyfunctional, exists in combination with more than one neighbouring chain molecule of cellulose and/or hemicellulose, forming a crosslinked structure (Bledzki et al. 1996).

Natural fibre is a hierarchial biocomposite itself where unidirectional cellulose microfibrils forms the reinforcing element and blend of hemicellulose and lignin form the matrix. The structure of a fibre is built with layers P, S1, S2 and S3 of cellulose microfibrils at different angles from the fibre axis. Depending on single fibre the spiral angle of layers have significant influence on properties of fibre. Also the crystallinity of the cellulose varies between different parts of the fibre (Faruk et al. 2012).

The understanding of the chemical nature and physical structure of different fibres is the key for fibre modifications and the development of natural fibres to be effective reinforcements in biocomposites, and tailoring for the best connectivity of fibres to polymers.

2.4.1 Micro- and Nanocellulose in PLA composites

In nature the hierarchial structure of natural fibres, as in Figure 8, is based on their elementary nanofibrilar components leading to their unique strength and high performance properties. This structure can be torn apart and the cellulosic nanoparticles can be extracted from the structure. The potential of nanocellulose and nanofibrillar cellulose is demonstrated as a functional particle is demonstrated in many studies over the past 20 years (Dufresne 2013). Nanocellulose can be extracted from all cellulosic plants and algae, and bacterial cellulose (BC) made using bacteria. For example, an intrinsic ingredient of wood is cellulose microfibrils that have a 20-100 nm cross-sectional size and a fibre length of 100-200 nm. The extraction of NC from natural resources includes pre-treatment of natural resources and the breaking of amorphous parts of cellulose to extract NC in forms of cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) (Kim et al. 2015).

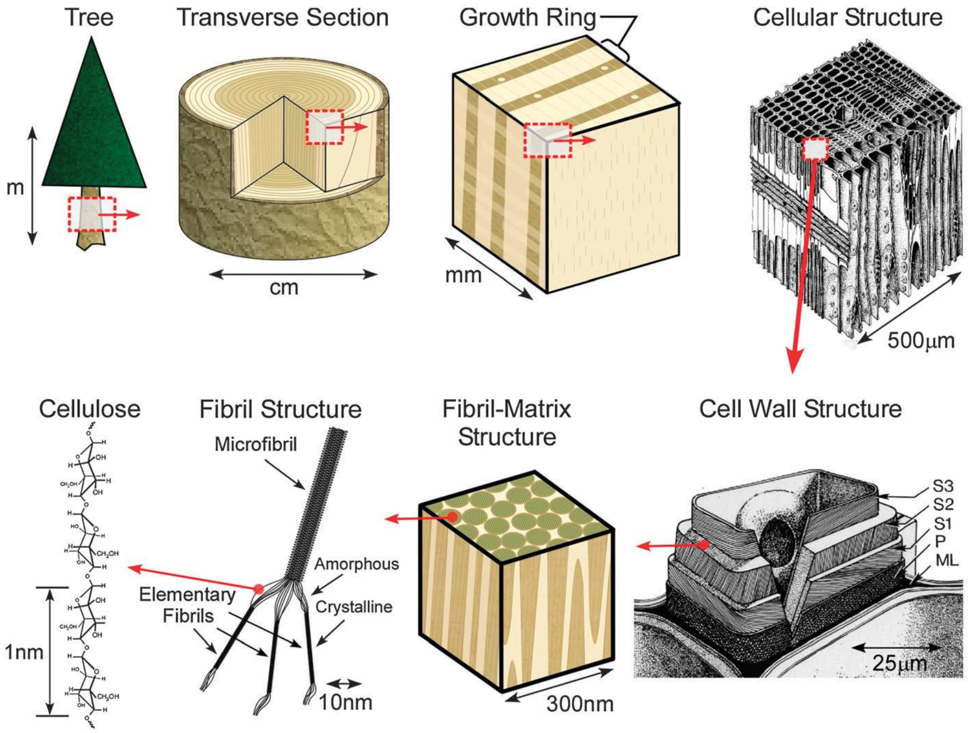

Figure 8: Hierarchial structure of wood from tree to cellulose (Moon et al. 2011)

The isolation of nanocellulose particles occurs in two stages. At first the wood or plant material is pretreated in addition to removing hemicellulose and lignin. In the second stage the cellulose is separated into fibrils using either mechanical treatments (e.g. high-pressure homogenisers, grinders/refiners, crycrushing, ultrasonic treatment or microfluidisation), acid hydrolysis (sulphuric acid, hydrochloric acid or maleic acid) or enzymatic hydrolysis. In addition to intensifying the fibril separation during mechanical treatments there can be used chemicals. The usual method is to employ 2,2,6,6-tetramethyl-piperidinyl-1-oxyl radical (TEMPO) (region-selective oxidation) or adsorption of charged polyelectrolytes (e.g., carboxymethyl cellulose treatment) (Moon et al. 2011).

Different cellulose particles can be gained by using the above mentioned cellulose isolation methods. Microcellulose (MC) or microcrystalline cellulose (MCC) is commercially available material used for mainly pharmaceutical and food applications. MC or MCC are made by acid hydrolysis from wood fibres, neutralised with alkali and spray-dried to porous particles with diameters of 10-50 µm. They are high in crystallinity and cellulose content. Microfibrillated cellulose (MFC) is 100% cellulose containing multiple elementary fibrils with both crystalline and amorphous regions. MFCs are used as thickening agents in the food and cosmetics industries. They have a high aspect ratio due to length variation from 0.5 to 90 µm and thickness from 10 to 100 nm. Nanofibrillated cellulose (NFC) resemble MFC but are finer. NFC length is typically 500-2000 nm and width 4-20 nm. The last class is cellulose nanocrystals (CNC), those are rod-like or whisker-shaped particles also and named nanocrystalline cellulose, cellulose whiskers, cellulose nanowhiskers or cellulose microcrystals. Those are highly crystalline (54-88%) cellulose particles with high aspect ratio, typical width from 3 to 5 nm and a length of 50-500 nm. Bacterial cellulose (BC) is a special cellulose produced by *Gluconacetobacter xylinus.* The advantage of bacteria-derived cellulose microfibrils is that it is possible to adjust culturing conditions to alter the microfibril formation and crystallisation. The average diameter of BC is 20–100 nm and micrometer lengths, entangle to form stable network structures (Abitbol et al. 2016). The specific strength properties of different nanocelluloses in comparison to other materials are presented in Ashby plot in Figure 9 (Moon et al. 2011).

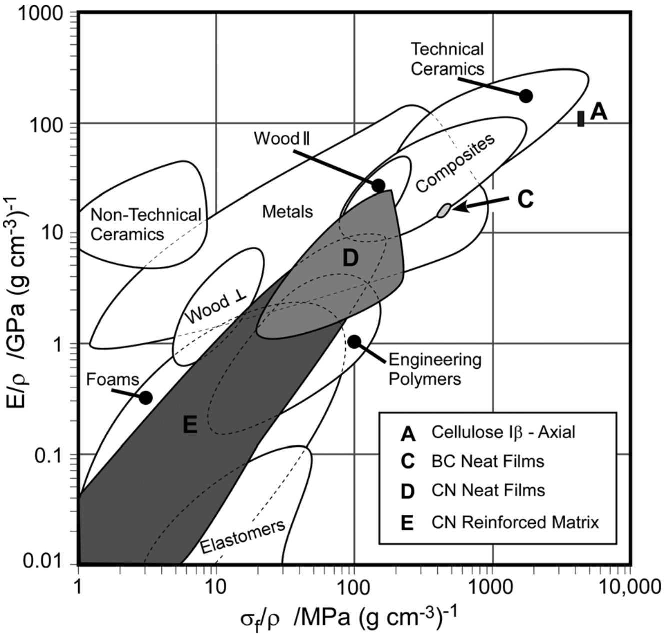

Figure 9: Ashby plot of specific modulus (E/ρ) versus specific strength (σ/ρ). Regions of crystalline cellulose Iβ (A), BC neat films (C), neat films of either CNC, t-CNC, MFC, and NFC (D), and NC-reinforced matrix composites (less than 30 wt% NC) (E). (Moon et al. 2011)

Nanocellulose is a promising biomaterial for medical applications due to its good biocompatibility and relatively low toxicity, as well as distinct geometry, surface chemistry, rheology, crystallinity and self-assembly. The addition of CNC to PLA has also showed the potential for controllable biodegradation. However, the interfacial strength between CNC and PLA is low due to hydrophobic PLA and highly hydrophilic

CNC, resulting in a decrease of mechanical properties. The high tendency of nanocellulose fibres for agglomeration also reduce mechanical properties. So the surface modifications of either PLA or CNC are potential ways to obtain improved composite properties. For example CNC has been studied in maleic grafted PLA (MPLA) composites for bone tissue engineering. The method for composite preparation was electrospinning of (MPLA/CNC)-containing solution to form nanofibre scaffolds. With only 5 % CNC content in MPLA the fibre tensile strength was improved from 1.6 MPa to 10.8 MPa and tensile modulus from 7.8 MPa to 135.1 MPa (Zhou et al. 2013).

Nanocelluloses CNC and NFC as reinforcements in thermoplastic composites for cost-effective, highly durable sustainable materials. The native crystallinity, high strength, and moderate to high aspect ratio (ca. 10–1000 length/diameter; type dependent) of nanocellulose are relevant for stress-transfer and load-bearing in thermoplastics, such as PLA (Abitbol et al. 2016). The solution based methods such as solution casting, electrospinning and preparation via hydrogels are currently the most promising methods for nanocellulose composite manufacturing even with thermoplastic polymers (Abitbol et al. 2016, Petersson et al. 2007). In addition to gaining good dispersion in thermoplastic polymer, PLA, and making the processing more feasible, the solution casting has been used as masterbatch preparation for further processing with extrusion or injection moulding. Promising results have been gained with nanomaterial loading below 5 % in the final material. The tensile modulus and strength increased in injection-moulded samples from 2.9 GPa to 3.6 GPa and from 58 MPa to 71 MPa, respectively, for nanocomposites with 5 wt-% CNF. However, the composites had clear agglomerates, which could even be seen visually (Jonoobi et al. 2010). In another study, MFC-PLA composites were made using solvent casting from acetone and melt kneaded to flat sheets, resulting in improvements in tensile strength of 25% and Young’s modulus by 40% in MFC content of 10% in PLA. In higher MFC amounts the flocculated nanofibres made the composites brittle and decreased the strength (Iwatake et al. 2008). In solution casting followed by melt processing, the typical solvent has been acetone, the use of which is not very industrially feasible. Wang and Drzal used water-based dispersions of PDLLA and utilised Polysorbate 80 (an ester of polyethoxylated sorbitan and oleic acid) as an emulsion stabiliser. This method provided a CNF sheet filled with polymer particles, which were stacked and compression-moulded. This method resulted in a 58% increase in tensile strength and 210% increase in modulus. However, according to conclusions, a higher suspension stability and a stronger fibre‒polymer interaction will be required to improve this method (Wang & Drzal 2012).

In addition to improve dispersion properties of nanocelluloses to PLA several modification are studied. Surface treatments such as coating with surfactants, controlled oxidation and functionalisation (e.g., silylation, carboxymethylation, isocyanate grafting and esterification with organic acids, etherification, alkylation, glyoxalisation and polymer grafting with PEG, PCL and PLA; Wang & Drzal 2012, Abitbol et al. 2016, Oksman et al. 2016).

The large surface area of nanocellulose with a high density of hydroxyl groups on it requires a high loading of chemicals for coating. More importantly, the reinforcing effect of cellulose in polymer composites is related not only to the high stiffness of cellulose, but also to its tendency to form percolating networks through hydrogen bonding. When nanocellulose is modified, its ability to achieve interfibrillar affinity is reduced, which may explain some observations of little or no property enhancement after the modifications despite improved dispersions (Wang et al. 2012). The critical challenge to achieving the transfer of good mechanical properties of single-fibre nanocellulose to the macroscale properties of the polymer nanocomposites is also to obtain well-dispersed hydrophilic-reinforcing nanocellulose in the polymer matrices, but also optimisation of the fibre–matrix interface and improved coupling of fibre and polymer for enhanced stress transfer. (Oksman et al. 2016).

2.5 Fibre-polymer interfaces and fibre modifications

In the development of high-strength biocomposites one of the key elements is to control fibre-polymer interfaces or interfacial bonding between fibre and matrix, which is agreed in many studies. The proper interfacial bonding enables stress transfer between matrix and polymer. Inherently hydrophilic cellulosic fibre and typically hydrophobic, polar polymeric matrix are poorly compatible with each other leading typically to poor bonding (Pickering et al. 2016). In short fibre composites, this can be seen as poor fibre dispersion, agglomerates and porosity, which are reflected as low strength properties, especially impact strength properties, and high water absorption.

Interfacial adhesion between fibre and polymer matrix can occur as mechanical interlocking, electrostatic bonding, chemical bonding and inter-diffusion bonding. Mechanical interlocking occurs when a fibre surface is rough and increases interfacial shear strength, but has less effect on transverse tensile strength. Electrostatic bonding can occur only via close interaction between fibre and other components in composite and requires different electrostatic charges in fibre and matrix or additives. Chemical bonding occurs when chemical groups on fibre surfaces can react with matrix or other additives, creating bonds between fibre and polymer matrix. In inter-diffusion bonding, the atoms and molecules of the fibre and matrix interact at the interface by, for example, chain entanglement and the strength is dependent on the length of the chains entangled (Beckermann 2007, Pickering et al. 2016,).

One important factor in creating good interfaces between fibre and polymer is sufficient wetting of fibres, when mixed with polymer melt. The wetting is in many cases a compromise between sufficient polymer melt viscosity to enable proper wetting of fibres and temperature in process (Beckermann 2007). With polymers having high melt viscosity in temperatures preferred for natural fibres (< 200ºC) the proper fibre dispersion and wetting may not be sufficient

The poor fibre matrix connection in final products has an effect on durability and abrasion properties, poor creep performance, wetting performance and microbe resistance. To tackle this challenge several fibre and polymer modification methods as well as additive systems are developed. The main methods are different physical, chemical and enzymatic modifications of fibres, modifications of polymers, especially focused on PLA in this study, and the use of coupling agents as well as plasticisers.

2.5.1 Physical modifications

Physical modifications of fibres contain several milling techniques, thermal treatments, calendaring, beating, cryo-crushing, steam explosion, plasma and corona treatments. The last two methods are seen as the ones with the most potential to increase fibre-polymer interaction. By milling, it is possible to control dimensions such as aspect ratio and fibrillation of fibre surface in addition to increased fibre surface area and potential dispersion properties of fibre to polymer. With physical treatments, it is possible to primarily increase the mechanical adhesion between fibre and polymer. The milling of surface can also provide hybrid fibres containing fibres from nanosize to micron size. In addition to manufacture nanosize fibres milling techniques such as high pressure homogenisers, fluidisers or ultra-fine friction grinders (so-called ‘Supermasscolloiders’) are in use. The milling methods are often combined with chemical or enzymatic treatment to get the highest effect on fibre. One way to release interfibrillar connections is ultrasonication, which can be applied on fibrous slurry in addition to generate microscopic gas bubbles in between fibres to cause fibre separation (Faruk et al. 2012, Adekunle 2015, Behzad & Ahmadi 2016). Ultrasound can also be used to activate chemical reactions on the fibre surface (Mason 1997).

Thermal modification of wood is typically carried out at temperatures of 180ºC to 260ºC. Beginning from temperatures above 200ºC, changes occur in wood fibre such as softening of lignin, decomposition of hemicellulose and modification of cellulose -OH groups, which causes an increase in fibre crystallinity. The effect of heat treatment can be seen as reduced wood hygroscopicity, improved dimensional stability and durability as well as increased resistance to microorganisms. The drawback of heat treatment is typically reduced mechanical properties and increased brittleness (Bhuiyan et al. 2000, Sivrikaya et al. 2015). The heat treatment induced increased crystallinity is also observed for kenaf fibres. The maximum tensile strength for kenaf fibres is obtained at 140ºC (Cao et al. 2007, Carada et al. 2016). In PLA composites compression moulded with ramie fabric was found to increase in HDT and mechanical properties (Chen et al. 2014). Tensile strength increases in heat treated sisal-PLA composites were also gained even though the fibre strength was reduced (Huang et al. 2015)

Corona discharge treatment changes the surface energy of materials, in this case fibres, using high frequency. The ozone from electrical discharge creates oxygenation in the fibre surface forming new groups. The corona effects only on the top molecule chains, which are 0.00001 microns thick. The effect of treatment is reversible and the more difficult a material is to treat the quicker it is likely to decay with time, usually a few hours (Vetaphone 2016). One advantage of corona treatment is that just a few minute treatment is needed to provide good adhesion between fibre and polymers (Faruk et al. 2012). In extractive-containing wood fibres, fibres that contain alcohol-benzene extractives, the corona treatment caused oxidation to produce aldehyde groups. The oxidation of the high hydrophobic surface layer of neutral fraction substances in the extractives leads to a reduction in hydrophobicity enabling improved connection to hydrophobic polymers (Sakata et al. 1993). Additionally, in a study of palm fibres treated with corona, it was found that under corona discharge treatment the area of peaks C=O, C-OH, O-C=O increased and the area of peaks O-H, -C-C and C-H decreased. Those were related to an increase of oxygen containing functional groups such as esters, carboxyl and carbonyl, by reaction with oxygen present in the fabric surface and atmosphere. Palm fibres contained cellulose 45%, hemicellulose 26%, lignin 5%, pectin 17% and other extractives 7% (Amirou et al. 2013).

The plasma treatment resembles corona, but it enables the utilisation of different gases applied with the treatment. The cold plasma treatment is used especially, a process which uses low gas temperature and high electron temperature enabling substrate to stay near ambient temperature. Depending on the type and nature of the gases used, a variety of surface modifications are achieved, which will introduce surface crosslinking while surface energy could be increased or decreased and reactive free radicals and groups could be produced. With low-temperature plasma treatment, chemical implantation, etching, polymerisation, free radical formation and crystallisation can be induced. In fibre treatments, the cold temperature plasma is used to bring polar groups to fibre surfaces (George et al. 2001, Beckermann 2007, Vetaphone 2016). In a study by Gibeop et al., jute fibres were treated with plasma polymerisation using acrylic acid. The batch plasma polymerisation time was maximum 120 s. After fibre treatment they prepared thermoplastic composites with PLA using compounding and injection moulding. Compared to untreated and alkali-treated fibres, the plasma led to a more than 20% increase in flexural strength in PLA (Gideop et al. 2013). The advantages of plasma are fast reactions and a wide selection of modifications, which makes it one of the highest potential methods for fibre treatments in sheet form. However the applicability on a porous fibre network or to 3D-structures is limited due to methods applied mainly on sheets.

2.5.2 Chemical modifications

The chemical modifications can focus on improving the hydrophobic properties of the fibre for improved miscibility to polymer or to modifying the fibre surface with different reactive components enabling improved fibre-polymer coupling.

One class of wood cellulose chemical modification is to use cellulose from different stages of the pulping process. In wood, the lignin-hemicellulose matrix around cellulose fibre acts as a natural hydrophobic element and during the pulping process or preparation of MFC it is possible to leave some residual lignin or hemicellulose on fibre. The improved dispersion of lignin and hemicellulose containing MFC to PLA and PCL was observed together with improved mechanical performance and thermal behaviour. This was seen to be related to improved dispersion and adhesion of cellulosic material to PLA (Herzele et al. 2015, Winter et al. 2017).

