PERFORMANCE AND PROCESSING EVALUATION OF THERMOPLASTIC WOOD FIBER COMPOSITES

DISSERTATION

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Dedicated to my family

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ABSTRACT

Thermoplastic based composites that contain a variable amount of wood and additives are commonly known as Wood Plastic Composites (WPC). Usually, WPC-manufacturers use wood flour as a filler, due to its relatively easy processability, low cost and good availability. Wood fibers compared to wood flour differ in size and shape. Fibers exhibit a high length to diameter ratio, which can potentially provide reinforcement to the polymer matrix. A drawback of wood fibers is their low bulk density and tendency to form bridges when processed with conventional compounding equipment, such as extruders. Thus, processing at industrial scale is difficult. Thermomechanical wood fibers, as one specific group of fibers, are processed by defibration of wood chips in a refining process. Characteristics such as a high aspect ratio make these fibers a promising candidate for the utilization in polymer composites.

The present thesis evaluates a novel compounding process, which enables the utilization of thermomechanical wood fibers in WPC. The potentials of thermomechanical wood fibers are identified by conducting a literature review and an experimental setup. The reviewed literature is catalogued according to wood fiber pretreatments, composite processing equipment, fiber contents, polymer types and coupling agents. Furthermore, the feed-in and dosing issue is described and possible solutions are discussed. It is concluded, that the composite properties are determined by the fiber morphology and the processing technology used. The reinforcement was found to be peaking at a fiber content of around 40 - 50 wt. %. The experimental study confirmed the challenge of wood fiber feed-in. Regarding the reinforcement of the composite, a threshold value is reached at fiber contents between 40 - 50 wt. %. No significant increment of tensile strength is observed at higher fiber contents. The mechanical properties decreased with increasing fiber content for wood fiber based composites without coupling agent. Additionally, the fiber length was investigated after compounding and injection-molding. The compounding process was found to be the major lever regarding fiber length degradation. The initial fiber aspect ratio of around 30 is reduced between 1 and 7 after injection-molding.

To solve the fiber feed-in challenge and fiber agglomeration, the novel developed process comprises an approach using refiner technology to defibrate wood chips simultaneously with polymer granulates under wet and pressurized conditions. Refiner systems are usually applied for fiber production in the panelboard or papermaking industry. For the experimental evaluation different refiner systems (Sprout-Waldron 12”, atmospheric, batch pressurized and continuous pressurized) were used. The process was found to be stable and continuously operating at different shares

of wood chips and polymer granulates. The obtained fiber / polymer compound showed typically high aspect ratio wood fibers with entangled chopped polymer flakes, which are inseparably attached to the fibres. However, issues regarding the defibration process, such as polymer behavior during defibration, are open and have to be improved in further studies. The compound was further proccesed to bulk material by different processes. The mechanical properties of the produced composite are depending on the further process applied. With each study, however, the mechanical properties of the composites were improved. It is believed that the novel compounding process can save production steps compared to the conventional WPC compounding process. Hence, a less expensive product is expected.

ZUSAMMENFASSUNG

Wood Plastic Composites (WPC) zählen zu den thermoplastisch basierten Verbundwerkstoffen, die aus unterschiedlichen Anteilen von Kunststoff, Holzpartikeln und Additiven zusammengesetzt werden können. Auf Grund der guten Verarbeitbarkeit und der günstigen Beschaffung wird üblicherweise Holzmehl als Füllstoff in WPC eingesetzt. Holzfasern haben im Vergleich zu Holzmehl, auf Grund ihres vorteilhaften Längen zu Durchmesser Verhältnisses (Aspekt-Verhältnis), zusätzlich das Potential die Festigkeiten der Kunststoffmatrix zu verstärken. Holzfasern haben jedoch ein geringes Schüttgewicht und die Neigung sich ineinander zu verhaken, was nachteilig bei der Verarbeitung mit den üblichen Aggregaten der Kunststoffindustrie ist. Daher ist der industrielle Einsatz von Holzfasern in WPC bisher schwer umsetzbar.

Die vorliegende Arbeit untersucht die Eigenschaften von thermomechanischen aufgeschlossenen Holzfasern, die in thermoplastischen Verbundwerkstoffen eingesetzt wurden. Des Weiteren wird ein neu entwickeltes Verfahren sowie die daraus hergestellten Werkstoffe, bzw. deren Eigenschaften, evaluiert. Die Arbeit basiert auf bereits veröffentlichten und nichtveröffentlichten Publikationen. Der bisherige Einsatz von thermomechanischen Holzfasern in WPC wurde durch eine Untersuchung der aktuellen Literatur und Forschungsarbeiten begutachtet. Die Ergebnisse der begutachteten Literatur wurden den eingesetzten Verarbeitungsverfahren und Technologien, dem verwendeten Fasergehalt im Komposit, dem Polymertyp und der Faser-Vorbehandlung zugeordnet. Des Weiteren wurden das Verarbeitungsproblematik von Holzfasern diskutiert und mögliche Lösungsansätze aufgezeigt. Es zeigt sich, dass das Verstärkungspotential von holzfaserbasierten Kompositen von der Fasermorphologie und dem jeweilig eingesetzten Verarbeitungsverfahren abhängig ist. Ein Effekt der Faserverstärkung kann bis zu einem Faseranteil von 40 - 50 mass. % erreicht werden. Das Verstärkungspotential von thermomechanischen Holzfasern in einer Polypropylen-Matrix konnte durch eine experimentelle Untersuchung bestätigen werden. Eine Faserverstärkung in spritzgegossenen Kompositen kann bis zu einem Faseranteil von 50 mass % erzielt werden, wenn ein Haftvermittler verwendet wird. Ohne Haftvermittler sinkt die Festigkeit mit steigendem Faseranteil. Unabhängig des Haftvermittlers steigt das E-Modul linear. Eine Untersuchung der Faserlänge nach der Compoundierung und dem Spritzgießen zeigte, dass bereits nach der Compoundierung die Fasern erheblich eingekürzt sind. Vor der Compoundierung lag

für die Holzfasern ein Aspekt-Verhältnis von 30 vor. Nach dem Herauslösen der Fasern aus der Matrix eines Spritzgußprüfkörpers konnte ein Aspekt-Verhältnis zwischen 1 bis 7 festgestellt werden.

Zur Lösung der schwierigen Faserdosierung und möglicher Faseragglomeratbildung, die die bisherige Verwendung von Holzfasern in WPC erschwerten, wurde ein neuer Verfahrensansatz entwickelt. Das entwickelte Verfahren kombiniert die herkömmliche Holzfasererzeugung mittels Refiner-Technologie und einer Mischung (Compoundieren) eines Thermoplasten in einem Verfahrensschritt. Dabei werden die nassen Hackschnitzel gleichzeitig mit Polymergranulaten unter Druck zerfasert und so untrennbar miteinander vermischt. Üblicherweise werden solche Refiner-Aggregate zur Faserstofferzeugung für Faserplatten oder Kartonage verwendet. Für die experimentelle Evaluierung des Verfahrens wurden unterschiedliche Refiner-Systeme (drucklos, batch unter Druck, kontinuierlich unter Druck) verwendet. Es konnte gezeigt werden, dass der Prozess der Holzzerfaserung mit gleichzeitiger Polymer-Vermischung stabil und kontinuierlich umsetzbar ist. Unterschiedliche Anteile von Hackschnitzel / Polymer wurden getestet. Das nach der Zerfaserung erhaltene Faser / Polymer Compound weist typische Refinerfasern mit hohem Aspekt-Verhältnis, auf, an denen angeschmolzene Polymerfragmente angebunden sind. Trotz der positiven Evaluierung des Verfahrens, ist die Frage des Polymerverhaltens während der Zerfaserung noch offen und muss in nachfolgenden Versuchsdurchführungen untersucht werden. Das Compound wurde mit unterschiedlichen Verfahren weiterverarbeitet. Mit fortlaufender Entwicklung des Verfahrens konnten die Eigenschaften der Komposite verbessert werden. Jedoch wurde aufgezeigt, dass die mechanischen Eigenschaften der geprüften Spritzgußprüfkörper in Abhängigkeit zur Weiterverarbeitungsmethode stehen. Mit der Entwicklung des neuartigen Verfahrens wird erwartet, dass im Vergleich zur herkömmlichen WPC-Herstellung Prozessschritte, wie das Trocknen und die aufwendige Mahlung sowie Fraktionierung, eingespart werden können. Im Vergleich zu herkömmlichen WPC-Verfahren werden erheblich größere Durchsätze erzielt, die schlussendlich zur Reduzierung der Herstellungskosten beitragen könnten.

CONTENT

CHAPTER 1

INTRODUCTION

1.1 WOOD PLASTIC COMPOSITES

Within material science wood plastic composites (WPC) are one specific group of wood based composites (WBC). WPC are defined differently worldwide and cover a wide range of products. In some regions WPC may comprise a material that contains any kind of natural material and thermoplastic or thermosetting polymer. Composites containing natural fibers (jute, hemp, flax or others) are defined as natural fiber composites (NFC). Composites made of wood, from virgin sources, like trees or wood residuals from manufacturing side-streams, are defined as WBC. However, WBC have to be further divided concerning the polymers used as binder or matrix material. Classical WBC products, like particleboards, oriented strand boards (OSB) and fiberboards (high or medium density fiberboards, HDF, MDF) use thermoset resins to bind the wood together. In Europe, WBC based on thermoplastic polymers commonly referred to as WPC, because “plastics” are typically associated with thermoplastics. However, the decisive factors between the two different polymer groups are (i) the present state before processing and (ii) the interaction between the polymer and the wood. Thermoset resins are present in a liquid state prior to processing. They form rigid solids after curing. After curing, unlike thermoplastics, they do not melt again. The curing leads to chemically cross-linked polymer chains that form a three-dimensional network (Hull and Clyne 1996). Thermoplastic polymers are present as solid granulates, flours or fibers prior to processing. In contrast to thermosets, thermoplastic polymers are not cross-linked and thus, thermoplastics are able to melt when heat is applied. Their melt generally features higher viscosity than liquid thermosets prior of curing and are therefore less suitable for impregnation purposes. (Madsen and Gamstedt 2013).

According to the standard EN 15534-1: 2014 WPC are a *“material or product made thereof being the result of the combination of one or several cellulose-based material(s) with one or several thermoplastics, intended to be or being processed through plastic processing techniques”*

The basic idea behind the concept of composites is, to combine at least two different constituents in a single material, whereby each constituent maintains its identity, resulting in a composite material with enhanced properties (Stokke et al. 2014). Next

to the property enhancement the addition of a less expensive filler material substitutes a share volume of the polymer and thus results in less expansive material (Callister 2001).

