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WOOD-FIBER REINFORCED BIO-POLYMER COMPOSITES AS ALTERNATIVE MATERIALS FOR INDUSTRIAL APPLICATIONS

Master of Science Thesis

Examiner: Assistant Professor Essi Sarlin
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ABSTRACT

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Wood-fiber reinforced bio-polymer composite (WFRBC) emerges as a promising material for many industrial applications due to its attractive properties. This work aims to evaluate the thermomechanical performance of WFRBCs, their benefits as alternative materials towards oil-based composites, current challenges, and potential applications within the automotive and construction industry.

This thesis is divided into four sections. The first covers the state-of-the-art of composites from raw material, fiber surface modification and processing technologies' point of view. In sequence, the second section discusses the importance and potential of switching traditional composites for bio-based composites within the automotive and construction industry, as well as their relevance related to WFRBCs. The third section includes the state-of-the-art of thermomechanical properties analysis by standardized testing methods. Lastly, bio-composites application cases found in the literature were selected, for performance evaluation mainly based on thermomechanical properties. The main benefits of bio-composites for replacement of traditional composites mainly made of synthetic reinforcements and polypropylene (PP) matrix were investigated. The composite performance analysis was performed focusing on its mechanical properties (tensile strength, tensile stiffness, flexural strength and impact strength) as well as the composite thermal stability.

From the performance evaluation of the WFRBCs considered in this work and their potential to replace traditional composites, promising results that confirm the possibility of switching traditional oil-based composites to this class of bio-composites were found. In this context, WFRBCs have shown competitive and, in some cases, even better mechanical properties in comparison with glass fiber PP composites that are extensively used in the automotive and construction industry.

PREFACE

The thesis was developed under Tampere University of Technology (TUT) collaboration and supervision. The topic was chosen according to imminent demand of bio-based materials development to support the circular economy context and their potential applications within the modern industry. The work involved thorough research related to the state-of-the-art of bio-composites, analysis of relevant industrial applications and performance evaluation based on the most recent results found in the literature.

Many people have supported me along this journey, and I would like to thank them all. First of all, my family for their love, endless support and encouragement. Secondly, I also want to thank my thesis supervisor and examiner, Mrs. Essi Sarlin, for all thesis guidance and revision reading. In addition, I wish to thank Dr. Jouni Lyly-Yrjänäinen, who has supported me since the beginning of my studies at TUT. I also owe a lot to Mr. Hannu Lepomäki, for all the guidance and mentoring over the past months.

After a fruitful and interesting journey, full of personal and professional growth, this work has substantially confirmed for me the potential of bio-composites to support the world's increasing demand for renewable materials, as well as to offer a better world for the next generations based on technology and innovation.

Tampere, 10.12.2018

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

ACF	Activated carbon fiber
APP	Ammonium polyphosphate
BKHF	Bleached kraft eucalyptus fiber
CB	Carbon black
CONE	Cone calorimeter
ECCs	Engineered cementitious composites
FRCCs	Fiber-reinforced cementitious composites
FRP	Fibre reinforced polymers
DNA	Deoxyribonucleic acid
FRC	Fiber reinforced composite
GP	General purpose
HB	Hardboard
HP	High-performance
HHR	Heat release rate
MPDI	Poly (*m*-phenylene isophthalamide)
ODA-PPTA	Copoly (*p*-phenylene-3,4-diphenyl ether terephthalamide)
PAEK	Polyaryletherketone
PAN	Polyacronitrile
PB	Particleboard
PE	Polyethylene
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBHx	Poly (hydroxybutyrate- co-hydroxyhexanoate)
PHBO	Poly (hydroxybutyrate-co-hydroxyoctanoate)
PHBOd	Poly (hydroxybutyrate-cohydroxyoctadecanoate)
PHBV	Poly (hydroxybutyrate-co-hydroxyvalerate)
PLA	Poly (lactide acid)
PP	Polypropylene
PPTA	Poly (*p*-phenylene terephthalamide)
PMC	Polymer matrix composites
PVA	Polyvinyl alcohol
PVAc	Poly vinyl acetate
PVC	polyvinyl chloride
RD	Random orientation
RNA	Ribonucleic acid
RTM	Resin-transfer molding
SEM	Scanning electron microscopy
SVM	Poly [5-amino-2(*p*-aminophenyl) benzimidazole terephthalamide]
UD	Unidirectional
VARTM	Vacuum Assisted Resin Transfer Molding
WFRBC	Wood-fiber reinforced bio-polymer composite

1 INTRODUCTION

Bio-composites have played an essential role in the industry by offering alternative materials for replacement of exclusively petroleum-based feedstock in a wide range of industrial segments, following the world's need towards sustainable, eco-efficient and environmentally friendly materials, products and processes. Wood-fiber reinforced bio-polymer composite (WFRBC) emerges as a promising material for many industrial applications due to its attractive properties. Throughout this thesis, the term "bio-composite" refers to fully bio-based composites.

Over the past years, the composite industry has developed several materials mainly made of glass, carbon and aramid fibers embedded on epoxy or unsaturated polyester resin matrices, for automotive, sports, aerospace, and building and construction applications. Recent studies and advances towards bio-fibers together with the new bio-polymer approach have been explored with the aim of meeting the industry demands concerning material requirements as well as tackling current environmental issues in relation to carbon footprint, degradability and waste-disposal.

Natural cellulose fibers are non-man-made materials available worldwide in the form of bast, seed, grass and reed fibers as well as other varieties such as wood and roots. It has been reported that natural fibers are environmentally friendly and low-cost materials capable of replacing and even achieving better properties than conventional synthetic fibers. Low weight, full biodegradability, low cost, low carbon footprint, relatively high specific mechanical properties, are among others, interesting aspects supporting the importance of this raw material in the composite industry. By contrast, high moisture absorption from the surroundings and low surface adherence to the matrix, for instance, are still drawbacks in the bio-composite development, making it weaker and more fragile. [1]

Recently, the development of bio-polymers has been an outstanding achievement for the modern industry. Bio-polymers have emerged as potential alternatives to replace fossil-based polymers, and some of them are available commercially while others remain under research. This class of materials is defined as naturally occurring long-chain molecules, as well as materials which have been derived from bio-based monomers. Most of these will also be biodegradable although this is not necessarily the case. A bio-polymer made from renewable resources which will biodegrade can appear to solve the significant problems associated with plastics and supports the composite industry need for alternative raw materials. When analyzing the whole value-chain of bio-polymers, the mitigation of environmental impacts boosts their industrial applicability nowadays. In consequence, bio-polymers arise as an alternative solution for replacement of conventional and petroleum-based thermoplastics (i.e., polyvinyl chloride, polypropylene, etc.), and thermosets (i.e., epoxy, unsaturated polyester and phenolic resins, etc.) as the matrix phase in composite applications. We can outline cellulosic plastics, polyvinyl alcohol (PLA), starch plastics, and soy-based plastics as competitive bio-polymers for composite applications. However, performance limitations, high production cost, demand for high production scales and degradability, are still hurdles to be overcome to increase their acceptance in the market. [2,4]

Despite the advances in the composite world over the past decades, continuous development of renewable materials and the clear demand for bio-based products in our society, the establishment of bio-composites based on economic, industrial and scientific aspects is still of great relevance. This work aims to evaluate the thermomechanical performance of WFRBCs, their benefits as alternative materials towards oil-based composites, current challenges, and potential application within the automotive and construction industry. Initially, the work consists of literature studies of natural fibers, focused on wood-based fibers, and bio-polymers. Secondly, fiber surface treatment methods and composite processing technologies will be exploited together with the challenges that researchers have faced over the past decades to make the bio-composite concept a reality. In sequence, a thorough assessment of the automotive and construction industry is discussed, by covering raw materials' requirements, market analysis and the potential of WFRBCs in these segments. The work also includes the state-of-the-art of thermomechanical properties analysis by standardized testing methods. Lastly, the potential of WFRBCs to replace glass fiber PP composites from the thermomechanical performance's point of view is also discussed.

2 STATE OF THE ART OF BIO-COMPOSITES

Composite materials have been used widely in many segments due to the demand for specific properties and materials performance in a multitude of industrial applications, such as automotive and aerospace industry. Their structure, which is primarily formed by two or more different materials, ensures the manufacturing possibility of several products capable of meeting broad end-users' requirements. The composite structure consists mainly of the matrix and the reinforcement phases, in addition to several other fillers and additives. The matrix phase deploys relevant functions: reinforcement phase protection and stress distribution among reinforcement materials. Whereas, the reinforcement phase ensures high mechanical properties, such as stiffness and tensile strength according to predefined directions. With respect to the final composite properties, these are determined according to the matrix and reinforcement phase chosen, geometry, processing technologies, surface adherence between the two phases, and resources volume content [3].

2.1 Conventional polymers overview

Oil-based polymers have historically played an essential role in the composite industry. Even though there is a clear demand for new renewable resources, this material group is still the primary resource of composite reinforcements and matrix phases.

Polymers are chemical components with long-chain molecules of repetitive units with similar identity. We can find several types of polymers in nature, such as cellulose, whereas synthetic polymers, such as polystyrene, polyethylene, and nylon, have been used extensively to produce a wide range of products lately. In this context, the word "*plastics*" are broadly used in industrial and commercial purposes for the materials derived from synthetic polymers. Thousands of new polymers have been synthesized over the past years, and thanks to the future demand for new materials for specific applications, the polymer variety tends to increase sharply. Among all the polymers classification, this class of material is often divided into two groups, based on their manufacturing processing characteristics or type of polymerization. It is also relevant to define thermosets and thermoplastics, that are the two polymers groups classified based on their thermal processing behavior. Thermoplastics are those polymers which can obtain pre-defined forms under heat applications, and any residues from manufacturing processes might be recovered for reutilization after temperature and pressure exposition. Polystyrene, polyolefins (e.g., polyethylene and polypropylene), among others, are notable examples of thermoplastics. By contrast, thermosets are polymers, in which their chain molecules are chemically linked by covalent bonds, formed mainly along the polymerization manufacturing phases, and by other chemical or thermal treatments. Once the thermoset polymer is formed, the structure is heat, softening, creep, and solvent attack resistant.

These properties assure proper performance for composites applications. Epoxy, phenol-formaldehyde resins, and unsaturated polyesters are prime examples of thermosets [5]. In parallel with the previous polymer classification, Figure 1 illustrates another polymer group definition based on the raw-material resource.

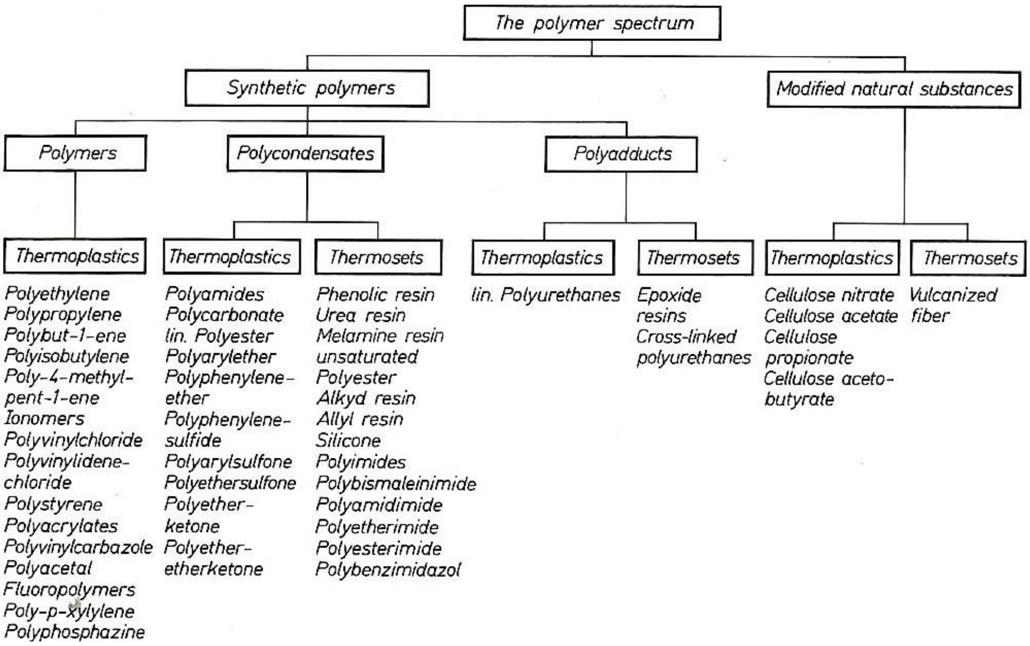

***Figure 1:** The polymer spectrum [6].*

In consequence of the composites classification available, when taking into account the matrix phase, composites are divided into three main classes: polymer matrix composites (PMCs); metal matrix composites; and, ceramic matrix composites.

PMCs provide attractive properties in many applications, including light-weight and high-performance, and their matrix plays a vital role in the composite structure. The matrix choice controls processability, upper use temperature, and flammability and corrosion resistance. Even though the reinforcement phase supports the external load, the composite performance also relies on the matrix modulus and failure strain, and the adherence ability between the reinforcement and the matrix. Unsaturated polyester and epoxy resins have been used as the primary matrix phases for composites applications. In some cases, the utilization of preformed and reinforced matrices, as long as it has been stored under proper conditions, i.e. compounded materials, has optimized some of the composite processing technologies available as exploited further in this work. The reduced volumetric shrinkage during the cure and excellent mechanical properties are other advantages in relation to epoxy resins for composite applications. Furthermore, phenolic resins also ensure good properties as composite matrices, especially when the end-product requires high flammability control, such as in aerospace and automotive industry. Thermoplastics demand has also increased for matrix application due to the following aspects: short processing time, allowing high production volume; better tolerance than thermosets; allowed for welding applications; better recyclability. However, its high processing temperature and viscosity are still drawbacks for thermoplastics applications in the composites development, especially by limiting the utilization of thermoforming or pultrusion processing technologies. [3]

2.2 Composite classification based on the reinforcement phase

The composites classification is based on the reinforcement and matrix phase nature. As stated before, most of the matrix phases are thermoset- or thermoplastic-based. Scientifically and commercially, it is common to classify the composites based on their sort of reinforcement phase and reinforcement orientation. The two main classifications based on the reinforcement phase are fiber reinforced composites (FRC) and particle-reinforced composites, see Figure 2. FRCs are reinforced by natural fibrous materials such as linen, wood-fibers, cotton fibres, etc., or synthetic fibers mainly in the form of glass, carbon and aramid fibers. Whereas, particle-reinforced composites have no defined shape for the reinforcement phase and it is usually made of fillers or a blend of fillers and fibers. Nowadays, the primary sort of reinforcements are fibers, particulates and whiskers materials [7, 24]. Structural laminates composites are built up by a stack of thin layers of reinforcements, each with different orientation, which are placed symmetrically above a center line, whereas sandwich panels composites consist of thin, stiff and strong layers of metallic or fiber reinforced composites separated by a thick layer of low-density material [69].

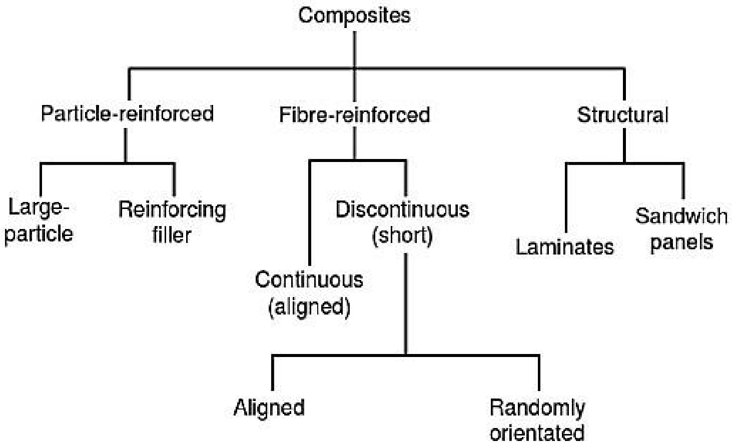

Figure 2: *Classification of composite materials [7].*

Reinforcements are vital components of composites, ensuring high strength, stiffness, high-temperature resistance, and other relevant properties to the final composite structure. The influence of the fibers depends significantly on the fiber length-diameter ratio, the fiber properties themselves, its orientation and the adherence capacity between the fiber and matrix phase [7].

Particulate composites are classified into two groups: large particles reinforced composites and filler reinforced composites. Large particles usually have a particle diameter of 30 µm or greater. The particle scale determines the contact surface area between the particles and matrix phase. By reducing the scale to micrometre or smaller, the contact area increases sharply, affecting the composite interphase positively. In comparison to the physical properties between the particulates and matrix phase, the particles are stiffer and harder than the matrix, playing a relevant role in the mechanical properties of the manufactured composite. Reinforcement fillers are small particles, which are often submitted to surface treatment procedures in order to improve their physical properties as well as the adherence with other materials. However, it should be noted that strengthening a specific feature might affect another one. Recently, the development of nanofillers has also contributed to larger surface contact area, tensile strength and better interaction between the fillers and matrix phase, improving impact resistance and stress transfer of the composite structure. Silica beads, carbon nanotubes, are extensively used in the composite industry as nanofillers. [7]

2.3 Bio-based alternatives for the matrix phase

Over the past decades, the composite industry, supported by materials science advances, has focused on the development of a new approach towards green plastics, or bio-polymers. Even though there is a multitude of synthetic polymers being produced nowadays, polymers are also found in nature, synthesized by plants, animals and microorganisms through biological reactions, or synthesized from renewable resources. The application of bio-polymers within the composite technology is of great relevance, and it is a new source of matrix phases. As the core of this work takes into account bio-based materials as an alternative towards traditional matrices, this section includes a brief explanation of bio-polymers and their properties. This class of material is also obtained from natural resources, and is classified into three main categories: proteins and polypeptides; polynucleotides; and polysaccharides. In parallel with industrial applications, those materials also have a relevant role concerning biological functions, where proteins act as catalysts substrates, polynucleotides control cell replications, and polysaccharides are primarily a sort of skeletal reinforcement in plants as detailed next [5]:

- Polysaccharides are essential materials for nature and the industry itself, including cellulose, starch, and glycogen. They are formed by the condensation of sugar molecules, and their polymerization degree ranges from 30 to 100,000. In the composite industry, starch and cellulosic materials are extensively used as matrix resource.
- Proteins are defined as heterogeneous polymers formed by different types of amino acids of general structure, which can obtain large biological and general performance. In the composite industry, proteins from grains have been used extensively as composite matrix resources.

- Polynucleotides, or nucleic acids, are found in nature in the form of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), the former stores genetic information, whereas the latter is responsible for information transmissions and protein synthesis when considering biological functions.

It is important to mention the degradability aspect of many bio-polymers due to their composition, including oxygen and nitrogen molecules. On the other hand, synthetic polymers, mainly made of carbon-carbon bonds lack these needed properties for sustainable materials. For industrial applications, bio-polymer may be extracted directly from nature, followed by refining procedures, and the material purity degree depends on its end purpose [15]. Starch (polysaccharide), proteins from grains, polyhydroxialkanoates (polyester), and PVA, are discussed intensely nowadays as competitive bio-polymers options to replace non-renewable polymers in the composite industry. Figure 3, illustrates some examples of bio-polymers and their synthetic pathways from the manufacturing point of view.

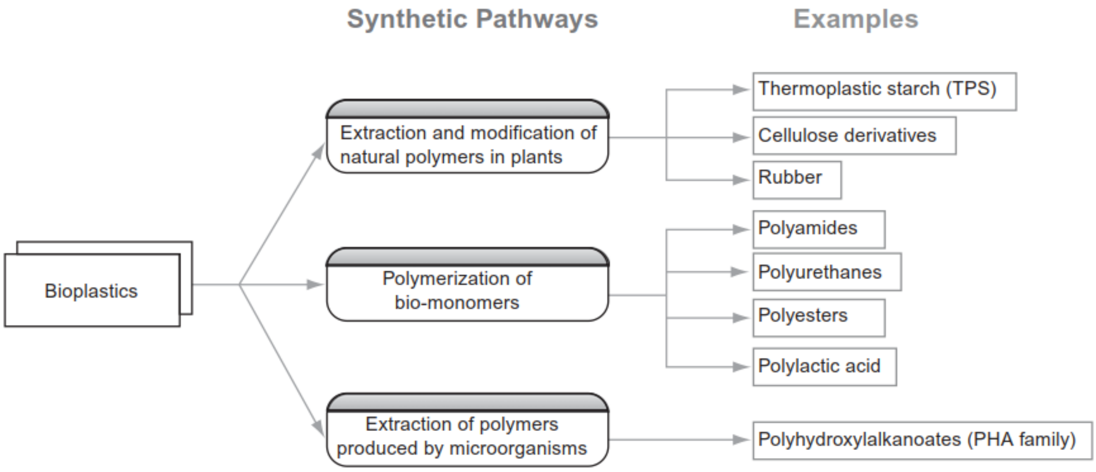

Figure 3: *Flow chart of different pathways to synthesize and examples [68].*

2.3.1 Starch

Starch is polysaccharide extracted from agricultural resources with the general composition $(C_6H_{10}O_5)_n$. The two main polymers forming starch are glucose polymers, amyloses and amylopectin, and their volume content varies according to the starch resource itself. It is mainly found in the form of crystalline granules in seeds, roots, stems, leaves, fruits and pollen grains of higher plants, functioning as the principal form of carbohydrates storage. For starch extraction, the raw materials are initially grinded, milled, for granule separation, followed by washing, centrifuging, dewatering and drying processes. Starch is primarily found as a white powder material, with 98 – 99.5% of purity, which in turns is insoluble in water, ethanol and many solvents [17].