Alkali treatment is maybe the oldest chemical modification for natural fibres. Treatment with NaOH, typically in concentrations of 1% to 10%, is also called mercerisation. The treatment removes some amount of lignin, hemicellulose, pecting, wax and oils covering the external surface of the fibre cell wall. One important aspect with alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing the surface roughness and affecting the wettability of the fibre and interfacial bonding between matrix and polymer. Alkali treatment with high alkali concentration can modify cellulose crystallinity to be more amorphous. The alkali treatment increases the internal strength of fibres, but in overly harsh conditions, it affects vice versa (Li et al. 2007, Faruk et al. 2012, Pickering et al. 2016). In a study with stereocomplex PLA (sc-PLA), a composite containing 10% alkali treated flax fibres (5% NaOH 2 h in 60ºC), crystallinity was found to increase from 17.2 % in sc-PLA to 27.1% in composite. The composites had increased Vicat temperature from 74.7ºC to 155.6ºC, opening new application possibilities for PLA-composites. Composites showed increased strength properties, those were however at the same level as untreated flax. The alkali treatment removed almost all hemicellulose from flax fibres and fibre bundles were more separated (Zhang et al. 2015). Even though alkali treatment has proved to be effective with many other polymer matrices it showed no or only minor improvement compared to non-treated fibres in short-fibre PLA composites (Aydin et al. 2011). It seems to be more beneficial when processing methods such as compression moulding and longer or even unidirectional fibres are used (Faruk et al. 2012).

In fibre esterification the hydrophilic OH groups are esterified with more hydrophobic chemicals or even polymers to coat the fibre surface with hydrophobic groups, including chemicals such as acetic anhydride, citric acid, malonic acid, malic acid, octadecanoyl chloride, dodecanoyl chloride, etc. (Vaca-Garcia et al. 1998, Pasquini et al. 2006, Spinella et al. 2016). The main esterification method for lingo-cellulose fibres in biocomposites is acetylation, where the hydroxyl groups able to react are those of the minor constituents of the fibre, i.e., lignin, hemicelluloses, and those of amorphous cellulose. That is because the hydroxyl groups in crystalline regions with close packing and strong interlock bonding are completely inaccessible. The acetylation provides a more hydrophobic, but fibrillated fibre surface. In PP composites, it provided improved tensile strength, but reduced impact strength, indicating no true connection between fibre and polymer (Bledzki et al. 2008). PLA composites with 5% acetylated and non-treated nanofibres using solvent cast master batch and melt processing techniques. The addition of nanofibres increased the thermal stability of the nanocomposites; the storage modulus was up to 28 times higher in pure PLA in 70ºC and the tan peak position moved by 7 degrees to a higher temperature. The acetylated nanofibres had the same effect as fibres without modification (Jonoobi et al. 2012)

Acrylation and acrylonitrile grafting, which are more known methods to modify glass, are used also in the modification of natural fibres. Acrylic acid (AA) can be grafted onto natural fibres in water by mixing in elevated temperature and alkaline conditions. The acrylic acid-treated flax showed improved tensile strength and reduced water absorption in HDPE, but in other studies with PE-matrix the strength increase was not gained. In PLA composites acrylic acid is more commonly grafted onto PLA by melt-mixing PLA and AA in 85ºC and in the presence of a catalyst. The free carboxylic end in acrylic acid can then react with carbohydrate hydroxyl groups to link PLA and in this case starch providing improved properties (Wu 2005). Acrylonitrile modification (AN) in PLA composites is presented for non-woven jute fabric. Modification was performed in the presence on potassium persulfate initiator and ferric sulfate catalyst in 70ºC for 90 minutes. Composites were prepared using press moulding with PLA-sheets and 10% fibre loading. A 2% Carboxymethyl cellulose (CMC) was also used as a binder mixed with fibres. The AN-modificated fibres resulted in simultaneously improved tensile and impact properties as well as reduced water up-take compared to un-treated fibres. The coupling of fibres and polymers was suggested even though the elongation was reduced (Khan et al. 2015).

In the benzoylation reaction, benzoyl chloride is typically used chemical in fibre treatment. Benzoylation reduces fibre hydroxyl groups and brings aromatic groups onto the fibre surface, which have the potential to improve fibre adhesion to polymer, matrix thermal stability, weathering and UV-stability in composites (Pandey and Chandrashekar 2005, Li et al. 2007). In benzoylation the alkali-treated fibres are soaked in 10% benzoyl chloride-containing solvent, mixed and washed with water or solvent. In press-moulded PLA non-woven jute composites with CMC as glue, the benzoylated fibres showed a more than 25% simultaneous increase in tensile strength as well as flexural and impact strength, but no significant increase in elongation, which indicates improved miscibility of fibres to PLA and entangling through hydrogen bonds (Khan et al. 2015).

Fibre treatment with aqueous tetraborate decahydrate (borax) solution provides an easy mean of fibre modification. It can also provide fire and biological resistance to fibres. Kenaf and palm oil fibres can be treated by soaking them in 5% borax water solution for 24 h in 25ºC and at pH 9.1 followed by washing until neutral pH and dried in oven at 60ºC for 24 h. Fibres compounded and compression moulded with PLA (40%). The borax-treated fibres provided higher tensile, flexural an impact properties as well as lower water absorption compared to composites without borax treatment (Birnin-Yauri et al. 2016).

Permanganate modification are oxidative reactions usually performed by potassium permanganate ($KMnO_4$) acetone solution with fibres. Permanganate treatment leads to the formation of cellulose radicals through (MnO_3^-)-ion formation. Those are then able to initiate graft polymerisation resulting in reduction of hydrophilicity in fibre. The radicals on cellulose fibre are also able to graft to polymer (Li et al. 2007). In the modification process the alkaline-treated fibres are stirred for a few minutes in low concentration permanganate solution and washed. The permanganate modificated non-woven jute fibres resulted in PLA composites, slightly improved tensile and impact properties as well as reduced water up-take compared to non-treated fibres. The coupling of fibres and polymers was suggested even though the elongation was reduced (Khan et al. 2015).

Literature also presents many other chemical modifications based on esterification (e.g. stearic acid) or radical grafting (e.g. different chloride compounds) or ring-opening reactions (e,g. lactide or caprolactone grafting), which are not discussed herein (Calmark et al. 2012). To mention some of the most interesting fibre modifications that use quarternary ammonium salts, polyvinyl acetate (Oksman et al. 2016), glutaraldehyde and 1,3-dimethylol-4,5-dihydroxyethyleneurea (Xie et al. 2010) or alkyl ketene dimer (AKD) modification (Hundhausen et al. 2009).

2.5.3 Chemo-enzymatic modifications

Enzymatic modifications maybe the oldest way to modify natural fibres such as flax for human use. The retting process made for fibres before converting them mechanically to fibre form is controlled degradation of plant stems to free the bast fibres from their bundles and separate the woody core. During retting bacteria and fungi release enzymes to degrade pectic and hemicellulose in middle lamella between cells. This helps the main fibres to become clean and more susceptible to other actions. The process is however time-consuming and fibre quality depends on water quality used in the process (Chavan 2014).

Enzymes are an increasingly interesting option in textile and fibre modification. This is because enzymes are highly specific, having focused performance, efficient catalysts and they work in mild, energy-saving conditions making the process environmentally friendly (Faruk et al. 2014). Enzymes can be used as such or combined with chemical and mechanical methods in modification and processing of biomaterials. The applications for enzyme modifications contain improvement of fibre surface properties by removing impurities, fibres bleaching, fibrillation, hydrophobisation, cross-linking, improved colouring and gluing properties.

Oxidative enzymes, such as laccases or peroxidases, can be used to activate and further functionalise lingo-cellulosic fibres. The primary reaction of laccase is the oxidation of phenolic hydroxyls to phenoxy radicals in the presence of oxygen. Laccases can thus be used to activate lignin, lignans, and different types of lipophilic extractives. Due to the high reactivity of the phenoxy radicals (either with each other or with a secondary substrate), further enzymatic or non-enzymatic coupling reactions leading to polymerisation, depolymerisation, co-polymerisation or grafting of lignocellulosic materials with selected chemicals can be concluded. So the laccase-catalysed functionalisation can be used in targeted tailoring (Saarinen et al. 2009). Research activities are reviewed for example hydrophobisation of lingo-cellulosic materials with *Trametes* and *Aspergillus* type enzymes and coupling for example with dodecyl gallates (Suurnäkki et al. 2006, Kudanga et al. 2011)

Abaca fibres were treated with enzymes at 50ºC, pH 7.5, for 4 h, washed and compounded with PP to fibre content 30%. The moisture absorption, mechanical and rheological properties were comparable or even better as with commercial (PP-MAH) containing composites (Bledzki et al. 2010)

Cellobiohydrolase and endoglucanase-treated seed flax fibres were prepared for compression moulded composites with PLA. Treated fibres showed improvement in adhesion with PLA even though no real mechanical improvements were gained (Hallila et al. 2014).

Laccase-assisted grafting of octyl gallate and lauryl gallate was made for TMP fibres and produced 3D-printable filaments with PLA in fibre contents 10% and 20%. The modified TMP fibres showed clearly increased hydrophobic properties and in composite filaments higher chemical compatibility with PLA. The octyl gallate-modified fibres showed tensile strength increase from 7 MPa (neat PLA) to 24 MPa in printed materials (Filgueira et al. 2017).

2.5.4 **Coupling agents**

Maleic anhydride (MA) grafting is a widely used coupling method to improve composite properties. Maleic anhydride is commonly grafted to the same polymer, which is used as a matrix in the final application. Compared to other coupling methods used for polypropylene, the coupling with MAPP (maleic anhydride polypropylene) can be regarded as the most successful. The treatment of cellulose fibre with MAPP in polymers melt during processing provides a covalent bond between fibres and polymer. The maleic group with two carboxyl groups are transformed to anhydride due to the cleavage of water in hot melt polymer (over 170ºC); this anhydride is able to react with cellulose hydroxyl groups to form a covalent ester bond coupling fibre and polymer presented in Figure 10 (Bledzki et al. 1996, Li et al. 2007) . Maleic anhydride can be grafted to PLA using dibutyl peroxide as a catalyst by simple melt-blending process and MA-g-PLA used either as such or as a coupling agent in fibre-PLA composites. With palm empty fruit bunch fibres MA-modified PLA facilitated the formation of strong interface adhesion with the fibres showing improved flexural and impact strength and elongation. (Birnin-Yauri et al. 2017). MA-g-PLA was used with microfibrillated henequen cellulose in fibre contents up to 20%. Increase in tensile, flexural strength were gained as well as HDT, but a decrease in impact strength was also observed. The results were also statistically significant (Dzul-

Cervantes et al. 2017). MA-g-PLA was used as a coupling agent with 3% microcrystalline cellulose (MCC) containing PLA composites. The coupling agent-containing composites showed increased crystallinity, tensile and flexural strength, modulus, improved elongation and more uniform distribution of MCC compared to composites without a coupling agent (Dogu & Kaynak 2016).

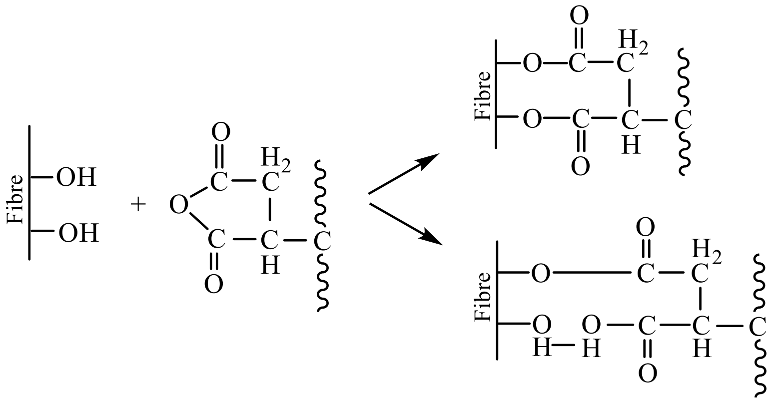

Figure 10. The reactions between cellulose fibre and maleic grafted polymer.

Silanes are commonly used as coupling or sizing agents in thermosetting glass fibre composites. The most commonly reported silanes used are amino, methacryl, glycidoxy and alkyl silanes and they usually contain different functional groups in one molecule. The interaction with fibres and polymer matrix can occur through hydrophilic groups to fibre and through hydrophobic groups to polymer. They reduce the amounts of OH groups providing increased hydrophobicity on fibre surface along with hydrocarbon chain in silane by forming covalent bonds with fibre. An effective way is to use hydrophilic silanes in blend with hydrophobic silanes such as phenyltrimethoxysilane. Mixed siloxane primers provide improved thermal stability, which is typical for aromatic silicones (Li et al. 2007, Adekunle et al. 2015, Pickering et al. 2016). In PLA composites with aminopropyl triethoxysilane-treated wood flour, the visual study showed no gaps between fibre and matrix, indicating increased compatibility between PLA and wood fibre. Tensile, flexural and elongation properties of composite were increased compared to neat PLA as well as reduced water absorption. The optimal silane content on wood flour was 1.5% (Lv et al. 2015). Coupling between wood fibre and PLA is explained. In solution the silanes are transformed into silanols with a large number of hydroxyl groups, at the same time occurs self-condensation of silanols forming -Si-O-Si- groups those are stable towards hydrolysis. When mixed with wood flour, the reactive silanol groups have high affinity toward hydroxyl groups in wood flour and are attached through hydrogen bonds. At the same time, free silanol groups react with each other forming a linked -Si-O-Si-network, which serves as coupling agents grafting to PLA carboxyl ends bonding fibre and polymer together. The reaction is controlled by adjusting pH (Lv et al. 2015).

In another study, PLA composites were prepared with kraft fibres and sisal fibres, which were treated with 3-aminopropyltriethoxysilane and 3-(trimethoxy) propyl methacrylate. The composite showed improved impact strengths with both fibres (from 10.1 J/m of neat PLA to 14.45 J/m with kraft and 24.61 J/m with sisal) (González et al. 2011). However, the effect of silanisation was small and may have been primarily due to improved fibre dispersion.

Isocyanates can be used to modify the fibre surface, but also as a coupling agent between fibre and polymer. The isocyanate group, -N=C=O, is highly susceptible to reaction hydroxyl groups present in cellulose and lignin. The isocyanate modified fibres are able to form covalent bonds to polymers such as PLA that have carboxylic end groups with hydroxyl group, which is able to react with isocyanate (Wang et al. 2001, Li et al. 2007). Non-woven jute fibres were modified using diphenyl methane di-isocyanate in toluene solution and stirred at 70ºC for one hour. Hot pressed composites with PLA showed decreased water absorption, increased tensile, flexural and impact properties as well as increased elongation, indicating the covalent connection between fibre and polymer (Khan et al. 2015)

Peroxide treatment of cellulose fibre provides a quite simple processing method for fibre modification. Peroxides such as hydrogen peroxide, benzoyl peroxide, and dicumyl peroxide, tend to decompose easily to form free radicals, which can react with the hydrogen groups of the matrix and cellulose fibre grafting them together. In PLA composites with alkali-treated and hydrogen peroxide-treated jute fibres in fibre content 5% to 25% were prepared by injection moulding. In peroxide treatment the alkali treated jute fibres were added to 10 ml/l hydrogen peroxide at room temperature and stirred for 45 min, washed with distilled water and dried in the oven at 50°C until it reached a constant weight. The composites showed improved flexural strength, decreased water absorption, and an improved biodegradation rate, but also decreased impact strength properties (Gunti et al. 2016).

Glycidyl metacrylate (GMA) is an effective modification chemical for fibre and for polymers due to two reactive functional groups: a very reactive epoxy group and an acrylic group. The free epoxy group can be easily reacted with hemp fibres in GMA/trimethylamine solution at 90ºC followed by washing. Polymers such as PP can be grafted in melt with GMA acrylate end using peroxides (Pracella et al. 2010) or carboxylic hydroxyl end of PLA grafted with epoxy head of GMA in 80ºC xylene using Zn powder as a catalyst. By using GMA fibres and polymers can be coupled together (Li et al. 2010).

2.5.5 Plasticisers for PLA

Plasticisers are low molecular weight compounds compatible with the polymeric material they aim to plasticise. Their focus is to improve flexibility and processability of polymers by lowering Tg, hardness, density, melt viscosity and electrostatic charge and increasing flexibility, resistance to fracture and dielectric constant of a polymer. Properties such as biological degradation, gloss, water absorption, fire resistance and crystallinity can also be changed due to plasticisers. Phtalic acid esters (e.g. dioctyl phthalate, DOP) maybe the best known plasticisers also known to cause unwanted effects on humans and the environment. The replacement of traditional plasticisers with new, safe to use, renewable-based, low-migration ingredients is increasing. The plasticisation effect on polymers is largely dependent on the chemical structure of the plasticiser, including chemical composition, molecular weight and functional groups and are in relation to polarity, dielectric constant and solubility parameters (Vieira et al. 2011, Mekonnen et al. 2013). The plasticisers are defined as internal or external plasticisers. The external plasticizers can interact with polymers chains without being chemically attached to them and can be lost from material by evaporation or migration. The internal plasticizers are co-polymerised into polymer structure or reacted with polymer (Vieira et al., 2010). The function of plasticiser in cellulose fibre-filled composites is to improve miscibility between fibre and polymer by reducing viscosity-improving interfacial interactions. (Halász & Csóka 2013)

Citrate esters (e.g., triethyl citrate and acetyl tributyl citrate), polyethylene glycol (PEG) (Ljungberg et al. 2005), glycerol, glycerol esters, oligomeric lactic acid, triacetin, fatty acid esters, are reported to be effective plasticisers for PLA. Polymers such as polycaprolactone, polybutylene succinate, polyvinyl acetate and polyhydroxybutyrate are also able to plasticise PLA and provide better impact properties and improved resilience. Besides good plasticising properties many of these ingredients show migration to PLA surface in time, especially low molecular weight molecules like citrate esters (Mekonnen et al. 2013).

Vegetable oils and their modificates with quite high viscosity, low volatility and high flash point are already applied in many applications as lubricants, coatings and polymer additives. With epoxy modification they can provide adequate reactivity to form chemical linkages. The fatty acid triglyceride chains (oleic acid, linoleic acid and linolenic acid, erucic acid, ricinoleic acid, vernolic acid or 10-undecanoic acid) having variable amounts of double bonds can be modified into more reactive groups via epoxidation, acrylation of epoxies reaction with maleic anhydride or transesterification. The epoxidized soy bean oil as a plastic additive has already marketed to sell at a rate of approximately 100000 tonnnes/year and one of the main uses is as a stabiliser/plasticiser in PVC (Samarth & Mahanwar 2014).

Epoxidised vegetable oils (e.g. palm, soy and linseed) have proved to be suitable plasticisers for PLA, showing good compatibility without voids and good interfacial adhesion. A 5 % addition of epoxidised palm oil and soy oil increased flexibility and thermal properties in PLA films, but decreased strength properties (Buong et al. 2014). 15% of epoxidised soy oil in PLA film, provided clear films, improved processability and thermal properties and provided very flexible films (Darie-Niţă et al. 2016). Epoxidised linseed oil is especially interesting due to its high content of linolenic acid, a substance which accounts for 56.6% of all fatty acids. The linolenic acid has three double bonds in its chain allowing a high degree of modification (Samarth & Mahanwar 2014).