With the beginning of the industrial production of WPC the interfacing of two different industry branches –the plastic and wood manufacturing industry- took place. The addition of fillers like talc, calcium carbonate and glass or carbon fibers had been well established within the traditional plastic industry. These traditionally produced composites have a broad range of applications. Before the industrial production of WPC, the utilization of wood in composites was mostly constrained by the plastic processors, because of using an inhomogeneous natural material that is difficult to process with the established processing equipment (Clemons 2002, Pritchard 2004). However, wood as filler or reinforcing element in composites has a number of advantages such as its ecological character, low cost, non-abrasive nature and low density (Ashori 2008). Therefore, since 1996, the utilization of wood in thermoplastic composites has gained interest (Clemons 2002) and has been investigated in a vast extent. For several load-bearing applications WPC and NFC pose a viable alternative to conventional glass or carbon fiber composites (Madsen and Gamstedt 2013).

The wood content in WPC can reach up to 80 % (Klyosov 2007). For injection-molded parts, wood contents between 20 % and 50 % are usual (Carus and Partanen 2017). Due to the low thermal stability of wood, process temperatures have to be lower than the degradation temperature of wood which is about 200 °C. This is one of the reasons why commodity thermoplastics like polyethylene (PE), polypropylene (PP) and polyvinylchloride (PVC) with melting points below 200 °C are widely used and currently common as matrix material (Carus et al. 2015, Oksman and Sain 2008). Another point is that the properties and the processing of these commodity polymers are well known, despite the fact that they are less expensive than other technical polymers.

WPC have a wide range of properties, depending on the resources and processing equipment used. Additives can improve the production process, enhance UV protection, flame retardancy and the resistance against biological decay (Oksman and Sain 2008). Coupling agents are needed to enhance the interfacial adhesion between the polar wood component and the non-polar polymer surface (Lu et al. 2000).

To date, WPC are well established products in different fields of applications. Most of the products are used for building, automotive and consumer applications. The

production volume of WPC in the European Union was 260,000 tons in 2012. In 2017, the total biocomposite production volume in the European Union reached 410,000 tons, including WPC and NFC. The highest growth rate (30%) is to be found in innovative applications, such as technical applications, injection-molding, furniture and consumer goods. Roughly 30 manufactures in Europe produce compound granulates for further processing. But only a few producers are able to produce more than 10,000 tons a year. The majority of the granulate producers have capacities of about 500-1000 tons a year (Carus and Partanen 2017).

1.2 PROCESSING TECHNOLOGIES FOR WPC-PRODUCTION

The manufacturing of WPC is based on the production technologies of the polymer industry (Clemons 2002, Schwendemann 2008). Exemplary some of these technologies are displayed in Figure 1.1.

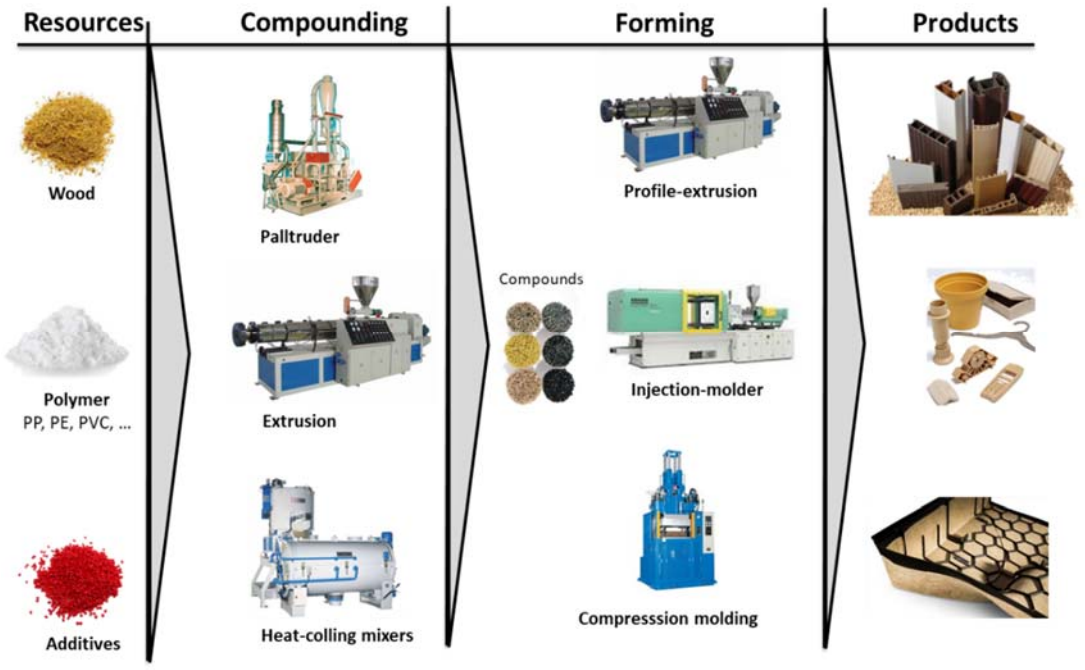


Figure 1.1 Processing technologies for WPC-production.

Independent of the processing equipment the overall process may be divided into a series of basic steps, feed-in, blending, compounding and forming. Additionally, a distinction has to be made between standalone (batch) and continuous operating technologies. The feed-in of the polymer granulate, filler particles and further additives needs to be precise at adequate speed. This can pose a challenge if wood is used as filler. The bulk density of particular wood may range from 70 - 350 kg/m³

(Schwendemann 2008). Fibrous materials cover the lower and flour particles the upper end of this range. The blending of the ingredients may be done as a standalone process with heating-cooling mixers, common in polyvinylchloride processing, where the temperatures stay below the melting point of the polymer and a homogeneous granular dry-blend is produced.

Compounding

The blending may also be integrated into the next processing step, the compounding, which is common in polyolefin processing. Compounding describes a process of changing the properties of a polymer by the addition of additives. Common technologies for compounding are co-rotating twin-screw extruders (Schwendemann 2008). During compounding the polymer is exposed to heat and shear, generated by narrow meshing screw elements, and thereby plasticized. The fillers and additives are dispersed to achieve a homogeneous melt, which is called compound. Dispersion is quite important especially for highly filled composites (Schirp and Stender 2010). If the compounding is not sufficient, reduced mechanical properties are obtained (Schwarzkopf and Burnard 2016). The compounding step also removes moisture and gases from the compound, which is particularly critical in the case of wood. Wood with high moisture contents can act as a foaming agent, which is undesired. To prevent this, atmospheric and vacuum degassing vents support moisture evaporation (Schwendemann 2008). Therefore, a wood moisture content of 1 - 2 % is recommended (Pritchard 2004, Clemons 2002). The venting units are also needed, to remove the air inside the system and to avoid a backward flow which maybe lead to a blocking of the feed-in section (Schwendemann 2008). With the processing of low bulk density materials, a great amount of air enters the extruder which then has to be removed. It has been found, that compounding with extruders is causing filler degradation (Teuber et al. 2013). After compounding the material may be directly formed into products (one-step process) or pelletized for later forming processes (two-step process) (Stark et al. 2010).

Forming

Combining the compounding and forming in a single process, extruders are the most common technologies for infinite linear WPC production. Next to co-rotating twin-screw extruder, single or counter-rotating twin-screw extruders are used. At the end of the process the plasticized melt is forced through a tool with a desired shape.

These types of extruders are mostly used for WPC deckings and profiles, as depicted in Figure 1.1.

To form more complex, three-dimensional structures, injection-molding equipment is used. These machines contain a rotating single screw, which melts the pre-manufactured compound and forces the melt into a mold. After a certain time of cooling the product is ejected. Injection-molding is used, when high production rates and high product qualities are desired.

In order to produce large-scale 3-dimensional structures, like car-indoor panels, compression molding equipment is used. Defined amounts of polymer, additives and wood or pre-manufactured WPC-compounds are placed in a mold. The upper part of the mold moves down, pressing and forcing the placed material into the mold cavity. The mold is equipped with a heating system to melt the polymer. After a defined time, the mold opens and the finished part is removed by an ejector-pin.

1.3 WOOD AS FILLER OR REINFORCEMENT COMPONENT IN WPC

Wood as natural composite, consisting primarily out of cellulose, lignin and hemicellulose, shows different characteristics which differ in a wide range among species, and between the same species and even between pieces of the same pieces (Stark et al. 2010). The natural fibrous structure of wood however, has excellent mechanical properties, which are accompanied by low density. For example, an isolated spruce fiber exhibits an ultimate tensile stress of 530 MPa and a modulus of elasticity of 10,100 MPa (Burgert et al. 2003). It is evident, that wood in WPC is not present in its natural fibrous structure. Wood from virgin sources or post-industrial byproducts like trimmings from sawmills, logging trimmings as well as sawdust and chips have to be chipped and grounded, before may be used for WPC (Schwarzkopf and Burnard 2016). To do so, mechanical breakdown technologies like hammer, attrition mills and refining aggregates are utilized. Due to mechanical and thermal treatment during breakdown, the wood structure is heavily altered and its properties are far away from those present in virgin wood. In dependency of the used technology, the resultant wood geometry may appear in a shape of particles or fibers.

Confusingly though, the term “wood fiber” is often used in general for any form of wood particles. The definition of fibers depends on the point of view: biologically or technically. From a biological perspective, fibers are cell types, specified as softwood

tracheids, hardwood tracheids and hardwood libriform fibers, that provide structural stability to the tree (Schirp and Stender 2010). From a technical point of view, wood fibers may contain single anatomical fibers or bundles, whole fibers or fiber fragments and are obtained through mechanical or chemical processes. Depending on the process, a different fiber geometry is obtained. In the present thesis the technical definition will be used.

In WPC usually wood flour is used, because of the good availability and easy feeding into conventional plastic processes (Oksman and Sain 2008, Clemons 2002, Stark and Rowlands 2003). Wood flour particles (size 100 - 500 µm) are less than 1mm in length and have a wide distribution of length to diameter ratio (aspect ratio or L/D ratio) (Schwarzkopf and Burnard 2016). Wood fibers differ from particles in that they exhibit a higher length to width ratio, i.e. aspect ratio. It is reported, that particle size characteristics, and in particular the aspect ratio is significantly influencing the composite strength and stiffness (Stark and Rowlands 2003, Nourbakhsh and Ashori 2008). Wood flour instead, is more acting as a filler, improving the stiffness but not the strength.

According to the composite theory, a reinforcement of the polymer matrix is achieved, when the resulting strength and stiffness of the composite is higher compared to the properties of the polymer matrix. If the added material only improves the stiffness, the material acts more as a filler (Ehrenstein and Wurmb 1977). For reinforcement effects the following conditions must be met (Ehrenstein 2006):

1. fiber strength σ_f > matrix strength σ_m
2. fiber modulus E_f > matrix modulus E_m
3. matrix fracture ε_m > than the fiber ε_f

If for example a tensile load is applied to a composite, the matrix expands more than the embedded fiber, due to a different stiffness of the components. Thus, shear stress occurs at the interface between fiber and matrix and the forces are finally introduced to the fiber. However the theory requires a good adhesion between the interface of the fiber and the matrix. With increasing fiber length a more efficiently force distribution is achieved (Ehrenstein 2006) which finally results in an strength improvement of the composite. The minimum fiber length that is required to obtain a reinforcement is known as critical fiber length (l_c). The critical fiber length may be calculated by the following equation, with fiber diameter d, fibre tensile strength σ_f and matrix shear strength τc.

$$l_c = \frac{\sigma_f \, d}{2\tau c}$$

The equation indicates that the smaller the fiber diameter, the shorter the fiber length may be and reinforcements are still feasible (Peltola et al. 2014). Tiny wood fibers with high aspect ratios have the potential to provide a good stress transfer, when a load is applied to the matrix.