In comparison with most of bio-polymers alternatives for matrix composite applications, Starch arises as inexpensive, abundantly available, non-toxic, biodegradable and compostable material. By contrast, starch's highly crystalline structure results in high brittleness, low strength properties, low thermal stability and retrogradation during storage over a period and high hydrophilicity behaviour. Therefore, it is common to apply starch with plasticizers, such as glycerol, and other polymers, such as PLA, in order to overcome the drawbacks mentioned. Recently, starch and PLA (in some cases clay addition has also been considered) as matrix phase, reinforced by jute fibers, have shown good results in comparison with flax PP composites, when mixing 50% starch and 50% PLA, concerning tensile strength and Young's modulus. When increasing the starch content, an improvement in the flexural strength and Young's modulus of the manufactured composites was noted, which is justified due to the strong interfacial adherence between jute fibers and starch. Good results can also be obtained by reinforcing starch with wood-fibers as covered further in this work. Therefore, attractive composites can be produced by utilizing starch as the main component of the matrix phase. [18, 61]

2.3.2 Poly (lactic acid)

PLA, a biodegradable synthetic polymer, has a key position in the bio-polymers market, being one of the most promising materials to replace high-carbon footprint matrices in the composite industry. Although there are still shortcomings towards PLA, the possibility to combine proper reinforcement fibers, fillers, other matrices, and additives, enhances its applicability as composite matrix. PLA has good mechanical properties (tensile strength, Young's modulus and flexural strength), in specific cases, even higher than conventional polymers such as polypropylene (PP) and polyethylene (PE). This material also offers easy processability and excellent degradability in most products. By contrast, PLA application for high stress loads without deformation is limited, as it is a brittle material and has low elongation at break (less than 10%) and toughness. PLA can be obtained by direct polymerization of lactic acid or by the ring-opening polymerization of lactide (cyclic di-ester). The first route englobes the removal of water by condensation and solvent utilization under high temperature and pressure, producing PLA of low molecular weight. The second route is based on a multistep procedure, which starts with condensation of lactic acid to produce low molecular weight PLA pre-polymer, which is then converted into a mixture of lactide stereoisomers. After the removal of impurities, the "meso" fraction is combined with low lactide fraction, ensuring, therefore, the possibility to produce PLA in several grades. PLA is biodegradable and biocompatible as well as a thermoplastic aliphatic polyester obtained by fermentation of polysaccharides from renewable resources, primarily extracted from corn, potatoes, cane molasses, sugar-beet, etc., ensuring the full biological cycle (biodegradation and the photosynthesis process) as displayed in Figure 4. [16]

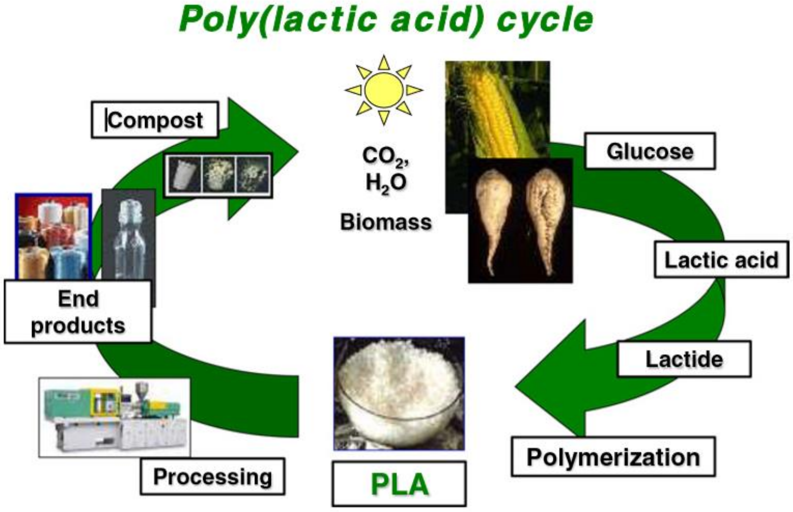

Figure 4: *PLA life cycle starting with sugar-beet and corn [16].*

Within the FRC context, PLA applications as matrix phase are limited by high temperature processing technologies, shearing and hydrolysis. Many natural fibers have been utilized with PLA matrices for composite application, such as flax, knaf, hemp, jute, wood, etc. Concerning the combination between PLA and glass fibers, its final properties are relevant, leading higher tensile and flexural strength in comparison with neat PLA and glass fiber PP composites. Cellulosic fibers, which includes wood-fibers, also emerge as attractive reinforcement towards PLA-based matrix, however the fiber susceptibility to swell due to its high-moisture absorption tendency, and consequently, its weak adherence to the matrix leads to the decrease of the composite’s mechanical properties. Anyhow, it is fundamental to point out the vast possibilities for surface modification of wood-fibers due to the hydroxyl groups on their surface, ensuring, therefore, further properties enhancements as exploited throughout this work. [16]

2.3.3 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are biodegradable polyesters that are obtained from microorganisms. Many microorganisms contain PHAs for carbon and energy storage, and the variety depends on the carbon substrates. Polyhydroxybutyrate (PHB) homopolymer, which is highly crystalline material with similar properties of polypropylene, is the primary variant of PHAs, and emerges as a promising material for the composite industry, being produced without petrochemical resources. By considering the degradability aspect, it is essential to mention the PHA’s rapid decomposition in aerobic, anaerobic, and saline environments. On the other hand, homopolymers also have shortcomings to be overcome such as high brittle behaviour, limited processability compared to conventional polymers due to their melt and thermal decomposition temperature. In order to overcome these issues, many copolymers have been synthesised from PHB such as poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), poly(hydroxybutyrate- co-hydroxyhexanoate)

(PHBHx), poly(hydroxybutyrate-co-hydroxyoctanoate) (PHBO), and poly(hydroxybutyrate-cohydroxyoctadecanoate) (PHBOd). In the composite industry, recent studies have observed consistent improvements of mechanical properties of fiber-reinforced PHB/PHBV composites, where flax fiber; jute fiber and yarn; wheat and rice straw; cellulose and wood-fibers, are among others, the main sorts of reinforcements utilized. In general, fiber-reinforced PHAs composites have high Young's modulus and tensile strength as well as good thermal properties. [19]

2.3.4 Poly (vinyl alcohol) (PVA)

PVA application in the composite industry has also been a remarkable achievement over the past years. PVA is a water-soluble, biodegradable and colorless synthetic polymer produced by polymerization of vinyl acetate, which forms poly vinyl acetate (PVAc), followed by further hydrolysis reactions. Along the hydrolysis reactions, the hydrolysis degree varies according to the extracted acetates groups, influencing the PVA's water-solubility directly [20]. It is important to note the weakness of pure PVA regarding physical-chemical stability and thermal resistance. Therefore, the use of PVA for composite applications is often dependent on PVA modifications such as utilization of silane precursors to modify PVA and form polymer-silica hybrid composites based on Si – O – C and Si – O – Si networks, ensuring better mechanical properties, functional performance and thermal stability [21]. Due to its high hydrophilic behavior, graphene oxides fillers have been used to improve water resistance, mechanical properties, as well as the thermal stability of PVA-based composites. Regarding the types of reinforcements utilized with PVA, the application of cellulosic reinforcements has offered promising results in the composite industry and emerges an alternative solution to replace traditional oil-based composites [22]. Table 1 lists the main physical and mechanical properties of bio-polymers and PP (the values are in range due to difference in literature results), and Figure 5 highlights the specific mechanical performance (tensile strength and stiffness).

Table 1: *Properties of natural polymers in relation to polypropylene [53].*

Polymer	Density (g/cm^3)	Melting Point (T_m °C)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break
Thermoplastic starch	1–1.39	110–115	5–6	0.125–0.85	31–44
PLA	1.21–1.25	150–162	21–60	0.35–3.5	2.5–6
PLLA*	1.25–1.29	170–190	15.5–65.5	0.83–2.7	3–4
PHB	1.18–1.26	168–182	24–40	3.5–4	5–8
PHBV	1.23–1.25	144–172	20–25	0.5–1.5	17.5–25
PP	0.9–1.16	161–170	30–40	1.1–1.6	20–400

*PLLA is the optical isomer of PLA.

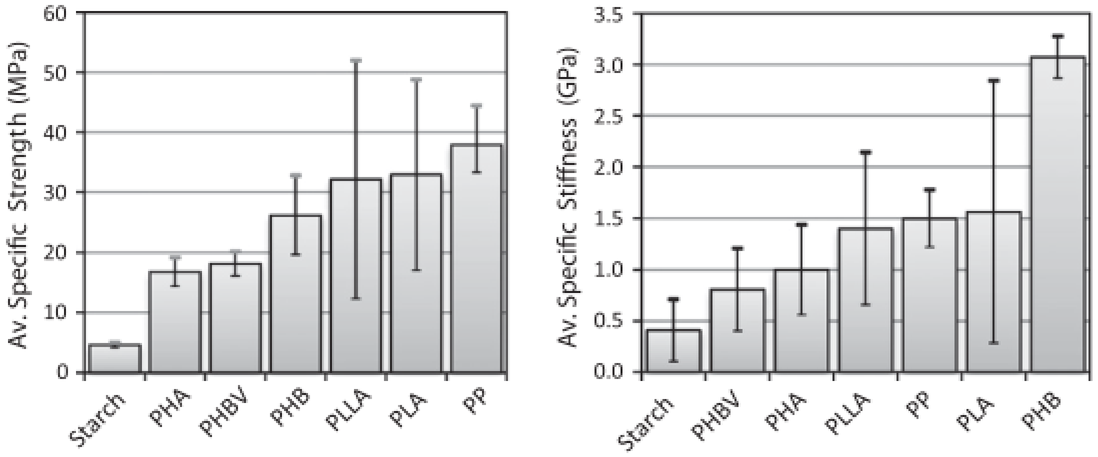

Figure 5: *Specific tensile properties of bio-polymers and polypropylene [53].*

2.4 Conventional reinforcements for the reinforcement phase

The reinforcement phase plays a crucial role in the composite structure, carrying on the external loads applied on the material and giving high strength, stiffness and other improved properties to the composites. The fibers' quality and morphology can change substantially along the whole composite value chain since the fiber cultivation phase to the composites manufacturing phase [24]. This section discusses the main types of conventional reinforcements applied in composite manufacturing over the past years and the introduction of alternative reinforcements, their properties, drawbacks and applicability within the composite industry. Natural fibers, wood-fibers in particular, is of great relevance in this work and will be exploited in details in Section 2.5.

2.4.1 Glass Fibers

Historically, glass fibers have been manufactured since 1893, however, commercial production was only introduced in 1931. Currently, glass fibers are one of the main reinforcement resources for composites due to their attractive properties, amorphous structure and low cost.

Glass fibers are mostly manufactured in the form of E-fibers and S-Fibers. E-fibers offer high electrical properties, and S-fibers ensure improved stiffness and strength properties as well as high-temperature stability. Furthermore, other varieties of glass fibers have been fabricated nowadays such as corrosion resistant fibers (ECR glass) and D-fibers offering low dielectric constant. Undoubtedly, a multitude of advantages within the composite industry such as high strength, corrosion resistance, thermal stability and low cost, flexibility towards particular requirements, highlights the importance of glass fibers. By contrast, low degradability and low stiffness are the main drawbacks of this class of reinforcement [24, 25].

2.4.2 Carbon Fibers

Carbon fibers have been studied for more than 150 years, and their excellent properties, make this material the best sort of reinforcement by obtaining high-strength and -stiffness composites. Carbon fibers have at least 92 wt. % carbon in composition. Concerning their morphology, they are applied in the form of short or continuous reinforcement. In most cases, the high crystalline modulus of carbon fibers is derived from the carbon layers that tend to be parallel to the fiber axis. Therefore, the fiber has higher modulus as well as higher electrical and thermal conductivity in parallel to the fiber axis than in transversal to the fiber axis. There are several types of carbon fibers, which are classified into three categories according to the composite's performance requirements: General purpose (GP); high-performance (HP) and activated carbon fibers (ACF) [25].

The manufacturing process of carbon fibers is based on pitch or polyacrylonitrile (PAN) precursors, in which both follow spinning techniques. Initially, the fibers must be modified in order to increase their thermal resistance carried out by oxidization processes at temperatures below 400 °C. In sequence, the removal of non-carbon elements takes place, followed by carbonization processes in inert atmosphere producing GP and HP carbon fibers. If high-modules is desired, graphitization at temperatures higher than 2500 °C is necessary, enhancing the material crystallinity and pureness. Finally, surface treatments are used to protect the fibers. With respect to ACF fibers, the fibers are obtained by activating in a reactive atmosphere. The high mechanical properties of carbon fibers are explained due to the strong carbon-carbon covalent bonds within the graphene layers and their degree of orientation. When increasing the temperature during graphization, the graphene layers are oriented in the fibers direction, increasing the tensile strength significantly [26].

The main advantages of carbon fibers are high-strength and high-modulus, lack of moisture sensitivity, low density in comparison with glass fibers and good thermal resistance. By contrast, high price and low ductility are the primary drawbacks of carbon fibers [25, 26].

2.4.3 Aramid Fibers

The development of aromatic polyamides (aramids) started in the early 1960s and combined with properties and structural variations, this material has also become relevant in the composite industry. One of the most important advantages of aramid fibers is their cost-effectiveness, by possessing a unique combination of high Young's modulus and tensile strength when compared to glass fibers and carbon fibers. Furthermore, due to their high degree of crystallinity and rigid molecular structure, aramid fibers have good thermal stability. The "aramid" term defines aromatic polyamide materials, which have at least 85% of amide linkages directly to two aromatic groups. In commercial terms, there are only four groups being produced in large scale: poly(*m*-phenylene isophthalamide) (MPDI), poly(*p*-phenylene terephthalamide) (PPTA), copoly(*p*-phenylene-3,4-diphenyl ether terephthalamide) (ODA-PPTA), and poly[5-amino-2(*p*-aminophenyl) benzimidazole terephthalamide] (SVM). DuPont company has been an outstanding player in the composite industry concerning research and development of materials. Concerning aramid fibers, the group has also developed PPTA fibers (trademarked as Kevlar), which is one most important sort of aramid reinforcement for composite applications. [27]

The manufacturing process of aramid fibers is based on solution spinning process. In this process, the powder polymer is dissolved in acid solution, sulfuric acid for instance, and extruded throughout small holes at temperature and processing speed of 80 °C and 0.1-0.6 m/s, respectively. The process is followed by a quenching step, where the fibers are cooled down at a temperature of 1 °C in a water bath, washing the fibers and removing acid residues. Finally, the fibers are then washed, dried and wound onto spools. [26]

Within the FRC context, aramid fibers have been used extensively together with different reinforcements, usually carbon fibers, ensuring the development of outstanding materials for aerospace, construction, sporting goods, ballistic armour, sailing boats, and heat-resistance applications [27].

2.5 Natural fibers as the reinforcement phase

Supported by environmental awareness, natural fibers and their attractive properties for the development of high-end engineering materials, have offered to the composite industry successful combinations of natural reinforcements with several types of matrices. Natural, or lignocellulosic fibers, are extracted from biodegradable sources and have been explored extensively to replace traditional synthetic fibers nowadays. Even though there are thousands of varieties, only a few of them are investigated for reinforcement purposes, and among the most popular; flax, jute, wood, hemp, sisal, ramie, and kenaf fibers are employed in many composites applications. Furthermore, abaca, pinapple leaf, coir, oil palm, bagasse, bamboo, wheat straw, and risk husk fibers are also being used as composites reinforcement. It is important to mention that there are variations regarding the fibers' properties and their quality, depending on the plant growth, harvesting, fiber extraction and supply stages as illustrated in Table 2. With important applications in many industrial segments, these materials have ensured substantial advantages towards the environmental and performance aspects in comparison with non-natural fibers resources: sustainability (carbon neutrality and natural-based resource); recyclability (easy decomposition and degradability); availability (numerous natural fibres resources available worldwide); good performance (lightweight, low-energy consumption and low-cost production) and flexibility (considered alternative solutions for oil-based reinforcements) [9].

Table 2. *Quality parameters towards fibers development from growing to storage phase [9].*

Stage	Factors effecting fiber quality
Plant growth	Species of plant
	Crop cultivation
	Crop location
	Fiber location in plant
	Local climate
Harvesting stage	Fiber ripeness, which effects:
	-Cell wall thickness
	-Coarseness of fibers
	-Adherence between fibers and surrounding structure
Fiber extraction stage	Decortication process
	Type of retting method
Supply stage	Transportation conditions
	Storage conditions
	Age of fiber

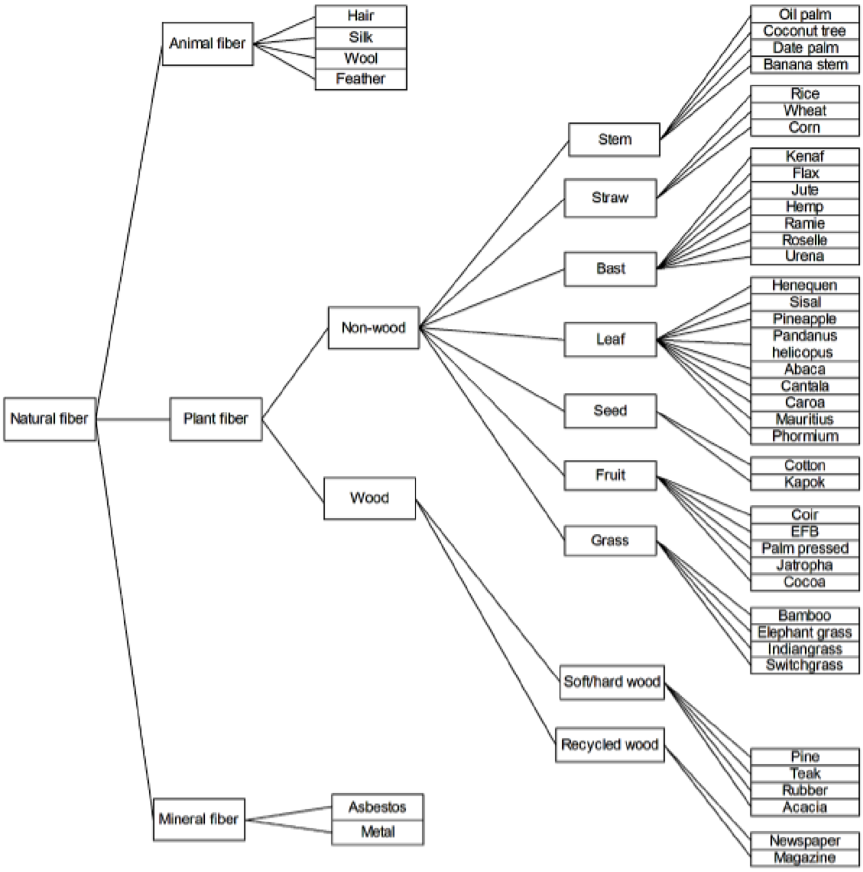

Figure 6: *Main natural fiber types [10].*

By contrast, some drawbacks still limit the use of natural fibres towards composite applications, such as shipping, storage, temperature restrictions for specific processing technologies and mainly the non-uniform dispersion in the matrix phase. The non-uniform dispersion is primarily caused by the natural polarity difference between the fibers and matrices. The processing temperature is also another restriction from natural fibers, where composite's processing technologies which rely on high-temperature processes cannot apply high temperatures to avoid the fibers' degradation, reducing, therefore, the process efficiency and production rate significantly. Also, the high-moisture absorption is considered another issue, being the main reasons for fibers' swelling and poor adherence between the fibers and matrix phase. Lastly, natural fibers are more prone to microbial degradation, being a challenge for composites mainly produced for durable applications. Figure 6 shows the natural fiber classification, divided into plant fibers, animal fibers, and mineral fibers [10]. Remarkably, natural fibers applicability ensures vast sustainable opportunities within the bio-composite industry. Table 3 summarizes the main physical and mechanical properties of natural and synthetic fibers used currently.

Table 3. *Natural and synthetic fibers' physical and mechanical properties. Adapted from [63, 64].*

Fiber	**Density (g/cm^3)**	**Diameter (µm)**	**Tensile Strenght (MPa)**	**Young's Modulus (GPa)**	**Elongation at Break (%)**
Flax	1.5	40-600	345-1500	27.6	2.7-3.2
Hemp	1.47	25-500	690	70	1.6
Jute	1.3-1.49	25-200	393-800	13-26.5	1.16-1.5
Kenaf			930	53	1.6
Ramie	1.55	-	400-938	61.4-128	1.2-3.8
Nettle			650	38	1.7
Sisal	1.45	50-200	468-700	9.4-22	3-7
Henequen					
PALF		20-80	413-1627	34.5-82.5	1.6
Abaca			430-760		
Oil palm EFB	0.7-1.55	150-500	248	3.2	25
Oil palm mesocarp			80	0.5	17
Cotton	1.5-1.6	12-38	287-800	5.5-12.6	7-8
Coir	1.15-1.46	100-460	131-220	4-6	15-40
Softwood Kraft Pulp	1.5		600-1020	18-40	
Hardwood Kraft Pulp	1.2		950	37.9	
E-glass	2.55	<17	3400	73	2.5
Kevlar	1.44		3400	60	2.5-3.7
Carbon	1.78	5-7	3400[a]-4800[b]	240[b]-425[a]	1.4-1.8

[a] *Ultra high modulus carbon fibers*

[b] *Ultra high tenacity carbon fibers*

2.5.1 Wood-fibers as reinforcement phase for composite applications

Woody biomass has been used since pre-ancient times as an energy source by human beings and currently represents one of the primary renewable feedstocks for the next generation of bio-products. As wood-fibers are considered the reinforcement phase chosen for this thesis, a thorough explanation of the structure and chemical composition of wood is presented in this section.