PLA composites with maleated microcrystalline cellulose (MAMCC) and epoxidised soy oil (ESO) were prepared with melt blending and reacted on cellulose surfaces by reactive extrusion. MCC was maleated to provide reactive carboxyl groups on the surface of MCC for increased reactivity to ESO. The results showed that ESO accumulated on the surface of MAMCC hence providing a hydrophobic layer on the surface of cellulose. Improved impact strength and elongation, but lowered Tg was observed in PLA composites (Dai et al. 2014).

The epoxidised tall-oil fatty acid ester (Figure 11) proved to be a good plasticiser in PLA composites with 30% birch pulp also facilitating coupling between fibre and polymer, which could be seen as simultaneously increased tensile strength, strain and impact strength properties. It was also possible to prepare a thermoformable extruded sheet with that material (Immonen et al. 2011).

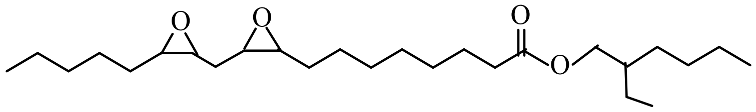

Figure 11: Epoxidised tall-oil fatty acid ester (TOFA 2-ethyl hexanoate).

2.6 Processing of PLA-based biocomposites

PLA-based thermoplastic biocomposites or green composites in general are manufactured in the same way as conventional composites: the processing methods can be widely categorised as open-mould or closed-mould processes, where open-mould processes serve the primarily purpose of thermosetting composites. The open-mould processes for thermoplastic processing contains primarily solvent casting. The most commonly used processing techniques are compounding followed by compression moulding, extrusion or injection moulding (Singh et al. 2017). In recent years novel additive manufacturing type processing techniques are becoming more common and PLA as well as PLA-composite filaments are one of the most used materials there. The sdditive manufacturing process, which uses thermoplastic filament, is fused layer manufacturing (FLM) also known as fused filament fabrication (FFF) or with commercial trademark Fused Deposition Modelling (FDM) (Quan et al. 2015, Hofstätter et al. 2017). There are also several other additive manufacturing techniques using powder, liquids and gels, they are not discussed herein.

The main challenge with natural fibres is the poor thermal resistance of the fibres, so they must be processed at lower temperatures, normally below 200ºC, to avoid thermal degradation of fibres, which limits the use of thermoplastic matrix polymers. Pure cellulose containing fibres can resist a short-time temperature over 200ºC, but lignin starts to decompose at 160ºC (Yang et al. 2007). PLLA is suitable polymer to be combined with cellulose due to its melt temperature being below 160ºC. Another drawback related to natural fibres is its high moisture absorption. Moisture swells the fibres changing dimensional stability and the mechanical properties of composites. The presence of residual moisture can lead to the formation of water vapour during processing, which can cause several problems. Especially if a venting or drying system is not present in injection moulding, it causes the formation of voids in the material and thus poor mechanical properties. So the first step before any thermoplastic process steps, it is to dry the natural fibres, which can be done via different methods such as hot air jets, rotating driers, and ventilated ovens, in order to reduce the humidity (Singh et al. 2017)

The processing conditions (shear, temperatures, mixing time, etc.) are determined by the type of equipment, the nature of dispersed phase(s), blend composition, desired end-use product properties, etc. A polyester-based matrix (e.g. PLA) is very sensitive to temperature, shearing and hydrolysis, such that all precautions should be applied to avoid its degradation. It is usually required to limit the water content in PLA and all mixed ingredients to 50–250 ppm in all processing conditions, which can be difficult with natural fibres (NFs) containing crystallisation water. (Murariu et al. 2018, NatureWorks 2018). Hajba suggested the suitable drying conditions for PLA 100ºC for 6 h, and 120ºC for 24 h for natural fibres (flax, cotton, jute), he also suggested maximum 10 minutes time between drying and thermoplastic processing (Hajba et al. 2015). For the drying of amorphous PLA grades, it is recommended to use temperatures below 55ºC for 4 hours and for crystalline PLA below 90ºC for a minimum of one hour. Desiccant beds capable of achieving a dew point of -40ºC in the supply air is recommended (NatureWorks 2018).

Courgneau et al. used 10% of cellulose fibres with PLA reinforcement as potential material for automotives with moisture content of roughly 0.5% before compounding. The mixing of cellulose fibres by melt-compounding using a twin-screw extruder caused a slight drop of PLA molecular weights due to the combined effect of the shearing at high temperature and hydrolysis of PLA chains. The composites showed changes in PLA molecular weight and odour emissions indication of PLA degradation, but also weak adhesion PLA–cellulose fibres, which was indicated by reduced impact strength properties (Courgneau et al. 2013). Moist bleached cellulose kraft pulp was compounded and injection moulded with PLA in quite high in moisture content, from 1 to 25% and found out that even 3% moisture content in fibre did not deteriorate the composite properties. Even though the molar mass of PLA was slightly reduced, it only had a minor effect on mechanical properties and the residual moisture even seemed to protect the fibre from high degradation. This phenomenon could be advantageous from a costs standpoint and save drying costs due to the difficulty of removing of fibre moisture to below 1% (Virtanen et al. 2016). The novel water based process of Aquacomp developed for wood cellulose fibre-polymer compound manufacturing also allows polymer and fibre blending and drying together with the presence of water (Ture & Nikkilä 2014).

Natural fibre type, length, aspect ratio, content and modification have a significant effect on composite properties. In thermoplastic composites the compounding process has significant influence due to fibrillation, shortening and thermal degradation of fibres, yet most of the fibres remain longer than 2 mm after compounding, are shortened to less than 2 mm during injection moulding (Peltola et al. 2011, Faruk at al. 2012). To avoid shortening of fibres, several methods have been developed to produce compounds for the injection moulding presented in Figure 12, yet the most common process for thermoplastic material preparation for injection moulding is extruder compounding.

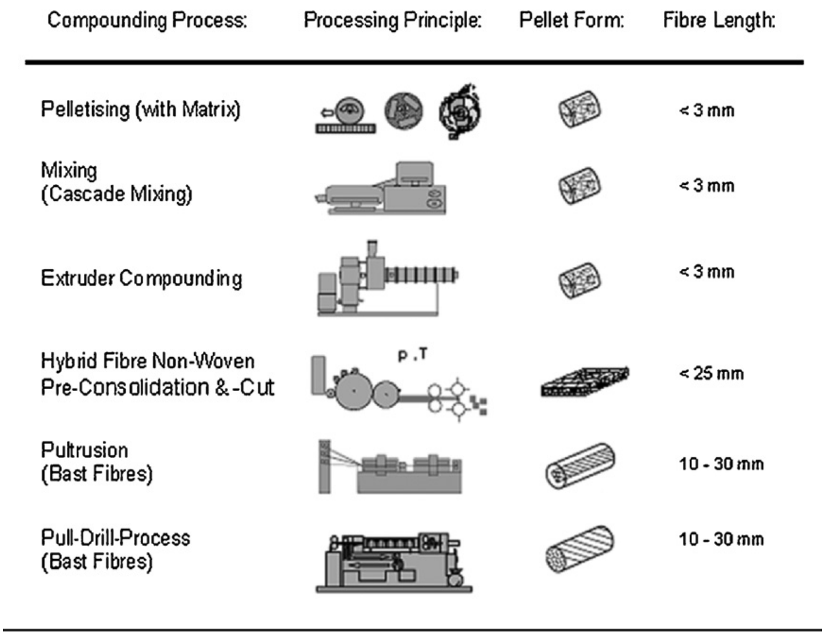

Figure 12: Compounding methods for injection moulding of natural fibre reinforced thermoplastic composite granules (Faruk et al. 2012).

Extruder compounding is an extrusion process using a single screw or twin-screw extruder which operates as either co-rotating or counter-rotating. For short wood fibre containing thermoplastic materials, this is the most common way to produce granules suitable for injection moulding or extrusion. Single screw extruder can be used, if the mixing effect does not have to be very high, but a preferable method for good dispersion is twin-screw extruder (Faruk et al. 2012). The screw element for temperature sensitive ligno-cellulosic fibre mixing needs to be designed in a way that provides good but sensitive mixture of fibres to polymer melt, so it is good to minimise sections with high kneading elements. Due to removal of residual moisture and volatile ingredients it is preferable to have a vacuum outlet. The bottleneck in the compounding of natural fibres has been the feeding of fibres the bulk densityof which is usually 50% lower than the reinforcements usually used with thermoplastic polymers. This is usually solved by chopping or grinding the fibres to increase the bulk density and flowability or by pelletising the fibres in various ways. (Sobczak et al. 2012). To minimise fibre cutting and friction between fibres and compounder, it is good to feed the fibre in polymer melt afterward and not with solid polymer granules (Beckermann 2017). The compounding process creates a string that is cooled in a cooling unit and cut to pellets after that. For moisture-sensitive PLA, it is preferable to use cold air cooling instead of the more commonly used method of a water bath.

The extrusion process for product manufacturing uses similar extruders as in compounding. The product manufacturing (e.g., wood polymer composite planks) can also be made without compounding in one stage by directly introducing fibres and additives to polymer melt. The critical point is in nozzle and after that to control the temperatures of the shaped die, calibration and cooling units in addition to minimise shrinkage and stability of the product. The extrusion process requires a polymer with high molecular weight and melt strength (Bledzki et al. 2002)

The injection moulding process enables fast single-item manufacturing using heat and pressure. The production machine can be divided into two units: an injection unit and a clamping unit. In an injection unit, the thermoplastic material is melted and transferred to clamping unit with a single screw moving backward and forward dosing the amount of material adjusted for the mould size. In the clamping unit, melt material enters into a mould through a gate and runners using pressure. The product is cooled and kept in the closed mould until the thermoplastic material is solid. Then the mould opens and ejector pins push the ready product out. The polymer used in injection moulding is typically a low molecular weight or a low viscous material enabling high speed and running through typically thin gates and runners (Bledzki et al. 2002, Abdennadher 2015). From a fibre-polymer interaction standpoint, the injection moulding is better than extrusion due to higher pressures, enabling closer contact between fibres and polymer.

Thermoplastic compression moulding is a process, which uses semi-finished sheets or pre-pregs, which combine fibres with various sizes with thermoplastic polymers in fibre form or sprayed on fibre mat or combination of fibre mats with thermoplastic sheets. Further, the compression of extruded sheets made with short fibres and thermoplastic polymers is possible. In sheets the fibres can be randomly mixed short fibres, carded, air-laid or wet-formed non-woven, unidirectional fibres or knitted mats with different knitting techniques. The compression moulding typically enables the production of relatively big products such as car door panels or ceiling structures (Bledzki et al. 2002, Faruk et al. 2012).

Solvent casting is a method used for PLA-natural fibre composites in a small scale, for example, in the bio-medical sector. In research publications the solvent casting that has been used many times for the preparation of PLA composites containing NC, CNC, BC or NFC. Due to solvents, the nanosize fibres are easier to keep separated and obtain an even structure for the composite. Due to an even fibre network in polymer the solvent casting and possibly followed annealing or compression stages provide materials with high strength (Murariu & Dubois 2016, El-Hadi 2017). The reinforcing effect of nanofibre in a polymer matrix is due to the formation of a rigid percolating filler network caused by hydrogen bond interactions of fibres. The formation of a percolating network is favoured by slow processing, which allows self-organisation of the CNC. Solvent casting when used with water-soluble polymers such as polyvinyl alcohol is a straight forward process of mixing two solutions and evaporating the water. The mixtures with non-water-soluble polymers such as PLA need an additional process step where nanofibre is a solvent exchanged with solvent, for example acetone, for mixing with dissolved PLA followed by the evaporation of solvents. To prevent aggregation in PLA due to poor compatibility different surfactants and chemical modifications, either on fibre or on PLA is introduced (Oksman et al. 2016, Stark 2016). Solvent casting has been used as premixing or a masterbatch production method for PLA-nanocellulose composites followed by melt processing which yielded mixed results. Composites have shown better nanofibre dispersion without strength improvement. The addition of liquid glycerol triacetate (GTA, 1%) as a plasticiser to PLA-CNF composite during extrusion led to an increase in elongation at a break from 2% to 31% and an increase of toughness from 1 to 8 MJ/m^3 (Herrera et al. 2015, Stark, 2016). Compared to extrusion, injection moulding or compression moulding, the solvent casting method is more time consuming and used more in the research or manufacturing of high-value medical components.

In fused layer manufacturing (FLM) the thermoplastic polymer or composite is prior to the final ‘printing’ stage made to filament with even thickness using extrusion. Some novel printing machine can also use granules and in some methods the fibre (natural, glass or carbon fibre) can be brought as continuous to the printing nozzle. In a nozzle the material is melted and placed on the product layer, where it cools and solidifies without external pressure. FLM as well as other additive-manufacturing techniques are processes of joining materials to make objects from 3D-model data, with layer-upon-layer being usually direct fabrication (from design data to realistic product, without tooling and machining) and layer-wise processing (from a bottom section up to a top section). Additive manufacturing enables the fabrication of complex shaped objects and large geometric design freedom with minimum tooling and assembling separate stages. Also shapes which are not possible with other processing techniques such as ball-within-ball without joints, novel woven structures and biomimicing of natural complex shapes (Quan et al. 2015). PLA in FLM is one of the most used materials due to biocompatibility, relatively low processing temperatures, safe processing without toxic fumes released during processing and good mechanical performance. The aim of fibres addition to PLA is to strengthen the material in terms of load, bring dimensional stability and enable larger and lighter objects to be printed. Additionally, natural fibres yiel cost-effectiveness and enable products with a natural look. In composite filaments the short fibres in micrometer scale or less is recommended to avoid clogging on a nozzle. If the fibres are chemically compatible and form a true connection between fibre and matrix, for example through chemical modification, there is potential for fibre alignment or orientation and strength improvements or tailoring. Meanwhile, due to pressure-less process the fibres and matrix material need to be linked at their interface to distribute stress so the materials need to be chemically compatible. Micro-cracks close to the interface between fibres and matrix lead to a significant loss of stiffness and strength. The high natural fibre (short fibre) containing prints also entails high porosity, leading to water absorption and swelling (Hofstätter et al. 2017). A 57% increase in tensile modulus and a 34% increase in tensile strength combined with a small increase in strain was gained using continuous jute fibre as reinforcement in PLA indicating real reinforcement of continuous jute fibre. With continuous fibre, the composite properties are affected by the configuration of the twisted yarn reinforcement, wetting of the fibre and achieving proper connection between fibre and polymer during solidification of the print (Matsuzaki et al. 2016). 3D-printing methods are currently very time consuming manufacturing methods compared to others, but the equipment is developing quickly, so these will be one of the main methods in the future. From a material point of view, there is a lot of recipe development needed in PLA-composites to gain high-strength materials.

2.7 Composite theories

There are several physical properties related to natural fibres which are good to know to get their highest potential in composites. A high aspect ratio (length/width) is very important as it gives an indication of possible strength properties. Fibre strength, fibre dimensions, defects, variability, crystallinity and structure all must be taken into consideration (Faruk et al. 2014). The basis is that fibres are stronger and stiffer than the thermoplastic polymer matrix and in optimal cases, strength and stiffness should increase when fibres are introduced and good interfacial strength is established. The stiffness of the composite is related to the fibre volume fraction, orientation and porosity, which is assumed to be zero in many calculations. When reasonable interfacial strength is obtained, the thermoplastic injection-moulded composite strength typically reaches its maximum in 40-55 m-% fibre content. When considering the volume fraction and porosity, the maximum is in 50-60 m-% and further addition of fibres typically results in higher porosity (Pickering et al. 2016).

The composite stiffness can be estimated by the rule of mixture. For composites with discontinuous and non-unidirectional fibres a combined rule of mixture is commonly used as presented in Equation 1 (Madsen et al. 2009):

Equation 1: $E_c = \eta_o \eta_l V_f E_f + V_m E_m$ (1)

where:

E is stiffness, MPa

V	is volume fraction, %
c, f and m	symbolises composite, fibre and matrix respectively
η_o	is fibre orientation efficiency factor, -
η_l	is fibre length efficiency factor, -

If the porosity of the fibre is taken consideration, it should be incorporated into the rule of mixtures as follows in Equation 2:

Equation 2: $E_c = (\eta_o \eta_l V_f E_f + V_m E_m)(1-V_p)^{n'}$ (2)

where:

V_p	is the volume fraction of pores, %
n	is the porosity efficiency exponent and quantify the effect of porosity, yielding stress concentrations in the composites. If n is equal to 0 there is no effect of having porosity inthe composite other than lowering the load-bearing volume.

Fibre length or rather fibre aspect ratio is important in short fibre composite in determining the critical fibre length (L_c). In a short fibre composite, tensile load is transferred into a fibre from the matrix through shear at the fibre/matrix interface. At the ends of the fibre, the level of tensile stress is zero and increases along the length of the fibre; therefore, a fibre needs to have a length of greater than a critical length (L_c) in order for the fibre to be able to be broken during tensile loading of a composite. Long and continuous fibres $L >> L_c$ will break without being pulled out of the matrix. Since the fibre fails to break, the composite rupture is determined either by the matrix strength or the interface resistance, whichever is smaller. Ideally, fibre length would be much greater than the critical fibre length to allow for efficient reinforcement of a composite such that the majority of the fibre could be loaded as if it were a continuous fibre. L_c can be expressed as follows according to the Kelly and Tyson model in Equation 3 (Pickering et al. 2016, Kalia et al. 2011):

Equation 3: $L_c = d\sigma_f / 2\tau_i$ (3)

where:

d	is fibre diameter, mm
σ_f	is tensile strength of fibre, MPa
τ_i	is the fibre/matrix interfacial shear strength (IFSS), MPa

L_c has been found to vary with fibre, matrix, fibre treatment and fibre content. For example L_c values for hemp-strand/PP composites with a coupling agent varied from 0.49, 0.67, or 0.62 mm for fibre contents 20, 40 and 50% respectively with IFSS 14.45 MPa (Vallejos et al., 2012). In another study, the L_c for sisal fibres in injection moulded PP composites with MAPP was 2.27 mm and interfacial strength 22.03 MPa (Sun et al. 2010). In a tomography study for injection-moulded wood cellulose fibres in PLA the fibres were degraded to a length below 0.5 mm (the main fraction being 0.05-0.1 mm) even with chain extenders (Chinga-Carrasco et al. 2013). Even though there is variation in the results above, already from these results can be seen that short wood cellulose fibres after injection moulding are well below the critical length needed to reinforce composites. So the reinforcing effect should come through the high aspect ratio or effective coupling of fibre-polymer interfaces. Meanwhile, it must be remembered that with natural fibres we are always dealing with the distribution of different lengths and aspect ratios, which makes the estimation and simulation of strength properties more complex in relation to glass or carbon fibres with specific length.

The effect of aspect ratio on Young's modulus in an optimal case such as a composite filled with unidirectional platelets or fibres is presented in Figure 13. Even though the estimation is not for natural fibres the effect of aspect ratio can be assumed to be quite similar in an optimal case without voids or other defects, if the fibre length and aspect ratio can be retained in the process.