It is maybe reasonable to classify fibers by their length. Wood fibers are classified as short fibers (1mm – 5mm) and are typically randomly oriented within the composite. Other natural fibers from crops, such as hemp, flax or jute, are classified as long fibers (5 - 50mm) and are typically aligned and oriented within the composite (Madsen and Gamstedt 2013). The effects of fiber length and alignment on mechanical properties of fiber reinforced composites are shown in Figure 1.2. Short fibers composites are preferably processed with injection-molding technology due to fast processing cycles and simplicity. For infinite linear products, short fiber composites are produced by extrusion technology. Long fiber composites are usually produced by open molding and autoclave processes (Ho et al. 2012).

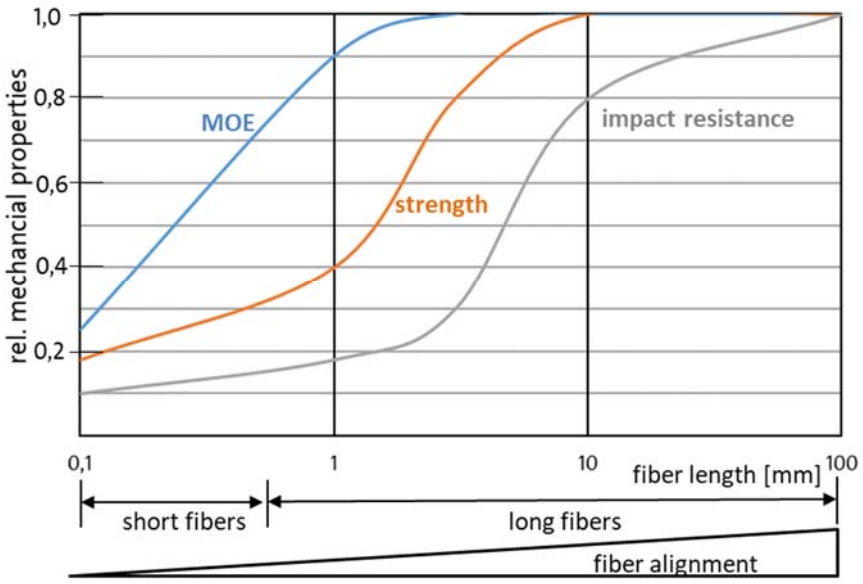


Figure 1.2 Relationship between rel. mechanical properties, fiber length and fiber alignment (modified from Buerkle et al. (2003))

In addition to the particle geometry and aspect ratio, the wood content of the composite is a crucial parameter influencing the mechanical properties. It was found that with increasing wood content the modulus of elasticity increases, whereas tensile strength decreases. By using coupling agents a positive effect of improved strength

properties can be achieved for wood contents of up to 50 wt.-% (Caulfield et al.). However, it was investigated that during compounding, high wood contents increase particle length reduction (Teuber et al. 2016a, Puglia et al. 2008). This is due to a stronger particle-particle interaction (Teuber et al. 2016a) and an increasing viscosity, accompanied by high shear forces (Peltola et al. 2014). In addition, with increasing fiber content, fiber distribution and orientation within the composite becomes more inconsistent. This increases the chance of areas with only partially covered fibers, leading to void formations, which then may have a negative effect on the composite properties (Thomason 2005, Erdmann 2017).

Despite the fact that wood fibers potentially can provide a reinforcement effect, their utilization in WPC is difficult with the traditional processing equipment. General drawbacks of wood fibers and other natural fibers are their low bulk density, the non-free flowing behavior and the tendency to form bridges during feed-in in continuous compounding processes (Thumm et al. 2011). With a low bulk density material, a high amount of air enters the process and has to be removed. If air is trapped in the process, the composite might include voids and finally reduces the composite performance.

In addition, dissolving fiber agglomerates during compounding is challenging with established technologies such as extruders (Le Baillif and Oksman 2009). The formation of agglomerates leads to a lack of fiber dispersion, influencing the composite performance. In case of natural fibers, the formation of agglomerates is believed to be a result of strong hydrogen bonds between the fibers (Gatenholm et al. 1993). The formation of agglomerates takes place by fiber volume collapsing of one to another fiber surface whereby the surfaces are connected by strong hydrogen bonds. Agglomeration maybe occur prior or during compounding. During drying, before compounding, the internal fiber volume shrinks irreversibly (Diniz et al. 2004), due to structural changes of removed water from the wood structure. The dissolving of fiber agglomerates during compounding is investigated by using dispersion aids (Qiu et al. 2003) or by increasing shear energy (Le Baillif and Oksman 2009).

1.4 THERMOMECHANICAL PRODUCED WOOD FIBERS

Thermomechanical produced wood fibers are technical wood fibers, which are usually utilized for:

- fiberboards (medium / high density fiberboard (MDF / HDF)
- paperboards (classified as thermomechanical pulp, TMP)
- insulation material

Principles of defibration

The main mechanism of fiber production is the defibration of the wood structure to fibers with thermal and mechanical energy (Sundholm et al. 1999). These fibers are obtained through a continuous pre-heating of wood chips in a digester followed by defibration in a pressurized system, which is done in a consecutively way (Wenderdel 2015). The thermal treatment of the moist wood chips is done by elevated temperature and pressure in order to soften the lignin within the wood structure. After the thermal treatment, the wood chips are continuously fed via a conveying screw into the defibration zone, where the mechanical treatment and fiber separation takes place. (Sundholm et al. 1999, Chapman 2006). The wood chips enter the eye of two discs, one rotating and the other stationary (Chapman 2006). The opposing discs have a specific pattern obstructed by grooves, bars and dams. The separation of the wood structure to fibers is achieved by contact with the disc pattern and by centrifugal forces. Centrifugal forces and pressure differences in the inner and outer part of the defibration zone, drive the wood outwards. Due to the harsh fiber-fiber collision and narrowing gap distance the fibers become defibrated and fibrillated (Sundholm et al. 1999). The disc is equipped with circumferential dams, that ensure a material movement radial forward, bringing the material back in contact between the grooves and bars. During the process the fibers are constantly flexed up to 5,000 times per second (Chapman 2006, Walker 2006b). During defibration the process heat increases the temperature of the water that is saturated in the fiber, and evaporates the water into steam. Thus, the temperature and pressure between the disc gap can be higher than those in the refiner system. After leaving the defibration zone, the separated fibers are discharged into a blow-line. The received fibers occur in different shapes and geometries, as single fibers, fiber bundles, and shives. The capacity of fiber production can range up to 60 tons/h (Chapman 2006). Figure 1.3 presents a typical refiner plant scheme and a refiner disc pattern as it used for fiber production.

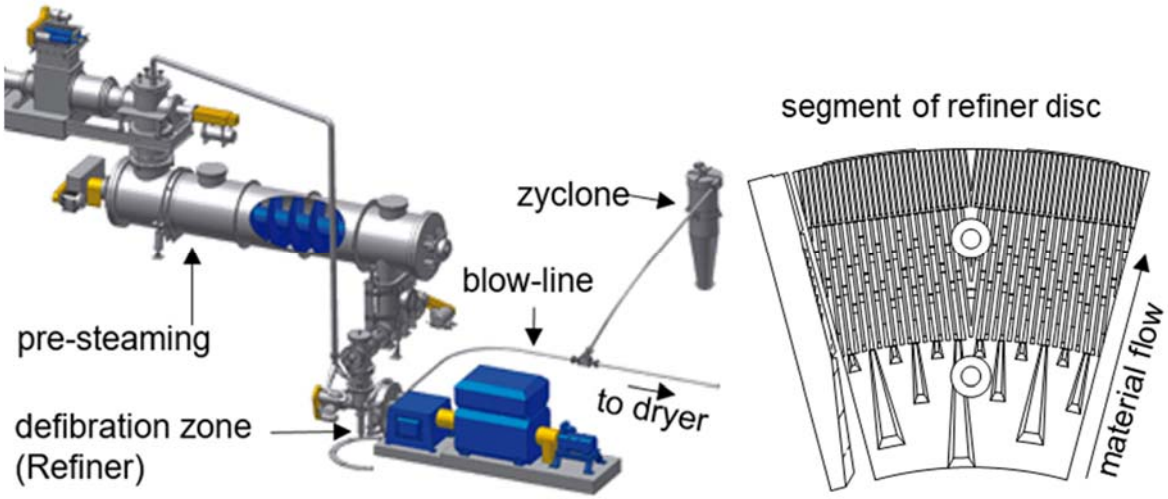


Figure 1.3 Refiner plant scheme and refiner disc pattern (Andritz AG)

MDF and thermomechanical pulp (TMP) production follow the same basic approach. Even the design of the used equipment is very similar. However, the processing conditions and the received fiber quality are different. The processing differences of MDF and TMP fiber production are compared in Table 1.1.

Table 1.1 Processing conditions for MDF and TMP fiber defibration (Walker 2006b, Chapman 2006, Wenderdel 2015, Sundholm et al. 1999)

Parameter	**MDF defibration**	**TMP defibration**
pre-steaming	> 150 – 190 °C (2 – 15 min.)	120 – 140°C (~4 min.)
defibration pressure	8 bar	1.5 – 5 bar
mechanical treatment	250 – 300 kWh/t	> 2000 - 2500 kWh/t
gap distance	0.2 – 0.4 mm	0.2 – 0.4 mm

Fiber morphology

The properties of the fibers after defibration are heavily influenced by the wood species (Krug and Mäbert 2008, Ohlmeyer et al. 2015), the initial shape of the wood resource, intensity of pre-steaming (pressure and temperature), disc gap (Wenderdel and Krug 2012, Ohlmeyer et al. 2015, Benthien et al. 2016) and disc pattern. In general, the MDF and TMP fiber production have two different approaches. MDF fiber production uses higher temperatures which are above the glass transition point of lignin, resulting in a fiber separation between the lignin-rich middle lamella. This leads to a lignin coated fiber surfaces, accompanied with poor hydrogen bonding

properties (Atack 1972, cited from Walker 2006b). In TMP fiber production, the higher mechanical treatment results in fiber surface which is more torn open and the polysaccharide rich regions are exposed, encouraging good hydrogen bonding properties (Walker 2006b).

The amount of individual fibers and fiber bundles can vary depending on the defibration conditions (Wenderdel and Krug 2012). Depending on the defibration conditions, the amount of fiber bundles vary between 40 - 60%, and single fibers between 8 - 32% and coarser dust >1% (Wenderdel 2015).

Figure 1.4 shows typical MDF fibers and fiber bundles after defibration and drying.

Figure 1.4 Visual (left) and microscopic (right) image of MDF fibers and fiber bundles obtained after defibration.