Wood, a composite fibrous material formed mainly by cellulose, hemicellulose, lignin, extractives and other chemicals, is the most relevant natural fiber resource. Wood-fibers are defined as living and dead cells, which are mostly orientated in the longitudinal direction of the stem, varying chemically and physically according to the age of tree and location, and at the microscopic level, it gives fibrous material with excellent performance, e.g. high strength to weight ratio. The word-fiber is often unclear, and non-well defined, where it englobes the wood-fibers itself (both in soft- and hardwood) as well as the woody-cells nominated tracheids (in the case of softwoods). The tracheids main functions are water and nutrients transport in the wood, and structural support for softwood, which is the same function performed in hardwood that has other fibrous elements. Cellulose, hemicelluloses, lignin and extractives, together, build the fibers' structure, each performing different functions, as exploited next [11, 12]:

- Cellulose, the major wood component (40-45%), is a long-chain polymer of β-D glucose, monosaccharide formed through photosynthesis from atmospheric carbon dioxide that is bonded by glycosidic links, forming, therefore, the cellulobiose residues. By consequence, it ensures the highly ordered structure together with the repeating units in the long cellulose chain. The amount of glucose units added is characterized by the polymerization degree, where $(C_6H_{10}O_5)_n$ is the glucose elementary form and n is defined as the polymerization degree, i.e., the number of glucose monomers per cellulose chain. The cellulose framework favours the formation of crystalline cellulose bundles linked by hydrogen bonds. However, cellulose also contains amorphous regions, and their content depend on the sort of cellulose considered.
- Hemicelluloses are also carbohydrates polymers, especially sugars others than glucose, both pentoses and hexoses. Although the degree of polymerization is much smaller in comparison with cellulose, their structure are similar.
- Lignin is the third major wood component (20-30%). It works as a fiber bonding and stiffening agent due to its aromatic amorphous polymer characteristics. In addition, it protects the wood cells against degradation. Although the chemical structure and its reactivity are not entirely known, lignin has nowadays ensured broad applications in

several industrial segments, including power generation and bio-products development. Lignin, hemicelluloses and cellulose perform essential structural functions in trees, as well as they influence the efficiency of wood-fibers applied in the composite industry.

- Extractives are wood inclusions components, mainly organic, and are water or organic solvent soluble substances. The extractives composition is broad, such as gums, fats, etc.

At the macroscopic level, wood-fibers are found in the wood xylem that is divided into heartwood and sapwood regions. When the tree has reached a certain age or diameter, heartwood is formed in the middle of the tree, being dryer than sapwood and primarily performs structural functions and synthesizes compounds to protect wood from decaying. The inner and dark part of the wood xylem is called pith. Sapwood contains living and dead cells carrying out transportation of water and nutrients throughout the whole tree. After a specific growing period, depending on the tree species, the living cells located in the sapwood regions stop functioning, forming, therefore, the heartwood. Due to the physical and chemical difference between heartwood and sapwood, there are notable differences related to the potential applications for the wood. For the composite industry, where the pulping process depends on chemical treatments for fiber isolation, sapwood is the main wood-stream for the procedure. By contrast, when the resistance for chemical liquid penetration in the pulping processes, drying content and high-strength of the heartwood is taken into account, these characteristics make the heartwood region more suitable for saw goods purposes. The cabium zone is a thin layer of tissue that consists of living cells between the bark (phloem) and the wood (xylem), where the radial wood growth takes place. Trees annually produce an annual growth ring (annual increment), controlled by the cabium and influenced by the external conditions such as weather, soil quality, wood type, among others. The annual ring growth is divided into two portions, earlywood (summerwood) and latewood (springwood), in which the former is developed during the first part of the growing season, whereas the latter is formed in the end of the season. Therefore, the wood stem, branches and roots are organized in concentric annual rings [47]. Figure 7 illustrates the wood framework.

Trees have been classified in several ways, and for scientific and commercial discussions, it is common to divide the tree species into softwoods (conifers) and hardwoods (dicotyledons). The most relevant differences between softwood and hardwood are related to the chemical composition, arrangement of structural elements and plant reproduction. Regardless of the type of wood, the polymers stated previously (cellulose, hemicellulose, lignin and extractives) are always present. In softwood, the cells are mainly fibrous, tracheids, with a length and width average between 1.4-6.0 mm and 20-50 µm, respectively, vertically orientated in the wood stem. On the other hand, hardwoods consist of several cell types, such as fibers (tracheids), vessels and perenchyma cells, where their fibers have length and width average of 0.4-1.6 mm and 10-40 µm, respectively. As consequence, tracheids are the primary wood structure constituent, around 90% over the volume of softwood and 50% of hardwood. Together, cellulose, lignin and hemicellulose are the main components of wood-fibers and are founded in the cell wall framework with different concentrations. With respect to the fibers' properties, they are mainly governed by separation process and chemical treatments, as exploited further in this work. Figure 8 illustrates the main cell types found in softwoods and hardwoods. [13]

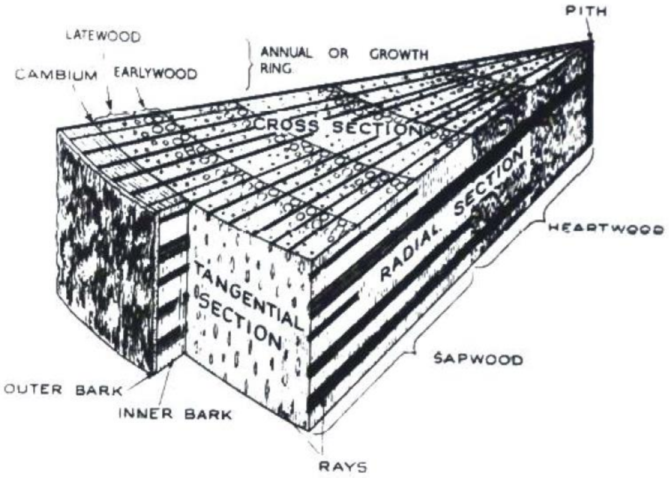

Figure 7: *Wood macrostructure [91].*

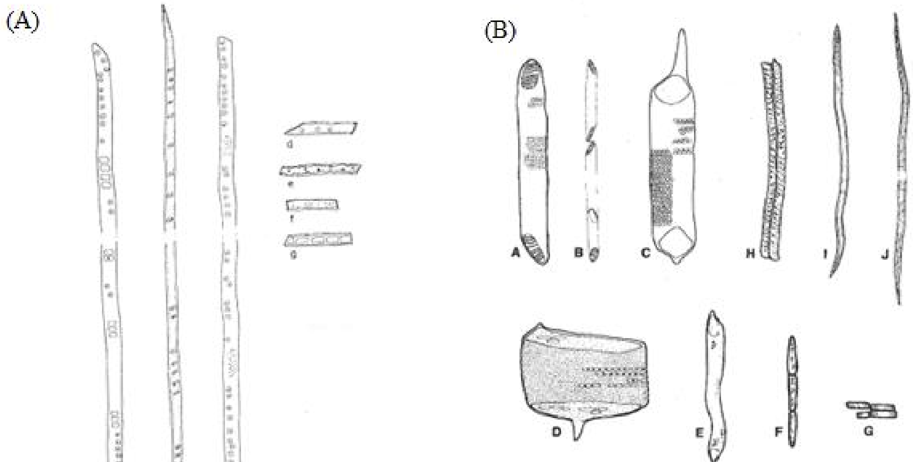

Figure 8: *(A) Major cell types in softwood. Earlywood (a) and latewood (b) pine tracheid, earlywood spruce tracheid (c), ray tracheid of spruce (d) and pine (e), and ray parenchyma cell of spruce (f) and pine (g); (B) Major cell types in hardwood. Vessel elements of birch (A), aspen (C), oak in earlywood (D), and oak in latewood (E), as well as a birch vessel (B), longitudinal parenchyma cells of oak (F), ray parenchyma of birch (G). Tracheids of oak (H) and birch (I), and libriform fiber of birch (J) [14].*

Regardless of the high concentration of tracheids in softwood and hardwood, the presence of other fibrous elements found in the wood framework can be noted such as ray cells, parenchyma cells, early and latewood fibers, and vessels (only present in hardwood), having different configuration and chemical composition (Figure 9). At the ultrastructural level, the wood-fibers are built up of concentric layers (also named interlayers) with different chemical composition and orientation, as illustrated in Figure 10. The wood-fibers framework in sapwood region is formed by the middle lamella (I), which is found in all fiber types with the main function to glue the fibers, where the lignin presence is high; the primary layer (P); secondary layers (S1-S3) performing structural functions; and the gelatinous layer (G). Another thin wart layer (w) is found in the inner part of lumen. Each of these layers plays a relevant role when defining the intrinsic mechanical properties of the wood-fibers [36].

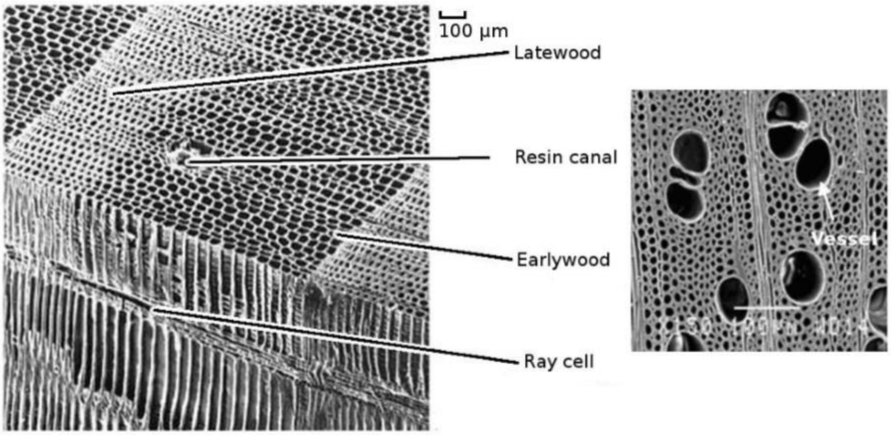

Figure 9: *Scanning electron microscopy (SEM) micrograph from a pine wood sap showing some of the cell types and their distribution within a wood. The SEM image on the right shows an example of sugar maple (a hardwood) and the size of the vessels [36].*

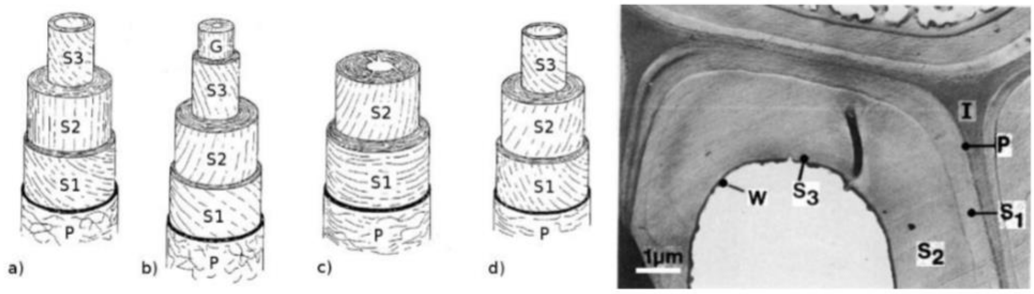

Figure 10: *Schematic illustrations of normal hardwood (a), tension hardwood (b), normal softwood (c) and tension softwood (d) fibres. The lines indicate cellulose microfibrillar angles in each layer. A transmission electron microscopy (TEM) image of ultrathin transverse section from a hardwood fibre. The lines indicate cellulose microfibrillar angles in each layer. A TEM image of ultrathin transverse section from a hardwood fibre (Fagus crenata) is shown on the right. Intercellular layer, i.e. middle lamella (I), primary layer (O), secondary layers (S1-S3) and wart layer (W) are marked [36].*

The wood-fibers processing technologies for composite purposes include two methods: pulping process and pulverization process. Pulping process is based on the reduction of the macroscopic wood structure to a fibrous material due to bond ruptures of the wood chemical elements, achieved by mechanical pulping, thermomechanical pulping or chemi-thermomechanical as explained next [36]. On the other hand, pulverization process reduces the wood macrostructure into smaller particles (180-425 μm), producing wood flour that is used mainly as fillers in polymeric materials and raw materials for saw goods (medium density fiberboard, for example).

- Mechanical pulping is extensively used to produce cheap papers such as magazines and newspapers. In this process, the wood is mechanically processed, releasing its individual fibers (strongly damaged with this technology), demanding appropriate amount of energy and pre-heating processes. It is common to see papers obtained by mechanical pulping with a yellowish tone due to the low processing efficiency of lignin extraction and concentration of heteropolysaccharides, pectins, inorganic materials and some extractives.
- Thermomechanical pulp (TMP) consists of a pulping method, where wood-chips are pre-treated with water steam before the refining process under pressurized conditions.
- Chemi-Thermomechanical Pulping (CTMP) involves the application of chemicals before the refining process. Even though there is a multitude of CTMP technologies available, kraft cooking is the most applied method nowadays for fiber isolation. The process is carried out in a digester under high-temperatures (140-170 °C for 2 h), where the wood-chips are fed, and reactive chemicals, mainly based on NaOH and Na_2S, impregnate the fibers with steam aid. One of the main objectives of chemical pulping is to isolate the fibers and to remove the lignin without damaging the fiber's walls physically. CTMP has ensured high-end pulp and paper production and several possibilities to utilize wood-fibers as reinforcement in the composite industry.

Although a multitude of pulping technologies is available currently, in order to achieve successful fiber isolation to be used as reinforcement phase, it is important to note that the more the fibers are free of lignin, the more effective might be the interactions between the composite phases, according to most results found in the literature [36, 40].

2.6 Preforms of natural fibers for composite applications

The preforms of cellulosic fibers used for composite manufacturing, obtained by the methods explained previously, are similar to the ones for synthetic fibers, and in some cases, concerns should be adequately addressed to ensure suitable applicability. In the pulp and paper industry, pulping processes produce wood-fibers in the form illustrated in Figure 11(a) to be mainly used in papermaking processes. In parallel, the composite industry utilizes the wood-fiber mats (Figure 11(b)) for composite manufacturing by impregnating the fibers with thermoplastic or thermoset materials by using several types of processing technologies as explained in details in Section 2.8. The papermaking industry detains huge structures for paper- and boards-sheets production, and is still is the primary user of wood-fiber mats, where the composite industry only absorbs small volumes of the global production [53].

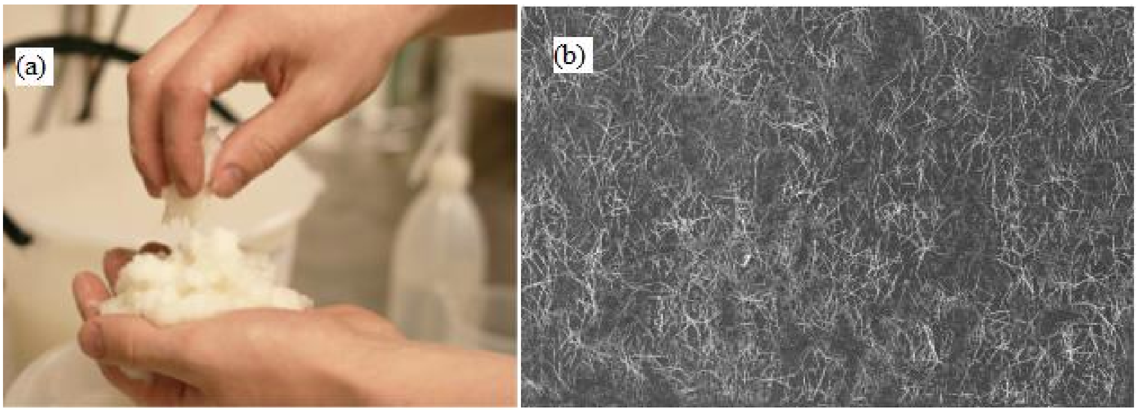

***Figure 11:** (a) pulp made from bleached softwood fibers. (b), wood-fiber mat showing fiber distribution (image height ~ 10mm) [53].*

2.7 Surface treatments for better reinforcement/matrix adherence

Even though there are many benefits from performance, environmental and operational points of view provided by natural fibers, their strong polar and hydrophilic character, and consequently weak surface adherence and even incompatibility with the matrix, is still the main hurdle to overcome in order to boost their use in the composite industry. In general, surface modification processes might ensure fiber homogenization, better degree of polymerization and crystallization, moisture repellence and flame-retardant properties, among other benefits. Hence, commercial fiber reinforced composites rely on analysis, adherence and modification of fiber surfaces, and the principal treatment methods are divided into two groups with different efficiency level regarding fiber-matrix adherence: chemical modification and physical modification. Although there are many surface treatment methods available, the next topics exploit briefly successful modification methods already applied for wood-reinforced composites.

2.7.1 Chemical Modifications

Chemical modification is an excellent surface treatment used especially with high polar and hydrophilic fibers. The method mechanism is based on modifying the surface structure or by adding hydrophobic layers onto the surface of the fibers [39]. There are many benefits achieved by chemical treatment, including better dispersion in the matrix, reduction of interactions between fibers, and the decreased ability of the fibers of absorbing moisture. The primary methods utilized nowadays are briefly explained next:

- Coupling modification optimizes the stress transfer of the composite interphase and is an excellent method for wood-fibers. Coupling agents are chemical substances and are classified as bonding agents or surfactants (surface active agents). The main functions of coupling agents are either to ensure reactions with the hydroxyl groups of cellulose or reactions with the hydroxyl groups of the matrices. Among several coupling agents applied in the composite industry, the most utilized coupling agents are silanes, isocyanates, and titan-based materials, all of them creating a bridge of chemical bonds between the fibers and matrices. Silane treatments are carried out by silane coupling agents forming chemical bonds, where the bifunctional silane molecules react with the cellulosic fiber surface, whereas the organofunctional groups bond to the polymeric matrix. The process efficiency relies on the structure, functionality, acidity, the drying condition and homogeneity, the topology of silanes as well as the chemical composition of the fiber surface. The chemical structure of the multifunctional silane molecule is X-Si-R. R is a chemical group that reacts with the matrix, e.g. vinyl, aminopropyl, methacreloxypropyne, etc., whereas X is group that reacts with the fiber surface, including methoxy, ethoxy, among others. Coupling modification commonly uses dispersion aids such as solvents and peroxides (initiators) to increase the number of chemical bonds and fiber interactions between the fiber and the matrix. The main advantage of silane treatments is the improvement of interfacial adhesion, and, consequently, significant enhancements towards the mechanical properties of the composites [35, 41].
- Alkali swelling, in special mercerization, is based on reactions of cellulosic fibers causing the fibers' swelling, breaking around 25% of the hydrogen bonds in the drying phase of the process. The broken bonds will re-bound having specific results: increasing the molecular direction, producing fiber fibrillation, decreasing the fiber diameter and increasing the aspect ratio as well as the surface area. These changes improve the fiber strength and consequently produce stronger composite materials. The process depends on temperature, time of treatment and concentration of the alkali solution. It is an efficient process towards better mechanical properties and fiber-matrix surface interaction [35, 41].
- Crosslinking is based on reactions of multifunctional compounds and cellulose hydroxyl groups. The process is always performed by etherification and esterification reactions and can reduce the transverse coefficient of hygroexpansion (moisture-induced dimensional changes) of wood-fibers, ensuring better environmental and dimension stability of FRCs [41].
- Grafting reactions are carried out by impregnation of the fiber surface by liquid monomers followed by polymerization with the support of heat, radiation and catalysts. The process starts when the fibers are exposed to high-energy ionizing radiation, releasing cellulose free radicals, which will initiate the grafting of alkyl acrylates (methyl, ethyl, butyl and propyl) and vinyl monomers (methyl methacrylate and acrylonitrile) onto the fiber surface. Among many successful grafting methods of natural

fibers, maleic anhydride (MA) has been extensively utilized in the manufacture of wood-fiber reinforced composites as covered further in this work [41].

- Enzymatic process has a relevant effect in the removal of non-cellulosic materials components, followed by cost reduction, energy and water savings [33].
- Acetylation reactions have been a promising surface treatment method towards ligno-cellulosic fibers, based on the reactions between the fibers' hydroxyls (-OH) with acetyl groups (CH3CO-). The method utilizes bases or acids, and, in some cases, is catalyzed by pyridine, sulfuric acid, potassium or sodium acetate. It is important to note the balance needed when choosing the catalysts for the reaction, where strong mineral acids or acid salts can damage the fibers (cellulose hydrolysis). According to recent studies, acetylation has already ensured up to 65% of moisture absorption reduction of pine fibers. In the composite context, acetylated fibers can increase the interfacial shear strength and surface free energy of the fibers. Figure 12(a) illustrates the acetylation process briefly [34].
- Steric acid treatment of cellulosic fiber by esterification reactions is a well-developed technology within the composite industry, where the surface treatment is carried out by fatty acids, such as steric acids. The method has provided an efficient solution for wood-fiber composites, where similarly to acetylation reactions, the fiber hydroxyls (-OH) react with carboxyl groups (-COOH) through esterification reactions. Thus, reducing the amount of hydroxyl available for water reactions. The long hydrocarbon chain of steric acid also improves the fibers' water resistance, since it is mainly hydrophobic. For the reaction with steric acid, the fibers are usually dissolved in a solvent. However, new methods for sizing with steric acid are available with no need of solvents, making the process simpler and reducing any possible environmental impact by the processes' effluents as shown in Figure 12(b). This surface treatment method has already been applied with several sorts of natural fibers [34, 70].
- Permanganate treatment is based on the formation of cellulose radicals by utilizing permanganate groups such as potassium permanganate ($KMnO_4$), under different concentration and reaction duration time. Initially, the method consists of MnO_3^- ion formation, where highly reactive Mn^{3+} is responsible for graft copolymerization onto the fibers' surface. The main advantage of this method is to reduce the fiber hydrophilic tendency. Although the higher permanganate group concentration in the method ensures lower fiber hydrophilic behavior, it is essential to control the cellulose degradation by the permanganate groups [40].
- Sodium Chlorite ($NaClO_2$), a chemical element often used in pulping processes, also ensures suitable fiber surface modification thanks to its delignification capacity. However, this method can also decrease the tensile strength of the modified fibers. On the other hand, the flexural strength increases due to higher fiber flexibility and stiffness after the delignification reactions [40].
- Benzoylation treatment is executed by first cleaning and drying the fibers, followed by soaking them in a NaOH solution for a pre-determined time. In sequence, the fibers are filtered and washed with water. The treated fibers are then suspended in a NaOH

solution and mixed with benzoyl chloride. Finally, the fibers are once more filtered and washed, to be soaked in an ethanol solution before their utilization in composite manufacturing. It has been reported that the method improved the tensile strength of bamboo fiber reinforced composites and palm leaf reinforced composites. Moreover, recent studies also concluded that flexural and compressive properties of FRCs are enhanced by benzoylation treatment [65].