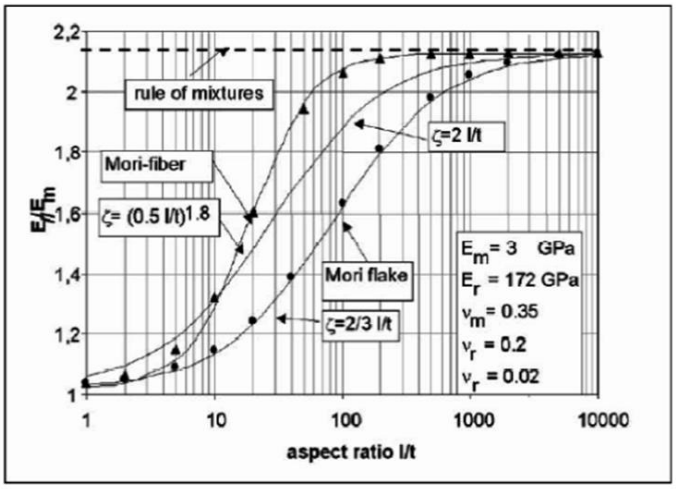

Figure 13: Plot of the computed Young's modulus of a unidirectional composite filled with flakes or fibres of different aspect ratios using the Tsai– Halpin and the Mori–Tanaka model. In both cases, a stronger reinforcing action of the fibres compared to platelets can be predicted (Gacitua et al. 2005)

For lignocellulosic fibres the weak fibre/matrix adhesion usually results in lower mechanical performance even if high-strength fibres are used as reinforcement. The adhesion or interfacial shear strength (IFSS) can be evaluated via different methods such as single fibre pull-out test, a critical-length pull-out (CLP) curve or a single-fibre fragmentation (SFF) test or microdebond, microintendation and microcompression test. Undirect estimation can be made by inferred critical length values from mechanical tests. The non-uniform shape and dimensions (length and diameter) as well as defects and porosity states limitations for L_c and strength estimations. The variations are more considered in the Weibull model, which is not discussed here. (Kalia et al. (eds.) 2011).

Fibre distribution and miscibility to polymers is improved when plasticisers are added to the mixture. This can be explained through theories for plasticising mechanisms enabling the fibre to penetrate better in between polymer chains. The suitable plasticiser also breaks down the interactions between fibres.

Several theories have been proposed to explain the mechanism and action of plasticisers on polymers. Among those theories, the following plasticising mechanisms have been widely accepted to describe the effect of plasticisers on polymeric networks (Mekonnen et al. 2013):
(a) The lubricity theory, where the plasticiser acts as a lubricant to reduce friction and facilitates polymer chain mobility past one another, consequently lowering deformation
(b) The gel theory, which suggests that a plasticiser disrupts and replaces polymer–polymer interactions (hydrogen bonds, van der Waals or ionic forces, etc.) that hold polymer chains together resulting in reduction of the polymer gel structure and increased flexibility
(c) The free-volume theory, which explains that for any polymeric material the free volume is defined as the internal space available in a polymer for the movement of chains. Rigid resins are typically limited by free volume and flexible resins have relatively large amounts of free volume. Plasticisers increase the free volume of resins and also maintain the free volume after the polymer–plasticiser mixture is cooled down in process. The free volume theory explains why the plasticisers lowering the glass transition temperature of polymers.

2.8 PLA-fibre composites in literature

Literature presents an increasing amount of different PLA-based natural or wood fibre based composites with different modification methods and processing methods. In addition to getting at least part of the whole picture of the effect of different composites, the properties with constituents and manufacturing methods are collected in Table 7.

Table 7: PLA composites with different natural fibres.

PLA	Fibre and content, (%)	Fibre modification	Process^1	Tensile strength, (MPa)	Tensile modulus, (MPa)	Strain, (%)	Impact strength, (kJ/m^2)	Reference
C-D^2	Flax 30	no	IM		2250			Aydin et al. 2011
C-D^2	Flax 30	NaOH	IM		750			Aydin et al. 2011
Ingeo 3052D	Oil palm 55 -Kenaf 5	no	C+CM	28.96	335.86	8.7	13 J/m	Birnin-Yauri et al. 2016
Ingeo 3052D	Oil palm 55 -Kenaf 5	Borax	C+CM	33.66	344.28	9.23	15 J/m	Birnin-Yauri et al. 2016
Ingeo 3052D	Oil palm 55 -Kenaf 5	Borax + MAH	C+CM	47.54	373.94	16.61	32.53 J/m	Birnin-Yauri et al. 2017
Ingeo 4042D	Man made cellulose 30	no	C+IM	92	5846		7.9	Bledzki et al. 2009

Ingeo 4042D	Long abaca 30	no	C+IM	74	8032		5.3	Bledzki et al. 2009
PLE001[3]	MCC 3	no	C+IM	57.5	2720	6.03	6.55	Dogu & Kaynak 2016
PLE001[3]	MCC 5	no	C+IM	56.5	2680	5.17	5.59	Dogu & Kaynak 2016
PLE001[3]	MCC 3	MAH	C+IM	58.8	2860	6.33	8.43	Dogu & Kaynak 2016
Ingeo 3251D	Microfibr. Heneq. 10	MAH 1	C+IM	56	3210		15.2	Dzul-Cervantes et al. 2017
Ingeo 3251D	Microfibr. Henq. 20	MAH 2.5	C+IM	46	3330		12.5	Dzul-Cervantez et al. 2017
Ingeo 4043D	TMP 20	enz.+Lauryl gallate	C+E (3D)	31				Filgueira et al. 2017
Ingeo 4043D	TMP 20	enz.+Octyl gallate	C+E (3D)	51				Filgueira et al. 2017
PL-1000[4]	Jute 20	NaOH 3	C+IM	37	3500	1.2		Gibeop et al. 2013
PL-1000[4]	Jute 20	Plasma	C+IM	53	4100	1.4		Gibeop et al. 2013
Ingeo 3051D	no	no	C+IM	59.1	1910	5.01	10.1 J/m	Gonzales et al. 2011
Ingeo 3051D	Euca cellulose 20	no	C+IM	56.3	2390	3.47	14.4 J/m	Gonzales et al. 2011
Ingeo 3051D	Euca cellulose 20	Amino silane	C+IM	57.0	2330	3.55	14.5 J/m	Gonzales et al. 2011
Ingeo 3051D	Euca cellulose 20	Metha silane	C+IM	55.0	2310	3.44	14.9 J/m	Gonzales et al. 2011
Ingeo 3051D	Sisal 20	no	C+IM	58.8	2210	3.63	24.6 J/m	Gonzales et al. 2011
Ingeo 3051D	Sisal 20	Amino silane	C+IM	58.2	2570	3.46	20.9 J/m	Gonzales et al. 2011
Ingeo 3051D	Bleached softwood kraft fibres 30	diethylene glycol dimethyl ether	Mixing + IM	65.3	6190	2.2		Granda et al. 2016
Esun[5] extrusion	Microcryst. cellulose 5	PEG 10	C+E	25.0	1450	3.8		Halás & Csóka 2013
Futerro	Banana CNF 1	Glycerol triacetate 20	C+ CM	28.8	800	31.1	8.0 MJ/m^3	Herrera et al. 2015
Ingeo 3051D	Sisal 8mm	Heat treatment	RM + CM	74				Huang et al. 2015
Esun[5] extrusion	Kenaf pulp CNF 5	Acetylation	S+C+ CM	69	3500	2.9		Jonoobi et al. 2012
Esun[5] extrusion	Kenaf pulp CNF 5	No	S+C+ IM	71.2	3600	2.7		Jonoobi et al. 2010
PLA 306D [6]	Wood flour 43	APS 1	C+E	44		4.4		Lv et al. 2015
Ingeo 4042D	Hemp bast fibre 20, 30	Retting and washing	C+IM	59.8 (20) 65.9 (30)	5500 7000	1.86 1.51		Sawpan et al. 2007
PLA Mw 100000 [7]	CNF 3	Lignin on CNF 4	SC	22.5	3400	2.5		Wang et al. 2014
Ingeo 3251D	MFCL 1	Lignin on MFC 17	SC	30.1	1077	6.6		Winter et al. 2016
PLLA 50 PDLA 50	Flax 4mm 50	No	C+IM	46.1	4150		4.6 (notched)	Zhang et al. 2015
PLLA 50 PDLA 50	Flax 4mm 50	NaOH	C+IM	44.2	3940		4.3 (notched)	Zhang et al. 2015

[1] Process: C=compounding, CM=compression moulding, E=extrusion, IM=injection moulding, SC=solvent cast, RM=roll mill

[2] PLA from Cargill-Dow

[3] PLA from NaturePlast, extrusion grade

[4] Miyoshi Oil and Fat Co.

[5] Shenzen Bright China Industrial Co.

[6] Ningbo Huanqiu Plastic Produscts Co.

[7] Shanghai Yishen Industry Ltd.

3 Aim of the work

The most important issue in tailoring PLA-fibre composites is to control the interfacial connections between fibre and polymer. The main issues affecting on interface are fibre length, fibre aspect ratio, fibre surface roughness and chemistry, fibre modification and additives used in composite such as plasticisers and coupling agents. Renewable, vegetable oil-based additives are potential plasticiser-coupling agents in short fibre composites. Epoxide-functional fatty acids are especially suitable materials for that purpose. It is proposed that in short fibre composites where fibre length is below the critical fibre length, one of the feasible ways to gain improved mechanical strength properties is to couple fibre and polymer together. One way to do that is with long-chain reactive additives those can simultaneously improve the fibre dispersion. When wood fibres are used in injection-moulded PLA-composites, the fibre length is below the critical fibre length due to fibre degradation in processing. Long chain processing additives typically used in composites can only aid in fibre dispersion, but are not able to provide cross-linking. There can be gained some improvements in impact strength especially with high aspect ratio fibres, but not in overall strengthening of composites. The industrial state of the art in coupling is to use maleic anhydride coupling between fibres and polymers. In many cases that is an effective coupling agent, but does not help to disperse fibres and can lead to brittle composites, as explained in the literature section of this study. Another aspect in fibre-PLA composites is the porosity and especially small gap between fibre and polymer, which can originate from some residual moisture in fibre or different shrinking behaviour of fibres and polymers during the material cooling stage. The use of long alkyl chain plasticisers improves the mobility of polymer chains during cooling and can fill up the gap between fibre and polymer. If these plasticisers also have reactive groups just as epoxidised vegetable oils do, they can also couple fibres and polymers together without any gaps, which can provide weak points in material.

The primary proposals of this study are the following:

- Regardless of ligno-cellulosic fibre dimensions in short-fibre PLA composites, the coupling is needed between fibre and polymer to obtain optimal properties for the composite.
- It is also suggested that especially suitable coupling agents are oils of renewable origin, such as epoxidised linseed oil (ELO), because it can provide coupling between the fibre and the polymer matrix, improved fibre dispersion of short fibres to PLA and reduced porosity in PLA composites, leading to improved mechanical performance.

4 Experimental work

This experimental work was made during several years in different projects. To get an overview of the work, the materials and methods used in each paper are presented in Table 8.

Table 8: Materials and methods used in the discussed papers.

Paper	Polymer matrix	Fibres	Modifications	Processes
I	PLA 3052D	BSKP	Epoxidised linseed oil (ELO)	Compacting, compounding, injection moulding
II	PLA 3052D	NC, HefCel, MC	Epoxidised linseed oil (ELO), fibre dispersion agent (DA)	Compounding, injection moulding
III	PLA 3052D	Hemp fibre, hemp pulp, shives, oxidised shives, hemp dust, SWP	Hemp fibre pulping, shives oxidation, nanofibrillation	Compacting, compounding, injection moulding
IV	PLA 3052D	BSKP	Fibre moisture adjustment	Compounding, injection moulding
V	PLA HM1011	Birch pulp	No modification	Compounding, injection moulding

PLA was selected as a polymer matrix due to being a polymer of renewable origin and biodegradable even though it is in industrial composting facilities. It is also very strong polymer possible to be applied on several different product lines. By being biocompatible it also enables use in medical applications (Farah et al. 2016). The combination of ligno-cellulosic fibres with PLA is a potential route for high-strength, environmentally sustainable composite materials with novel properties. That is why several different size lingo-cellulosic fibres were selected for this study. One aim was to see the difference in materials containing fibres of different sizes and challenges in material from a development point of view. In quite early phases of studies, a gap in between the fibre and the polymer matrix was found indicating poor bonding. Also agglomeration of fibres in injection-moulded materials was quite significant. That is why the dispersion agents and additives capable of coupling of fibres and polymer was introduced in compounds. Epoxidised vegetable oil and especially linseed oil seemed to provide a proper, environmentally sustainable solution for both fibre dispersion and coupling of fibres with PLA.

The main tested properties for composites were tensile strength, Charpy impact strength, heat distortion temperature (HDT) and melt viscosity. The main analytical methods to study materials more closely were differential scanning chromatography (DSC), Fourier transfer infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and different fibre-length analytics depending on available equipment at the time of study.

4.1 Materials

Poly(lactic acid) (PLA) (Ingeo™ 3052D from Natureworks®) was used as a matrix polymer in works presented in Papers I-IV. PLA 3052D is a semi-crystalline polymer. It has a melt flow index of 14 g/10 min (210 °C, 2.16 kg), specific gravity 1.24 and relative viscosity 3.3 (NatureWorks 2018). It has a weight average molecular weight Mw 228.2 kg/mol and a number average molecular weight Mn 154.8 kg/mol presented in Paper IV. The polymer used in work presented in the older Paper V was a PLA HM1011 from Hycail with a melt flow rate 2-4 g/10 min.

Fibre for work described in Papers I and IV was never-dried bleached softwood kraft pulp (BSKP) made from spruce and delivered by Stora Enso in a dry material content of 32.6%. The average fibre length was 1.79 mm and an average width of 23.5 µm was measured with FiberLab (Metso Automation) according to TAPPI standard. Fibre content in work described in Paper I was 40%. Fibre content described in work in Paper IV was 30% in moisture contents 1, 3, 16 and 25%.

Fibres used in work described in Paper V were bleached cellulose birch pulp (MetsäBotnia, Finland) used in moisture fibre contents 20% and 40% and in moisture content below 2%.

Fibres used in work described in Paper II were powdery microcellulose (MC) Arbocel B600 (Rettenmeier and Söhne GmbH, Rosenberg, Germany), cellulose nanofibrils (CNF) and high-consistency nanocellulose prepared from dried bleached softwood kraft pulp (HefCel) (MetsäFibre, Äänekoski, Finland) by the methods explained later. Cellulose nanofibrils were also made from softwood dissolving pulp (CNFSD) (Domsjö Fabriker, Örnsköldvik, Sweden). The typical topological polar surface area of MC is 40.8 m^2/g (Chemical trading quide 2017) and the average fibre length is 60µm.

Fibres used in study presented in Paper III were hemp bast fibres, hemp shives, and hemp dust as a side stream from fibre production (HempRefine). Softwood cellulose pulp (SWP) (MetsäFibre, Äänekoski, Finland) was used as a reference. Also prepared were hemp pulp, oxidized shives and fibrillated hemp fractions.

A reactive coupling agent-plasticiser additive epoxy functional linseed oil (ELO) Vikoflex 7190 from Arkema was used as an additive on fibres in works presented in Papers I and II. According to the manufacturer, Vikoflex 7190 linseed oil is recommended for food contact packaging and medical applications. In Vikoflex 7190, the double bonds of linoleic oil, α-linolenic oil and oleic acid are epoxidised to contain several oxirane rings (minimum 9% of oxirane oxygen), which are able to react further (Arkema epoxides 2018).

In work presented in Paper II, the fibres were treated with Arosurf PA780 from Evonik (Essen, Germany). It is a quarternary blend of non-ionic and cationic surfactants and contains <20% imidazolium compounds, 2-C17-unsaturated-alkyl-1-(2-C18-unsaturated amidoethyl)-4,5-dihydro-N-methyl, Me sulfates (Evonik 2017). The aim of this additive was to improve the hydrophobic properties of fibres used mainly as dispersion agent (DA).

4.2 Methods

4.2.1 Nanomaterial preparation

In the study in Paper II, two different nanomaterials were prepared, cellulose nanofibrils and high-consistency nanocellulose.

Cellulose nanofibrils (CNF) were produced using BSKP and softwood dissolving pulp from mechanical treatment with a high-shear grinder as described in the following. The pulps were first soaked at 1.8% consistency for one day and dispersed using a high shear Ystral Dispermix (Ystral, Markgräflerland, Germany) for 10 minutes at 2070 rpm. Suspension was then fed into a Masuko Supermasscolloider (Masuko Sangyo Co., Kawaguchi-city, Japan) type MKZA10-15J. The BSKP was ground with six passes and the dissolving pulp was ground seven passes in order to obtain the CNF. The rotation speed was fixed at 1500 rpm. The gap width was approximately 0.14–0.25 mm depending on the fibrillation cycle. The production yield of ground material was 95% based on mass balance calculation. The material was stored at +5 °C until used.

BSKP was used as a raw material for high consistency nanocellulose (HefCel). The enzymatic treatment for BSKP was carried out at a consistency of 25 w-% for 6h at 70 °C using a two shaft sigma mixer (Jaygo Incorporated, NJ, USA) running at 25 rpm. The pulp batch size was 300g on a dry basis. After the treatment enzyme activity was stopped by increasing temperature of the mixer to 90 °C for 30min. The fibrillated material was diluted with deionised water, filtered and washed thoroughly with deionised water. The fibrillated material was dewatered to a consistency of ~20% by filtration. The gravimetric yield of the fibrillated material was 90%. The material was stored at +4°C until used.

Nano-fibrillated hemp materials in Paper III were made using bast pulp, unbleached shives and TEMPO-oxidised hemp bast fibres. The fibrillated hemp fibres were produced using a high-shear grinder Masuko Supermasscolloider MKZA10-15J. In TEMPO mediated oxidation, made for hemp bast fibres before fibrillation, the sample amount was 50 g and the pulp was suspended in 3 l of purified water. TEMPO (1 g) and NaBr (24 g) were used to catalyse the oxidation reaction with 10% NaClO (744 ml). The pH was kept at 10.3 by adding 1 M NaOH during the reaction. After the pH level stabilised, the reaction was stopped by adding ethanol into the oxidised pulp suspension. Finally, the pH was adjusted to 7 by adding 1 M HCl. The oxidised hemp pulp was washed with deionised water and stored in a fridge at +6 °C before fibrillation.

4.2.2 Fibre treatments

For work described in Paper I, the fibres were treated with additives using the fibre compacting methods presented in chapter 4.2.3.

For work described in Paper II, the additives were introduced on CNF and HefCel water dispersions and MC powder in a dough mixer. DA was added to 20 w-% of the fibre amount and VF was added to 10 w-% of the fibre amount. Before compounding with PLA HefCel and CNF were dried using a freeze-drying method. Freeze drying agglomerated fibrils to some extent, but it was the best available methods for this purpose. The water-containing slurry was frozen at -40 °C followed by freeze drying in a Supermodulyo 12K Freeze Dryer (Edwards High Vacuum International, Crowley, UK). The modified MC was oven dried at 50 °C overnight.

Hemp pulp in work described in Paper III was prepared using soda cooking. Cooking time was 90 minutes at 165 °C. Total alkali (NaOH) was 4.5 mol/kg. The liquid-to-solid ratio was 7.5. Oxidized shives were also prepared via ozonation. Medium consistency (12%) ozonation was carried out in a flow-through reactor at room temperature with ozone charge of 2%. After the ozone stage, the pulp was diluted to a 5% consistency with deionised water. After dewatering, the pulp was washed twice with cold, deionised water with an amount equivalent to ten times the absolute dry pulp amount. The hemp fibre, hemp pulp, hemp dust and BSKP used in work described in Paper III were also treated with the compacting methods presented in Chapter 4.2.3. to improve feeding into a compounder.