With increasing steam pressure and retention time in the digester, fiber length decreases while the amount of short fibers increases (Benthien et al. 2014). Also the color of the fibers gets darker with increasing steam pressure and retention time (Lerche et al. 2014, Benthien et al. 2016). Groom et al. (2006) found extensive fiber delamination, darker fibers and high quantities of fine fraction at high steaming pressures (18bar). In a previous work, Groom L. et al. (2002) found that with increasing pressure the hemicellulose content decreases and the fiber surface tears open, leading to an increase in fiber surface roughness.

The influence of the defibration conditions on the chemical composition of wood was investigated by Kelly et al. (2015). With increasing pressure during softening the amounts of extractives and glucose increase, while the amount of hemicellulose is decreasing. With increasing pressure and retention time an increasing amount of lignin on the fiber surface was observed by Krug (2010).

Benthien et al. (2016) investigated the influence of the disc gap distance and wood species on fiber morphology. It was found that increasing the disc gap is accompanied with an increase in fiber coarseness. A small disc gap is resulting in finer fibers. Using the same defibration conditions, shorter fibers are obtained from hardwoods (beech and poplar) than from softwoods (pine).

For composite designing or for predicting of composite properties, the fiber strength is important as explained in Chapter 1.3. It is evident, that the above mentioned different processing conditions alter the fiber properties and thus strength properties. Groom et al. (2002) and Mott et al. (2002) showed a differences in tensile strength and modulus of elasticity between juvenile and adult macerated single pine fibers. Tensile strength of adult pine fibers is between 410 – 1422 MPa and a tensile modulus of 6.55 – 27.5 GPa. Tensile strength of juvenile fibers is 33 % and modulus of elasticity 73 % lower. The range of properties depends on tree height and position within the trunk. The same results were obtained by Eder et al. (2008). They stated that the lower tensile strength for juvenile fibers are related to thinner cell walls. The crack initiation of juvenile fibers compare to adult fibers was found to be in relation with the cell wall pits. The pits of juvenile fibers are larger than pits of adult fibers. This different structural nature is leading to different crack initiation accompanied with different tensile strength properties. This observation was confirmed by Mott et al. (2002), who stated that pits serve a strain concentration in fibers under stress and are therefore points of failure.

For defibrated wood fibers, Wenderdel (2015) stated that the properties are extremely influenced by hydro-thermal and mechanical treatment during processing. Due to the variations of fiber geometry distribution, Wenderdel (2015) investigated the tensile strength and modulus of elasticity of single fibers and fiber bundles, depended on the defibration conditions. For single fibers tensile strength between 300 – 600 MPa and a modulus of elasticity between 4 – 16 GPa was observed. Compared to the single fiber strength, the values for fiber bundles are reduced to a half. With regard to the entire investigation higher and lower values as outliers are observed. Wenderdel (2015) as well as Groom et al. (2006) found no linear relationship between tensile strength and defibration conditions, which is discussed by Groom et al. (2006) with regard to the glass transition temperature of the different wood components.

It can be concluded, that thermomechanical produced wood fibers show promising characteristics for the application in thermoplastic composites. Additionally, thermo-mechanical produced wood fibers are readily available at commercial scale which is an advantage over other agricultural-based fibers (Wolodko et al. 2015).

1.5 WORKING HYPOTHESIS AND INTEGRATION OF THE PUBLICATIONS

Based on the introduction, there are indications that thermomechanical wood fibers have distinct characteristics for the utilization in WPC. However, the processing of thermomechanical wood fibers in thermoplastic polymers with standard technologies seems to be limited due to the low bulk density of the fibers and fiber agglomeration. Therefore, the following working hypothesis is drafted:

"The novel process, of simultaneous wood chip and polymer defibration using the refiner technology to obtain a wood fibers based thermoplastic compound, solves the problem of the fiber feed-in challenge and fiber agglomeration, whereby the high aspect ratio of the wood fiber is maintained."

In order to confirm the drafted working hypothesis, the present thesis is divided into two research scopes.

1. **Identify the potentials of thermomechanical wood fibers as resource in thermoplastic polymers.**

   To identify the potentials, a literature review and an experimental study is conducted.

2. **Evaluation of the novel developed process of simultaneous defibration and compounding of thermomechanical wood fibers and thermoplastic polymers**.

   The evaluation of the simultaneous defibration and compounding process is conducted in three different steps:

   1. Preliminary study
   2. Proof of concept
   3. Up-scaling to industrial level

The present thesis is primarily based on four peer-reviewed publications, which are:

Paper I: *Mertens O, Gurr J, Krause A (2017) The utilization of thermomechanical pulp fibers in WPC. A review. Journal of Applied Polymer Science 52:10.*

Paper II: *Mertens O, Krause KC, Weber M, Krause A (2018) Performance of thermomechanical wood fibers in polypropylene composites. Submitted to Wood Material Science and Engineering (under review)*

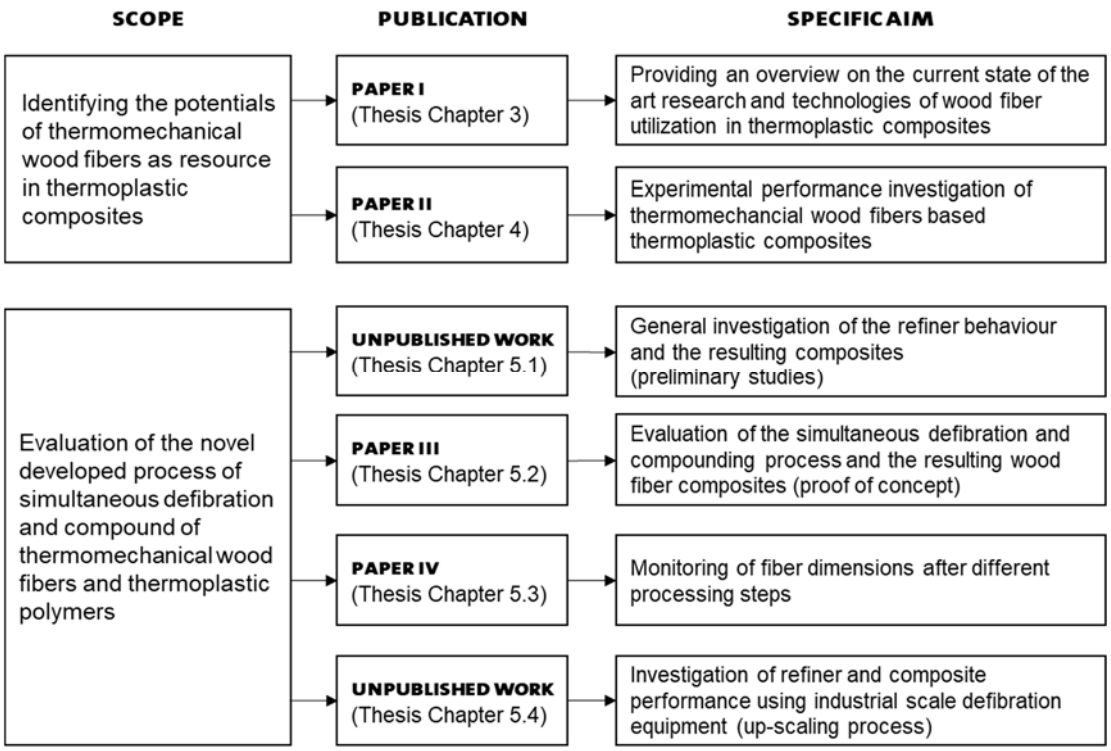
Paper III: *Mertens O, Krause KC, Krause A (2017) Evaluation of wood fiber composites based on a novel simultaneous defibration and compounding process. Journal of Applied Polymer Science 99:45859.*

Paper IV: *Mertens O, Benthien JT, Krause A (2017) Monitoring of fibre dimensions after a novel wood-plastic compounding approach. European Journal of Wood and Wood Products 46(2):175*

Additionally, the thesis includes two sub-chapters (Chapter 5.1 and 5.4) which include unpublished work.

Integration of the publications

The peer-reviewed publications are integrated into the present thesis and refer to the defined scopes and following the below shown scheme. The entire conducted research is finally interrelated discussed in Chapter 6.



CHAPTER 2
MATERIALS AND METHODS

The following Chapter will give an overview on the materials and methods used to confirm the working hypothesis. More detailed information about the materials and methods, can be found in the corresponding Chapters (publications and unpublished work) of the present study.

(1) Identifying the potentials of thermomechanical wood fiber as resource in thermoplastic composites.

The literature review in Chapter 3 was done by the revision of 50 peer-reviewed publication, conference proceedings and technical reports. The publications were searched by using the following web based scientific literature search engines:

- SCOPUS (www.scopus.com)
- Web of Knowledge (www. webofknowledge.com)
- KVK - Karlsruher Virtueller Katalog (www. http://kvk.bibliothek.kit.edu)

In order to provide an overview on the current state of thermomechanical wood fiber utilization in WPC, the cited publications is catalogued according to:

- thermomechanical wood fiber production conditions,
- pretreatments,
- batch or continuous procedures, processing at laboratory or industrial scale,
- fiber contents,
- polymer types, coupling agents as well as wood species.

For the experimentally (Chapter4) investigation of the performance of thermomechanical wood in thermoplastic polymers a broad experimental set-up was scheduled and conducted. Several wood fiber based PP composites with fiber contents from 20 wt.% to 60 wt.% were produced using a twin-screw extruder. Different mechanical properties were tested. The characteristics of fiber length after compounding and injection-molding were investigated applying a dynamic image analysis system.

(2) Development of an alternative compounding process for utilizing thermomechanical wood fiber in thermoplastic composites

A novel process of simultaneous defibration and compounding was developed. For the process the refiner technology was applied, which is basically used for the production of thermomechanical wood fibers. For all conducted experiments a 12” Sprout-Bauer (Waldron, Andritz) refiner was used. For all conducted experiments a PP and HDPE polymer was used as matrix material. Commercially wood chips, consisting out of spruce (Chapter 5.2) and pine (Chapter 5.4) were used for the defibration process. The received wood fiber polymer compound was further processed to investigate the composite performance. The characterization of the composites and the fiber length was done by applying X-ray micro-computed tomography (Chapter 5.2 and 5.4) and dynamic image analysis (Chapter 5.3 and 5.4).

CHAPTER 3
THE UTILIZATION OF THERMOMECHANICAL PULP FIBERS IN WPC (PAPER I)

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Authors contribution:

	CD	EX	ED
Oliver Mertens	70%	100%	70%
Julius Gurr	10%	0%	20%
Andreas Krause	20%	0%	10%

CD: Conceptual Design
EX: Conducting experiments
ED: Editing

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ABSTRACT

Thermomechanical pulp, among other natural fibers, features characteristics that make it a promising candidate for the utilization in polymer composites. This review is providing an overview on the current state of research on TMP reinforced polymer composites. More than fifty references were reviewed. The cited literature is catalogued according to pretreatments, batch or continuous procedures, processing at laboratory or technical scale, fiber contents, polymer types, coupling agents as well as wood species. The reinforcing potential of TMP utilized in composites is demonstrated. The reinforcement was found to be peaking at a fiber content of around 40 wt-%. Fiber morphology is presumed to be an important determinator for composite properties. Specific mechanical energy (SME) is presented as an indicator suitable to compare the influence of various processes on fiber morphology. Furthermore, the feed-in and dosing issue that generally accompanies the utilization of cellulosic fibers is described and possible solutions are discussed.