- Peroxide bleaching treatment of fibers is carried out by removing non-cellulosic materials, utilizing sodium hypochlorite or calcium hypochlorite and hydrogen peroxide. The method is also used in the pulp and paper industry, which in turn also enhances the cellulosic fiber isolation as well as ensuring whiter and brighter fibers. It has been reported that peroxide bleaching can improve interfacial adhesion between fibers and matrix caused by increased surface roughness and therefore better mechanical interlocking of both composite phases [66].
- Triazine-based fiber surface treatment is a suitable method for cellulosic fiber modification, allowing large-scale implementation and good fiber functionalities. It has been successfully applied onto cellulosic nanocrystals (CNC's) surface and is considered versatile and straightforward, usually executed either by affixing amino-reactive dyes onto cellulose fibers or grafting of fluorescent dyes, porphyrin and N-lipidated oligopeptides onto the fiber surface. The method can be used either as a standalone surface modification or as a building block for subsequent modification, showing good capabilities to form a stable suspension in organic solvents and better fiber compatibility with polymeric matrices by tuning the polarity of fibers [67].

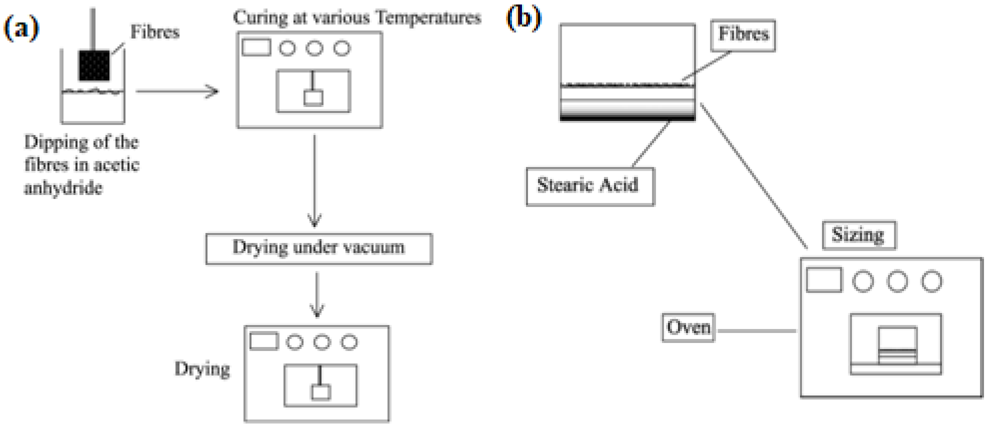

Figure 12: *(a) Fiber surface treatment by acetylation process. (b) Fiber surface treatment with steric acid as sizing agent [34].*

2.7.2 Physical Modifications

Physical modification changes and improves the structure and properties of the fiber surface by utilizing electric discharge and fibrillation treatments. The main examples of physical modification are listed next:

- Fibrillation is usually carried out by mechanical devices, increasing the fiber-fiber interaction and flexibility, surface area of the fiber and improving the mechanical interlocking.
- Corona modification (electric discharge) is based on surface oxidization and therefore the change of cellulosic fiber surface energy by increasing the amount of aldehyde groups [39].
- Cold plasma treatment (electric discharge), includes methods under low-temperatures and varies according to type and nature of the gases used, which in turn enhances chemical implantation, polymerization, formation of free radicals for particular reactions as well as the control of the surface energy of the fibers. The method is executed by using electrons, ions and radicals' discharges [35].
- Ultrasound modification involves a set of chemical and physical processes under high-pressure, and -temperature, where shock waves and severe shear forces are responsible to break up chemical bonds found on the fibers surface [33].

The methods mentioned previously assure improvements of wood-fiber surface as already reported over the past years. The most promising scenarios for cellulosic fibers surface treatment should rise the amount of continuous covalent bonds between the fiber surface and the matrix.

2.8 Processing Technologies for composite manufacturing

Apart from the importance of the right choice of the reinforcements, matrices and fiber surface treatments, composite processing technologies also play a relevant role when fabricating materials to meet pre-defined design and operation requirements. Nowadays, a multitude of composite manufacturing methods have been applied, each of them has its advantages and drawbacks as exploited next.

2.8.1 Open Mold Technologies

A single-sided mold, male or female, treated by a mold-release agent, is used to give form and cosmetic surface. The reinforcements are applied by hand lay-up process and wet-out, followed by the matrix addition, or by spray-up process that applies the chopped reinforcements together with the matrix onto the mold. Then, additional laminates are added in order to make the material thicker and stiffer according to the material's requirements. Open molding technology is the most flexible method, which can offer a wide range of composite production concerning design parameters, low scale production and an alternative solution for those materials which cannot be fabricated by automated processes. A gel resin (gel coat) layer (approx. 0.5 mm) is usually applied onto the mold in order to ensure environmental protection of the composite produced [24, 37].

- Hand layup process is the simplest composite manufacturing technique. The resin is applied, distributed and compacted on top of the gel coat, forming a laminate stack, as shown in Figure 13(a). In sequence, the dry reinforcement layer is added uniformly with a hand-held roller. When the reinforcement layer has been satisfactorily impregnated, another resin layer is applied. In sequence, the process is repeated until reaching the desired number of layers. In some cases, when better surface appearance is needed, some additives can be applied [37].
- Spray up molding process can produce a multitude of composite materials with a similar mechanism presented by hand layup process. However, it significantly reduces the labor intensity where a spray gun sprays pre-chopped reinforcement and the matrix onto the mold. The gun feeding system defines how the reinforcements and matrix are mixed, being possible to have isolate system blending both on the way to the mold or mixing it internally before the application on the mold surface. In general, the spraying of a predetermined ratio of fibers, which are fed in continuous form and then chopped into short lengths, and matrix starts after coating the mold with mold-release, gelcoat and/or the surface film as illustrated in Figure 13(b). The process ends when workers compress the layers applied onto the mold by hand-held rollers, followed by the curing, cooling and removal phases [24, 37].

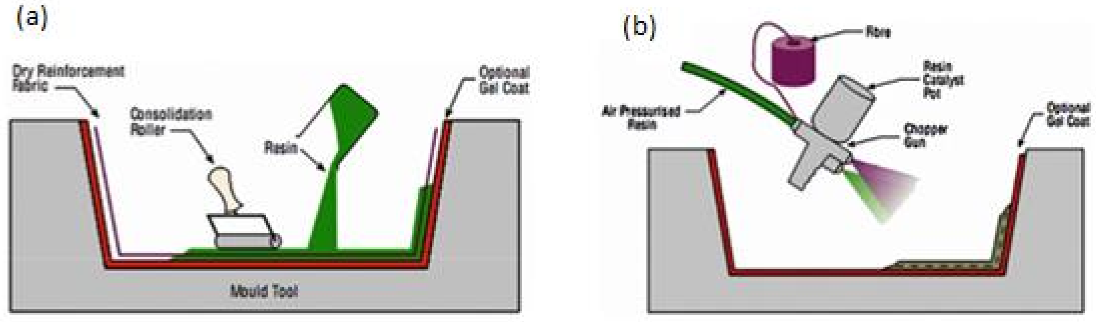

Figure 13: *(a) Hand layup and (b) Spray-up composite processing technology [37].*

2.8.2 Closed Mold Technologies

- Resin-transfer molding (RTM) is considered one of the most important composite processing technologies, being able to fabricate large components with wide dimension variations, good surface finish and high integration framework. It is well-known processing technology also due to its cost-effectiveness [37]. The process starts when the dry reinforcements are fed into the mold, then the mold is closed by pneumatic or hydraulic systems. Following the mold closure, the catalyzed thermosetting matrix is injected, i.e. transferred, into the mold in order to impregnate the reinforcement as shown in Figure 14. The injection is carried out by pressurized systems that can vary their complexity according to the type of composite being fabricated. If the matrix viscosity is too high, high-pressure devices are needed, and the risk of displacing the fibers in the mold ("fiber wash" phenomenon) increases. Finally, the curing phases start, and, therefore, the mold is opened to remove the part from it [24].

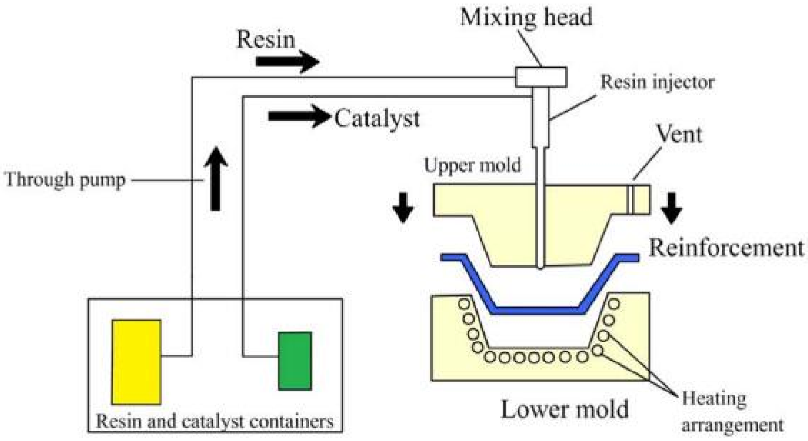

Figure 14: *Resin transfer mold [http://www.eppcomposites.com/rtm-process.html].*

- Vacuum Assisted Resin Transfer Molding (VARTM), Figure 15, is similar to RTM method with its main distinguishing characteristic being the matrix injection method executed by vacuum systems, whereas RTM utilizes matrix injection under pressurized systems. Therefore, the vacuum draws the matrix from the storage system into the vacuum bag along its channels, ensuring the reinforcement impregnation. The more fibers are used, the more the time needed for full impregnation. VARTM is a simple, practical, and low cost method, allowing the fabrication of composites with various geometry, size and other design requirements [37].

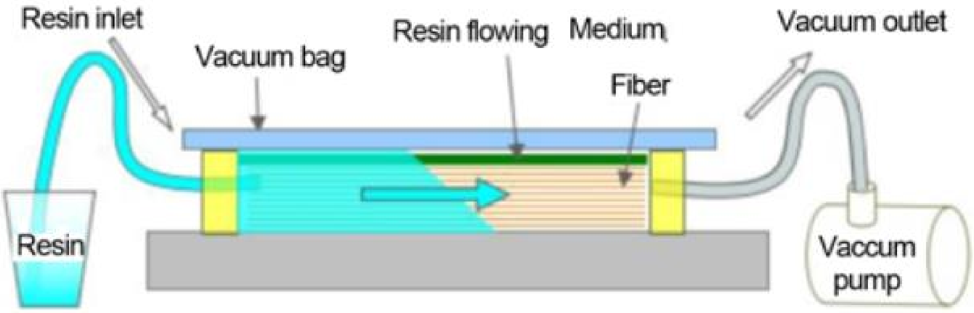

Figure 15: *VARTM schematic diagram [38].*

2.8.3 High Volume Molding Methods

High volume molding methods are covered below.

- Extrusion, Figure 16, is an outstanding method for wood-fiber reinforced composite development, which in turns allows the possibility to use a wide range of biodegradable polymers for matrix purposes such as starch and PLA [41]. The process starts when the mixture of fiber and resin material in fed from a top mounted hopper into the barrel of an extruder. Other materials, such as additives, colorants, and UV inhibitors can also be introduced in the resin. Then, the fed material comes in contact with the screw and is forced to flow throughout the barrel that is heated to specific temperatures, according to the resin melting temperature. In this phase, the heating controlling system is usually operated by proportional-integral-derivative controllers, achieving optimal temperature distribution from the resin fed area to the front, and ensuring the gradual resin melting. In the front area of the barrel, the material is filtered, and contaminants might be removed (breaker plate is usually positioned in order to avoid the screens to break due to high operation pressure). In sequence, the composite material enters the die, obtaining the final shape and profile desired with a constant cross-sectional area. Finally, the product is cooled down in a water bath or in heat exchange systems according to machine design [24]. The two types of extruders used currently are single-screw and twin-screw [41]. Excellent compounding capability, good functional versatility, among other advantages, make this method by far the most suitable for wood-fiber reinforced composites. It is also important to mention the importance to control the processing variables such as screw speed, screw configuration, material throughput rate and barrel temperature correctly, to maintain the integrity of the reinforcements, avoiding mainly fibers' thermal degradation and significant changes towards their morphology.
- Compression molding, Figure 17(a), is based on the distribution of the thermosetting matrix excess. In this method, a male and female mold is compressed by external forces, ensuring the matrix stream towards pre-designed channels. The process starts by loading the lower fixed mold half with thermosetting materials, usually a stack of material that is described as compound or charge. The mold is then closed with the upper movable mold half by hydraulic press, forcing the charge flow to fill the mold [24].
- Injection molding, Figure 17(b), is also used for engineering thermoplastic manufacturing such as PP polystyrene, etc., accounting for around one-third of polymeric materials produced nowadays. The process mechanisms consist mainly in forcing or injecting the composite material into a closed mold of desired shaped and is executed through 4 phases [37]:
    - Clamping: Closure of the two halves of the mold by hydraulic power, in which both halves are attached and fixed to the injection machine, whereas the second one is free to slide when the clamping phase is concluded.
    - Injection: The compound material is inserted in the injection machine and routed towards the mold injection unit under high temperature and pressure.
    - Cooling: The injected material starts to cool down immediately when in contact with the mold surface. It is important to note that during the cooling phase,

it is common to face the shrinkage of the part. Therefore, the injection machine is usually set up to add additional material if needed.

  - Ejection: After the cooling phase, the part is usually attached to the mold surface, and the ejection system takes it away when an external force is applied. In most of the cases, the mold-release agent ensures more efficient part ejection, without damaging the part surface.

- Pultrusion (Figure 18) is a popular high-volume processing technology [37] for structural fiber reinforced composites such as storage tanks, pipelines, gas cylinders, etc., with a constant cross-section. The technique requires little labor, the process waste is minimum, and the fiber volume fraction is relatively high (60-70%), being one of the most cost-effective and energy-efficient composite processing technology available. According to the possibility to apply thermosetting and thermoplastic matrix, the process can be categorized in thermosetting pultrusion technology and thermoplastic pultrusion technology [43].

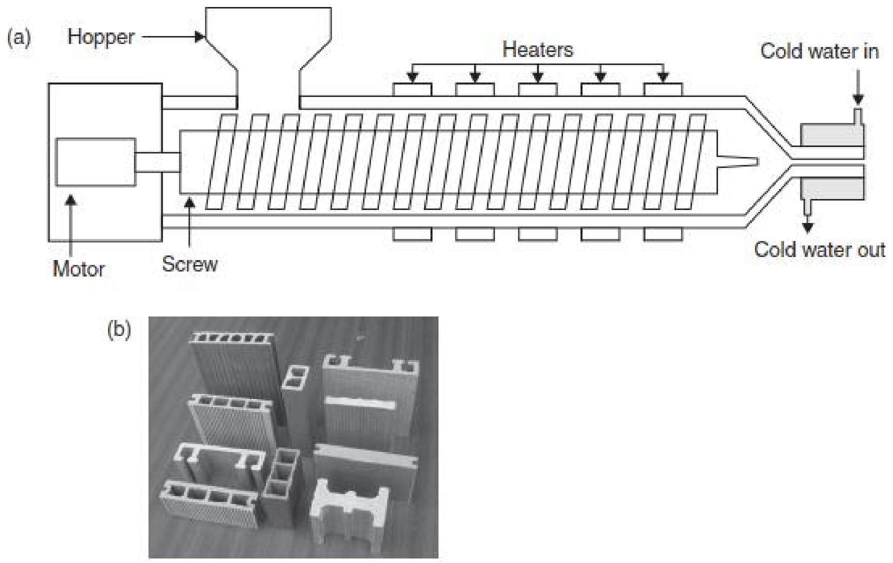

Figure 16: ***(a)*** *Schematic of extrusion molding and (b) extrusion molded wood-fiber composite products examples [41].*

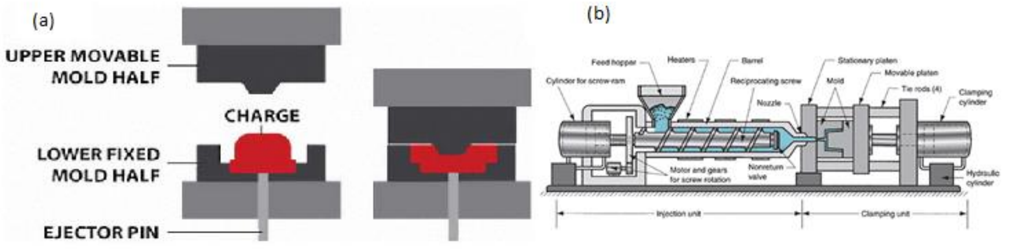

Figure 17: *(a) Compressing mold schematic diagram. (b) Injection mold schematic diagram [37, https://www.xcentricmold.com/injection-molding-process/].*

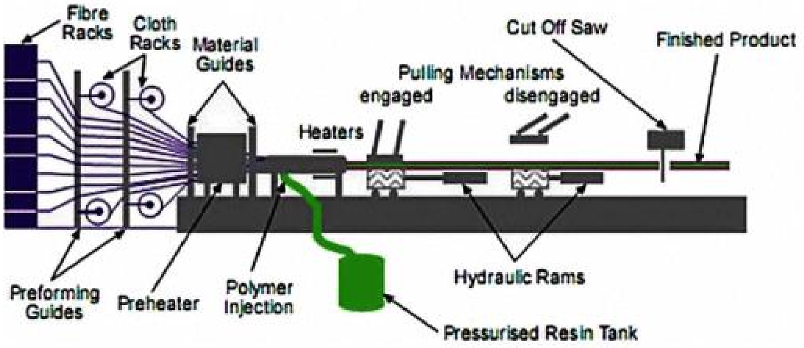

Figure 18: *Pultrusion technology [37].*

Although there are several composite processing technologies available nowadays, the technology selection is a crucial step for a successful composite development it is usually defined according to final product design, performance attributes, raw materials (feeding form is also a key parameter), and cost-effectiveness of the method [72]. Concerning wood-fiber reinforced composites, compression, injection molding and extrusion are the most popular techniques applied nowadays within the construction and automotive industry. These technologies allow the production of intricate and simple shapes, a wide range of 3-D structures, possibility to use high reinforcement volume without damaging the fiber morphology, among other benefits [60,71].

Among some key parameters to control throughout the manufacturing phase, moisture generation after molding is the most relevant to be monitored, strongly influenced by temperature and relative humidity. Besides, due to natural fiber degradation in the order of 150 and 220 °C for long and short processing durations, respectively, makes the control of processes' temperature and the utilization of fast processing technologies strategic factors related to composite production [41,72].

Compounding processes have been extensively used in composite manufacturing centers, where the technique consists of the blending of reinforcement and matrix phase, producing a palletized feedstock that can be processed further in the composite manufacturing phase. The technique ensures a high-degree of consistency feasible in the pallet form. Processing technologies like injection molding, extrusion and compression molding demand compounds for their operations. Appendix 1 outlines the processing technologies covered previously, and their main advantages, disadvantages and applications in the composite industry.

3 INDUSTRIAL APPLICATIONS OF WOOD-FIBER REINFORCED COMPOSITES

Although the application possibilities related to wood-fiber reinforced composite are broad nowadays, the automotive and building industry are the largest consumers of wood-fibers for composite purposes in Europe and America, respectively, as illustrated in (Figure 19(a). In consequence of this and being the main industrial applications considered for this work, this section covers a thorough analysis of each sector mentioned previously, as well as assesses the properties requirements and the potential applications and challenges related to bio-composites. Despite showing a favourable scenario concerning the development of innovative sustainable materials and the possibility to utilise bio-composites in the modern industry, these materials still struggle to increase their market penetration in the composite industry, whereas synthetic composite market share has remained in growth trend and still dominates the market as shown in Figure 19(b). The building and automotive industry are the main users of bio-based composites, accounting for 70.8% and 12.5% of the natural fiber reinforced composite market share, respectively. In this context, wood-fiber reinforced composites possess 80% of the market share of the natural fiber reinforced composites [41, 53].

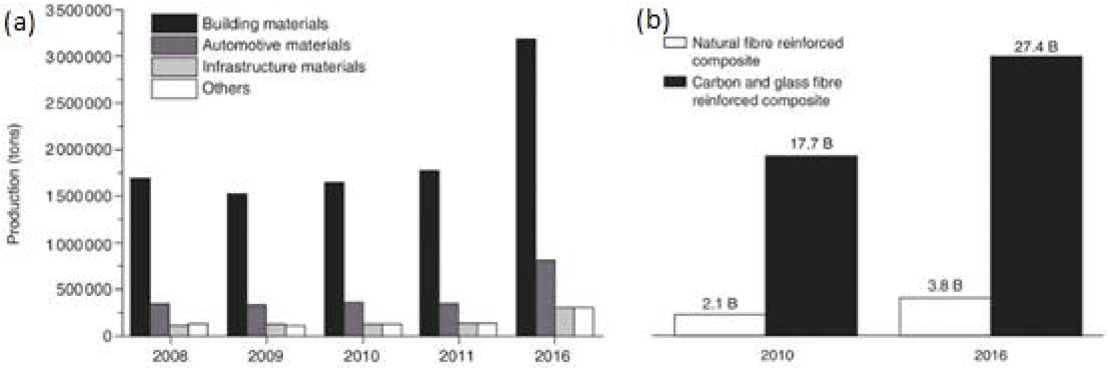

Figure 19: *(a) Global application of natural fiber composites, (b) Comparison of composite market of natural and synthetic composites (US$ billions) [41].*

3.1 Automotive Industry

The automotive industry has pushed a relevant change towards an eco-friendlier product chain by applying natural reinforced composites in various vehicle components. A wide range of factors has boosted this concept such as environmental awareness, the need for lighter and less harmful materials, new market opportunities, improvement of natural fibers performance and their increasing production globally, technological advances in the chemical and automotive industry, as well as new legislation standards. Moreover, the fact that the transportation industry accounts for 20-25% of the global greenhouse gas emissions nowadays, also pushes the segment to encourage the development of bio-composites materials as a strategic resource to tackle this environmental issue. In the production landscape, a reduction of production costs between 10 to 30% when replacing conventional synthetic fibers such as glass fibers to natural fibers in vehicles components has been reported. Wood-fibers reinforced composite within automotive applications, for instance, allowed automotive manufacturer Mercedes to produce door panels of its Mercedes SL sedans, achieving 20% weight reduction and showing satisfactory performance results [51, 93]. Considering the market penetration of these products, it can further increase when developing cost- and competitive-efficient processing technologies as alternative solutions towards the main present injection-molding thermoplastics applied broadly in car parts manufacturing nowadays. Recently, material experts estimate that advanced bio-composites are capable of reducing up to 67% the weight of modern steel auto-body due to its lower density compared with traditional materials. In addition, the trend of electric vehicles consolidation in the next decades will also need lighter and efficient materials in order to make up for the extra added weight of batteries [51]. The facts mentioned before are considerable advances in the modern industry, contributing to a greener society, cost-effectiveness production, client satisfaction without compromising the vehicles quality and performance.