In work described in Paper IV, fibres were adjusted to different moisture contents 1, 3, 16 or 25% prior to compounding. The moisture contents 16% and 25% were adjusted in conditioning chamber (WTB Binder KBF-115) at 30ºC and 75% RH for 24 hours. The sample with 16% moisture was dried in a flow drier at 30ºC for 15 minutes. The sample with 3% moisture was dried in the flow dryer at 50 °C for 30 minutes. A sample with 1% moisture was dried in the flow dryer at 50 °C for 30 minutes, the drying was continued in an oven at 50 °C for 4 hours and in a vacuum-oven at 50 °C for 2 hours before compounding.

4.2.3 Fibre-compacting method

In work described in Paper I, the fibres were treated with additive (ELO) and densified using a compacting device, a compactor developed at VTT (Technical Research Centre of Finland) (Sivonen & Valta 2011) before compounding with PLA. The compactor device is a modified pelletising equipment (Figure 14), which allows the processing of high dry material content (50-85%) cellulose fibre material to loose pellets without increasing the friction temperature too high during the compacting process for sensitive carbohydrate materials. There is still a small temperature increase (max 50°C), which, in combination with press can, at this stage, already lead to some reactions between additives and cellulose. Before the compactor, the additives were introduced to fibres by spraying them onto the fibre surface in amounts of 5, 8 or 12% of fibre dry material content in a blade-type blender (Figure 14) (F-60, Halvor Forberg A/S, Larvik, Norway). Then the additive containing fibre mass was pressed through the compactor to form additive pellets suitable for addition to the compounder. The method was first published by Immonen et al. in 2011.

The fibre pellets were dried in the oven over night (for 12 hours) at 50°C after which they contained 3% moisture.

Figure 14: A blade-type blender (right) and the compactor device for fluffy fibre material treatment (left).

Fibre compacting was also used in work described in Paper III for compacting fibrous hemp (fibre, pulp and dust) and BSKP materials before compounding with PLA.

4.2.4 Processing of composites

Compounding

The compounding of fibres with PLA was made using a co-rotating twin-screw extruder (Berstorff ZE 25x33 D, Berstorff GmbH, Hanover, Germany). The extruder zone temperatures ranged from 60 to 195°C, a speed of 100 rpm and an output of 2 kg/h. The residence time of the compound inside the compounder was measured to be approximately 2.5 minutes. The compounding was made in the same way in all papers.

Injection moulding

Injection moulding was made with an injection-moulding machine (Engel ES 200/50 HL, Engel Maschinenbau Geschellschaft m.b.H, Schwefberg, Austria) to dog-bone shaped test specimens according to ISO 527 and presented in Figure 15. The processing temperatures during injection moulding were from 180 to 190°C in the screw and 200°C on the nozzle. The injection moulding was performed in the same manner in all the papers.

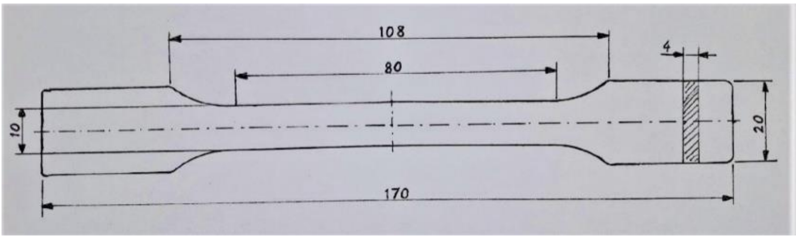

Figure 15: Injection moulded dog-bone shaped test specimen according to ISO 527-2:1993) used for material testing. Dimensions are in millimetres.

4.2.5 Analysis methods and characterisation

DSC

DSC (Differential scanning chromatography) analysis was run for PLA-BSKP compounds using NETZSCH DSC 204F1 Phoenix 240-12-0287-L (NEZSCH GmbH, Selb, Germany). The heating profile was 10°C/min from 0°C to 190°C followed by cooling 10°C/min to 0°C. The second identical heating and cooling cycle can be made to see, if the first heating induces some reactions or changes in material. By DSC it is possible to analyse how the heat capacity of material is changed by temperatures. The parameters analysed normally from polymeric materials are glass transition temperature (Tg), melting temperature (Tm) and melting behaviour, crystallisation temperature (Tc), melting enthalpy (ΔH) and wheather the heat flow change is endothermic or exothermic.

Fibre analysis

For determination of the BSKP fibre lengths, the fibre fraction of injection moulded PLA samples was Soxhlet-extracted. A small amount of composite sample was placed into the Soxhlet thimble and continuously fluxed with a hot solution of chloroform for 48 h. The remaining kraft pulp fibre fraction was collected and the fibre lengths were determined using a Kajaani Fiberlab analyser. Some 0.23–0.30 g of each sample was soaked in 500 ml of deionised water and they were dispersed using a high shear laboratory blender (IKA Ultra-Turrax T18) for five minutes. After dispersing, the samples were left in deionised water overnight. Next day the samples were further mixed in five litres of water with an impeller for 10 minutes. Some 50 ml of dispersed sample was pipetted into the analyser and fibre analysis was performed with two repeat measurements. Fibre length results were reported according to TAPPI standard method T271. This method was used in work described in Paper IV

In work described in Paper III, the coarse fractions of hemp were difficult to analyse using a fibre analyser so a Malvern Particle size analyser was used after dispersing the fibrous material in water. The extraction of PLA was made as above.

The fibre dimension analysis presented in older Paper V was made by at first dissolving PLA with methylene chloride by heating the chemical to its boiling point (39.8ºC) and the dissolved components were filtered with glass sinters and washed with methylene chloride. The dimensions (length, width, aspect ratio and proportion of fines) of the remaining fibres were analysed using the automated fibre analyser L&W STFI FibreMaster (FM).

In work described in Paper II, the fibre size of nanocelluloses was analysed using optical microscopy pictures. The samples were a water suspension of nanofibrillated fibres in fibre content 3%. Before the imaging of fibrillated cellulose samples, they were dyed with 1% Congo red solution by mixing fibrillated cellulose and dye in a ratio of 1:1 and further diluting the dyed mixture on the microscope slide (2:1). Optical microscopy was performed with Olympus BX 61 microscope equipped with WH10X-H eyepieces, fluorite objectives and ColorView 12 camera (Kangas et al. 2014).

FTIR

FTIR (Fourier transfer infrared) spectra of cellulose fibres were analysed with Perkin Elmer FT-IR Spectrum BX (Perkin Elmer Inc., Llantrisant, England) equipment with a wavelength from 400 to 4000 1/cm using tablets prepared with KBr in a Specac tablet press (Perkin Elmer GmbH, Uberlingen, Germany). Before analysis the cellulose fibres were extracted from the injection moulded samples by dissolving the PLA matrix in hot chloroform with Soxhlet-extraction for 48 hours and then dried. The purpose of the cleaning process was to see, wheather the fibres contain any covalently coupled PLA or additives on the fibre surface. The residual additives or PLA can be seen, for example, in increased carbonyl bonds related to ester linkages.

In the FTIR method, infrared radiation is exposed on a sample, some radiation is absorbed by the sample and some passes through (i.e., is transmitted). The resulting signal at the detector is a spectrum representing a molecular ‘fingerprint’ of the sample. Each molecular linkage is giving a signal on specific wavelength, which can be used to analyse chemical structures of the sample.

HDT

HDT (Heat distortion temperature) was measured according to the ISO-75 standard using method A, where the stress on the sample is 1.80 MPa. HDT was determined by using the Ceast HDT 3 VICAT P/N 6911.000 (Ceast S.p.a., Torino, Italy) and for three parallel samples.

HDT is one of the most important analyses for polymers and composites. It gives an indication of the temperature at which the material begin to soften or deflects by 0.25 mm, when exposed to fixed temperature and loaded with standard weight. The heat distortion temperature of amorphous materials is related Tg and in crystalline materials to melting temperature. It gives a good indication of the maximum use temperature for structural applications.

Mechanical testing

Tensile tests were performed using an Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA, USA) and an Instron 2665 Series High Resolution Digital Automatic Extensometer (Instron Corp., Canton, MA, USA) with a 10 kN load cell and a 5 mm/min cross-head speed. A minimum of six parallel samples were tested. The tensile tests were performed according to ISO-527.

Charpy impact tests were made according to ISO-179 standards. Impact strengths were measured for ten parallel unnotched specimens in a three-point bend configuration and using a Charpy Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy).

The mechanical test specimens were kept in standard conditions (23°C, 50% relative humidity) for at least five days before testing to minimise the variation caused by temperature and moisture.

In a tensile test, a dog-bone shaped sample (Figure 16) is pulled in opposite directions from both end of the sample with specific load. In fibre composite samples this gives an indication of how well the sample is able to resist the pulling force without structural changes. The more the fibre loading is or the bigger the fibre surface area is inside the polymer matrix the more the structural changes are in relation to fibre-polymer interface strength.

The Charpy impact strength test is to measure how much kinetic energy is needed to initiate a fracture on a sample until it is broken when it is stroked with a sharp headed hammer in the middle of the sample. In fibre composite samples, the fracture is transferred through the sample in the weakest points, those usually occur in the fibre-polymer interface, if no coupling is used.

SEM

The morphology of the injection-moulded samples was studied by an SEM (scanning electron microscopy) from a cross-section of the test bars. The sample surface was coated with gold to prevent surface charging. Gold film thickness on the sample surface was 50-70 nm. Analyses were made using JEOL JSM T100 (JEOL ltd., Tokyo, Japan) with a voltage of 25 kV.

Viscosity

The apparent melt viscosity of the compounds was analysed using a Göttfert Rheograph 6000_3/V 4.45 Messwertdatei capillary rheometer (Göttfert Werkstoff-Prüfmaschinen GmbH, Buchen, Germany) at a temperature of 190°C, where polymer PLA is in the melting stage. Viscosity was measured from samples after compounding, before injection moulding.

5 Results and Discussion

The result and discussion part of the work is divided into different sections where the results from different papers are collected on topic at a time and discussed together.

5.1 Mechanical results

The mechanical results from tensile and impact tests of all five of the papers are collected in Table 9. Figure 17 shows a tensile strength versus strain distribution for all the results and Figures 18 and 19 displays tensile modulus and tensile strength versus impact strength distribution for the results respectively.

Table 9: Mechanical results of all the papers discussed.

Paper/ Fibre (%)/ Additive (%)	Tensile strength at break, MPa	Young's modulus, MPa	Strain at break, %	Charpy Impact Strength, kJ/m^2
I / PLA	62.7 ± 0.3	3380 ± 130	3.9 ± 0.0	16.4 ± 1.1
I / BSKP (40)	75.8 ± 3.3	6380 ± 130	2.4 ± 0.1	13.1 ± 0.9
I / BSKP (40) / ELO (5)	80.7 ± 0.9	6700 ± 180	2.1 ± 0.1	16.5 ± 2.6
I / BSKP (40) / ELO (8)	80.5 ± 0.8	6550 ± 280	3.7 ± 0.1	18.0 ± 1.5
I / BSKP (40) / ELO (12)	75.1 ± 1.7	6200 ± 150	5.6 ± 0.3	17.9 ± 3.0
II / PLA 3x processed	50.9 ± 0.5	4820 ± 609	5.9 ± 0.7	16.8 ± 1.5
II / PLA / DA	51.5 ± 0.7	3475 ± 167	4.6 ± 0.6	17.0 ± 1.6
II / CNF (3%)	56.6 ± 0.7	3907 ± 202	2.3 ± 0.1	14.7 ± 0.7
II / CNF (3%) / DA	54.5 ± 1.5	3962 ± 244	2.5 ± 0.4	18.7 ± 2.4
II / CNF (5%)	56.1 ± 1.6	3551 ± 104	2.3 ± 0.3	13.7 ± 1.6
II / CNFSD (5%)	55.4 ± 0.6	3489 ± 20	2.3 ± 0.1	11.9 ± 1.6
II / HefCel (5%)	55.9 ± 1.0	3924 ± 103	2.6 ± 0.3	17.8 ± 1.8
II / HefCel (5%) / DA	51.3 ± 1.2	3865 ± 106	2.5 ± 0.4	21.6 ± 4.1
II / HefCel (5%) / ELO	56.8 ± 0.8	4171 ± 246	2.3 ± 0.2	20.9 ± 2.7
II / MC (5%)	53.1 ± 0.5	3821 ± 159	3.1 ± 0.5	24.1 ± 7.4
II / MC (5%) / DA	51.1 ± 0.8	3923 ± 132	2.4 ± 0.3	34.1 ± 5.5
II / MC (5%) / ELO	51.9 ± 0.6	3797 ± 123	3.8 ± 0.7	29.5 ± 8.5
III / SWP (40%)	59.5 ± 1.9	6950 ± 356	2.4 ± 0.1	9.9 ± 2.2
III / Hemp pulp (40%)	86.6 ± 0.8	7440 ± 596	1.9 ± 0.1	19.9 ± 3.2
III / Hemp fibre (40%)	67.8 ± 3.0	6607 ± 184	1.2 ± 0.1	9.8 ± 2.5
III / Hemp shives (40%)	51.1 ± 1.4	6869 ± 113	0.8 ± 0.0	7.5 ± 1.5
III / Oxidized shives (40%)	59.9 ± 0.3	6734 ± 491	1.2 ± 0.1	7.1 ± 1.2
III / Hemp fibre (30%)	67.4 ± 1.5	5667 ± 128	2.0 ± 0.2	12.1 ± 1.9
III / Hemp dust (30%)	48.0 ± 0.3	4486 ± 93	1.6 ± 0.1	9.8 ± 1.1
IV / BSKP (30%) / Moist. 1%	72.8 ± 0.7	6190 ± 100	1.9 ± 0.1	14.3 ± 1.6
IV / BSKP (30%) / Moist. 3%	73.1 ± 0.3	6210 ± 100	1.9 ± 0.1	13.9 ± 1.7

IV / BSKP (30%) / Moist. 16%	70.6 ± 1.2	6670 ± 100	1.5 ± 0.1	13.1 ± 1.7
IV / BSKP (30%) / Moist. 25%	70.4 ± 0.8	5910 ± 300	1.8 ± 0.1	14.2 ± 1.3
V / Birch pulp (20%)	62.7 ± 1.2	5617 ± 151	2.7 ± 0.3	15.4 ± 1.2
V / Birch pulp (40%)	74.1 ± 1.8	8018 ± 96	1.5 ± 0.2	13.8 ± 2.3
V / PLA HM1011	63.9 ± 0.2	3771 ± 55	4.2 ± 0.1	18.4 ± 0.9

The results presented in Table 9 are comparable and even exceed the values presented in the literature in Table 7. Especially the results obtained for PLA composites containing BSKP fibre and ELO as well as hemp fibre composites are showing enhanced properties compared to literature presented in Table 7.

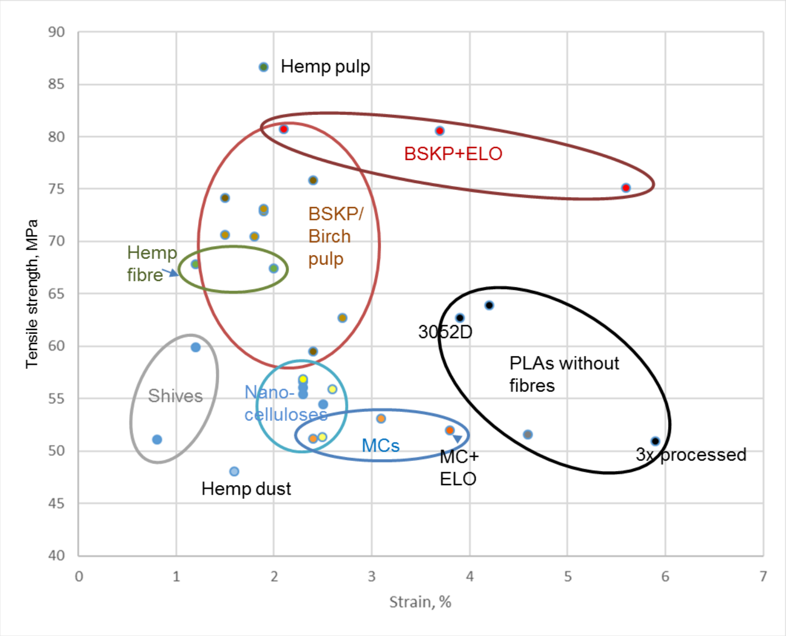

Figure 17: Tensile strength versus strain distribution for all the results in five papers. The circles around results are grouping the composites with similar fibre types and also indicated with the same colour as text.

The tensile results collected from all of the five papers show the best tensile properties for hemp pulp-PLA composite, where hemp fibres were cooked in alkaline conditions (NaOH) removing most of the lignin and waxy materials out of the fibres, yet retaining the fibre length, which is discussed more in Paper III. Results for washed hemp fibre PLA composites in literature are in line with our studies for hemp fibres (Sawpan et al. 2007). With 30% hemp fibre content, tensile strength 65.9 MPa and strain 1.51% were lower compared to our results (67.4 MPa and 2.0%). However, the use of the hemp pulp in PLA composites seems to be novel according to literature. We found in the level of 45%

improvements in tensile strength with hemp pulp compared to hemp fibre. Compared to neat PLA 3052D, the best overall improvements for tensile strength was obtained with BSKP containing over 8% ELO, from 62.7 MPa of neat PLA to 80.5 MPa with PLA+40% BSKP containing 8% ELO. The strain at break was reduced in all other fibre-containing composites except a 12% ELO containing BSKP-PLA composite. In literature, the tensile strength for PLA containing a 30% solvent treated, bleached pine fibres was 65.3 MPa (Granda et al. 2016). No improvements on tensile strength or strain was obtained with short fibres such as hemp dust or more particle form shives or oxidised shives, those were acting more like fillers, probably due to the small aspect ratio. The microscopy pictures of those materials presented in Paper III are already showing their particle form structure before processing.

Nanocelluloses (CNF and HefCel) and MC are to be compared to 3x-processed PLA, which gives an indication of strength improvement with nanocelluloses up to 11% improvement with 3% to 5% nanocellulose addition. On the strength of the 5% HefCel-containing composites the ELO addition has a positive effect on the contrary to DA addition. The ELO addition also has a positive effect on the strain properties of 5% MC containing PLA (3x processed). With MC composites the addition of DA, a pure dispersion agent, also enabled improved strength properties. Strain was reduced in all MC and nanocellulose-containing composites compared to reference, which was due to increased breaking points inside PLA caused by partially agglomerated nano and microparticles. Those are more discussed in Paper II.

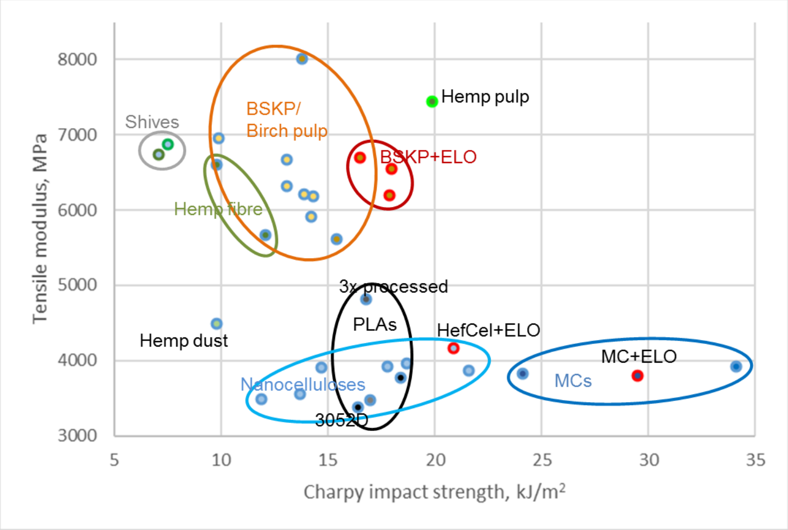

Figure 18: Tensile modulus versus Charpy impact strength distribution for all the results in five papers. The circles around results group the composites with similar fibre types and also indicated with the same colour as text.