3.1 INTRODUCTION

Wood based materials such as OSB, fiber- or particleboard that utilize thermosets as adhesives are well established and are used in many applications. In addition to these products wood-plastic-composites (WPC) have increasingly gained interest in recent years (Paulitsch and Barbu 2015, Clemons 2002), offering a unique set of properties. WPC consist of a thermoplastic polymer, such as polypropylene (PP) or polyethylene (PE), wood particles in different sizes and shapes, such as wood flour (WF) or fibers, as well as additives. The combination of thermoplastics and wood particles offers new opportunities for wood-based products (Marutzky and Thole 2005). In terms of application WPC are particularly used for building and construction purposes and in the automotive industry (Carus et al. 2015, Oksman and Sain 2008).

Commercially available WPC usually contain WF. WPC-manufacturers use WF due to its good processability, its low cost and high availability (Schirp and Stender 2010, Stark and Rowlands 2003, Clemons 2002). However, the utilization of wood fibers as reinforcement in composites is gaining interest. Confusingly though, the term “wood fiber” is often used in general for any form of wood particles. The definition of fibers depends on the point of view, biological or technical. From a wood biological point of view, fibers are cell types, specified as softwood tracheids, hardwood tracheids and hardwood libriform fibers, that provide structural stability to the tree (Schirp and Stender 2010). From a technical point of view, wood fibers or WF may contain single anatomical fibers or bundles, hole fibers or fiber fragments and are obtained through mechanical (thermo-mechanical pulp, TMP) or chemical (bleached or unbleached pulps, e.g. kraft pulp) processing. Wood fibers differ from WF in that fibers are significantly longer than wide, rather than particle like (Warnes et al. 2006). In this review the technical definition will be used and the terms fiber and flour will be used specifically.

In general, the reinforcing performance of fibers in composites depends on fiber and matrix polymer properties as well as on the interfacial bond quality (Callister 2001). The fibers strength and stiffness need to be higher than of the matrix polymer. Also, the matrix should not fail before the fibers (Ehrenstein 2006). In addition, in order to have a reinforcing effect fibers need to have a minimum ratio of length to diameter (aspect ratio). This minimum aspect ratio is also influenced by the matrix properties

and is expressed as the critical fiber length. The critical fiber length may be calculated by the following equitation, with critical fiber length l_c, diameter d, fibre tensile strength σ_f^* and matrix shear strength τc.

$$l_c = \frac{\sigma_f^* \, d}{2\tau c}$$

The equation indicates that the smaller the fiber diameter, the shorter the fiber length may be and reinforcements are still feasible (Peltola et al. 2014). Furthermore, a composite may only perform well if induced forces are transferred from the matrix onto the fibers, for which fiber-matrix adhesion is required. However, the compatibility of many commonly used polymers with wood is low (Nygård et al. 2008). In order to enhance the composite properties several studies investigate possible enhancements of fiber-matrix adhesion.

In recent years the interest in the utilization of thermomechanical pulp (TMP) instead of WF has grown (Lerche et al. 2014) due to several advantages. TMP is usually produced for medium density fiber boards (MDF) using a refiner process. Relatively high yields are obtained by TMP refining, resulting in cheaper pulp compared to e.g. chemical pulps (Lee et al. 2001). Due to processing conditions, the surfaces of TMP fibers are predominantly covered by lignin. Lignin is less polar than polysaccharides and therefore more compatible towards nonpolar polyolefin matrices (Schirp et al. 2014). The high aspect ratio of TMP fibers has a reinforcing effect on the composite, increasing their strength and stiffness properties (Stark and Rowlands 2003, Schirp and Stender 2009, Schirp and Stender 2010, Horbens et al. 2012, Lerche et al. 2014). In contrast to TMP, WF, with its cubical particle shape, tends to only increase the stiffness of composites, but does not improve their tensile strength (Stark and Rowlands 2003). After refining, fiber lengths may vary from 20 µm to 4500 µm and fiber widths from less than 1 µm to 80 µm (Lohmann and Blosen 2010). The aspect-ratio of TMP fibers range from 24 (Gehrmann et al. 2004) to 72 (Nygård et al. 2008, Peltola et al. 2014, Horbens et al. 2012). From an economical perspective, compared to other natural fiber composites and glass fiber composites, composites containing TMP have a good price-performance ratio (in terms of specific strength and specific modulus). Furthermore TMP is readily available at commercial scale, which is a significant advantage over agricultural based fibers (Wolodko et al. 2015).

By revision of a number of references that address the utilization of TMP as reinforcement for polymers, this review aims to answer the following questions:

- What kind of technologies are used to process TMP polymer composites?
- How does the refiner process influence the fiber morphology and the resultant composite properties?
- What kind of compounding and forming technologies are utilized and do they influence the concerning composite properties?
- Is it possible to give a general overview on the mechanical properties that have been achieved and are they comparable?

3.2 METHODS

To answer the stated questions, we collected peer reviewed articles, conference proceedings, patents and project reports related to TMP polymer composites. Literature was searched by using the following web based scientific literature search engines:

- SCOPUS (www.scopus.com)
- Web of Knowledge (www. webofknowledge.com)
- KVK - Karlsruher Virtueller Katalog (www. http://kvk.bibliothek.kit.edu)

The following Keywords were used:

- TMP fibers, thermoplastic
- Refiner fibers WPC
- TMP fiber, composites

The term “wood fiber” was consciously avoided since it is often used unspecifically for any form of wood particles. Including the term wood fiber would have led to an unmanageable amount of references. In a second step the references of the reviewed literature were analyzed and further related literature was selected.

3.3 THE CONVENTIONAL WPC PROCESS

The manufacture of WPC is based on the production technologies of the polymer industry. Independent of the processing equipment the manufacture may be divided into few basic steps, feed-in, blending, compounding and forming. The feed-in of the polymer, filler and further additives needs to be precise at adequate speeds. In the case of natural fillers this can pose a challenge, which will be addressed in this review. The blending of the ingredients may be done as a standalone process, com-

mon in polyvinyl chloride processing, in which the temperatures stay below the melting point and a homogeneous granular dry-blend is produced. The blending may also be integrated into the next processing step, the compounding, which is common in polyolefin processing. During compounding the polymer is exposed to heat and shear and thereby plasticized. The fillers and additives are dispersed to achieve a homogeneous melt, which is called compound. The compounding step also severs to remove moisture and gases from the compound, which is particularly critical in the case of WPC. After compounding the material may be directly formed into products (one-step process) or pelletized for later forming processes (two-step process) (Stark et al. 2010).

3.4 THE FEED-IN CHALLENGE OF NATURAL FIBERS

Several options are available for compounding WPC, using either batch (internal or high-intensity mixer) or continuous (extruders) mixers (Clemons 2002). For industrial scale processing (e.g. twin-screw extrusion) high feed rates are desired (Teuber 2016a) and thus, continuous and precise feed-in technologies are required. TMP and natural fibers in general have a low bulk density, a non-free flowing behavior and tend to form bridges. This makes continues feed-in into the compounding process quite challenging. Moreover, dissolving fiber agglomerates within the extruder is difficult to achieve and poor fiber-matrix bonding is expected. As a consequence, many investigations related to cellulosic fiber composites use laboratory batch processes for compounding (Lee et al. 2001, Gehrmann et al. 2003, Marutzky and Thole 2005, Warnes et al., Nygård et al. 2008, Bengtsson et al. 2007, Schirp et al. 2015, Schirp and Stender 2010, Stadlbauer 2010).

Several references discussed the issue of fiber feed-in. Nygård et al. (2008) pelletized TMP to increase its bulk density. Pelletizing allowed for portioned feed-in into the extruder. Though, due to occurring shear during pelletizing, a significant reduction in fiber length was observed. The pelletizing approach was also adopted by Bengtsson et al. (2007) and Le Baillif and Oksman (2009), while using bleached kraft pulp. They also observed fiber length reduction. Stadlbauer (2010) adapted a cutting compactor technology, which is originally used for foil agglomeration. Their results showed that the utilized method can provide for constant feed-in, but the fiber length reduction was observed to be comparable to the pelletizing approaches (Stadlbauer 2010). To overcome these feed-in difficulties during compounding Horbens et al. (2012) used a modified ball-mill to produce dosable fiber agglomerates for extruder-

type processes. A complete resolve of the agglomerates after injection-molding was observed.

Warnes et al. (2006) developed a method for using the MDF process technologies to produce MDF fiber pellets which are ready to use for extruders. After refining the fibers are transported through a conduit (blow-line); meanwhile a liquid polymer formulation is applied onto the surface. After a drying stage the fibers are pressed to thin solid panels and cut into pellets. These temporarily bound fibers are then able to be used in further extrusion production steps.

3.5 PROCESS PARAMETERS INFLUENCING FIBER MORPHOLOGY

Fiber morphology has a large impact on composite properties and therefore factors that influence the fiber morphology have to be considered. The major processes that influence the TMP-fiber morphology are:

- TMP processing parameters (e.g. temperature (Solala et al. 2016, Lerche et al. 2014), residence time (Lerche et al. 2014), disc gap (Schirp et al. 2014) and plate pattern)
- composite processing equipment, conditions and fiber pretreatments

a) Influencing TMP-processing parameters

Lerche et al. (2014) investigated different defibration conditions and their influence on properties of maleic anhydride modified HDPE/TMP reinforced composites. TMP was produced with different boiling times, temperatures and pressures. Higher temperatures and longer defibration times caused darker and shorter fibers. The obtained data from mechanical tests revealed that differing defibration conditions led to statistically significant differences in flexural, tensile and impact properties. They argue that not necessarily great fiber lengths, but mild defibration conditions, associated with lower thermal wood degradation and less lignin coverage on fiber surfaces, could be advantageous. Nygård et al. (2008) stated that high amounts of surface lignin may impair the effect of coupling agents and thus, decrease the mechanical properties of the resultant composite.

In contrast to these assumptions, Solala et al. (2016) investigated the reinforcing effect of high temperature (HT-) TMP on melt-compounded PLA composites. Fiber contents of up to 20 wt-% were investigated and no coupling agents were used. It was observed that higher defibration temperatures (150 to 170°C) led to higher lignin

surface coverage, weaker fiber-fiber bonding, and a loss of hemicelluloses. Due to the high amount of lignin on the fiber surfaces and its hydrophobic nature, relatively high compatibility to nonpolar thermoplastics is expected. The TMP of higher defibration temperatures probably had a lower level of fiber surface fibrillation and thus weaker fiber-fiber interactions, leading to less agglomeration.