Historically, the automotive industry has been a leader in the research, development and use of natural fibers reinforced composites. They arise as alternative materials to replace conventional metal- and oil-based automotive materials, as they can provide attractive impact and tensile strength, improved aesthetics, maximum potential for weight reduction (which in turns means low fuel consumption), easy mold-ability, and low carbon footprint related to the segment [48]. Globally, the automobile sector has changed dramatically and the increasing demand for sustainable materials and fuels-efficiency are crucial material science subjects that require from the modern industry relevant movements to meet global carbon emission reduction standards. Among many strategies taken into account, the evolution of low-weight green materials, supported by natural fiber reinforced composites, has significantly helped the development of an environmentally-friendlier supply-chain in the automotive industry as explained further in this work.

In parallel with a suitable reinforcement selection, as stated beforehand, the matrix selection also defines the final properties of composites. For automotive purposes, it has been reported that thermoplastic matrices offer suitable composite production when the part size is relatively small and thermoforming techniques are acceptable, where injection molding technology offers high production rates and fast reacting resin systems. By contrast, thermosetting resins are used for relatively large size parts mainly by VARTM. By applying suitable composite processing technologies listed in Section 2.8, a multitude of automotive components is produced nowadays such as dashboards, car disk-brakes, door panels, trunk panels, headliners, trunk components, floor panels and insulations, as shown in Figure 20. Regardless of the complex task of material selection, basically the materials are expected to meet the following specific requirements in the automotive context [49, 50, 52, 71]:

- Good mechanical properties, i.e., reasonable strength/weight and stiffness/weight;
- Shatterproof performance under extreme temperature changes;
- Lightweight: ensuring lower carbon emission, fuel efficiency, and reduction of metal-based composites demand;
- Economic effectiveness: determining whether the material has the potential to be used as a vehicle component by lowering processing time and costs;
- Safety: to be able to absorb impact energy and assure controlled failure modes and mechanisms to preserve the integrity of the passengers;
- Recyclability and life-cycle consideration: supporting the global need regarding the protection of resources, and, therefore, boosting the recycling possibilities and mitigating environmental damages;
- Thermo-acoustic insulation properties;
- Structural rigidity as well as ductility over a wide range of temperature;
- Good fitting tolerance and tight radius contouring;
- Ability to form both simple and complex shapes and contours;
- Ability to hot stamp thin decorative films and attach decorative upholstery;
- Ability to mass produce the door trim panels commercially with very few rejects.

Figure 20: *Natural fiber composites in a Mercedes E-Class [51].*

The well-established applications of natural fiber reinforced composites in the automotive industry are illustrated in Table 4.

Table 4. *Vehicle manufacturers and use of natural fiber composites [50].*

Automotive Manufacturer	Size	Model Applications
Audi	A2, A3, A4 and (Avant), A6, A8,	Roadster, Coupe, Seat backs, side and back door panels, boot lining, hat rack, spare tire lining
BMW	3,5,7 series, BMW i series	Door panels, headliner panel, boot lining, seat backs, noise insulation panels, molded foot well linings, door trim
Citroen	C5	Interior door panelling
Daimler-Chrysler	A, C, E and S-class models, EvoBus (exterior)	Door panels, windshield, dashboard, business table, pillar cover panel
Fiat	Punto, Brava, Marea, Alfa romeo 146, 156	Door cladding, seatback linings, floor panels, seat bottoms, back cushions, head restraints, under floor body panels
Ford	Mondeo CD 162, Focus, Freestar	Door panels, B-pillar, boot liner, sliding door inserts
Lotus	Eco Elise (July 2008)	Body panels, spoiler, seats, interior carpets
Mercedes-Benz	TRUCKS, Mercedes-Benz A	Internal engine cover, engine insulation, sun visor, interior insulation, bumper, wheel box, roof cover
Peugeot	406	Seat backs, parcel shelf
Renault	Clio, Twingo	Rear parcel shelf
Rover	2000 and others	Insulation, rear storage shelf/panel
Saturn	L300s	Packing trays, door panel inserts
Toyota	Brevis, Harrier, Celsior, Raum	Door panels, seat backs, spare tyre cover
Vauxhall	Corsa, Astra, Vectra, Zafira	Headliner panel, interior door panels, pillar cover panel, instrument panel
Volkswagen	Golf, Passat, Bora	Door panel, seat back, boot lid finish panel, boot liner
Volvo	C70, V70	Seat padding, natural foams, cargo floor tray

3.1.1 New concept towards automotive industry developed by UPM-Kymmene

The immediate demand for new renewable materials in the automotive industry due to reasons outlined beforehand has created a new business landscape worldwide, highlighting the importance of having innovation, high-quality products and sustainability in the same track. This section shows a brief example of bold research and development projects that might create alternative solutions towards the traditional automotive supply-chain.

UPM-Kymmene, a Finnish company operating within the forest industry, has recently launched in partnership with Helsinki Metropolia University, the “Biofore concept car”, showing the potential of bio-materials as real alternatives to traditional oil-based resources throughout the automotive value-chain, without compromising quality, durability and safety.

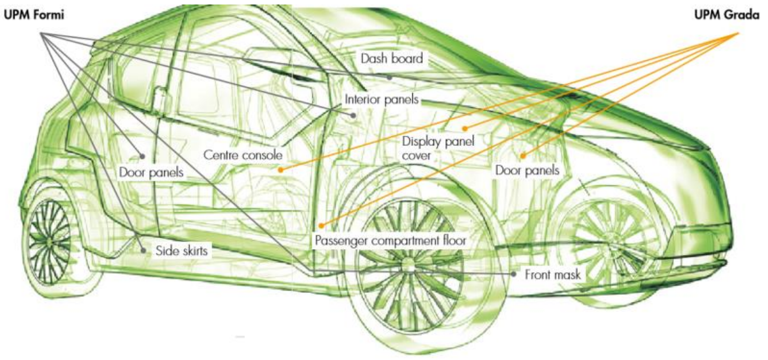

Figure 21: *The Biofore Car developed by UPM-Kymmene and Helsinki Metropolia University. Adopted from [59].*

The innovative and advanced utilisation of cellulosic fiber-based composites was responsible for developing the biofore concept car (Figure 21), weighing approximately 12% less than a conventional equivalent sized car, leading, consequently, to significant fuel consumption reduction and less greenhouse gas emissions. The vehicle utilizes UPM biomaterials trademarks such as UPM Formi® bio-composites and UPM Grada® thermoformable wood material to manufacture the primary car components. UPM Formi®-based materials are made by certified cellulosic fibers and clean polymers that allow reduction of the oil-based material dependence up to 50% by adding renewable fibers. Recyclable, clean, odourless, UPM Formi® was used to produce the front mask, side skirt, dashboard, door panels and interior panels of the biofore car. UPM Grada®, material that consists of thin wood-based panels pressurized and heated up to 95 °C, was used to fabricate the passenger compartment floor, centre console, display panel covers and door panels of the biofore car. The car still relies on carbon fiber reinforced composites and metals as primary resources to manufacture the car chassis and load-bearing parts, respectively. Nonetheless, the majority of the car parts are biodegradable and can be further recycled and reused. Moreover, the possibility to use UPM trademark renewable fuel, nominated as UPM BioVerno®, which reduces the greenhouse gas emissions up to 80% in comparison with conventional fossil fuels, illustrates a promising case that can be overspread among the automotive manufacturers, backing the development of a new automotive value chain based on renewable materials and sustainability. [59]

3.2 Construction Industry

Building and infrastructure are fundamental components to support economic and social development worldwide. The construction industry value chain is strongly dependent on materials and energy, which in most cases, are still obtained by non-renewable resources. In consequence, a wide range of research is being performed in order to assess how environmentally friendly these materials, technologies, and buildings are, and what can be done to mitigate environmental impacts as well as achieve a more sustainable construction industry. Within this context, it is essential to define the embodied energy and operation energy. The first includes the energy used for construction, maintenance, renovation and demolition of the building environment, being strongly related with this work objectives. The latter covers the energy need towards the building environment operation [55]. Therefore, these two parameters are relevant to define the carbon footprint of the construction industry in modern society, which in turn tell us the environmental impacts and their contributions regarding the greenhouse gas emission. Based on extensive research and life cycle assessments (LCAs), construction industry including mainly the manufacturing of concrete and steel, accounts heavily for the world energy consumption as illustrated in Figure 22(a), and the sector still remains as one of the most relevant carbon dioxide emissions sources as shown in Figure 22(b) [56]. Therefore, since CO_2 emissions cause global climate change, environmentally conscious builders, aim to develop energy-efficient buildings, from embodied and operation energy point of view, to tackle these issues, allowing then a larger scope towards the use of bio-based materials, where wood-fiber reinforced composites emerge as a promising solution within this context as explained in further details next.

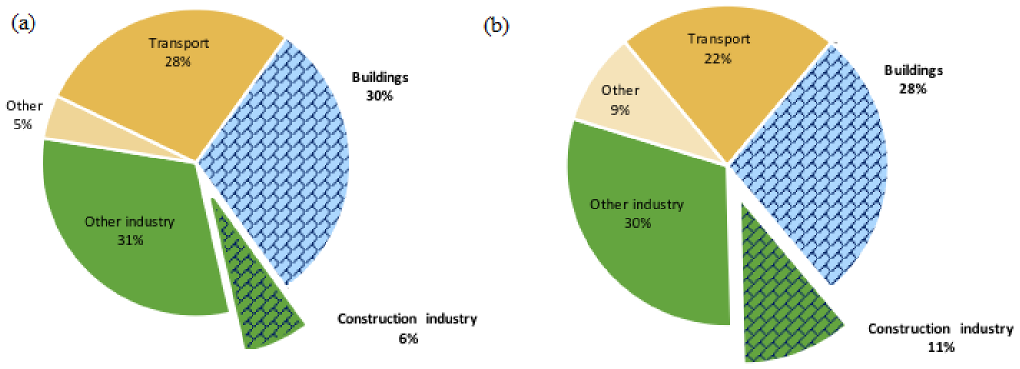

Figure 22: *(a) Share of global final energy consumption by sector, 2015. (b) Share of global energy-related CO2 emissions by sector, 2015. Adapted from [56].*

The utilization of wood-fiber reinforced composites has the longest history with regarding natural fiber composites and dates back more than 1200 years in China when wood-fiber clay composites had been applied in rural dwelling, showing excellent mechanical durability and environmental performance [41]. Due to the need for environmentally friendly materials and the reduction of the carbon footprint in the segment, the building industry has boosted the application of bio-composites towards housing and infrastructure products.

The new concept of green materials towards the building sector was first developed and applied by the US housing industry and nowadays has been successfully overspread worldwide. In most cases, the extensively used material for these purposes are wood-fiber reinforced composites, with optimized design and interface adhesion, offering a multitude of opportunities to manufacture housing decks, structural insulated panels, exterior moldings, window frames, trim products, etc. Moreover, blending wood-fiber reinforcements obtained from sawmill residues with recycled high-density plastics such as PE and polyvinyl chloride (PVC) also provides promising alternatives for housing purposes as shown in Figure 23(a). These materials are obtained in the form of hollow profiles and in many cases, can become more flexible under hot weather and more rigid in cold weather than other conventional building materials. Plastic trim products are another sort of wood-fiber based composites, obtained by blending wood flours (volume ranging from 40 to 60%) with thermoplastic matrices (PE, PP or PVC) manufactured by pultrusion technology. Hence, due to the manufacturing flexibility of pultrusion technology, many building materials can be pultruded such as exterior trims, shingles and sidings as illustrated in Figure 23(b). [50]

The mechanical performance relies strongly on the matrix selection as well as the composite density, where the higher the density, the better the dimensional stability, material resistance itself and indentation resistance. Undoubtedly, wood-fiber reinforced composites have clear potential towards building applications, however low cost-effectiveness based on low-production volume, and high-cost for high-quality fibers production, are still some drawbacks that demands more research and investment for further development. [50]

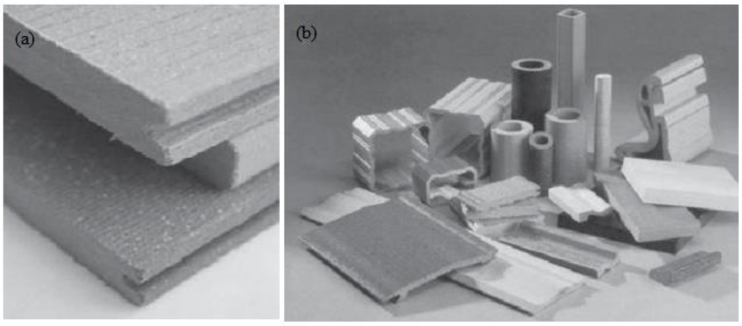

Figure 23: *(a) Decking produced from wood reinforced composite. (b) Pultruded natural fiber composite products [50].*

Still going through other applications, wood-fibers have also been successfully applied in the form of [41]:

- Board engineering materials including MDF (medium density fiberboard) and hardboard (HB) (Figure 24(a,b)), usually stronger and denser than particleboard (PB) with large applications related to building materials. MDF are used extensively as advanced wall coverings, offering better resilience to wear, tear and temperature changes in comparison with PB, plastic wall and solid wood panels.
- Wood-fiber composites also offer an alternative solution towards insulation materials, which are named as wood-fiber insulated boards as illustrated in Figure 24(c,d). These materials are usually applied in the form of wood-fiber fabrics and can be produced by using 80% recycled newspaper, cardboard and paperboard, wherein most of the cases are chemically treated in order to ensure fire resistance and other specific properties. It has excellent acoustic properties and similar insulation performance when compared to traditional insulation materials such as glass fibers.
- Wood-fiber cement composites (Figure 24(e,f)), are relevant materials applied in the modern building industry that are used to manufacture insulating concrete forms, noise barriers, among other products, based on their dimensional stability under moisturized atmospheres and fire resistance properties.

Although these materials offer a multitude of applications within the construction industry, particular cases might require different composite properties and performance. Hence, the majority of composites manufactured for the construction industry usually need to match with the performance requirements listed next [57, 58]:

- Good mechanical properties such as strength and stiffness per unit weight;
- Mechanical resistance, including wind loads, harsh outdoor conditions, and the building load itself;
- Resistance againt moisture absorption, large variations in temperature, freeze-thaw regimes, sea-water, alkaline environments;
- Chemical reactions resistance between the material and the atmosphere gases, pollutants, rainwater and acid environments;
- Photo-degradation resistance, due to polymer chains and chemical bond degradation under continuous energy uptake from global radiation;
- Long-term performance and durability;
- High durability against corrosion;
- Ease of installation and reduced manufacture time.

Due to the photosensitive polymer chains and hydrophilic behaviour of wood-fibers, their use towards composite outdoor construction materials is still limited, where weathering effects such as UV light, temperature and moisture negatively influence their performance, degrading mechanical properties and also changing surface appearance.

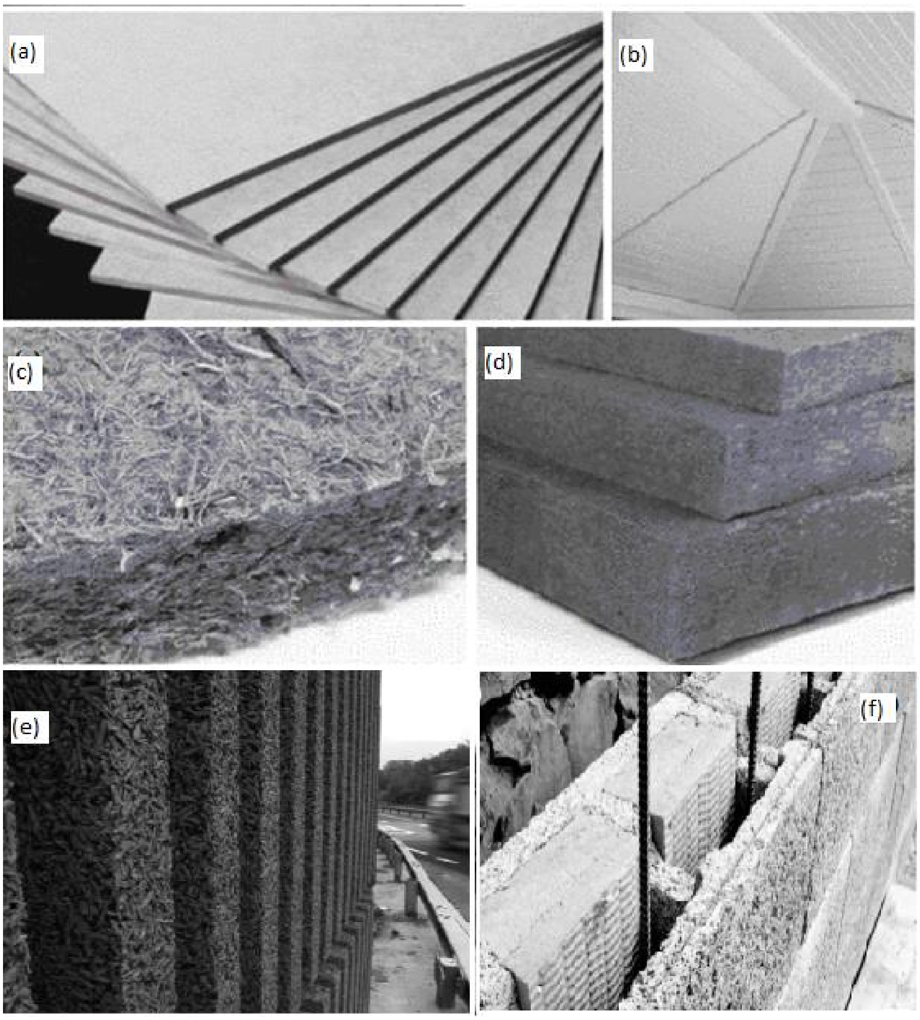

Figure 24: *MDF in building construction: (a) MDF raw material; (b) roofing. Wood-fiber board as insulation: (c) non-woven mat; (d) soft board. Wood-fiber cement composites: (e) sound wall: (f) wall [41].*

3.3 Market analysis of natural fiber reinforced composites towards the automotive and construction industry

Dealing with exterior automotive components demands special attention due to the extreme and hard operation conditions, thus, automakers are aware of the wood-fiber drawbacks such as low dimensional stability under moist conditions, low thermal resistance, and others as listed in Chapter 2, making the automotive industry sceptical of applying natural fiber reinforced composites in exterior vehicle components [54]. By contrast, as already well-developed and applied over the past years, natural fibers reinforced composites are successful and potential materials towards interior car components, mainly to manufacture interior trims for high-value doors and dashboards, rear shelves, trims for trunks and spare wheels, etc., as listed in Table 4.

As stated previously, remarkable applications of wood-fiber reinforced composites are taking place towards the automotive and construction industry in European markets. It is estimated that between 10-15% of the composite market in 2012 was supplied by natural and wood-fiber composites, with primary utilization in decking, siding and fencing, as well as automotive interior parts. The production of wood-polymer composites in the European Union in 2012 was 260,000 tonnes, where 65% of the volume was used for decking materials and 23% for the automotive industry. Furthermore, 92,000 tonnes of natural fiber reinforced composites were manufactured to meet mainly the automotive demand. In that year, the composite industry, covering traditional materials such as glass and carbon reinforced composites manufactured 2.4 million tonnes of composite materials, showing a low natural fiber reinforced composite market share of 15%. [60]

With the increasing price of polymer and the strong foothold of the bio-based economy in Europe, a consistent growth of the bio-based composite market share is expected over the coming years. By 2020, it is predicted that the production and use of 150,000 tonnes of natural and wood-fiber reinforced composites in the automotive industry in 2012, will expand to over 600,000 tons. Even though the future scenario is promising, it still relies strongly on political incentives to increase the bio-based material presence in the automotive industry. Otherwise, the increasing production can be reduced to around 200,000 tonnes. According to the well-established market of extruded wood-fiber composites for decking, fending and facade elements, its market is still growing nowadays and might surpass the level of tropical wood in most of the European countries by 2020. Approximately 190,000 tonnes of wood-fiber reinforced composites was manufactured in 2012 for the construction industry, and by 2020, the production is estimated to increase to 400,000 tonnes. Table 5 lists the composite market numbers in 2012 and forecasts of the segment. [60]

Table 5: *Production of bio-composites in the Europe Union in 2012 and forecast in 2020 (in tonnes) including the sort of materials and processing technologies. Adapted from [60].*

Composites	Production in 2012	Forecast production in 2020 (without incentives for bio-based products)	Forecast production in 2020 (with strong incentives for bio-based products)
WOOD-POLYMER COMPOSITE			
Construction, extrusion	190,000 t	400,000 t	450,000 t
Automotive, compression molding & extrusion/thermoforming	60,000 t	80,000 t	300,000 t
Technical applications, furniture and consumer goods, mainly injection molding	15,000 t	100,000 t	> 200,000 t
Traded granulates for extrusion and injection molding	40,000 t	200,000 t	> 300,000 t
NATURAL FIBER REINFORCED COMPOSITE			
Automotive, compression molding	90,000 t	120,000 t	350,000 t
Granulates, injection molding	2,000 t	10,000 t	> 20,000 t

4 THERMOMECHANICAL PERFORMANCE ANALYSIS AND TESTING METHODS

The absence of a composite database due to its recent development, dated back in the 1950s, increases the need of testing methods to evaluate this class of engineering materials. Based on composite end-use applications, in which most are related to loading environments and service conditions, the mechanical properties are often the most relevant parameters to be assessed and tailored in order to meet performance requirements. Hence, the material selection in many cases is usually made according to the analysis of tensile strength, Young's modulus, elongation at break, flexural strength and impact strength. Moreover, the thermal properties of composites including flammability and thermal degradation are also relevant, which should be appropriately evaluated in order to comply with thermal safety requirements of the materials. Thus, a thorough understanding of properties analysis by laboratory tests becomes a crucial step to ensure proper material design and, consequently, optimum thermomechanical performance and suitable lifecycle as covered next.