Looking at the results for tensile modulus presented in Papers I, III, IV and V (BSKP, birch pulp and hemp material), which contain PLA composites compared to neat PLA 3052D we can find a significant increase in modulus with all the fibres indicating stiffening of the material due the addition of fibre, which is in line with literature (Granda et al. 2016). The biggest increase in modulus was gained with 40% hemp pulp from 3380 MPa of PLA 3052D to 7440 MPa with hemp pulp. A nearly similar increase was yielded with 40% birch pulp (8018 MPa) in Hycail PLA (3770 MPa). Further, the shives, which were more like fillers, showed a quite high modulus of 6869 MPa in 40% loading in PLA 3052D. With most of the fibres being without a coupling agent, the stiffening of the material caused a simultaneous drop in impact strength except with 40% hemp pulp. The impact strength result of which is higher than in neat PLA (19.9 kJ/m^2 vs. 16.4 kJ/m^2). Additionally the ELO-containing BSKP materials showed a small, sub 10%, increase in impact strength value.

In PLA composites with birch, BSKP and hemp materials, the amount of lingo-cellulosic fibres was 20-40%, which enabled the fibre network formation inside the PLA. That has an effect on the modulus increase, because the hydrogen bonds on the fibre network also resist the shape transformation during pulling even though there are gaps in between fibre and polymer.

The tensile modulus results for nanocellulose and MC-containing PLA composites are 14 to 27% lower than in reference PLA (3x processed). However, the Charpy impact strength results for all HefCel (from 17.8 to 21.6 kJ/m2) and MC (from 24.1 to 34.1 kJ/m2) containing materials were higher than in reference PLA (16.4 kJ/m2). This is discussed more properly in Paper II. Increased impact strength values for PLA composites with ball-milled BSKP fibre with specific fibre size are in line with our studies. With 20% milled BSKP in particle size 120 µm and 39.7 µm, the unnothed Charpy impact strength values were 27.7 kJ/m2 and 28.8 kJ/m2 respectively (Gao et al. 2017). The particle size in our MC was 60 µm. The modulus drop is due to a low amount of partially agglomerated nano- and micro-size fibres unable to form a percolation network to increase the stiffness of materials. The addition of ELO to HefCel was able to disperse the HefCel nanofibres in PLA, enabling improved fibre network formation and probably also fibre straightening. That and also the coupling of fibres to PLA made the material more resistant to shape formation during tensile tests (pulling) showing as improved modulus. That also caused improvement in impact strength.

With microcellulose having a short aspect ratio and low MC amount, the improved dispersion due to ELO and DA was not able to form a real network. MC just acted as breaking point during tensile test (pulling) without an increase in modulus. Impact test being a test with fast strike on material, the improved fibre dispersion with DA and ELO was more able to resist the break than material with MC without modification.

The literature presents the minimum aligned plant fibre volume fraction able to provide tensile improvements to be 8.1% and maximum theoretical fibre volume content 58.9% in polyester composites (Shah et al. 2012).

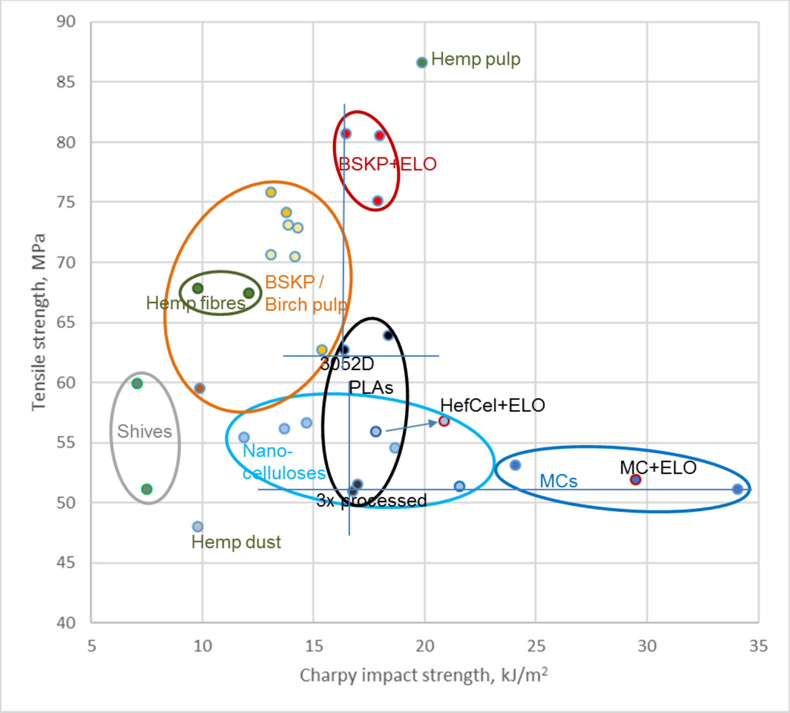

Figure 19: Tensile strength versus Charpy impact strength distribution for all the results in five papers. PLA 3052 is the reference for hemp materials, BSKP and birch pulp. 3x processed PLA is the reference for nanocelluloses and MCs. The circles around the results are grouping the composites with similar fibre types and also indicated with the same colour as text. The horizontal and vertical lines are fixed in PLA 3052D pulp and hemp composites and 3x processed PLA for nanocellulose and MC composites with the aim of visualising the strengthening effect in composite causeds by fibres.

Figure 19 presents tensile strength results versus Charpy impact strength results from all five papers to visualise the real strengthening effect in PLA-fibre composites due to the addition of lingo-cellulosic fibres with different lengths. The horizontal and vertical lines in Figure 19 are fixed in PLA 3052D to compare pulp and hemp composites and in 3x processed PLA to compare nanocellulose and MC composites with the aim of visualising the strengthening effect in composite caused by fibres. When comparing the results presented in Papers I, III, IV and V we can see that the real strengthening of the composites has occurred with 40% BSKP+ELO and 40% hemp pulp containing composites, which is indicated by the simultaneous increase in tensile strength and impact strength compared to PLA 3052D. The best overall improvements were obtained with BSKP fibres containing over 5 % of ELO. The increase in Charpy impact strength was 25%, 37.4% and 37% with an ELO amount in fibre of 5% to 8% and 12%, respectively. The simultaneous increase in tensile strength for 5% and 8% ELO containing BSKP fibres was 6%, but stayed on the original level with 12% ELO in fibres. However, due to the plasticising effect of ELO, the strain at break increased from the value of 2.4% without ELO to 5.6% with 12% ELO in fibre and even exceeded the value of neat PLA 3.6%. This is an indication of the real connection between fibres and PLA.

In hemp pulp, the lignin, waxy material and part of hemicelluloses are removed compared to hemp fibres and shives (Thomsen et al. 2005). In hemp pulp 22% of fibre lengths in the injection moulded material is over the critical fibre length of 0.36 mm calculated for cellulose fibre presented in work in Paper V. According to the theory, if the fibre length exceeds the critical fibre length, it is able to transfer the stress and strengthen the composite material.

The strengthening effect of nanocelluloses (CNF and HefCel) and MC are to be compared to 3x processed PLA in Figure 19 and Table 9, which gives an indication of the strengthening effect already due to 5% HefCel addition, providing a 9.8% increase in tensile strength from 50.9 MPa to 55.9 MPa, and a 6% increase in Charpy impact strength from 16.9 kJ/m^2 to 17.8 kJ/m^2. The addition of ELO (10% on fibre) to HefCel provided an additional increase of 1.6% to tensile strength and 17.4% to Charpy impact strength (20.9 kJ/m^2), which indicates the real fibre-polymer coupling due to ELO. Literature presents the effect of maleated-PLA grafting of nanofibrillar cellulose in amount of 5% to PLA showing tensile strength 60.3 MPa and impact strength 12.5 kJ/m^2 (Ghasemi et al. 2017).

With CNF addition of 3% and 5% without any additives the results show roughly an 11% and 9% increase in tensile strength respectively, but a reduction in impact strength. When DA was added to CNF, the impact strength increased by 27%, but the tensile strength was reduced by 4%. DA also caused the same phenomena with HefCel, impact strength increased by 21% and tensile strength decreased by 8%. However, the DA addition was not able to increase other properties simultaneously, hence indicating no connection between fibre and polymer.

The 5 % MC addition was able to strengthen PLA (3x processed) as such showing a 4.3% increase in tensile strength results and a 43.5% increase in Charpy impact strength results. The addition of 10% ELO on MC yielded and additional 22.4% increase to Charpy impact strength, which was 75% higher than PLA (3x processed) (from 16.8 kJ/m^2 to 29.5 kJ/m^2), but a slight decrease in tensile strength (51.9 MPa) yet keeping it over the reference PLA (50.9 MPa). This may be due to an excessively high amount of ELO in fibre and is in line with the results for pulp fibres. The addition of DA (20% on MC) gave superior impact strength results, 34.1 kJ/m^2, which was 103% better than in reference PLA. However, there was no improvement in tensile strength properties due to DA. Literature gives tensile strength value of 56.5 MPa and impact strength 5.59 kJ/m^2 MPa for PLA containing 5% microcellulose, and processed with compounding and injection moulding (Dogu & Kaynak, 2016). Our results showed an indication of improved impact properties compared to literature.

Part of the strengthening improvement with HefCel and MC is coming from improved fibre dispersion, because similar impact strength improvements were achieved by using a pure dispersing agent (DA) with an amount of 20 % on fibre. The DA addition was not able to increase other properties simultaneously, indicating no connection between fibre and polymer. However the mechanical results for HefCel and MC are showing the true connection between fibres and PLA due to ELO addition. These results are more closely discussed in Paper II.

The fibre distribution and fibre length are correlated to the strength of composites. Distributions for injection-moulded materials with different fractions of hemp and softwood pulp (Paper III) are presented in Figure 20, and length-average fibre lengths for materials without DA and ELO described in Papers IV and V in Table 10. The removal of PLA from ELO-containing fibres composites was difficult due to coupling of fibres to polymer and so the fibre length results are not available for those samples.

The average fibre lengths for nanocelluloses and MC presented in Figure 21 and Table 10 are values before processing, assuming that no significant reduction in fibre length has occurred due to small fibre length at the beginning. The average fibre length used in Figure 21 for MC was 60µm, for CNF 10µm and for HefCel 0.3µm as reported in Paper II.

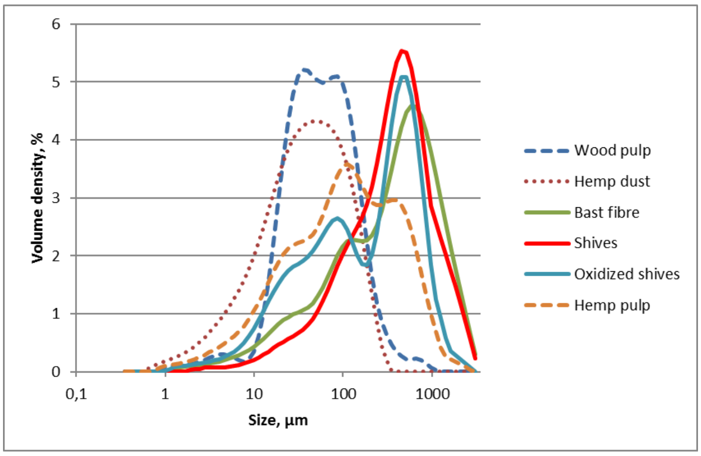

Figure 20: Particle size distributions of fibre materials removed from injection moulded PLA-fibre composites from work described in Paper III. Wood pulp is softwood cellulose.

In Figure 20 can be seen how lignin, hemicellulose and other materials containing hemp (bast) fibres, shives and oxidised shives contain more coarse material with a fraction of longer fibres than pulped fibres have. After the pulping process with NaOH, which removes lignin and hemi, the hemp fibre is still able to retain some of the longer fibres during thermoplastic processing compared to softwood pulp. In addition, compared to purified cellulosic fibre, the hemp pulp containing material had an indication of the widest fibre length distribution also containing a fraction of very long fibres, over 1 mm, which are able to provide stress transfer to some extent. Even though the average fibre length for hemp pulp in Table 10 shows a quite low value of 113 µm, the fibre length distribution in Figure 20 shows the high fraction of long fibres. In work described in Paper V, the minimum theoretical fibre length was counted for birch pulp fibre to be able to provide a reinforcing effect. The calculated fibre length is 143-357 µm depending on the amount of fibre. According to that the hemp pulp composites contain fibres that are able to act as real reinforcement material in PLA even though most of the fibres are degraded in processing to smaller fibres. The literature presents the fibre length for BSKP after injection moulding (1 process) to be average of 514 µm (Granda et al. 2016), and for hemp fibres after compounding and injection moulding an average of 544 µm (Peltola et al. 2011).

In processing PLA-cellulose fibre composites it is suggested by the PLA manufacturer to dry the fibres and PLA to moisture content below 250 ppm, which is in fact very difficult for ligno-cellulosic fibres containing moisture in fibre cell walls. The effective drying is also very difficult to realise on an industrial scale. In work described in Paper IV, the effect of fibre moisture content was studied more closely and it was found that even the 3% moisture content in fibre gave reasonably good properties for the PLA-BSKP composite and the length of the average fibre was higher than with fibre moisture contents of 1%, 16% or 25%, that is presented in Table 10.

Table 10: Average fibre lengths for PLA composite materials after processing.

Paper / fibre material (amount in composite)	Average fibre length, (µm)	Measurement method
II / CNF	10	Microscopy
II / HefCel	0.3	Microscopy
II / Microcellulose	60	Material specification
III / Softwood pulp (40%)	58 (excluded Fig. 21)	Malvern[a]
III / Hemp pulp (40%)	113 (excluded Fig. 21)	Malvern[a]
III / Hemp fibre (40%)	404	Malvern[a]
III / Hemp shives (40%)	400	Malvern[a]
III / Oxidized shives (40%)	253	Malvern[a]
III / Hemp dust (30%)	40	Malvern[a]
IV / BSKP (30%, moisture 1%)	290	Kajaani FiberLab[b]
IV / BSKP (30%, moisture 3%)	350	Kajaani FibreLab[b]
IV / BSKP (30%, moisture 16%)	280	Kajaani FibreLab[b]
IV / BSKP (30%, moisture 25%)	290	Kajaani FibreLab[b]
V / Birch pulp (20%)	423 ± 4	FibreMaster[c]
V / Birch pulp (40%)	361 ± 11	FibreMaster[c]

[a] No standard deviation available, the value is average size of particles in volume (%)

[b] No standard deviation available, the value is a length-weighted length fraction

[c] Results are length weighted average length

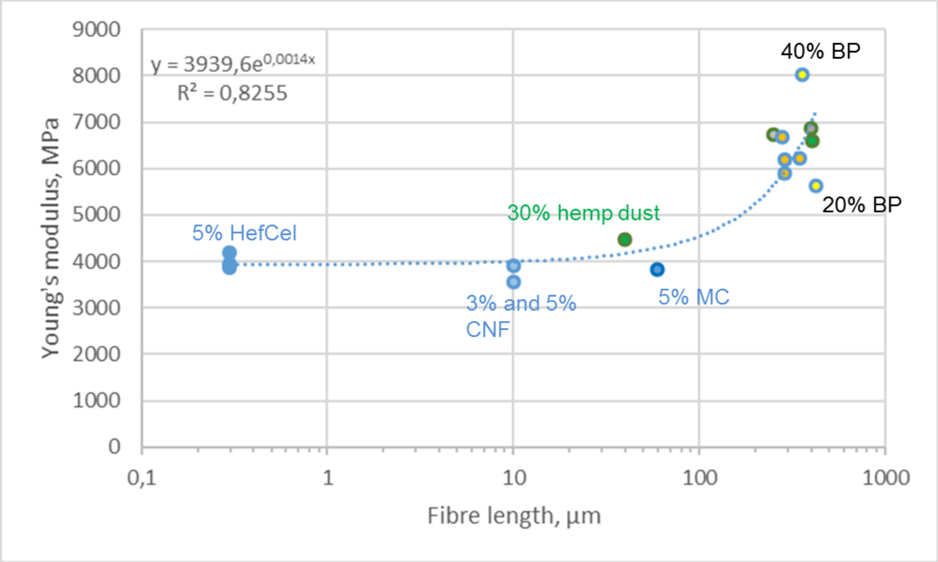

Figure 21: Fibre length in correlation to tensile modulus (Young's modulus). Fibre lengths are after compounding and injection moulding except with CNF, HefCel) and MC those are values before processing. The probability R^2 for exponential fit is 0.8255.

The stiffening of the short fibre composite material starts roughly when the average fibre length exceeds roughly 150 µm, see Figure 21. In work presented in Paper V, suggests a value of 143-357 µm for short birch pulp fibre. Literature presents the critical fibre length of 505-635 µm for chemically treated bleached pulp fibres with PLA (Granda et al. 2016), and 120 µm for man-made cellulose with PLA (Bledzki & Jaszkiewicz 2010). The critical fibre length is found to vary depending on fibre type, modification, type of matrix polymer and fibre content (Pickering et al. 2016). In most of the wood pulp containing short fibre composites, the fibre length is below that. The failure in composites during tensile stress is assumed to occur in the fibre-polymer interface.

The hemp pulp fibre was left out from Figure 21 because the average particle size measured by Malvern is not able to represent the wide size distribution that the hemp fibre has. There are some uncertainties in the average values for softwood pulp and hemp fibres of Malvern-results, because it measures more particles than fibres and also estimates the fibrous material to round particles. However, the shives, oxidised shives and hemp dust were more in particle form than fibrous material, so the method is relevant for those. By leaving out clearly fibrous material such as hemp pulp and softwood pulp the exponential estimate in Figure 21 fairly well explains the fibre length relation to tensile modulus with a probability of R^2 0.8255. The results are in line with calculated results in Paper V, but also in line with previous studies in terms of estimation of critical fibre length. However it must be kept in mind that the fibre length of ligno-cellulosic fibres is a wide distribution containing fibres from nanosize to millimeter size and the fraction of each size class also has an effect of its own and follows the theoretical rule of mixture.

The effect of aspect ratio is not considered here because of the short cellulose fibre composites have wide particle size distribution.

The stiffening of the composite material can be seen as simultaneously increased tensile and impact strength that is due to the coupling of fibres and polymers with ELO enabling stress transfer inside the material. Due to ELO also acting also as a plasticiser for PLA the modulus is not necessarily increased in all cases as can be seen in Figures 18 and 19 and discussed in literature (Buong et al. 2014).

5.2 Morphological results and melt viscosity

The visual outlook of the injection-moulded PLA-BSKP composites with and without ELO for CNF, HefCel and MC containing PLA composites can be seen in Figure 22 and for 40% BSKP-containing composites in Figure 23.