Yam et al. (1990) compared the influence of acetylated and heat treated aspen TMP on recycled HDPE composites. No coupling agents were used. Composites containing untreated or acetylated fibers showed higher tensile and flexural strength than those containing heat treated fibers. The authors conclude that the untreated fibers retain most of their lignin and natural waxes and therefore show better compatibility to the non-polar HDPE matrix.

Schirp et al. (2014) analyzed the influence of beech wood particle geometry (flour compared to fibers) and various modification treatments on composite properties. The influence of refiner disc gaps between 0.15 to 1.00 mm on pulp geometry were evaluated. As was expected, an increase in refiner disc gap resulted in coarser pulp. An important result was that the flexural strength of TMP-composites increased with increasing refiner gap width. Under the applied conditions (batch process) the longer the TMP-fibers, the higher the flexural strength of the composite. Interestingly though, TMP did not improve the flexural strength considerably compared to wood flour or wood particles. Furthermore, the authors conclude that the effect of hornification may have a large influence on fiber and ultimately composite properties. Hornification takes place in lignocellulosic materials up on drying or water removal. During drying the internal fiber volume shrinks irreversible because of structural changes. This leads to stiffer fiber properties (Diniz et al. 2004). It was suggested, if pre-drying of the fibers before compounding could be avoided, a positive influence on the properties of the fibers and resulting composites may be achieved. It was also obtained that TMP modified with emulsifiable methylene diphenyl diisocyanate (EMDI) could be used as an effective coupling agent in WPC. The use of EMDI resulted in reduced water absorption and increased flexural strength (Schirp et al. 2014).

Winandy et al. (2008) pretreated red pine chips with oxalic-acid and diethyloxalat. They pointed out that the treatments do affect the mechanical properties of TMP-HDPE composites. The modulus of elasticity of composites containing treated TMP was decreased compared to composites containing untreated TMP or wood flour. A

conclusive interpretation of the mode of action of the modifications was not provided by the reference.

Refiner plate patterns were not discussed in any of the analyzed references. This is surprising, as the plate pattern would be expected to influence fiber length and morphology considerably.

b) Influencing WPC processing parameters

To date, a wide range of process types and processing conditions for compounding and forming are utilized. Most investigations used low feed rates at laboratory scale (Teuber 2016a). Teuber (2016a) mentioned that a laboratory process such as an internal mixer is not directly comparable to industrial relevant processes such as twin-screw extrusion. During compounding and forming, the filler is subject to high temperature and shear which may cause severe morphology changes. Composites properties are largely influenced by filler size and morphology. Thus, it is important to take the applied processes into account in order to be able to draw conclusions from the results of the different investigations (Teuber 2016a). Various aspects such as initial parameters and conditions need to be considered.

The literature to date regarding the process types and processing conditions of TMP polymer composites are listed in Table 3.1. The overview is divided in pretreatment, compounding and forming. Furthermore, it is being distinguished between:

- laboratory scale processes (batch, e.g. kneading mixers, and continuous, e.g. micro-extruders).
- industrial scale processes (batch, e.g. high-intensity mixers, and continuous, e.g. twin-screw extruders and injection molding.

Table 3.1 Overview of the different compounding and forming processes used in the cited literature. The pretreatment process is tagged with different numbers for different processes ([1]Pelletizing after patent from Warnes et al.[2] Pelletizing with Amandus Kahl pelletizing machine, [3]Granulation drum). rpm = rounds per minute used for the different compounding processes. SME = specific mechanical energy. The temperature column indicates which temperature (for batch processes) or which temperature range (for continuous processes, mostly extruders) were applied during the compounding process.

	Pretreat-ment	**Compounding**							**Forming**	
		laboratory scale		*industrial scale*		rpm	*temperature*	*through put*	*laboratory scale*	*industrial scale*
Reference	Pelletizing	continuous	batch	continuous	batch		[C°]	[kg/h]		
Solala et al. (2014)	-	x	-	-	-	225	190	-	x	-
Teuber (2016a)	x[1]	-	-	x	-	200-400	180-210	6-24	-	x
Zierdt et al. (2015)	-	-	x	-	-	50	196	-	x	-
Schirp et al. (2015)	-	-	x	-	-	50	190	-	x	-
Dickson et al. (2014)	x[1]	-	-	x	-	-	< 200 C°	-	-	x
Lerche et al. (2014)	-	-	x	-	-	50	160	-	x	-
Peltola et al. (2014)	x[2]	-	-	x	-	200	60 – 190	2,5	-	x
Schirp et al. (2014)	-	-	x	-	-	50	160	-	x	-
Horbens et al. (2012)	x[3]	-	-	x	-	-	-	-	-	x
Peltola et al. (2011)	x[2]	-	-	x	-	200	60 – 190	-	-	x
Thumm and Dickson (2013)	x[1]	-	-	x	-	-	-	-	-	x
Schirp and Stender (2010)	-	-	-	-	x	-	-	-	-	x
Schirp and Stender (2009)	-	-	-	-	x	-	-	-	-	x
Nourbakhsh and Ashori (2008)	-	-	x	-	-	50	180 – 200	-	x	-
Nygård et al. (2008)	x[2]	-	-	x	-	200	190	-	x	-
Zhang et al. (2007)	-	-	x	-	-	50	150	-	x	-
Lu et al. (2004)	-	-	x	-	-	60-90	150 – 180	-	x	-
Li and Sain (2003)	-	-	-	-	x	4600	190	-	-	x
Stark and Rowlands (2003)	-	-	-	x	-	-	< 190	-	-	x
Kazayawoko et al. (1999)	-	-	-	x	-	3300	180	-	-	x
Ren and Hon (1993)	-	-	x	-	-	-	-	-	x	-
Yam et al. (1990)	-	-	-	x	-	100	150 - 210	-	x	-
Woodhams et al. (1984)	-	-	x	-	-	90	225	-	x	-
Kokta et al. (1983)	-	-	x	-	-	-	-	-	x	-
Sean (2010)	-	-	x	-	-	10-30	155-175	-	x	-
Winandy et al. (2008)	-	-	-	-	x	5000	196	-	-	x
Caulfield et al.	-	-	-	-	x	4600	190	-	-	x

Warnes et al.		x[1]	-	-	x	-	150-200	160-210	-	-	x
Gehrmann et al. (2003)		-	-	-	x	-	-	-	-	-	x
Total number of references: 29	**8**	**1**	**11**	**12**	**5**					**14**	**15**
		12			**17**						

According to table 3.1, in twelve references continuous compounding processes, such as twin screw extruders, which are able to mimic industrial processes, were used. In eight references the TMP was pretreated in order to compact the fibers before compounding. This was done to achieve constant feed-in into the extrusion process. A significant fiber length reduction was observed when pelletizers were used as compaction technology (Nygård et al. 2008, Bengtsson et al. 2007, Le Baillif and Oksman 2009). In several investigations in which continuous compounding processes and injection molding were used significant fiber length reduction was determined (Dickson et al. 2014, Peltola et al. 2014, Horbens et al. 2012, Peltola et al. 2011, Thumm et al. 2011, Stark and Rowlands 2003, Yam et al. 1990), independent from the processing conditions, fiber loading and kind of polymer. Thermo-degradation, leading to the darkening of the fibers, occurred with increasing mixing time (Yam et al. 1990) and increasing shear forces due to e.g. high viscosity polymers (Peltola et al. 2011).

In all studies, with the exception of Schirp et al. (2014), in which laboratory scale compounding equipment was utilized fiber length reduction was not investigated after compounding, but rather observed after forming. Schirp and Stender (2010) stated that a heating-cooling mixer, as a batch process, is an economically feasible way to process TMP with only minor fiber damage compared to twin-screw extrusion.

Process parameters derived by different processes are often not directly transferable to other setups, as they produce different outcome. Finding a key variable that is applicable to different compounding processes would aid further research in this field. Teuber (2016a) mimicked industrial extrusion conditions by compounding TMP composites with a laboratory twin-screw extruder. They chose feed rates and screw speeds that resulted in commercially relevant specific mechanical energy (SME) values. SME $[kWh/kg]$ is an important process parameter influencing the final product characteristics. SME represents the amount of dissipated mechanical energy per unit mass, that is applied by the engine driven screw to the material(Godavarti and Karwe 1997) and can be deduced according to:

$$SME = \frac{E}{t_c Q}$$

with consumed energy by the engine E [kWh], compounding time t_c [h] and feed rate Q [kg/h]. To avoid attrition and thermal degradation of natural fibers it is desirable to keep the SME to a minimum. Teuber (2016b) confirmed that fiber breakage could be

reduced by choosing low SME values, which are still in a range applicable in industrial processes.

According to the previous conclusions it appears that the SME may be a suitable processing parameter to compare different compounding processes and their influence on fiber morphology.

3.6 MECHANICAL PROPERTIES OF TMP POLYMER COMPOSITES

We have well established that a comparison of the composite properties of different investigations is difficult since varying processing parameters and fibers were used. In addition to the production processes and settings (Graupner and Muessig 2016) major influencing factors on composite properties are (Oksman and Sain 2008, Klyosov 2007, Rowell 2005):

- characteristics of the fibers and matrix itself
- fiber/matrix adhesion
- fiber length and fiber length distribution
- fiber dispersion
- fiber compaction

Figure 3.1 provides an overview of tensile strength values as a function of modulus of elasticity (MOE) of various TMP- and wood flour-polypropylene composites. The plotted data was derived from the references listed in Table 3.1. The tensile strength values are related to fiber contents of up to 50 wt-% illustrated in an Ashby-plot. The values for the TMP composites are subdivided in laboratory and industrial scale production. As a point of reference, the tensile strength and MOE of wood flour composites are also displayed. The strength values derived for the wood flour composites were all compounded utilizing twin-screw extruders (Peltola et al. 2011, Nygård et al. 2008, Li and Sain 2003, Winandy et al. 2008, Stark and Rowlands 2003).

As one can see Figure 3.1 depicts a broad range of tensile strength and MOE values of TMP composites, produced by either laboratory or industrial scale processes, as well wood flour composites. Independent of the fiber content, industrial scale TMP composites display higher MOE in comparison with laboratory scale TMP composites. This might be explained by the added pressure formation as well as dispersion during continuous compounding by means of industrial scale extruders. Additionally, injection molding was utilized in all cited industrial scale investigations, in contrast to mostly compression molding in the cited laboratory scale investigations. Graupner and

Muessig (2016) compared injection molded to compression molded Lyocell fibers and PLA matrix composites. They came to the general conclusion, that injection molding leads to better compaction and fiber/matrix adhesion compared to compression molding. This may explain the higher MOE of the injection molded, industrial scale produced TMP-polymer composites. The industrial scale TMP composites and the wood flour composites do exhibit comparable MOE.