4.1 Standardized testing methods for mechanical properties analysis

This section explains the most relevant standardized testing methods and their requirements briefly:

- Tensile test: Test specimens are prepared mainly by injection or compression molding and are submitted to ASTM D3039, ASTM D638 EN 61, ISO 3268, ISO 527 standardized tensile testing methods, following strict requirements concerning specimens' dimensions, conditions and test parameters. Since the properties of many materials might change even with small temperature variations, it is recommended to execute the test in the standard laboratory atmosphere of 23 ± 2 °C and 50 ± 5% relative humidity. The prepared samples are tested under constant stress-strain test, determining the tensile strength, Young's modulus and elongation. A stress-strain curve is obtained throughout the test, determining the tensile modulus and elongation values and other tensile parameters [50].
- Flexural properties: Flexural strength is the ability of the material to resist loads applied perpendicularly to its longitudinal axis, creating, therefore, a combination of tensile and compressive stresses in the material framework. Flexural properties are calculated according to stress and strain that occur in the material surface, and the test is executed according to ASTM D790 and ISO 178 standards. There are two main flexural testing methods: three-point bending method and four-point bending method.

The former is carried out by loading in the constant rectangular cross-section material in one single point (symmetrically with respect to the two-supporting points) and is usually applied to composites that break at small deflections. The latter utilizes the same type of specimens, and two loading points are considered, which are equally spaced from the supporting points. The test is designed mainly for materials that withstand larger deflections. A load-deflection curve is plotted if the flexural module is desired [50].

- Impact/toughness properties: The ability of the material to absorb energy without rupture is defined as toughness, which is divided into two types: equilibrium toughness and impact toughness. Equilibrium toughness is related to the area of under stress-strain curve determined by the tensile test at low strain rate. Impact toughness test is one the most common method, where an impact load is applied onto the material, assessing the internal material deformation to accommodate the impact. The tests are mainly performed by standardized Izod and Charpy tests (ASTM D256), where a pendulum is released from its highest position, striking the specimen, and breaking it up and then stopping on its lowest height. Therefore, the toughness is defined according to energy conversion principles, where the height difference and consequently the potential energy differential is proportional to the energy absorbed by the material. Toughness tests can also be performed by falling dart tests (ASTM D5628) [50].

4.2 Thermal properties analysis

Due to the sensitivity of organic materials to flame, the majority of reinforcement and matrix phases tend to alter their features under high-temperature conditions. Thus, the flammability of wood-fiber reinforced composites is also another relevant aspect to be considered from the performance point of view. It is mainly determined by the matrix phase, since natural or synthetic reinforcements slightly influence this parameter when compared with the matrix effects. However, it is important to note that natural fiber reinforced composites generally possess higher flammability than carbon or glass fibers in the same matrix according to the significant flammability contribution of natural fibers themselves [72]. Therefore, the study of composite’s fire-resistance is of great relevance in order to ensure proper thermal performance and fulfil safety measures.

With the aim to improve and control the thermal stability of composites, different procedures are undertaken such as flame-retardants, fire barriers, coatings and additives, among others. Generally, the mechanism of most of these methods is based on the formation of a protection layer to minimize mass flow, flux and heat exchange towards the matrix, resulting therefore in better composite fire resistance. A well-known technique applied to natural reinforced composites, which is carried out by increasing the char formation over the composite burning, has also offered enhanced composite thermal stability by expanding the char formation during the burning and reducing the combustion [70].

Furthermore, flame-retardants, including phosphonates, magnesium hydroxide, silica, nanoclay particles and ammonium polyphosphate (APP), are commonly applied into the composite framework to enhance the composite thermal stability. However, their addition negatively affects the composite mechanical properties by reducing tensile strength, impact strength and elongation at break. It is mainly attributed to the poor compatibility between the fire-retardant materials and matrix phase according to the agglomeration of large particles onto the fibers surface and the formation of mechanical failure points that boost the fracture of the material. [72]

Among several methods available for thermal stability analysis, the following techniques have been greatly utilized:

- Official tests: The cone calorimeter (CONE) executes the most common test based on the ISO 5660 or ASTM 1454 standards, which provides the fundamental combustion characteristics such as ease of ignition, heat release rate, weight and temperature of sample as it burns, rate of weight loss, rate of smoke release and yield of smoke in a wide range of ignition and temperatures. In parallel, the automotive industry tests plenty of vehicle components by flame spread index (ASTM E162) and smoke density generating rate (ASTM E662) [72]. CONE technique is based on the oxygen consumption and measures numerically the heat release rate (HRR) in the calorimeter along the test. High-efficiency flame-retardant system shows low HRR value. The method plots the heat flux in the function of time [73].
- Laboratory tests: Utilized for material development and improvement, where the most common and accurate standardized method is limiting oxygen index (LOI) based on ASTM D2863 procedure. LOI is defined as the minimum concentration of oxygen that sustains the combustion of a polymeric material. High LOI results are associated with low material flammability [73]. The vertical burn test (ASTM D568 and D3801) and the horizontal burn test (ASTM D635) are other alternatives for flammability analysis [72].
- TGA: The method is usually applied to assess the thermal stability of polymeric materials as well as their composition under high-temperatures. The testing mechanism analyses the weight change of material over different temperatures in an inert atmosphere, plotting the weight of the material as a function of temperature. By this method, it is possible to obtain the polymer decomposition temperature, thermal stability, oxidative stability and compositional analysis [74].

5 THERMOMECHANICAL PERFORMANCE ANALYSIS OF CONVENTIONAL AND WOOD-FIBER REINFORCED COMPOSITES

Considered one of the most relevant raw materials within the automotive and construction industry, PP and its applications in these fields as the matrix phase have gained significant attention over the past years. PP shows excellent performance when reinforced with synthetic and natural reinforcements due to its flame resistance, impact strength, dimensional stability, and so on [75]. In the automotive industry, PP is considered an outstanding engineering polymer and has been extensively used for composite manufacturing, offering, therefore, a multitude of products capable of meeting the broad requirements from the automotive components [71]. In parallel, the utilization of PP reinforced with several types of fibers in the European construction industry, mainly for decking manufacturing, has also increased over the past years [60]. For composites purposes, this sort of polymer can be reinforced by various types of fibers, where carbon fibers, glass fibers and aramid fibers are still substantially applied for the manufacturing of PP-based composites according to their excellent properties as exploited previously in this work. The utilization of glass fiber reinforcements, for instance, embedded in several sorts of polymers is by far the largest group of materials applied in the composite industry over the past years according to literature reports [77]. By reinforcing PP matrix with glass fibers, the tensile strength, Young’s modulus, heat distortion temperature and other properties are greatly improved in comparison with neat PP [88].

Consequently, the strong foothold of PP towards the automotive and construction industry, as well as the high demand for synthetic fibers in the composite industry, justifies the relevance of alternative biomaterials capable of meeting the broad requirements of quality, performance and cost-effectiveness. In this context, this chapter gathers data from recent studies found in the literature, with the primary aim to evaluate the potential of WFRBCs to replace PP composites reinforced with traditional synthetic fibers from the thermomechanical performance’s point of view.

5.1 Mechanical and structural properties of glass fiber-reinforced PP composites

Kallel et al. (2018) [88] investigated the mechanical and structural properties of glass fiber PP composites and the influence of PP grafted with MA (PP-g-MA) on the composites' performance. It was utilized glass fibers of 10 µm and 4.5 µm in diameter and length, respectively. Carbon black (CB) was applied as a black colorant and a UV stabilizer, and two PP composites were manufactured with different content of fibers and PP: PPGF30 (30 wt % GF, 68 wt % PP and 2wt % CB) and PPGF30M (30 wt % GF, 63 wt % PP, 5 wt % PP-g-MA, and 2wt % CB). The composites were processed by a twin-screw extruder at a barrel temperature of 240 °C. Lastly, the compounded extrudates underwent a cooling process in water and cooled air ill ambient temperature. A Batenfeld injection molding machine prepared the testing samples. Tensile tests were performed on a Galdabini 1890 QUA-SAR device, and the samples were fabricated following the ISO 527-2/1A standards. The impact strength analysis of the samples was carried out by Charpy and Izod testing methods.

The results of mechanical properties are listed in Table 6 and the stress-strain curves obtained are shown in Figure 25. In contrast of some cases where the elongation at break of polymer composites are reduced by reinforcement addition [89], despite the effectiveness of the interphase, in this case, the presence of MA-PP mitigates the negative effect of reinforcement to some degree as shown in Figure 25. By comparing Young's modulus of PPGF30 and PPGF30M, it can be observed that the composite's elasticity is positively influenced by MA-PP addition. Moreover, in agreement with the results found in the literature, due to the improved fiber/matrix interfacial strength, the tensile strength of PPGF30 is sharply increased by 91% with the incorporation of MA in the composite framework. Figure 26 illustrates the impact strength results. From figure 26 (a), it can be noted a sharp increase of the Charpy impact energy from 12 to 45 kJ/m2 when PP-g-MA was added. Izod impact energy (Figure 26(b)) test also confirmed the positive influence of PP-g-MA towards the composite's impact resistance. Therefore, it shows the better ability of PPGF30M composites at absorbing energy under impact loads compared to PPGF30. Concerning the reinforcement morphology, it was noted from the fiber distribution analysis a considerable decrease of their length, based mainly on the fibers' fractures during the compounding and injection steps.

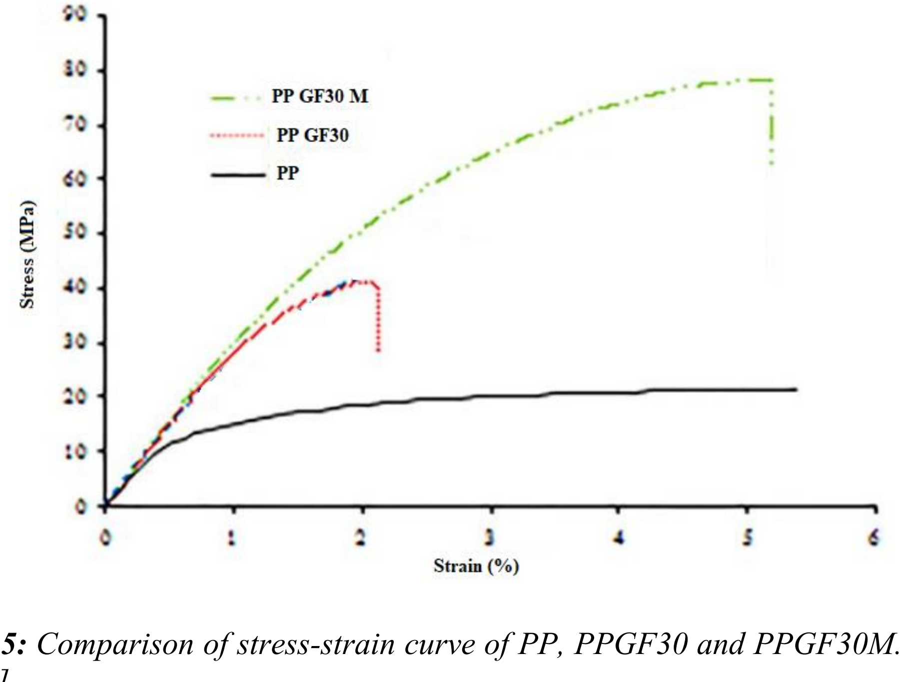

Figure 25: *Comparison of stress-strain curve of PP, PPGF30 and PPGF30M. Adapted from [88].*

***Table 6:** Values of tensile strength and Young's modulus of the studied material. Adapted from [88]*

	Young's Modulus (GPa)	Tensile strenght (MPa)
PP	1.4	33
PPGF30	7.01	42.65
PPGF30M	7.21	81.74

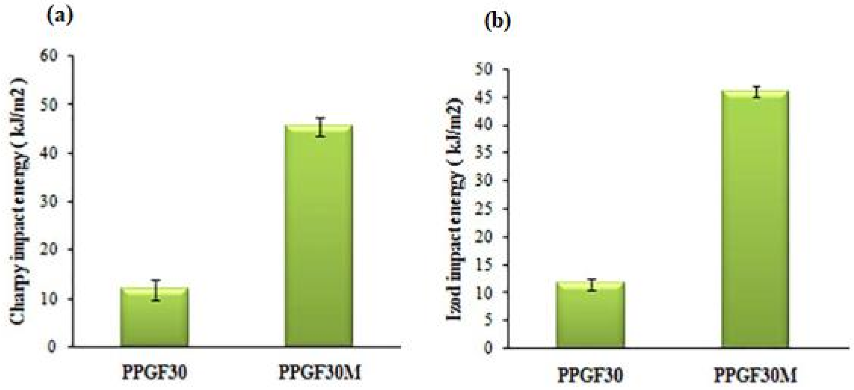

***Figure 26:** (a) Variation of Charpy impact energy and (b) Izod impact energy of PPGF30, PPGF30M. Adapted from [88].*

5.2 Polypropylene composites with natural fibers and wood – General mechanical property profiles

Sobczak et al (2012) [76] investigated the mechanical property profile of natural PP composites manufactured by injection molding technology. The PP composites considered are reinforced with natural fibers and wood particles (named in the article as NFCs and WPCs, respectively) at different volume content, ranging up to 70% of the composite mass. Besides, due to the competition of this class of material in several industrial segments with traditional PP composites reinforced with talc (mineral reinforcement), carbon fibers, glass fibers and aramid fibers in PP matrix, the performance results of both sorts of materials found in the literature are also evaluated by Ashby plots. Thus, a comprehensive overview was given in order to discuss the potential of replacement of traditional PP-based composites by NFCs and WPCs. The mechanical properties analysis includes the generation of Ashby plots as tensile strength vs. tensile modulus and impact strength vs. tensile modulus. In order to assess the potential of lightweight material design, the specific mechanical properties (i.e. absolute values divided by the respective material density) of the materials are also considered. Figure 27 illustrates the tensile properties of PP composites reinforced with the various material types in absolute and specific terms.

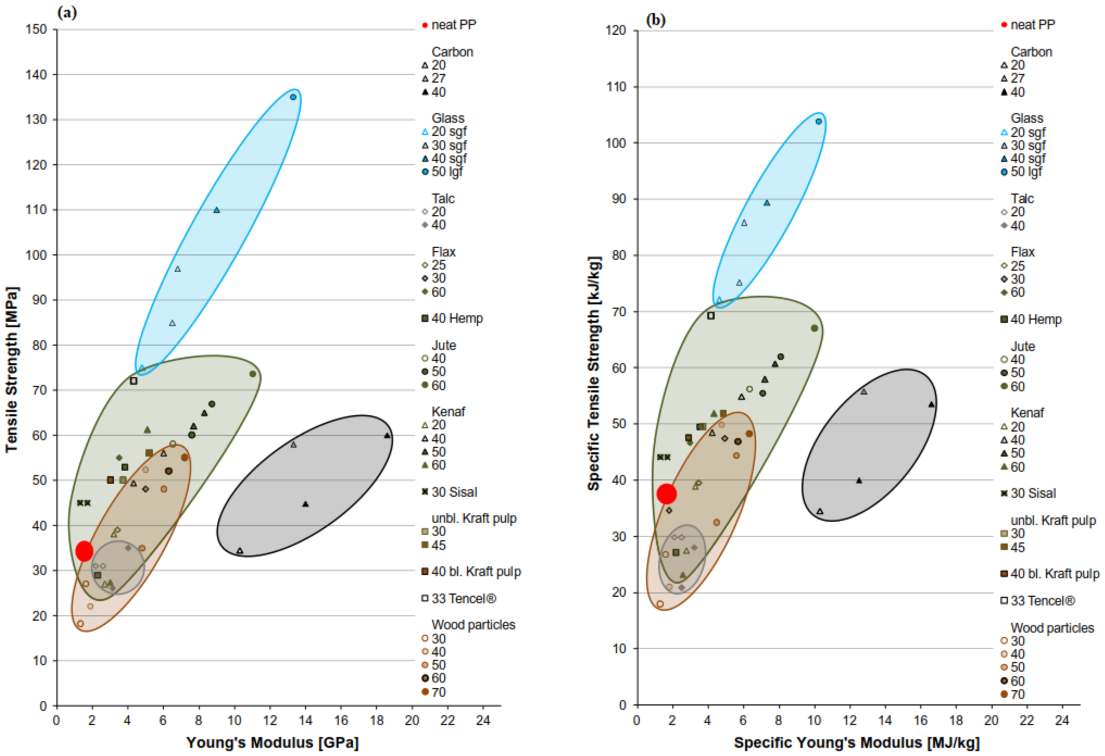

Figure 27: *Ashby plot presenting (a) the tensile strength vs. the Young's modulus of various PP compounds and (b) the specific tensile strength vs. the specific Young's modulus of various PP compounds (property divided by density). The numbers in the caption give* the fiber/filler content in (m%) [76].

From Figure 27 (a), it can be observed that the tensile strength of NFCs and WPCs do not differ significantly in comparison with traditional and commercial PP-based composites (with some remarkable exceptions), where the property regions approach one another. NFCs show modulus/strength of up to about 7 GPa/55 MPa, whereas 11 GPa/75 MPa is noted from WPCs. By contrast, short and long glass fibers (named as sgf and lgf, respectively, in the above plots) PP composites cover a broad modulus/strength regime varying from 5 GPa/75 MPa to 13 GPa/135 MPa, offering higher tensile properties than NFCs and WPCs. A similar tendency is noted towards the specific tensile strength, as displayed in Figure 27 (b), primarily justified by the density difference between natural and synthetic reinforcements.

The impact strength of the PP composites is illustrated in Figure 28 as untouched Charpy values vs. Young's modulus values. The remarkable Young's modulus of NFCs reinforced with Tencel® wood-fiber without compromising the composite's impact strength is noted. Tencel® fibers are obtained from hardwood, which contains cellulose in high purity with little hemicellulose and low lignin concentration [90, 91]. On the other hand, apart from the Tencel® PP composites, all of the other PP composites show inferior impact strength than neat PP. WPCs and NFCs display the most significant reductions.

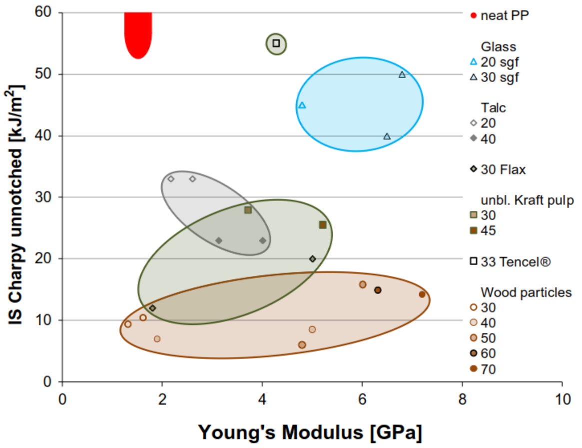

Figure 28: *Ashby plot presenting the unnotched Charpy impact strength vs. the Young's modulus of various PP compounds. The numbers in the legend give the fiber/filler content in (m%) [76].*

5.3 Tensile strength performance analysis of natural fiber reinforced composites in traditional oil-based matrices

Madsen et al. (2013) [53], evaluate the similarities and differences between wood-fibers and plant fibers, as well as comparing the mechanical properties (tensile strength and stiffness) of natural reinforced composites with glass and carbon fiber reinforced composites. The matrix contribution is also taken into account. Table 7 illustrates the results found.

From Table 7 it can be observed that cellulosic fiber reinforced composite, including wood and plant fibers, with a nominal in-plane random orientation (RD), have moderate Young's modulus and tensile strength in the range of 4-8 GPa and 30-60 MPa, respectively. Regarding glass fiber composites also randomly oriented, Young's modulus is noted in the range of 5-7 GPa and tensile strength in the range of 80-100 MPa, showing, therefore, that cellulosic fibers reinforced composites have comparable stiffness and slightly lower strengths. The tensile properties are remarkably increased by the utilization of unidirectional fibers, with Young's modulus and tensile strength in the range of 2-32 GPa and 130-340 MPa, respectively, as listed in Table 7, based on the better fiber packing ability of oriented fibers than randomly oriented ones. In this context, most synthetic reinforcements provide the best packing ability, explaining the outstanding performance of this sort of reinforcement in the composite industry. Recent research has estimated the contributing stiffness of cellulosic fibers related to the composite Young's modulus, ranging widely from 20 to 90 GPa [79] due to their quality parameters as explained in Chapter 2. Hence, considering the best fibers from quality point of view, they can offer similar stiffening properties compared to glass fibers with intrinsic Young's modulus ranging from 70-87 GPa [80].