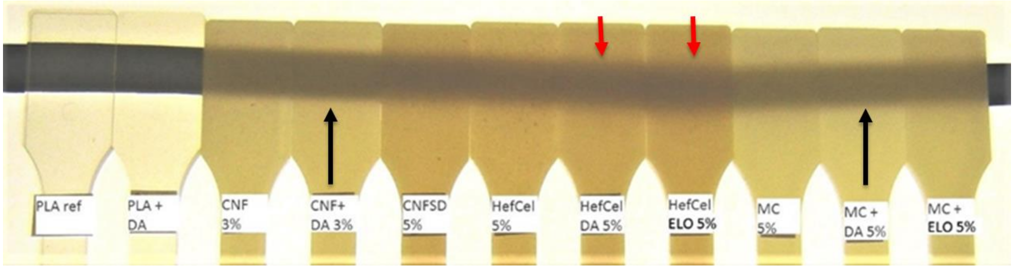

Figure 22: PLA composites with 3% or 5% CNF, 5% HefCel and 5% MC with and without DA and ELO. Red arrows showing the effect of DA and ELO in PLA-HefCel composites. Black arrows shows the effect of DA on 3%CNF and MC PLA-composites.

The improved dispersion of HefCel in PLA discussed in Paper II is due to DA and ELO added on the fibre surface before the thermoplastic process, see Figure 22. In material containing 5% HefCel without additives, the fibre agglomerates can clearly be seen. The agglomerates were clearly reduced in the additives DA and ELO containing test bars (red arrows) with 5% HefCel suggesting that they were both able to disperse the fibres in PLA. The improved dispersion in 5% MC and 3% CNF-containing PLA composites with DA can be seen as reduced light scattering through test bars (sharper line marked with black arrows) as compared to other MC and just 3% CNF-containing test bars. The main effect of ELO in MC-containing composites can be seen in SEM-pictures in Figures 25 and 26, those are presenting a closer look for fibre attachment on PLA matrix.

Figure 23: Injection moulded test samples from left to right PLA, PLA with 40% BSKP (Ref), PLA+40% BSKP with 5% ELO (1), PLA+40% BSKP with 8% ELO (2) and PLA+40% BSKP with 12% ELO (3).

Dark colour of the injection moulded composites in Figure 23 suggests quite high thermal degradation of fibre, which is highest in material without ELO. Even though the melt viscosity increased with ELO (as presented in Paper I) the colour is lighter. ELO is known to act as an acid scavenger and PLA is an acid-functional polymer (Samarth and Mahanwar 2014). Cellulose at high temperatures is degraded by acids, but the presence of ELO reduces the degradation of cellulose and gives a lighter colour to the product. The small colour increase in materials with higher additive amounts of 8% and 12% is due to the increased melt viscosity of materials causing increased friction during processing followed by thermal degradation of cellulose. The melt viscosity was measured from PLA-fibre compounds after the compounding stage and presented in Paper I and in Figure 24. A clear increase in melt viscosity is found with increasing ELO content. It is suggesting that the reaction has taken place between fibre and polymer. If the ELO is acting only as plasticiser the melt viscosity would have decreased, but here it increased.

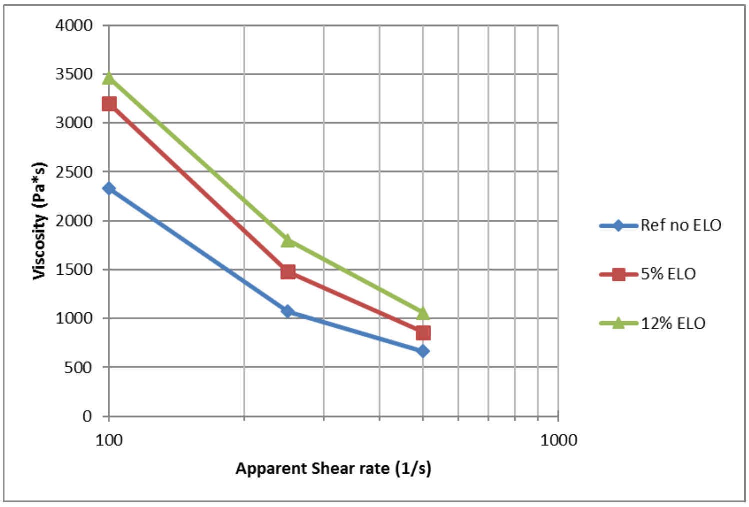

Figure 24: Apparent melt viscosity at 190°C for 40% BSKP fibre-containing PLA samples.

The connection between BSKP fibre and PLA is presented in SEM-pictures in Figures 27 and 28.

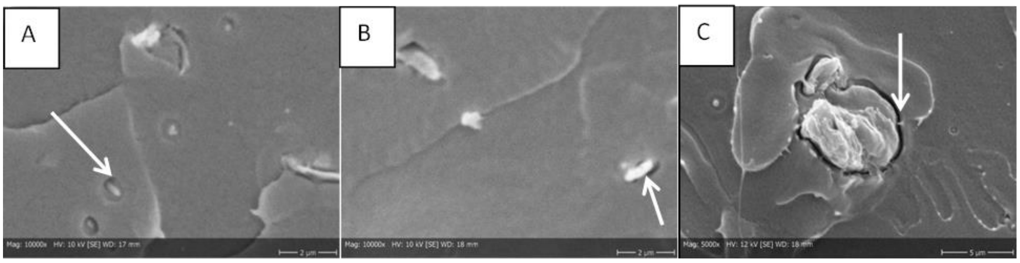

Figure 25: SEM-pictures of 5% CNF (A), HefCel (B) and MC (C) containing PLA composites without additives. The arrows indicate the gap between fibre and PLA.

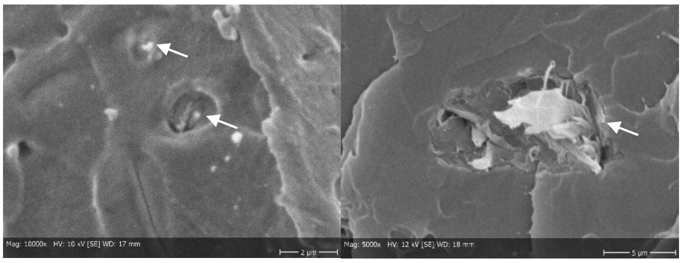

Figure 26: SEM-pictures of 5% HefCel- (left) and MC-containing (right) PLA composites with ELO as additive. The arrows indicate the interface between fibre and polymer.

SEM-pictures for 5% CNF-, HefCel- and MC-containing PLA composites without additives from work described in Paper II are presented in Figure 25. There can be clearly observed a gap in fibre polymer interface, which is reduced or even disappeared when ELO is used as an additive. The effect of ELO for 5% HefCel- and MC-containing PLA composites is presented in Figure 26. The effect of ELO is also quite similar to BSKP-PLA composites presented in Figures 27 and 28. The poor interfacial bonding between the fibre and PLA is presented in literature for CNF (Mosley 2018), wood fibre (Joffre et al. 2014) and also generally (Pickering et al. 2016).

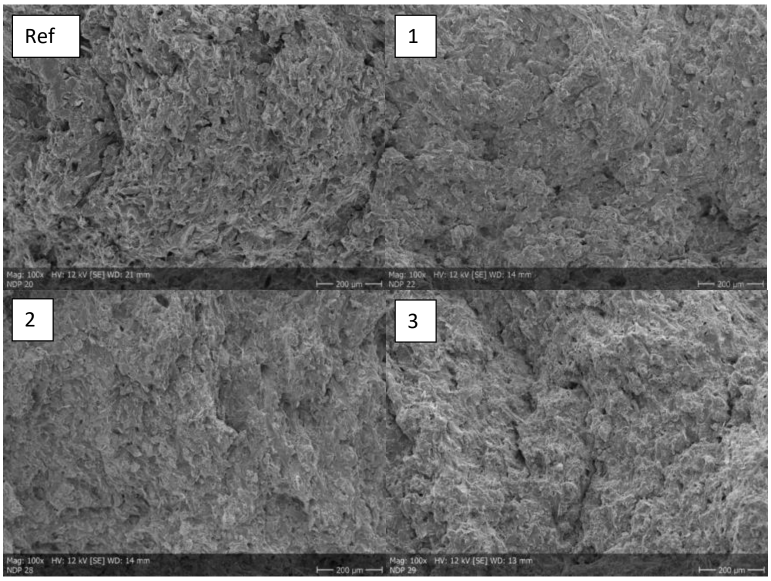

Figure 27: SEM-pictures of samples PLA with 40% BSKP (Ref), PLA+40% BSKP with 5% ELO (1), PLA+40% BSKP with 8% ELO (2) and PLA+40% BSKP with 12% ELO (3) with enlargement of 100.

The SEM-pictures of crosscut of injection-moulded specimens with enlargement of 100 reveal less porosity in 5% and 8% ELO-containing samples than the sample without ELO in Figure 27. The connection between fibre and polymer is tighter and visually there are less pull-outs of fibres which can be seen in pictures 1 and 2 in Figure 27. With an ELO amount of 12% the porosity in the matrix seems to increase even though the fibre-polymer connection is good.

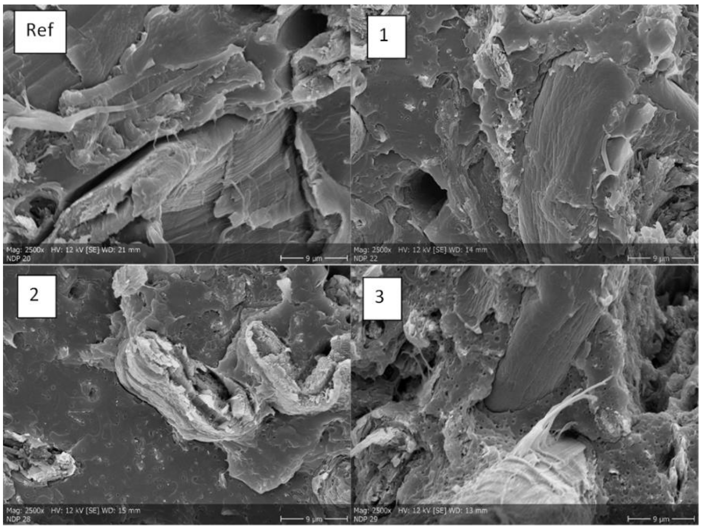

Figure 28: SEM-pictures of samples PLA with 40% BSKP (Ref), PLA+40% BSKP with 5% ELO (1), PLA+40% BSKP with 8% ELO (2) and PLA+40% BSKP with 12% ELO (3) with enlargement of 2500.

Figure 28 shows the improved connection between fibre and polymer in all ELO containing PLA-BSKP composites. The increasing ELO content in composites caused some porosity in the PLA matrix, which can be seen as small circular pores and quite clearly in composites containing 12% ELO on fibre (picture 3). There are two explanations causing those small pores, which still need to be clarified by further studies. The most probable explanation is that with increasing hydrophobicity in the fibre-polymer interface due to increasing ELO amount the moisture migrates out from the interface to polymer melt during processing, but is stuck on polymer causing small pores. This entrapping of moisture to polymer is supported by the increased melt viscosity of the material with higher ELO contents as presented in work described in Paper I. In the second explanation, there is an excess of ELO, which has not reacted, but stays in a separate phase as small pores in PLA. However, ELO is compatible with PLA and should not stay as a separate phase inside a PLA matrix. From a processing point of view, this increased porosity of the composite material is stating challenges related to better drying of fibres, which contain reactive vegetable-oil based additives, and improved mixing and moisture removal conditions during compounding.

In work described in Paper IV, was studied the effect of fibre moisture content in PLA composites. The moisture is known to act as a plasticiser for cellulose fibre (Salmen 1982), but is not very compatible with hydrophobic PLA. The increasing moisture content of BSKP fibre can be seen as increasing gaps and fibre pull-outs in SEM pictures in Figure 29. Results for composites with increasing moisture content show that if the fibre is dried properly to a moisture content well below 1% and possibly to below the 250 ppm suggested for PLA, a better connection between fibre and polymer can be obtained

(NatureWorks 2018). The gap between fibre and polymer can be minimised, which is reflected mainly as improved impact properties of the composite. It is however industrially very energy consuming to get out all the residual moisture which can even be located in between the fibril structure of the cellulose fibre.

When the moisture is present in fibre and causing gaps, it is even more important to find suitable coupling agents able to connect fibre and polymer together in composite materials. It is even better for mechanical performance, if the coupling agent is acting as a fibre-dispersing additive and is also able to fill the gap between fibre and polymer, which is how ELO behaves.

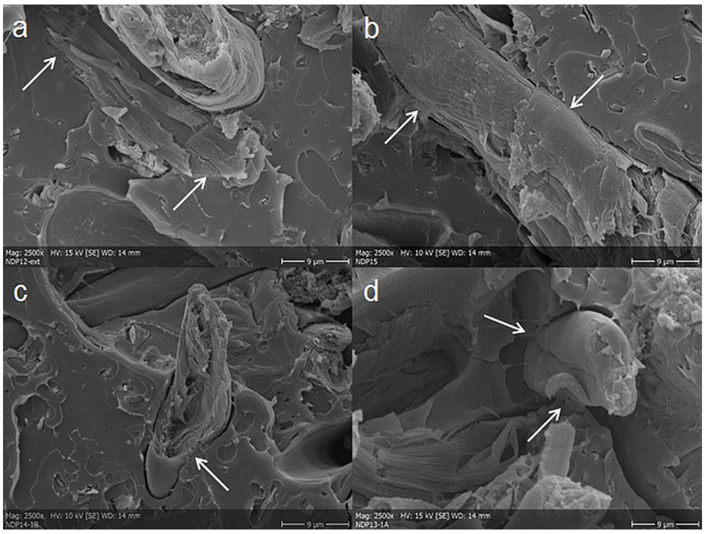

Figure 29: SEM-pictures of samples PLA+30% BSKP with 1% moisture (a), 3% moisture (b), 16% moisture (c) and 25% moisture (d) in fibre at the beginning of compounding. Pictures with enlargement of 2500. The arrows indicate fibre-polymer interfaces.

The gaps in the fibre-polymer interface were also found out in PLA-birch pulp composites, where the fibre was dried to fibre moisture content below 2% and presented in Figure 30 and in Paper V.

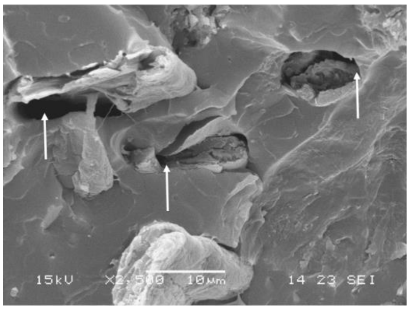

Figure 30: SEM-picture of PLA-birch pulp (20%) composite with the enlargement of 2500. The arrows indicate the gap in polymer-fibre interface.

5.3 Thermal performance

The results of how the thermal resistance and melting behaviour of the PLA-BSKP composite materials is affected by the addition of ELO is presented in Table 11.The results are from work described in Paper I.

Table 11: HDT and DSC results from PLA-BSKP composites with and without ELO and in BSKP fibre content 40%. At melting temperature (Tm) the bigger melting peak is marked as bold.

Sample	HDT		DS C			
	°C	s.d.	Tg, °C	ΔH, J/g	Tm_1 / Tm_2 , °C	Tc, °C
PLA 3052D	58.4	0.8	60.6	-39.34	**148.4** / 154.0	56.6
PLA-BSKP	56.6	0.8	60.4	-28.01	150.5 / 157.1	56.2
PLA-BSKP-ELO(5%)	54.1	0.9	56.0	-26.61	149.6 / **156.8**	51.0
PLA-BSKP-ELO(8%)	52.4	1.0	52.8	-26.05	147.8 / **156.1**	50.3
PLA-BSKP-ELO(12%)	51.4	0.9	48.0	-23.94	- / **155.6**	48.3

Both HDT and DSC results are showing decreasing temperatures and melting enthalpy (ΔH) in correlation with fibre addition to PLA and increasing ELO content.

The BSKP fibre addition to PLA is already causing a slight decrease on PLA thermal resistance, which can be seen as a roughly as 2°C drop in HDT results (from 58.4ºC of neat PLA to 56.6ºC) and minor reduction in Tg and Tc. During the HDT test, there is a load (1.8 MPa) applied to the middle of sample and when the polymer matrix starts to soften the sample starts to bend. If there is no connection between fibre and polymer and even a gap in interface, the material starts to bend at lower temperature. In DSC analysis there is no stress applied on sample, so the effect of increasing temperature is smaller. The higher drop in melting enthalpy (ΔH) is more related to the amount of melting material, which is only PLA in a reference sample and PLA+ELO in the samples containing ELO. The fibre addition to PLA is however causing a 1.5 to 2% increase in the melting temperature of PLA, which is related to limited polymer chain mobility during melting due to the presence of fibres.

When ELO is introduced to the composite, the HDT results show an increasing drop in correlation with ELO amount, a 9% drop with ELO amount of 12% in fibre and a 4.6% drop with the ELO amount of 5% in fibre. Even though the ELO is coupling the fibres and polymer together, it is acts as a plasticiser to both PLA and cellulose fibre (Buong et al. 2014, Miao et al. 2014). This plasticising effect and increased soft material amount in composite is dominating the mechanical changes under elevated temperature over the fibre-polymer coupling effect.

In DSC results, the plasticising effect of ELO can be seen as decreased glass transition (Tg) and crystallisation temperature (Tc). Tg of PLA with 40% BSKP is 60.4ºC with a 5% ELO addition the reduction of Tg is 7% and with 12% ELO, the addition of fibre in the reduction in Tg is 20%. The changes in Tc are at the same level as Tg. During composite melting the presence of ELO changes the double melting peak towards a higher temperature peak (Tm_2) simultaneusly decreasing it by 1.5°C from 157.1°C to 155.6°C without and with 12% of ELO on fibre respectively. The increase of higher melting peak temperature (Tm_2) due to fibre addition indicates the slightly increased crystallinity of PLA, which is also found in other studies (Pilla et al. 2009, Kamthai and Magaraphan 2015). The introduction of ELO connects fibres and polymers together, which still increases the crystallinity, but at the same time plasticises the polymer, which can be seen as a Tm_2 shift to lower temperature presented also in literature (Chieng et al. 2014).

The long-term temperature resistance was studied for the same samples as in work presented in Paper I in a Bachelor’s Thesis (Rauta S.-T. 2018). An aging test was performed for these PLA-BSKP samples without ELO and with 5%, 8% and 12% ELO applied to fibre. The samples were kept in a climate chamber at 50°C and 80% relative humidity for six weeks. Tensile and impact strength were measured from the samples after a two-week and six-week aging period. It was found that in PLA-BSKP samples with 40% fibre content and without ELO, the impact strength dropped from 13.1 kJ/m2 to 7.0 kJ/2 corresponding to a 43% drop in six weeks. With 5% ELO in fibre, the impact strength drop over the course of six weeks was 11%, from 16.5 to 14.5 kJ/m2 and with 12% ELO the drop was only 1.2%. The tensile strength dropped in PLA-BSKP samples without ELO by 47.7%, from 75.8 MPa to 39.6 MPa. When ELO was added in amount of 5% on fibre, the tensile strength drop was 27% from 80.7 MPa to 58.7 MPa. With 12% ELO addition on fibre, the tensile strength drop was 24.5% from 75.1 MPa to 56.7 MPa. The ELO addition to PLA-BSKP composites is stabilising the composite through fibre polymer coupling. This is reflected as more stable impact and tensile strength properties even when the composite is exposed to temperature close to composite Tg and increased humidity during a six-week period. This stabilisation was, however, not reflected to stiffness or tensile modulus (Auto Young) result. The drop in modulus was 15.8% without ELO, 17% with a 5% ELO on fibre, and 16.5% with 12% ELO on fibre. This is because the ELO is also acting as plasticiser and the increased ELO amount eliminates the potential effect stiffening, which is coming from fibre-polymer coupling. The stabilisation of the composite due to improved fibre-polymer coupling properties is suggesting that in fibre polymer composites the coupling is essential for retaining the mechanical properties during a product's life time. ELO as a coupling agent is suitable for that purpose in amounts of over 5% in fibre.