Wood flour composites display similar tensile strength properties to the laboratory scale TMP composites, but wood flour composites reveal higher MOE. An explanation for this phenomenon may be, that smaller particles with lower aspect ratio disperse more easily in the polymer matrix resulting in additional homogeneity and therefore stiffer composites (Shahi et al. 2012, Nygård et al. 2008). Furthermore, it is assumed here, that twin-screw extruders have a larger free volume within the mixing barrel compared to laboratory scale compounding technologies. This may lead to an increment of fiber dispersion, especially when processing aids are used. Good dispersion with extruders can also be achieved by high screw speeds (Le Baillif and Oksman 2009) and proper screw design (Teuber 2016a).

The tensile strength of laboratory scale composites ranges from 20 MPa to 40 MPa. The tensile strength of industrial scale composites ranges from 25 MPa to 52 MPa. The tensile strength of wood flour composites ranges from 27 MPa to 44 MPa. The strength properties of the industrial scale TMP composites exhibit a large range, with a considerable portion displaying higher values than laboratory scale and wood flour composites. However, an also notable portion exhibits comparable strength properties. According to the plotted strength values here, it is evident, that a certain reinforcing effect can be achieved by TMP in comparison to wood flour. Teuber (2016a) discovered that fiber lengths are considerably reduced just after fibers are fed in during compounding. Therefore, the processing is presumably a major lever in the discovery of the full reinforcing potential of TMP. Furthermore, Schirp et al. (2014) stated that next to the aspect ratio and fiber length the fiber surface, i.e. its topography as well as its surface chemical composition, have to be considered. In contrast to that, Nygård et al. (2008) came to the conclusion that high aspect ratios do not improve the MOE, because of the non-linear alignment of the fibers in the polymer.

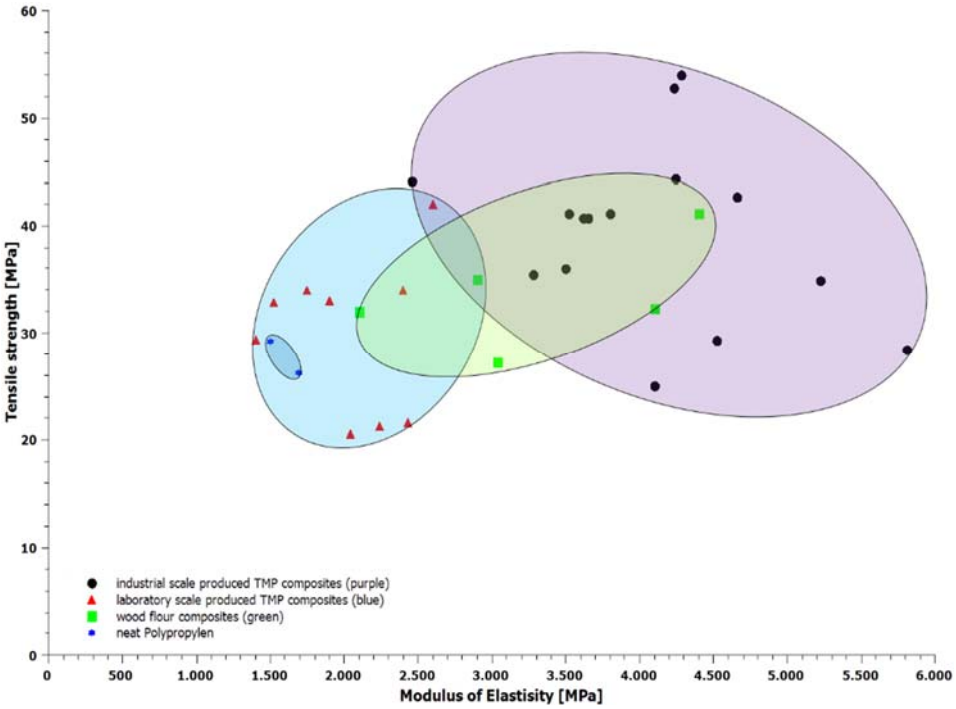

Figure 3.1 Tensile properties of TMP- and wood flour- PP composites with a fiber content ≤50 wt. %. Comparison of laboratory (blue area) and industrial scale (purple area) TMP composite and wood flour composites (green area) values illustrated in an Ashby-plot. Data for TMP composites were derived from references listed in Table 3.2.

3.7 INFLUENCE OF FIBER CONTENT ON MECHANICAL PROPERTIES

WPC properties are strongly affected by their wood content (Sain and Pervaiz 2008). The following Table 3.2 gives an overview on tensile strength and MOE values regarding to different TMP contents used. Also the utilized polymers, coupling agents are listed. In two thirds of the cited literature fiber contents between 30 and 40 wt.% were used. Fiber loadings greater than 65 wt.% are difficult or not feasible to process (Ehrenstein 2006) due to the low bulk density of TMP. Materials with low bulk density contain high shares of air. Because air hinders the plasticization of a polymer (Kohlgrüber 2007) and leads to voids in the composites it has to be removed during compounding. In more than half of the cited literature PP was used as matrix polymer. In the majority of the cited literature coupling agents were applied to enhance material properties. The mechanism of coupling agents and their effect on mechanical properties is well documented but not subject of this review.

Table 3.2 Overview of tensile strength and tensile Modulus (tMOE) in dependency of fiber content, matrix polymer and coupling agents (CA). Also listed are the processing methods (IS = industrial scale, LS = laboratory scale). In the references at the bottom of the table no tensile strength and tMOE were determined.

	tensile strength [MPa]						tMOE [GPa]						polymers						
fiber content [%]	**20**	**30**	**40**	**50**	**60**	**>60**	**20**	**30**	**40**	**50**	**60**	**>60**	**PP**	**PE**	**PLA**	**others**	**CA**	**IS**	**LS**
(Caulfield et al.)		29,3						4,5					x				x	x	
			34,9						5,2				x				x	x	
				28,4						5,8			x				x	x	
					25,6						6,9		x				x	x	
(Dickson et al. 2014)			44						4				x				x	x	
(Gehrmann et al. 2003)					25				4,1				x				x	x	
(Kazayawoko et al. 1999)		44,1						2,4					x				x	x	
(Lee et al. 2001)	20,6						2,04						x				x		x
		21,3						2,2					x				x		x
			21,6						2,4				x				x		x
(Lerche et al. 2014)				x						4,5				x			x		x
(Migneault et al. 2008)		22,7						2,7						x			x		x
(Nourbakhsh and Ashori 2008)	29,4						1,4						x						x
		32,9						1,5					x						x
			34						1,7				x						x
(Nygård et al. 2008)				54						4,2			x				x	x	
(Peltola et al. 2011)		35,5						3,2							x				
(Ren and Hon 1993)					33,7						2,5		x				x		x
(Schirp et al. 2014)						10,3							x				x	x	
(Sean 2010)	33						1,9						x						x
		34						2,4					x						x
				42						2,4			x						x
(Solala et al. 2016)	55,3						5,1								x				x
(Stark and Rowlands 2003)			52,8						4,2				x				x		
(Teuber 2016a)		41						3,6					x				x		
(Thumm and Dickson 2013)													x				x	x	
(Warnes et al.)		36						3,5					x				x		
			42,7						4,6				x				x		
(Winandy et al. 2008)		37						2,2						x			x		
(Woodhams et al. 1984)			44						4,5				x				x		x
			39						4,4					x					x
No tensile strength or tMOE were determined in the references below																			
(Horbens et al. 2012)	x												x				x		x
(Kokta et al. 1983)		x														x	x		x
(Li and Sain 2003)			x										x				x	x	
(Lu et al. 2004)				x										x			x		x
(Michaud et al. 2005)						x							x				x	x	
(Schirp et al. 2014)					x									x			x		x
(Yam et al. 1990)	x													x				x	
		x												x				x	
				x										x				x	
(Zhang et al. 2007)	x													x			x		x
			x											x			x		x
(Zierdt et al. 2015)		x														x			
			x													x			
				x												x			

Mechanical properties depend on various parameters (Krause and Krause 2012), whereby wood or fiber content is one of the main factors (Schirp and Stender 2010). Figure 3.2 displays tensile strength values of industrial scale TMP (red), laboratory scale TMP (black/grey) and wood flour (blue) composites as a function of fiber content. The plotted data is based on references for PP composites presented in Table 3.2. It is known that MOE increases with increasing fiber content, but tensile strength increases only to a certain fiber content (Yam et al. 1990, Woodhams et al. 1984). Several studies observed that the tensile strength increases up to fiber contents of 40-50 wt.%. Fiber loadings beyond led to decreasing strength values (Yam et al. 1990, Woodhams et al. 1984, Sean 2010, Caulfield et al.). Sean (2010) stated that strength properties with fiber contents beyond 40 wt-% are no more linear and reach an asymptote. These phenomena indicate poor fiber dispersion. The efficient stress transfer is reduced due to imperfections such as agglomerates which do not contribute any strength to the composites. Woodhams et al. (1984) pointed out that beyond 40 wt.% composites gave lower strength values because the viscosity of the melt was too high to mold properly. According to these references it seems that in general tensile strength increases up to a fiber content of approximately 40-50 wt.%.

Krause and Krause (2012) stated that mechanical properties depend on the production method as well as that the highest strength values are achieved by using injection molding in contrast to extrusion. In Figure 3.2 the industrial scale composites show higher strength values up to a fiber content of 40 wt.% than laboratory scale composites. Graupner and Muessig 2016 (2016) found that the tensile strength of injection molded cellulose fiber-reinforced PLA composites decreased significantly at a fiber content of 40 wt.% compared to compression molded samples. They argued that the fiber aspect ratio of injection molded samples is below the critical fiber length. Moreover, at a fiber loading of 40 wt.% an increased occurrence of voids was observed, which may cause the reduced tensile strength (Gehrmann et al. 2003). Comparing wood flour composite strength values and TMP strength values beyond a fiber content of 40 wt.%, it appears that wood flour values are in between. This could be due to the fact that during compounding of fiber contents of 40 wt.% and above, fiber-fiber interaction increase, leading to fiber length reduction below the critical fiber length.

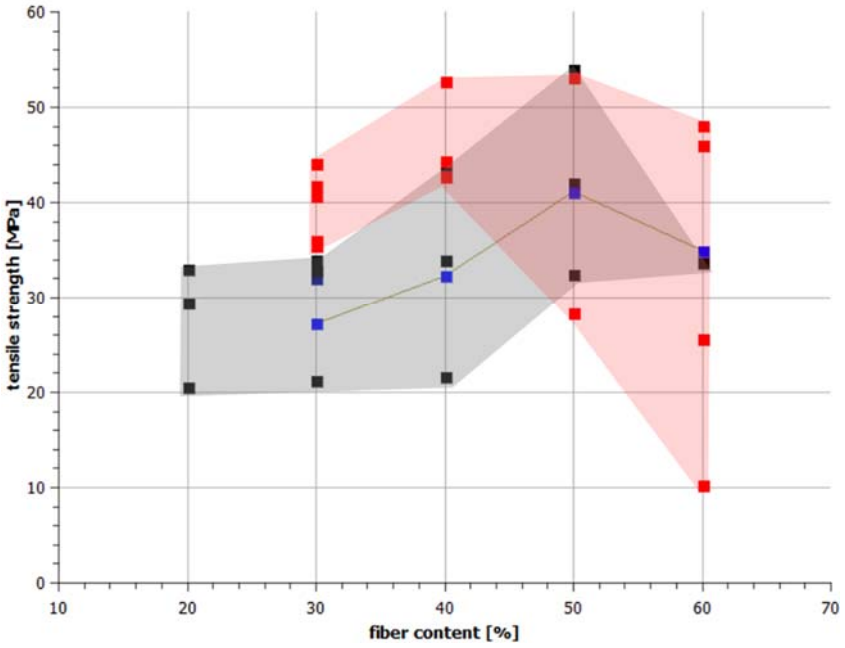

Figure 3.2 Tensile strength as a function of fiber content for industrial produced TMP composites (red dots and area), laboratory produced TMP composites (black dots and grey area) and wood flour composites (blue dots).