***Table 7:** Tensile properties of wood and plant fiber composites. The type of fiber preforms used for the composites is given, in addition to their nominal fiber orientation; in-plane random (RD) and unidirectional (UD). For means of comparison, tensile properties of glass and carbon fiber composites are shown. Adapted from [53].*

	Fiber content (%v/v)	Tensile Properties	
		Young's Modulus (GPa)	Tensile Strenght (MPa)
Wood fiber composites			
Wood pulp/PP[1]; RD	27	4.2	28
Eucalyptus saw dust/UP[1]; RD	46	6.2	60
Kraft + TMP/PP; RD	40	4.5	43
Sulphite pulp/PP[1]; RD	50	3.9	51
Kraft/PF—paper; RD	72	[a]26.2	247
Kraft/PF—paper; RD	72	[b]11.7	156
Plant fiber composites			
Flax/starch—loose fibers[1]; RD	37	8.3	51
Jute/PP—non-woven mat; RD	32	8.4	39
Jute/PP—non-woven mat; RD	30	5.2	40
Flax/PLA—non-crimp fabric; UD	39	19.5	150
Flax/epoxy—non-crimp fabric; UD	35	19.8	234
Flax/epoxy—yarn[2]; UD	40	28.0	133
Flax/PET—yarn[2]; UD	48	32.0	344
Glass fiber composites			
Glass/PP—loose fibers[1]; RD	30	7.3	100
Glass/PP—chopped strand mat; RD	20	5.4	77
Glass/epoxy—roving; UD	55	39.0	1080
Glass/PP—roving[2]; UD	60	45.0	1020
Carbon fiber composites			
Carbon[c]/epoxy—roving; UD	60	313.0	1140
Carbon[d]/epoxy—roving; UD	60	142.0	2140

[1]Injection molding; [2]filament winding
[a]Machine direction; [b]cross direction; [c]high modulus fibers; [d]high strength fibers

5.4 Thermomechanical performance analysis of wood-fibers PP composites

Zhang et al. (2011) [73] investigated the thermomechanical properties of wood-fiber PP composites at different concentration of APP and silica as flame-retardant agents. PP-grafted-MA and poly (styrene)-blockpoly (etheneco-1-butene)-block-poly (styrene) triblock copolymer (SEBS-g-MA) were utilized as surface treatment methods. APP is made of phosphate chains of high molecular weight. Considered an effective flame-retardant, APP is mainly utilized with polymeric materials, where the increase of char formation generally drives the flammability enhancements. Silica is utilized in some cases to improve the mechanical properties of composites such as tensile strength and toughness. Besides, silica has also been recognized as a flame-retardant agent [73]. From the mechanical performance context, tensile properties and impact strength were measured. The thermal properties analysis was carried out by TGA, LOI and CONE tests. Extrusion technology utilizing a twin-screw extruder initially prepared the wood-fiber PP composites. The compounded material produced was palletized and dried under vacuum at 80 °C for 24 h in order to control the samples moisture. Lastly, the composite testing samples were manufactured by injection technology with temperature ranging from 150 to 180 °C. The wood-fibers used are LIGNOCEL C120 (wood-flour obtained from softwood) with aspect ratio between 5 and 10, particle size ranging from 70 to 150 µm and 1.45 g/cm^3 of density. Table 8 summarizes the samples prepared and LOI results by varying the concentration of APP and silica.

In agreement with results found in the literature, from Figure 29, a negative influence of the flame-retardant agents towards the tensile strength and elongation at break can be observed, primarily justified by the poor interphase between the matrix and the flame-retardants; cavities formation due to the filers' thermal decomposition and the formation of stress concentration points. As illustrated in Figure 29(a), without the addition of APP, the tensile strength and elongation at break of the composites are 38.5 MPa and 9%, respectively, however, a drop to 33 MPa and 5.8% is noted when APP is added at 40 phr. Similarly, the tensile strength and elongation at break of the composites are sharply reduced by 8.4% and 26.4%, respectively, with silica content at 10 phr as shown in Figure 29(b). In relation to impact strength, it is also noted a decreasing trend by increasing the concentration of flame-retardants. This fact is also correlated to the poor compatibility between the matrix and the flame-retardants, as well as the inferior ability of the matrix to absorb impact energy according to discontinuities created by high fiber content.

Table 8: *Formulation of wood-fiber PP composites and LOI results [73].*

Samples	APP[a]	Silica	LOI[b]
a	0	0	21.4
b	10	0	24.5
c	20	0	26.5
d	30	0	27.4
e	40	0	27.9
f	20	2	27.1
g	20	6	28.4
h	20	10	28.9

* Base material is PP 65 phr; wood-fiber 30 phr; PP-g-MA 5 phr; SEBS-g-MA 5 phr.

[a] Ammonium polyphosphate

[b] Limiting oxygen index

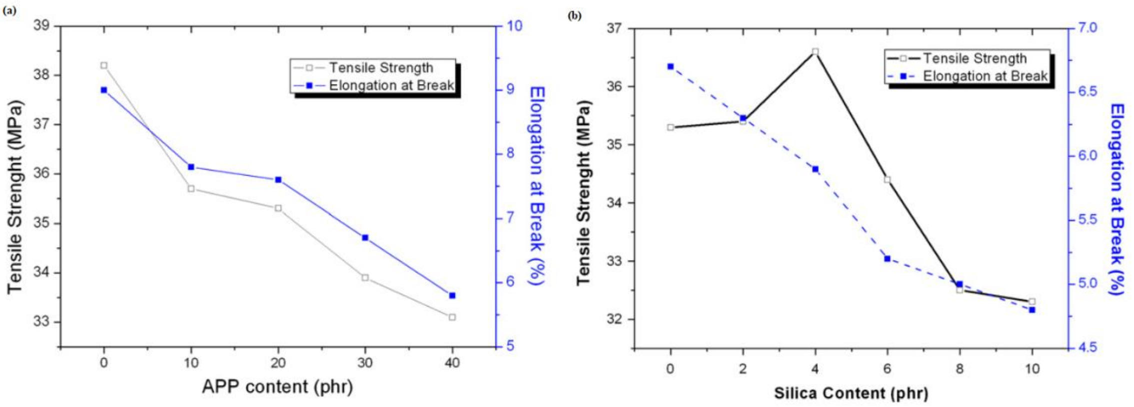

Figure 29: *The effect of (a) APP and (b) silica content on tensile strength and elongation at break of wood–fiber/PP composite [73].*

Concerning the composite flammability, the LOI indexes summarized in Table 8 show the high-efficiency of APP as a flame-retardant agent. The LOI index of neat wood-fiber PP composites is increased by 30% when adding APP at 40 phr due to the effective catalysis of wood-fibers to form char.

The thermal degradation of the composites is also considered. From Figure 30, the degradation of all composites in two steps can be noted. Although the presence of the APP speeds up the first degradation step, the temperature of the second degradation is shifted to higher temperatures. It is mainly explained based on the formation of a protection layer at the first step, which decomposes in sequence to yield a compact charred layer on the surface of the materials that avoids mass and heat transfer between the matrix and the surface.

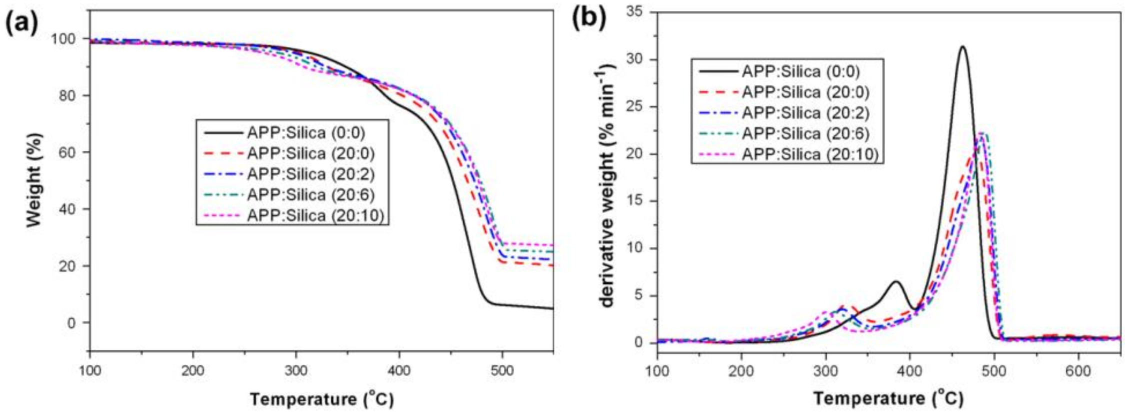

Figure 30: *Thermogravimetric (a) and difference thermogravimetric (b) curves of the wood–fiber/PP composites with different loads of silica [73].*

5.5 Wood-fibers reinforced PLA/TPS bio-composites

Raghu et al. (2017) [61] combined the attractive properties of PLA and starch as well as utilizing glycerol and maleic anhydride (MA), as the plasticizer and reacting interfacial coupling agent, respectively. The bio-composites fabricated in the case, with different reinforcement and matrix concentration, were processed by twin extrusion and injection molding technology and then submitted to thermomechanical properties analysis. The case assessed different scenarios by considering the presence of MA and wood-fibers (at two different weight portions, 20 and 40% regarding the TPS concentration). The wood-fibers were obtained by pulverization and sieving process. Untreated and defect-free *Melia Dubia* wood (softwood) was converted into wood chips, followed by a 24 hour drying process in an oven and then pulverized. In sequence, the pulverized wood was sieved into different particle sizes with standard BSS meshes obtaining - 80 +100 wood powder, that was dried at 105 °C for 24 h to be used for compounding with TPS/PLA. Tensile strength and flexural strength experiments were performed following ASTM D638 and ASTM D790 testing methods, respectively. Also, thermostability and decomposition temperature of the samples were assessed by thermogravimetric analysis, measuring the mass loss as a function of temperature. Table 9 summarizes the bio-composite samples prepared for testing and the mechanical properties of PLA70/TPS30 and PLA50/TPS50, in different scenarios according to the reinforcement volume and surface treatment utilization.

The tensile and flexural strength of the PLA/TPS alone blend is 33 and 24.12 MPa, which are used as reference numbers to further assessment of properties changes by wood-fiber addition and surface treatment with MA. Tensile and flexural strength are improved by 3% and 25%, respectively, with 20% wood-fiber addition. At 40% wood-fiber volume, it results in 35% and 158% increase of tensile strength and flexural strength, respectively. Hence, in this case, the wood-fiber concentration is directly proportional to mechanical properties enhancements, confirming the effectiveness of wood reinforcements in composite structures. By adding 10% MA-grafted-TPS to 30% TPS blend, it ensures a sharp increase of 31% and 103% of tensile and flexural strength, respectively, due to more efficient adhesion between TPS and PLA. When considering an addition of 20% wood-fiber and 10%-MA-grafted-TPS at the same time, the tensile and flexural strength of the blend has significantly increased by 38% and 135%, respectively. Moreover, by increasing to 40% the wood-fiber content, the best results among all samples were reached (51.24 MPa, tensile strength and 65.11 MPa, flexural strength). Thus, it proves the mechanical properties improvements and synergy between the blend, wood-fiber and coupling agents. No significant improvement of tensile and flexural modulus was noted by adding 10%-MA-TPS, whereas slightly improvement was noted by increasing wood-fiber volume.

The same tests were carried out by PLA50/TPS50, and the results followed similarly the conclusions stated previously concerning wood-fiber volume and MA presence. However, it is meaningful to outline the following conclusions:

- Low mechanical properties in comparison with PLA70/TPS30 due to higher concentration of TPS, which displays low mechanical properties.
- Relevant improvement of tensile and flexural strength, probably attributed to the better compatibility between the reinforcement and TPS.

- The effect of wood-content on tensile and flexural modulus was mainly affected by high Young's modulus of wood-fibers and the more efficient stress transfer in the bio-composite framework.

Table 9: *Composition of blends/bio-composites prepared and tensile strength (σ_{TS}), flexural strength (σ_{Flex}), Young's modulus (E), flexural modulus (E_{Flex}), and unnotched impact strength at 70/50% PLA. Adapted from [61].*

Batch name	PLA (%)	TPS (%)	WF (%)	MA-grated -PLA (%)	σ_{TS} (MPa)	σ_{Flex} (MPa)	E (GPa)	E_{flex} (GPa)	Impact strength (J/m)
PLA70/ TPS30	70	30	0	0	33 ± 2.79	24.12 ± 0.74	2.3 ± 0.07	2.4 ± 0.07	100.51
PLA70/ TPS30 (WF20)	70	24	6	0	34.0 ± 1.8	30.25 ± 2.52	1.7 ± 0.1	2.6 ± 0.1	84.24
PLA70/ TPS30 (WF40)	70	18	12	0	44.73 ± 0.5	62.30 ± 1.9	2.7 ± 0.03	3.8 ± 0.1	112.64
PLA60/ GPLA10/ TPS30	60	30	0	10	43.25 ± 1.38	49.09 ± 0.86	2.0 ± 0.04	2.2 ± 0.09	168.59
PLA60/ GPLA10/ TPS30 (WF20)	60	24	6	10	45.65 ± 1.44	56.75 ± 2.00	2.7 ± 0.03	2.8 ± 0.1	111.26
PLA60/ GPLA10/ TPS30 (WF40)	60	18	12	10	51.24 ± 1.26	65.11 ± 0.9	2.8 ± 0.1	3.8 ± 0.08	113.21
PLA50/ TPS50	50	50	0	0	19.45 ± 4.96	21.85 ± 3.15	2.2 ± 0.07	2.4 ± 0.1	75.06
PLA50/ TPS50 (WF20)	50	40	10	0	23.65 ± 3.0	25.59 ± 2.04	1.9 ± 0.1	2.8 ± 0.06	67.03
PLA50/ TPS50 (WF40)	50	30	20	0	32.10 ± 1.62	49.80 ± 1.41	3.0 ± 0.04	4.9 ± 0.04	77.79
PLA40/ GPLA10/ TPS50	40	50	0	10	34.16 ± 1.33	39.68 ± 1.69	1.9 ± 0.04	2.1 ± 0.03	99.17
PLA40/ GPLA10/ TPS50 (WF20)	40	40	10	10	36.29 ± 1.08	45.12 ± 1.59	2.4 ± 0.1	3.1 ± 0.1	74.27
PLA40/ GPLA10/ TPS50 (WF40)	40	30	20	10	44.45 ± 1.26	61.19 ± 1.41	3.1 ± 0.02	5.4 ± 0.06	86.21

Thermal degradation of the blend and bio-composites were analysed by TGA. The temperature of 5 % mass loss of PLA70/TPS30 was 252.30 °C, whereas it reduces to 215 °C in PLA50/TPS50. The temperature reduction is mainly justified by higher content of plasticizer (glycerol) and therefore its volatility and water loss by heating processes. On the other hand, 10%-MA-PLA has slightly decreased the thermal stability of the composites. At 5% mass loss, the respective temperature of PLA70/TPS30 reduced to 194 °C, whereas to 192 °C for PLA50/TPS50. It is explained due to early degradation of grafted PLA. The maximum mass loss is noted in the range between 360 – 380 °C thanks to highest degradation of PLA, TPS and wood-fibers.

The increasing volume of wood-fiber in both PLA/TPS blends has ensured better thermal stability. By increasing the wood-fiber content to 40% in PLA60/GPLA10/TPS30(WS20) and PLA40/GPLA10/TPS50(WF20), the temperature related to 5% mass loss was increased by 26% and 34%, respectively. Therefore, the results confirm a suitable combination of PLA, TPS and wood-fibers supported by thermal properties improvements. Figure 31 shows two different derivative weight behaviours of the matrix blend and matrix blend reinforced with wood-fibers. Two different derivative peaks for PLA/TPS blends are illustrated, whereas only one peak is noted when the blend is reinforced with wood-fibers, i.e., in this case, the bio-composites degradation takes place in one single step due to the thermal degradation of wood-fibers overlapping with same thermal degradation range of TPS and PLA (250 to 350 °C).

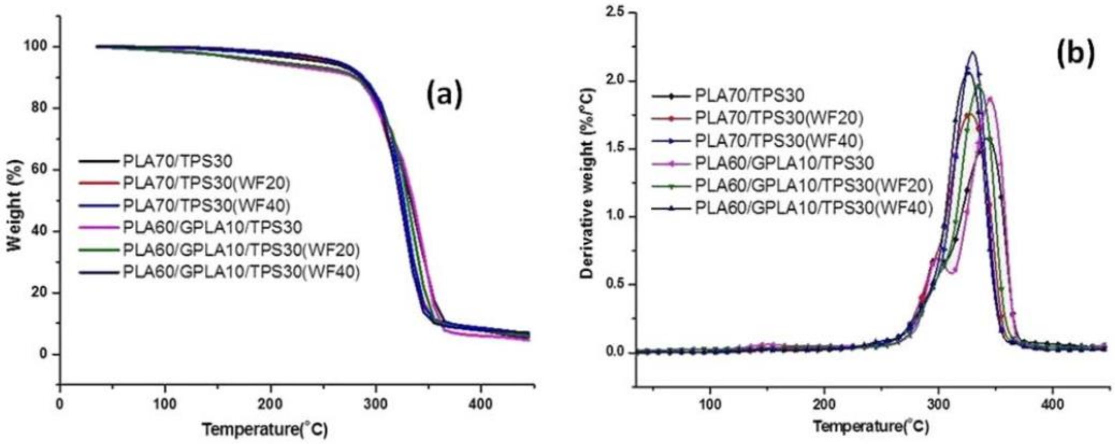

Figure 31: *(a) Thermogravimetric curves of 30% TPS blends/composites and (b) DTG curves of 30% TPS blends. Adapted from [61].*

5.6 Bleached Kraft Eucalyptus fiber PLA bio-composites

Marc et al. (2018) [62] investigated bleached kraft eucalyptus fiber (BKHF) PLA bio-composites, manufactured without any surface modification methods. The bio-composite obtained showed competitive properties in comparison with glass fiber PP composites, where the effects of mechanical properties (tensile strength, strain at break and Young's modulus), interfacial adhesion and the fiber morphology on the composite's performance were analysed. In this case, the wood-fibers were isolated by kraft pulping. With respect to mechanical properties evaluation, micromechanics analysis was performed based on the models available in the literature. The fiber preparation phase was carried out by the pulping process in an aqueous solution of 2/4 of Dygleme to avoid hydrogen bonds between fibers. In sequence, the fibers were dried at 105 °C and shred by knife mill. The reinforcement and matrix were mixed by Gelimat kinetic mixer initially at 300 rpm, then increased to 2500 rpm for 2 min. The composites were made in different BKHF content

(10, 20 and 30% w/w). The mixed material was stored in an oven at 80 °C, avoiding moisture absorption before the composite manufacturing carried out by injection molding technology. The BKHF morphology was previously assessed by mean arithmetic length and diameter with morphological fiber analyser (MorFi Compact) device. Due to possible variations along the injection molding phase, the real impact on the fiber morphology, i.e., length and width, were assessed using a Soxhlet apparatus dissolving the matrix and extracting the fibers from the bio-composites fabricated. Micromechanics methods were used in the case to assess the impact of each phase in the final properties of the fabricated composites.

The fiber morphology results show that the fibers' length is reduced during the mixing and injection phase, mainly due to shear in both processes. The decrease of the fiber length was higher when the fiber volume was increased, in which the high viscosity of the solution demanded more energy to perform correct mixing. Regarding the fiber width, it changed substantially due to the collapse of their lumen. The fiber length and width distribution are shown in Figure 32, from extracted fibers of composites at 30 % w/w reinforcement content. By the results of arithmetic mean of length and width of BKHF, 191.0 and 18.7 μm, respectively, it was possible to calculate the aspect ratio of the reinforcements (length divided by width), showing 10.21 as the result. The literature reports that fibers with aspect ratio higher than 10 have proper strengthening and stiffening capabilities [62].

Table 10-A summarizes the tensile strength (σ_t^C), strain at break (ε_t^C), and Young's modulus (E_t^C) of the bio-composite produced according to different fiber fraction. The case also tabled the contribution of the matrix to tensile strength of the bio-composite, σ_t^{M*}, evaluated as the tensile strength of the matrix at the ultimate strain of the composite. A consistent increase in the tensile strength of PLA, by BKHF reinforcement addition, where the composite tensile strength with 10, 20, and 30% of fiber content was 10.5, 38.6 and 54.3% higher than alone PLA can be observed. There was also a linear relation between the tensile strength of the composite and reinforcement content (correlation coefficient of 0.9934), which in turn shows proper reinforcement dispersion in the matrix as well as good reinforcement/matrix adherence. In comparison with PP, based on literature numbers, PLA alone, due to its high mechanical properties (49.6 ± 0.23) has offered 43% higher tensile strength than PP matrix used by many researchers [81]. Even though in most cases the interphase efficiency of PP based composites, mainly reinforced with glass fibers, are improved by surface treatment methods, the results of this case show that BKHF-PLA bio-composites without surface treatments detain similar properties of glass fiber PP composites from tensile strength point of view. Similarly to the tensile strength, Young's modulus also behaved linearly with the reinforcement content (correlation coefficient of 0.9981). However, it was slightly influenced by the reinforcement volume. Still, the bio-composites developed showed higher Young's modulus than glass fiber PP com-

posites at the same reinforcement content, mainly justified by PLA higher modules compared with alone PP (1.5 GPa) [82]. Therefore, it proves from stiffness point of view, good results for BKHF/PLA bio-composites as alternative solutions towards glass fibers PP composites.