5.4 Analytics - Coupling of materials

The FTIR spectra was analysed for BSKP fibres extracted from the injection moulded test bars in work described in Paper I. Free PLA, which was not connected to fibres, was dissolved out before analysis using Soxhlet-extraction and hot chloroform. The results are combined in Figure 31.

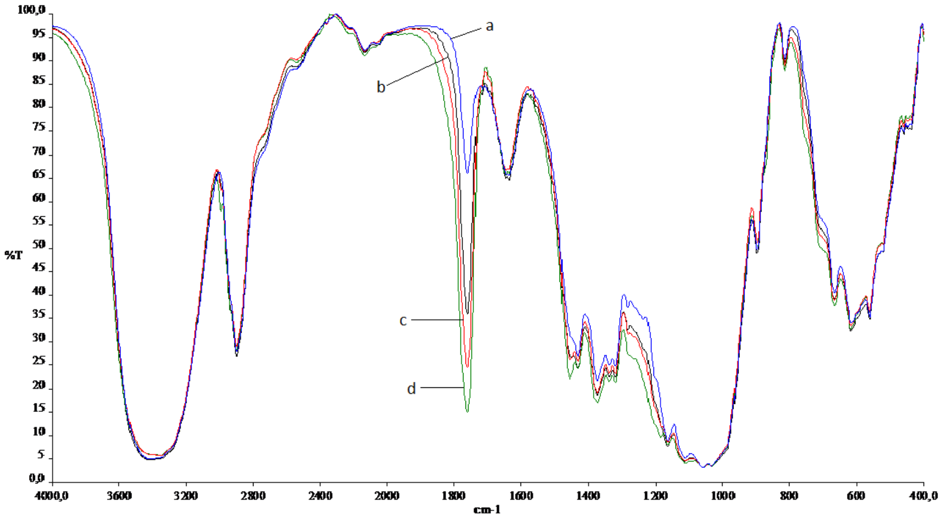

Figure 31: FTIR-spectra of cellulose samples after dissolving out the loose PLA. Spectrum a) is PLA with 40% BSKP (Ref), b) PLA+40% BSKP with 5% ELO, c) is PLA+40% BSKP with 8% ELO (2) and d) is PLA+40% BSKP with 12% ELO.

FTIR-spectra in Figure 31 is compared cellulose from injection-moulded samples with samples where ELO was used. With ELO there can be found increasing response in peaks 1200-1300 /cm, 1375 1/cm, 1450 1/cm and 1760 1/cm as correlation with the increasing amounts of ELO used in compounds. All those peaks can be linked to ELO or increasing amounts of ELO connected to the fibre. The one, which is proving the presence of ELO instead of PLA is peak 1450 1/cm coming from CH_2 vibration and the most CH_2 present in the materials used is in fatty acids of ELO as presented in Figure 31. The other increasing peaks can also be originating from PLA are CH_3 vibration in 1375 1/cm, peak area 1200-1300 1/cm from C-O vibration and peak 1760 1/cm coming from ester C=O vibration (Fan et al. 2012, Hayes et al. 2014). The high increase in peak 1760 1/cm is because esters are present in both ELO, in connection between ELO and PLA and in PLA. It should be absent from a reference sample, containing only BSKP fibre, but it is possible that some residues of PLA is still present on fibre even if it is dissolved and washed out before analysis. During extraction process of PLA from fibre for FTIR analysis, the free ELO is also removed. However, the increasing amount of ELO and PLA on fibre surface proves the true fibre-polymer connection provided by ELO and presented as reaction schema in Figure 32.

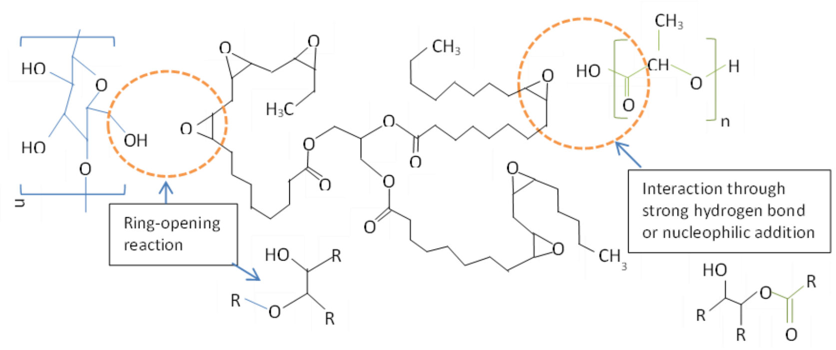

Figure 32: Suggested reaction schema for cellulose fibre PLA coupling with epoxidised linseed oil (ELO).

According to the reaction schema in Figure 32 the coupling between cellulose, ELO and PLA can be seen in FTIR as increased ester carbonyl peaks and increased amounts of CH_3 and CH_2, which was proved and presented in Figure 31.

In ELO the double bonds of linoleic oil, α-linolenic oil and oleic acid are epoxidised to contain several oxirane rings able to further react with cellulose and PLA at elevated temperature. According to the literature, presented in Paper I, the epoxy reaction can take place at 115-136ºC and at higher temperatures it should occur in only minutes (Doszlop et al. 1978). The oxirane ring is able to react in slightly acidic condition at 180°C through nuclephilic substitution (S_N1) mechanism (McGraw-Hill, 2000). At room temperature hexane dissolved epoxidized soy oil has been attached on cellulose paper surface with stannous chloride catalysed reaction in 30 minutes (Huang et al. 2017). According to the literature and the FTIR results, it is suggested that at temperatures over 180°C used in processing and under ten minutes´ time in process, the reaction between cellulose, ELO and PLA has took place. The coupling effect of ELO was proved, but the percentage of reacted ELO was not studied more closely.

5.5 Summary of results

As a summary of findings made in research related to the ELO addition on PLA-fibre composites is collected a Table 12. It shortly presents the positive (+) and negative (-) effects of ELO even though the coupling of fibre and polymer matrix is proved.

Table 12: The positive and negative effects of ELO in PLA-fibre composites.

Effect of ELO in PLA-BSKP composite	Effect
Fibre-polymer connection	+
Fibre dispersion	+
Tensile strength	+
Stiffness	+
Impact strength	+
HDT	-
Composite colour	+
Renewable based raw materials	+
Material processing	-
Suitability to normal injection moulding and extrusion	+
Composite material aging	+

6 Conclusions

Materials based on renewable raw materials are gaining more importance in several injection moulded applications. PLA is one of the main bio-based commodity polymers. The addition of natural or wood-based fibres to PLA brings stiffness to the composite, reduce the costs, lower the carbon footprint, provide special visual look and haptic feeling and compared to glass fibres less abrasion in process and safe materials to use. The introduction of ligno-cellulosic fibres have challenges related to fibre-polymer interface, which is reflected mainly as decreased impact strength. To give a real reinforcing ability for the short fibres a proper bonding is needed between fibre and polymer enabling the stress transfer without cracks over the material in PLA composites containing mainly fibres below critical fibre length, which is one aim to show in this work.

To create totally renewable-based composite materials novel renewable-based additives are also needed. One aim of this work is to prove that vegetable-oil based additives can be used as effective plasticiser-coupling agents in short fibre composites. Good candidate is epoxide-functional linseed oil (ELO) with high linolenic acid content enabling a high degree of reactive epoxide groups. The use of long alkyl chain plasticisers improves the mobility of polymer chains during cooling and can fill up the gap between fibre and polymer and enable better fibre dispersion. If these plasticisers also have reactive groups, as ELO do, they can couple fibres and polymers together providing improved performance for the composite.

This thesis is based on five papers summarizing research of PLA-fibre composites with bleached softwood kraft pulp (BSKP) presented in Papers I and IV, birch pulp (BP) in Paper V, nanocellulose (CNF), high consistency nanocellulose (HefCel), microcellulose (MC) presented in Paper II and hemp fibre, hemp pulp, hemp shives, oxidized shives, hemp dust and softwood pulp presented in Paper III. ELO is used in work described in Papers I and II. The processing methods used were compounding of fibres and PLA with a twin-screw compounder followed by injection moulding. In work described in Papers I, III, IV and V, the fibres were treated before compounding using a special compacting method presented in Immonen et al. 2011.

The characterisation of material was made visually, using SEM, by mechanical tests (impact and tensile strength), and thermal analysis using HDT and DSC. Analytical studies such as melt viscosity of the compounds and fibre length and FTIR of the fibres extracted from injection-moulded test bars were made. The hypothesis was that if the reaction between fibre and polymer has taken place, it should be seen as improved mechanical performance, improved fibre-polymer coupling and increase in melt viscosity of composite material. The FTIR should show the bonding of ELO on PLA and a fibre surface through ester coupling and increased amounts of CH_3 and CH_2 groups on a fibre surface.

The simultaneous increase in tensile strength and Charpy impact strength compared to neat PLA was found for PLA composites containing 5% ELO on BSKP fibre with fibre content 40%, and 10% ELO on HefCel and MC fibres with fibre content 5 % indicating a real connection between fibre and the polymer matrix. A similar effect was found with hemp pulp, which is because the fibre length distribution in hemp pulp has a significant amount of fibres over critical fibre length enabling some reinforcing effect without coupling agents. The fibre length in BSKP, nanocelluloses and MC was all below critical fibre length in injection-moulded composites. However, it must be taken account that the fibre length of ligno-cellulosic fibres is a wide distribution and the fraction of each size class has effect of its own and follows the theoretical rule of mixture. This closer examination of different fibre size fractions is not included in this study. Also, the closer examination related to fibre aspect ratio was excluded from this study.

The visual characterisation of test bars showed improved dispersion of HefCel in PLA due to ELO addition. The SEM-pictures for nanocelluloses (CNF and HefCel) and MC showed a tighter connection between fibres and PLA in composites where ELO is used. Visual characterisation of PLA-BSKP composites shows less colour formation in materials containing ELO than without. Even though the melt viscosity increased with increasing ELO content, the colour is lighter in those compounds. Cellulose in high temperatures is degraded by acids coming from PLA, but the presence of ELO reduces the degradation of cellulose and gives a lighter colour to the product, which supports the use of ELO in fibre-PLA composites with fibre contents over 30%.

SEM-pictures for PLA-BSKP composites with increasing moisture content showed that with proper drying and a fibre are moisture content below 1 %, a better connection between fibre and polymer can be obtained. When the moisture is present in fibre and causing gaps, it is even more important to find suitable coupling agents to be able to connect fibre and polymer together, enable better fibre dispersion and also fill the gap in between fibre and polymer, which is how ELO is acting.

Increasing hydrophobicity in the fibre-polymer interface due to increasing ELO amount and increased melt viscosity is causing small pores in PLA matrix. From a processing point of view, this is stating challenges related to better drying of fibres containing reactive vegetable oil based additives, and improved mixing and moisture removal during compounding. The optimal ELO amount on fibre is, according to this study, below 8 %.

Temperature performance such as HDT and Tg of the ELO containing composites is lower than in just BSKP fibre containing PLA composites due to plasticising effect of ELO supporting the use of ELO in lower amounts (e.g. 5%). However, the ELO addition stabilises the composites because of fibre-polymer coupling against long term changes induced by temperature and moisture. The increase in melting temperature indicated increase in PLA crystallinity due to fibre addition and coupling of fibres with PLA. The increased crystallinity, however, will require further study.

The FTIR analysis for BSKP fibres extracted from injection moulded samples showed increasing response in peaks 1200-1300 /cm (C-O), 1375 1/cm (CH_3), 1450 1/cm (CH_2) and 1760 1/cm (ester carbonyl) as correlation to an increasing amount of ELO used in compounds proving the true fibre-polymer connection provided by ELO and presented as reaction schema in Figure 32. The coupling effect of ELO was proved, but the percentage of reacted ELO was not more analytically studied.

As final conclusions, the use of renewable-oil based additive, epoxidised linseed oil in PLA-ligno-cellulosic fibre composite is recommended. However, more research is needed related to the thermal resistance of the product, which limits the upper use temperature to 50°C. Further, the treatment of fibres adds two processing steps to manufacturing; introduction of additive to fibres and compacting of fibres to a form suitable for plastic processing.

The current research stated questions which remains open and initiated ideas of how to proceed in the studies with natural oil-based additives. There are open questions regarding the real cross-linking degree of fibre and polymer and the optimisation of additive amount even though this research gave an indication of how much ELO is needed on fibre to provide a good bonding. Those studies could be proceeded using NMR-analytics. With nanocelluloses the increase of dispersion should be more thoroughly studied, for example, by TEM-analytics to see the real dispersing effect of ELO. The limitations in thermal resistance of the material could be improved by selecting a PLA grade with higher temperature resistance or by using stereocomplexing approach by adding PDLA and chain extenders to the compound. Additionally, the increase of PLA nucleation speed through mineral nucleation additives such as talc or nanosilica in combination with ligno-cellulosic fibre could help to increase the HDT.

It is now proved that high linolenic acid containing ELO can act as combined plasticiser coupling agent in ligno-cellulosic fibre PLA composites. However, other renewable based oily additives also can be considered. In a study at VTT, was found that epoxy modified tall-oil is a potential wood-based additive to composites (Immonen et al. 2011). That study should be continued together with industry in aim to get a wood-based additive instead of a field-based on the market. Another approach for wood-based coupling agents could be functionalised lignin as a glue between fibres and PLA to simulate an artificial wood.

In injection moulded and extruded composites ligno-cellulosic fibres are degraded during processing due to friction and heat. To study of how to retain the fibre length in wood and natural fibre-based composites should be continued. One approach would be to introduce plasticising and coupling agents to fibre network using a foam-forming technique followed by cutting pellets suitable for injection moulding. Another way could be to protect fibres from breaking through internal cross-linking and strengthening of fibres.

The modelling of composites is a good tool to minimise the amount of trials. However, to create a good model that also enables the simulation of composites with additives, a lot of work will be needed. So one of the further works is to create better models based on the real research results. Therefore, an understanding of the phenomena in the fibre-polymer interface is crucial.

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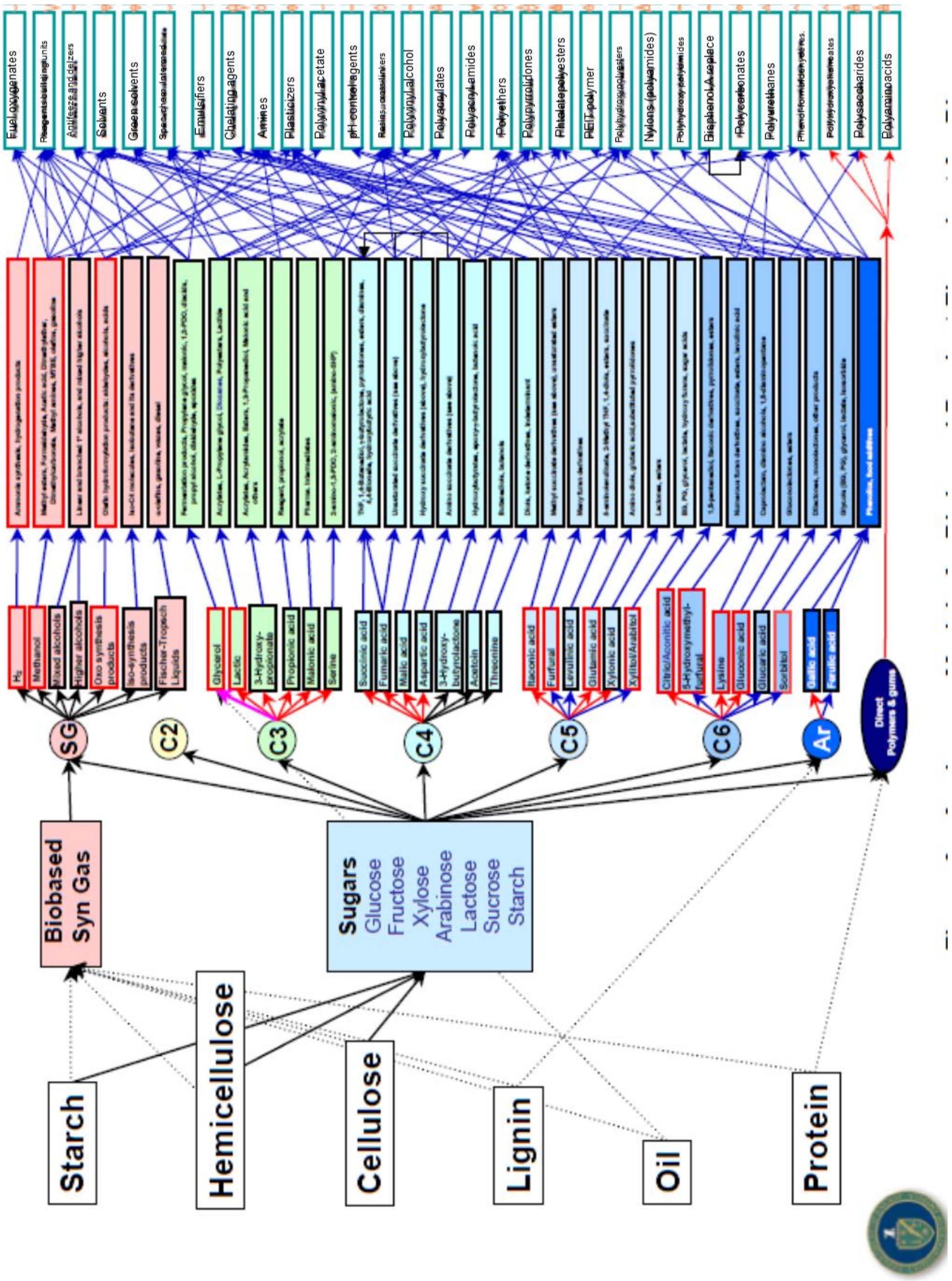
Appendix A: Renewable chemical platform, biobased chemicals and raw materials (Werpy & Petersen 2004).



Publication I

Immonen, K., Wikström, L., and Anttila, U.

Coupling of PLA and bleached softwood kraft pulp for enhanced properties of biocomposites

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Publication II

Immonen, K., Lahtinen, P., and Pere, J.
Effects of Surfactants on the Preparation of Nanocellulose-PLA Composites

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Publication III

Immonen, K., Lahtinen, P., Isokangas, P., and Torvinen, K.
Potential of Hemp in Thermoplastic Biocomposites - The Effect of Fibre Structure
Conference article from ICNF2016

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Publication IV

Virtanen, S., Wikström, L., Immonen, K., Anttila, U., and Retulainen, E.
Cellulose kraft pulp reinforced polylactic acid (PLA) composites: effect of fibre moisture content

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Publication V

Sippola, M., Immonen, K., Miettinen, A., Laukkanen, A., Andersson T., Peltola, H.,
Harlin A., and Holmberg, K.

Predicting stiffness and strength of birch pulp - Polylactic acid composites

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