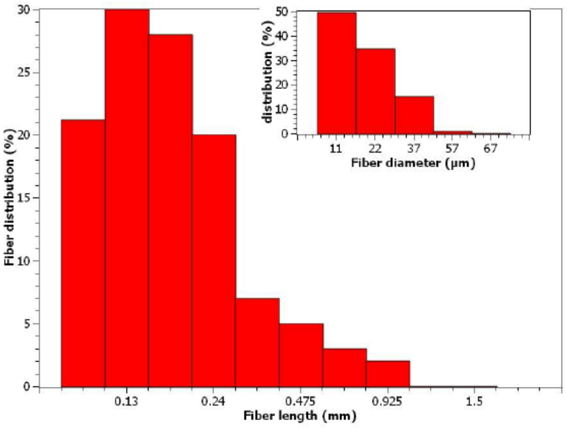

Figure 32: *Distribution of the lengths and diameters of the BKHF, extracted from bi-composites with 30 % w/w reinforcement content [62].*

Table 10-A: *Fiber fraction (V^F), tensile strength (σ_t^C), strain at break (ε_t^C), Young's modulus of the composite (E_t^C) and contribution of the matrix to the tensile strength of BKHF-based composites (σ_t^{M*}) [62].*

BKHF (%)	V^F	σ_t^C (MPa)	ε_t^C (MPa)	E_t^C (GPa)	σ_t^{M*} (MPa)
0		49.6 ± 0.23	3.3± 0.18	3.4 ± 0.11	
10	0.085	57.3 ± 0.48	2.9 ± 0.12	4.4± 0.18	48.4
20	0.172	68.7 ± 1.08	2.6 ± 0.15	5.7 ± 0.22	46.2
30	0.263	76.5 ± 1.31	2.3 ± 0.07	6.8 ± 0.26	44.2

In order to assess the fiber contribution of the bio-composite mechanical properties and the quality of the interphase between reinforcement and matrix, the fiber tensile strength factor (FTSF) and fiber tensile modulus factor (FTMF), were also calculated as illustrated in Figure 33. The FTSF obtained, 176.75 MPa, was clearly higher than softwood reinforcements in the same matrix (123.98 MPa), indicating the higher efficiency of hardwood fibers as reinforcement in comparison with softwood fibers [83]. The FTSF was higher than wood-fiber reinforced PP composites (109.4 MPa), however lesser than fiber glass PP composites without surface treatment (273.85 MPa). Regarding the FTMF obtained, it reveals similar results, with a value of 16.376 MPa, higher than that of natural fiber reinforced PP composites (10.87 MPa), but lower than fiber glass PP composites (32.6 MPa) [84]. As a consequence, it can be outlined that the quality of interface slightly affects Young's modulus of short fiber reinforced composites, and the high FTMF indicates high-efficiency interphase as well as excellent mechanical properties of the fibers.

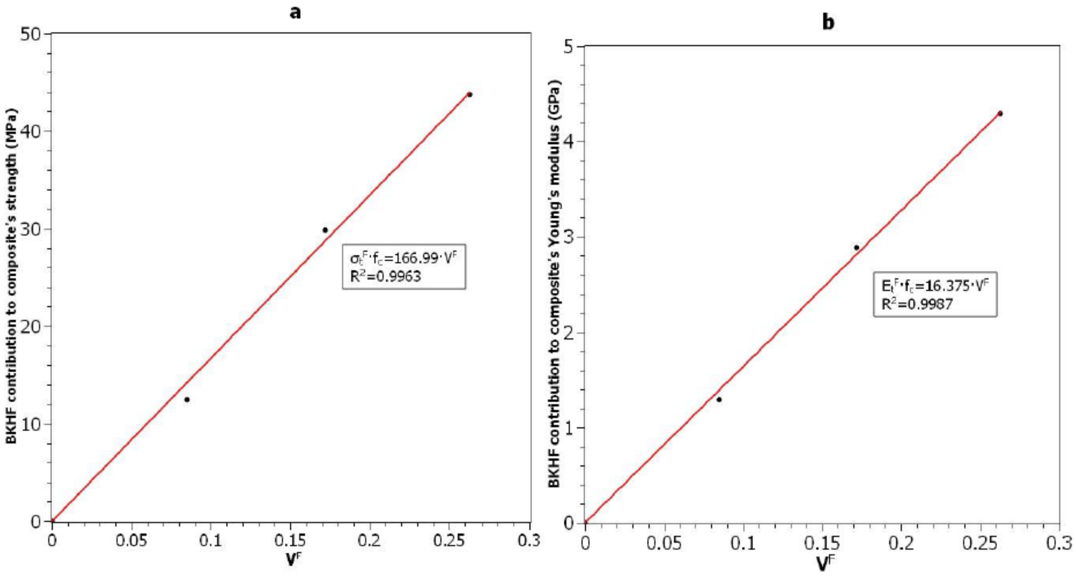

Figure 33: *Net contributions of the reinforcement to the (a) tensile strength and (b) Young's modulus of the bio-composites manufactured [62].*

Micromechanics analysis of the tensile strength and Young's modulus was also performed to confirm previous results as well as further assessments of the effects of intrinsic fiber properties (morphology and orientation) in final bio-composite performance from mechanical properties point of view.

As listed in Table 10-B, the intrinsic BKHF tensile strength, interfacial shear strength and fiber orientation factor were calculated as 768.4 MPa, 27.8 MPa and 0.284, respectively. The interfacial shear strength was near to Von Mises models for high-efficiency interphases ($\sigma_t^M/3^{1/2}$), 28.6 MPa, confirming the strong interphase between PLA and BKHF. Based on Kelly and Tyson model, it was found that the reinforcements contributed 57.4 % to the bio-composite tensile strength, in agreement with high-stiffening characteristics of BKHF according to its FTSF analysis. Based on literature results, coupling factors of around 0.2 ensure optimal interphases, therefore, as also noted from Table 10-B, the coupling factors of the bio-composites produced in the case were higher than 0.2, confirming excellent adhesion between both bio-composites phases [85]. In consequence, it is also concluded by micromechanics methods the high-quality adherence between BKHF and PLA, based on the interfacial shear strength and coupling factor.

Initially, based on Hirsch's model, the fiber intrinsic properties and effects towards the bio-composite Young's modulus were calculated and listed in Table 10-C. The mean intrinsic fiber Young's modulus found was 28.8 ± 1.661 GPa, which is higher than the literature results of bleached soofwood fibers (21.2 GPa) [86]. According to this result, hardwood fibers can perform better regarding stiffening agents than softwood fibers. However, the stiffness properties of BKHF are considerably inferior to glass fibers, with Young's modulus of 71.6 GPa [87]. It is also noted in this case, higher effects of length efficiency than orientation factors, with mean values of 0.92 and 0.6, respectively. In other words, the impact in the bio-composite Young's modulus was mainly driven by the reinforcement morphology, whereas slightly influenced by the reinforcement orientation.

Table 10-B: *Intrinsic tensile strength of the BKHF and micromechanics parameters for modified rule of mixtures of the tensile strength of the composites [62].*

BKHF (%)	σ_t^F	f_c	χ_1	χ_2
10	768	0.20	0.284	0.704
20	768	0.23	0.284	0.810
30	768	0.22	0.284	0.774

Table 10-C: *Intrinsic Young's modulus of BKHF and micromechanics parameters for a modified rule of mixtures of the Young's modulus of the composites [62].*

BKHF (%)	$E_t^F\ (GPa)$	η_e	η_1	η_2
10	28.09	0.541	0.905	0.598
20	31.41	0.533	0.917	0.581
30	29.84	0.547	0.931	0.587
Mean	28.78	0.541	0.918	0.589
S.D.	1.661	0.007	0.013	0.008

5.7 Conclusions from the cases analyzed

The complexity of material selection for composite manufacturing can be addressed by a thorough understanding of how each composite phase contributes to the final composite performance. Based on the results found in the previous cases analysed and the content of this work, the effects of wood-fibers, surface treatment methods and other important parameters in the composite technology are summarized in this section. Also, the influence of wood-fibers and flame retardants towards the composite's properties is briefly discussed. In sequence, the potential of WFRBCs for the replacement of conventional glass fiber PP in the automotive and construction industry is also included in the scope of this section.

5.7.1 The influence of wood-fibers, surface treatments and flame retardants on the composites' performance

- Wood-fiber type is a significant factor: Hardwood fibers should be more favourable than softwood fibers concerning the composite's tensile properties, where better tensile strength and Young's modulus can be achieved according to the higher stiffening capability of hardwood fibers. Even though natural fibers can offer competitive properties compared to traditional synthetic fibers, the utilization of this sort of reinforcement for composite applications relies significantly on proper quality control, according to several parameters and variations that influence their reinforcement capabilities along the fiber cultivation as listed in Table 2.

- Fiber isolation method / Pulping process: Wood-fibers obtained by kraft pulping methods have ensured the highest mechanical properties of the composites (tensile strength and tensile stiffness). Even though the lignin effect related to composites' mechanical properties is still controversial based on literature results, in this work, it was found that high-efficiency pulping methods, concerning the fiber production with high purity cellulose and low lignin content, are the most promising techniques to improve the composite's mechanical properties. Remarkable results related to the composite's impact resistance, as explained in the next, should also be related to the fiber isolation methods and their parameters.
- Fiber fraction and morphology: Wood-fibers have excellent potential to increase the tensile strength, tensile stiffness, and flexural strength of several polymer-based composites. However, impact strength and elongation at break tend to decrease by wood-fibers addition. With regards to the composites’ processing technology, by increasing the fiber fraction in the composite framework, the fibers' length is significantly reduced, based on the fibers’ fractures and high shear rates that occur along the processing steps. Hence, the mechanical properties are negatively influenced by the reduction of the fibers' length, according to the synergy between the mechanical performance and fiber morphology.
- Fiber orientation: The composites' tensile properties are remarkably improved by the utilization of unidirectional fibers, justified by better packing ability of the reinforcement phase. By contrast, Young’s modulus is lightly influenced by the fibers' orientation.
- Surface treatment of wood-fibers: In agreement with the results found in the literature, it was noted that surface treatment methods are excellent techniques to improve the composites’ mechanical properties (tensile strength, flexural strength and impact strength), according to the high-quality interphase obtained. Moreover, the development of composites with excellent mechanical properties without any surface treatment methods is also a reality in the composite industry, as experimentally proved by BKHF/PLA (Section 5.6). Regarding composite elasticity, it was noted that Young’s modulus of composites is slightly affected by surface treatments and, consequently, the interphase quality.
- Flame retardants and thermal stability: By increasing the wood-fiber content, it is possible to improve the thermal stability of bio-composites. Alternatively, the use of flame retardants such as APP and silica in composites has ensured great enhancements towards the thermal stability of the composites, where the temperature of specific mass loss rates is increased mainly due to the charred layer formation, and, consequently, the reduction of heat and mass transfer between surface and matrix. By contrast, the application of flame retardants significantly decreases the composites' mechanical properties (tensile strength, Young’s modulus, impact strength and elongation at break), mainly justified to the poor adhesion between the flame retardants and the matrix. Therefore, the development of flame retardants capable of mitigating adverse effects towards the material mechanical performance is still of great need.

5.7.2 The potential of WFRBCs as alternative materials towards traditional glass fiber PP composites

From the performance evaluation of the WFRBCs considered in this work and their potential to replace traditional composites, promising results that confirm the possibility of switching traditional oil-based composites to this class of bio-composites were found. In this context, WFRBCs have shown competitive and, in some cases, even better mechanical properties in comparison with glass fiber PP composites that are extensively used in the automotive and construction industry as explained next.

- Tensile Strength: The application of WFRBCs, BKHF30/PLA70 (Section 5.6) and PLA60/GPLA10/TPS30/WF40 (Section 5.5) as alternative materials towards PPGF30 (Section 5.1), can offer bio-composites with higher tensile strength, 82% and 22%, respectively, in comparison with PPGF30 (42 MPa). Thus, wood-fiber PLA/TPS composites backed by surface treatment methods confirm the possibility to develop bio-composites with excellent mechanical properties due to the high tensile strength of PLA/TPS blend and high compatibility between the composite's phases ensured by surface treatments. In applications where surface treatment methods and coupling agents cannot be used, BKHF/PLA is a powerful bio-composite able to ensure high tensile properties mainly justified by excellent compatibility between wood-fibers and PLA, as well as the high-contribution from hardwood fibers on the composite's tensile strength. Alternatively, unbleached kraft (at 30 wt %) PP composites and bleached kraft (at 40 wt %) PP composites (Section 5.2) also give competitive tensile properties when compared with PPGF30, where the tensile strength is higher by approximately 20% with the utilization of both wood-fiber PP composites. Thus, it also proves the possibility to obtain good materials in comparison with PP-based composites by replacing synthetic reinforcements by wood-fibers.
- Young's Modulus: Differently from what was noted with regards the tensile strength, the application of PLA60/GPLA10/TPS30/WF40 is still limited if elasticity plays a significant role in the material selection and composite design phase. The Young's modulus of PLA60/GPLA10/TPS30/WF40 is 60% inferior to the Young's modulus of PPGF30 (7.01 GPa). Similar results can be noted from unbleached kraft (at 30 wt %) PP composites and bleached kraft (at 40 wt %) PP composites. By contrast, BKHF/PLA ensures similar Young's modulus (6.8 GPa) when compared with PPGF30 based on the high stiffening capability of hardwood fibers. It is also explained due to the higher Young's modulus of neat PLA (3.4 GPa) than PLA/TPS blend (approximately 2.2 GPa), as listed in Table 10-A and Table 9. Hence, the utilization of bleached hardwood fibers embedded in PLA can be a promising solution when it is necessary to manufacture composites with high tensile properties.
- Impact Strength: In cases which require materials with high-impact resistance, exterior automotive components, for instance, the application of cellulosic fiber reinforced composites is generally restricted. However, wood-fiber reinforced composites show good impact resistance compared with glass fiber PP composites, where unbleached kraft (at 30 wt %) PP composite detains great energy impact resistance of 28 kJ/m2,

while PPGF30 detains only 12 kJ/m2. In addition, as highlighted in Section 5.2, the utilization of Tencel® fibers, which have a high content of pure cellulose, embedded in PP matrix offers an outstanding material with 55 kJ/m2 of Charpy impact resistance. Therefore, it indicates that wood-fibers are materials capable of increasing the impact resistance of PP-based composites, as well as that fibers with high purity cellulose and low lignin content should affect the composite impact resistance positively.

- Elongation at break: In composite applications where the material ductility plays a significant role and good thermal stability is also required, the replacement of PPGF30, which detains elongation at break of 2%, by wood-fiber (at 30 phr) PP (at 65 phr) composites, with insertion of flame retardants (APP or silica) and surface treatments is a promising solution. Wood-fiber PP composites with APP (at 40 phr) and silica (at 10 phr) can increase the elongation at break of PPGF30 to 5.8% and 4.6%, respectively. Regardless of the positive results related to the elongation at break and thermal stability, the application of the APP and silica as flame retardants, significantly reduces the composite’s tensile properties.

6 CONCLUSIONS

The increasing demand for bio-based materials to address industrial environmental impacts and to offer high-quality resources for modern society has been extensively investigated nowadays. In consequence, bio-composites developed by using bio-polymers such as PLA, starch, etc., and naturally available fibers such as wood-fibers have been gaining considerable attention because of their environment-friendly nature, competitive properties and potential to replace oil-based composites.

Wood-fiber reinforced composites have been successfully applied in the automotive industry, considered a relevant material for manufacturing interior vehicle components. However, due to its low-performance for harsh environmental conditions, the application scope of this class of materials towards exterior vehicle components is still limited. Within the construction industry context, wood-fiber polymer composites have consolidated their market share for housing materials over the past years, according to increasing rates of decking materials production. Even though wood-fibers have been utilized for many purposes in the form of composites in the automotive and building industry, as well as the market trends showing increasing demand for wood-fibers for the upcoming years, the combination of these renewable reinforcements with bio-polymers is still modest and under development.

Composites' performance is highly affected by material selection of reinforcements and matrices. Wood-fiber reinforcements can substantially increase the composites’ tensile strength, tensile stiffness and flexural strength, whereas the impact strength and elongation at break are negatively affected by wood-fiber addition. The thermal stability of composites is also positively influenced by wood-fiber addition and can be further enhanced by applying flame retardant materials in the composite framework. However, these materials tend to decrease the mechanical properties of the composites. Thus, the development of flame retardants capable of improving the thermal properties of composites without compromising the mechanical properties is of great need. The fiber morphology also plays a relevant role towards mechanical properties, where the more aligned the fibers are in the composite framework, the better properties are obtained. By contrast, fiber orientation slightly affects mechanical properties.

Regarding the wood-fiber types, hardwood fibers ensure better interphase efficiency and stiffening effects in comparison with softwood fibers according to the higher stiffening capability of hardwood fibers. Among all the fiber isolation technologies, kraft pulping has shown better results towards the properties of wood-fiber reinforced composites. Hence, the pulping efficiency concerning the production of fibers with high purity cellulose and low lignin content should be also properly evaluated when utilizing wood-fibers as reinforcements in the composite industry. As scientifically proven and noted in this work, fiber surface treatments are powerful methods to improve adhesion between the reinforcement and matrix phase, and, consequently, enhancing the composite mechanical properties. Furthermore, the possibility to obtain WFRBCs with competitive properties compared to traditional composites without any surface treatment methods was also observed throughout this work. Regarding the composite's matrix, PLA bio-polymer detains attractive intrinsic properties, which are sharply improved by wood-fibers addition. Therefore, continuous development and research of wood-fiber PLA composites might boost the consolidation of WFRBCs in the composite industry.

The wide variation in properties with the formulation provides an opportunity to tailor the properties of bio-composites to offer a new class of materials towards the modern industry. From the cases analyzed in this thesis, WFRBCs have shown competitive mechanical performance when compared to conventional composites that are extensively applied in the automotive and construction industry. Therefore, WFRBCs confirm the possibility of replacement of traditional oil-based composites by this class of bio-composites, according to their capabilities of performing competitively in relation to glass fiber PP composites. Softwood-fiber PLA/TPS and hardwood-fiber PLA bio-composites, for instance, emerge as promising alternatives towards conventional PPGF30, where the tensile strength of both bio-composites are 82% and 22% superior to PPGF30, respectively. Besides, hardwood-fiber PLA bio-composites are capable of providing similar elasticity properties (6.8GPa) regarding Young’s modulus of PPGF30 (7.01 GPa) without utilizing any surface treatment methods. Regardless of the low impact resistance noted from most of the natural fiber reinforced composites, the utilization of wood-fiber has shown clear potential to improve the composites’ impact resistance. In addition, the development of composites based on wood-fibers with high cellulose purity and low lignin content embedded in the PP matrix can be considered a promising strategy towards applications where impact resistance is one of the most critical requirements.

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Appendix 1

Composite processing technologies. Adapted from [37, 41, 43, 45].

Processing Technology	Advantages	Disadvantages	Applications
Hand lay-up	- Low Cost - Widely used - Low tolling costs - High fiber content possibility	- Skilled person is needed - Health and safety considerations are required for resin handling. - Low viscosity of resin generally compromises their mechanical/thermal properties due to the need for high diluent/styrene levels	Wind-turbine blades, production boats, architectural moldings
Spray Up	- Low labour and operation costs for depositing fiber and matrix in the mold - Low tooling costs - Applicable towards a wide range of composite design	- Laminates tend to be very resin-rich and therefore excessively heavy - Only short fibres are incorporated which severely limits the mechanical properties of the laminate - Resins need to be low in viscosity to be sprayable. This generally compromises their mechanical/thermal properties - The high styrene contents of spray lay-up resins generally mean that they have the potential to be more harmful and their lower viscosity means that they have an increased tendency to penetrate clothing	Simple enclosures, lightly loaded structural panels, e.g. caravan bodies, truck fairings, bathtubs, shower trays, some small dinghies

Resin Transfer Molding (RTM)	- Provides a convenient fabrication route for a variety of application ranging from high-stress components to non-structural items with modest level of reinforcement concentration - High fibre volume laminates can be obtained with very low void contents - Applicable to various forms of fiber reinforcement - Both sides of the component have a molded surface	- Matched tooling is expensive and bulky in order to withstand high pressures - Fibre washing, edge flow and fibre concentration should be controlled accurately - Generally limited to smaller components - Non-impregnated areas can occur resulting in costly scrap parts	Small complex aircraft, automotive components, train seats.
Vacuum Assisted Resin Transfer Molding (VARTM)	- Inexpensive process - Can be set up without highly sophisticated equipment - Requires less space for set up - High fiber volume ratio can be achieved	- Thickness is uneven - Low surface quality - No control over curing - Dimensional control is difficult	Parts being used in transportation, wind energy, marine, infrastructure, and aerospace applications
Extrusion	- Suitable for the production of profiles with any thermoplastic and thermoset composite - Excellent compounding capability, good functional versatility, end performance characteristics, and production throughput	- Demand accurate control of processing parameters in order to avoid the materials thermal degradation - Required a polymer with higher molecular weight for better melt strength	Production of high-performance wood-reinforced composites for structural and construction industry applications

Compression Molding	- No gates, sprues or runner are required - Good for large parts fabrication - Low cost tolling and can be connected with other processes (injection, extrusion - Good for small productions	- More wastage and the mold can be damaged - High labour cost - Slower process time - Contamination - Difficult to control flash	Automotive industry applications
Injection Molding	-The wide range of materials enables almost exact matching of the physical properties required, and multi-layer molding allows tailoring of mechanical properties and attractive visual appearance - In volume, it is a low cost process, arguably with minimal environmental impact. There is little waste created in this process, and it can be re-used	- Requires low viscosity materials - The investment in tooling - making the mold - typically requires high volume production to recover the investment - High control is needed in other to ensure the right process temperature and fibre length - Producing the tooling takes development time, and some parts do not readily lend themselves to a practical mold design	Wire pools, packaging, bottle caps, and several automotive industry applications
Pultrusion	- This can be a swift, and therefore economic, way of impregnating and curing materials - Resin content can be accurately controlled - Fibre cost is minimised since the majority is taken from a creel - Structural properties of laminates can be excellent since the profiles have very straight fibres and high fibre volume fractions can be obtained - Resin impregnation area can be enclosed thus limiting volatile emissions	- Analysis of its physics, dynamics and definition of optimal processing parameters are complex tasks - Some process-induced defects such as premature cracks and potential delamination are inevitable - The presence of unwanted residual shape distortion in the final product is another challenge	Beams and girders used in roof structures, bridges, ladders, frameworks, decks