3.8 CONCLUSIONS

Overall, there are strong indications that long or rather high aspect ratio TMP fibers have a reinforcing effect on composites. However, although not consistently reported in all references, it appears that the majority of thermo-mechanical pulping, feed in, compounding and forming processes do potentially alter fiber morphology as well as chemical composition. Consequently, in order to realize the reinforcing potential of TMP fibers all processing steps and their influence need to be taken under consideration.

The feed in issue continues to be unsolved. Varying approaches did lead to improved fiber dosing, but were accompanied by either fiber agglomerates in the final composite or fiber length reduction. Additionally, further promising approaches were investigated, but fiber agglomeration and fiber length reduction were not evaluated or reported on. As fiber agglomeration and length reduction both presumably lead to diminished composite properties, in the future, considerable efforts towards finding a solution for the feed in issue should be put in.

TMP processes alter the morphology as well as the chemical composition of TMP fibers. Harsh defibration conditions may lead to thermal degradation and shortening

of the fibers as well as an increase of surface lignin. There are strong indications, that changes in the fibers chemical composition affect the fiber matrix adhesion or the mode of action of certain coupling agents. Depending on the polarity of the matrix polymer, high or low shares of surface lignin may be advantageous. The TMP process should be adjusted accordingly. Furthermore, coupling agents need to be chosen under the consideration of the TMP process or more specifically the chemical composition of the resultant fibers. Ultimately, in order to achieve optimum composite performance, it is inevitable to take the TMP's chemical composition, the polymer type as well as the coupling agents under consideration.

WPC processes also alter the morphology as well as the chemical composition of TMP fibers. In several investigations in which continuous compounding processes, extrusion and injection molding were used significant fiber length reduction was determined. In those investigations this reduction in fiber length was found to occur independently from the processing conditions, fiber loading and polymer type. Thermodegradation, leading to the darkening of the fibers, occurred with increasing mixing time and increasing shear forces due to e.g. high viscosity polymers. Therefore, the processing is presumably a major lever in the discovery of the full reinforcing potential of TMP. In general though, it is difficult to provide an overview on the influence of different compounding and forming processes on fiber morphology and degradation. In one reference the specific mechanical energy (SME) was introduced as figure suitable to compare different processes and there influence on fiber and composite properties with one another. It was demonstrated that low SME values lead to less fiber breakage. Further investigation of the SME could provide a way to mimic industrial scale processes with laboratory technologies and predict composite properties.

It is well known that the fiber content have a significant influence on the mechanical properties of composites. In the cited references the MOE of TMP composites increases with increasing content. In the case of tensile strength, this relation appears to be true only for TMP contents of up to around 40 wt-%. In several references tensile strength values started to decrease at TMP contents between 40 and 50 wt-%. This was attributed to poor dispersion and increased agglomeration, leading to inefficient stress transfer. Although the decreasing tensile strength of fiber contents beyond 50 wt-% were only investigated by few studies, it appears that the optimum fiber content resides between 40-50 wt-%. To determine the cause of the decreasing strength properties as well as a possible solution further investigation is needed.

CHAPTER 4
PERFORMANCE OF THERMOMECHANICAL WOOD FIBERS IN POLYPROPYLENE COMPOSITES (PAPER II)

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Authors contribution:

	CD	EX	ED
Oliver Mertens	70%	70%	80%
Kim C. Krause	10%	10%	15%
Matthias Weber	0%	20%	0%
Andreas Krause	20%	0%	5%

CD: Conceptual Design
EX: Conducting experiments
ED: Editing

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ABSTRACT

Thermomechancial wood fibers, as usually used for medium density fiberboard or cardboard production, feature promising characteristics, like a high aspect ratio, for the utilization in thermoplastic composites. The present study investigates the influence of fiber loading and fiber geometry on the mechanical properties of wood polypropylene composites in order to confirm the results that were found in a previous published literature review. Composites were compounded at fiber contents from 20-60 wt.%, using a co-rotating twin screw extruder and subsequently injection moulded to test specimens. Field emission scanning electron microscopy was carried out to evaluate the fracture morphology of the composites. Fiber length was evaluated using a applying a dynamic image analysis system. The compounding process was found to be the major lever regarding fiber length degradation. The mechanical properties decrease with increasing fiber content for composites without coupling agent. The addition of a coupling agent increased the tensile and flexural strength up to a fiber content of 50 wt.%. However, it was found, that the processing of these fibers into conventional compounding equipment is still challenging.

4.1 INTRODUCTION

Wood polymer composites (WPC) consist of wood particles in different shape and size, a thermoplastic polymer and additives. The most common polymers for WPC are polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) (Clemons 2002). To date, WPC are well-established with products in different fields of applications. Most of the products are used for decking, automotive and siding applications. The production of WPC in the European Union was 260.000 tons in 2012 (Partanen and Carus 2016). The wood content in WPC can reach up to 80 % (Klyosov 2007). The manufacturing of WPC is based on the production technologies of the polymer industry. These technologies (e.g. extruders) require dry material in order to avoid an excessive moisture evaporation during the process. Due to its low cost and good availability and its relatively easy processability, WPC-manufactures usually use wood flour as a filler (Schirp and Stender 2010, Stark and Rowlands 2003, Clemons 2002). Wood flour particles are less than 1mm in length and have a wide distribution of length to diameter ratio (aspect ratio or L/D ratio) (Schwarzkopf and Burnard 2016). Stark and Rowlands (2003) as well Nourbakhsh and Ashori (2008) showed that the particle size characteristics are significantly influencing the composite properties. They concluded that the aspect ratio and not particle size has the greatest effect on strength and stiffness. If the added material does not improve strength and stiffness, the material largely acts as a filler rather than reinforcing (Ehrenstein and Wurmb 1977). However, it has to be kept in mind that during processing of wood fiber composites the fiber geometry and thus the aspect ratio is heavily altered.

Wood fibers obtained through mechanical defibration have a promising high aspect ratio and a good price-performance ratio (Wolodko et al. 2015) and thus are may a candidate for the application in WPC. Compare to the traditionally used wood flour, wood fibers are rather long compared to their width. Basically, these fibers are used for medium density fiberboards (MDF) or cardboards (TMP). Both fiber types are using refiner technology. The process of fiber production differs in that way, that the process for MDF fibres is using a low energy thermomechanical defibration. The TMP process used for paper is much higher in temperature and shear forces (Walker 2006a). The high temperatures during MDF fiber production, which are above the glass transition point of lignin, resulting in a fiber separation in the lignin-rich middle lamella. This leads to a lignin coated fiber surface accompanied by poor hydrogen bonding properties (Atack 1972, cited from Walker 2006b). Due to higher mechanical

treatment during TMP fiber production, the resulting fiber surface is more torn open and the polysaccharide-rich regions (first and secondary cell wall, S1 and S2 lamella) are exposed, encouraging in good hydrogen bonding properties (Walker 2006b). The defibration conditions do affect the fiber properties and the ratio of single fibers and fiber bundles (Wenderdel and Krug 2012). Depending on the defibration conditions Wenderdel and Krug (2012) showed, that the amount of single fibers vary between 8-32 % and for fiber bundles between 40-60 %.

In a previous study (Mertens et al. 2017a) the utilization of thermomechanical fibers in WPC were investigated. The promising characteristics of thermomechanical wood fibers are highlighted in many publications. Overall, there are indications that long or rather high aspect ratio wood fibers have a reinforcing effect on composites. The performance of these fibers depends on the production method used (Mertens et al. 2017a). However, the determination of the fiber length which is present after the last process step applied is important to conclude about the reinforcement potential of fiber. The reinforcement potential of a composite is expressed with the critical fiber length (l_c). The critical fiber length is the minimum fiber length that is required to ensure a sufficient stress transformation from the matrix to the fiber. Additionally, the modulus of the fiber has to greater than of the matrix, the fracture of the matrix has to greater than the fiber and the strength of the fiber is greater than thus of the matrix. The critical fiber length is calculated with

$$l_c = \frac{\sigma_f^* \, d}{2\tau c}$$

According to the given equation, fiber tensile strength and the matrix shear strength (τc) have to be known. These two parameters are difficult to measure for small wood fibers (Thumm and Dickson 2013) and differ therefore to other natural fibers. The common models of analytical approaches to determine the composite properties are based on assumptions like that the particles are impermeable, the particles/fibers have a cylindrical shape, the bonding between the components is perfect and that the components are isotropic (Schwarzkopf and Muszynski 2015). All these assumptions do not meet the properties of wood fibers. On the one hand, thermomechanical wood fibers are present as fiber bundles and single fibers in different ratios, which makes the calculation of an appropriate fiber tensile strength difficult. On the other hand, thermomechanical wood fibers show a wide distribution in their length and width. Since the fiber diameter is important parameter for the determination of the critical

fiber length, it is difficult to define a diameter for thermomechanical wood fibers due to their wide distribution.

The present study aims to investigate the performance of thermomechanical wood fibers in polypropylene composites. The study is conducted to verify the findings regarding the maximum threshold for tensile strength the results of the maximum tensile strength at a fiber content of around 40 wt.%, which was previously investigated based on a literature review by Mertens et al. (2017a). The publications found in the literature review are dealing all with different fiber contents. However, a consistent study that evaluates the performance of thermomechanical wood fibers at several fiber contents in composites and a consideration of fiber length reduction during processing was missing. Thus, in the present study, several fiber loadings from 20 to 60 wt.% were produced and the mechanical properties are investigated. Additionally, the literature review found, that fiber length is observed rather after composite forming than after compounding. However, it is important to know what kind of process step leads to a sever fiber length reduction. In the present study for all composites formulations fiber length and aspect ratio is determined after compounding and injection-molding. The determination of the fiber characteristics after injection-molding aims to draw conclusions regarding the mechanical properties achieved.

4.2 MATERIALS AND METHODS

MATERIALS

Industrial produced thermomechanical wood fibers (Steicozell©, Steico, München, Germany), were used as a reinforcement material. The pine fibers were delivered as bulk material. The wood fibers are originally used as insulation material for building purposes. According to the fiber manufacturer, the fibers were defibrated with a pressure of 10 bar and 180 °C, respectively.

Polypropylene (PP), PP 575P from Sabic (Saudi Basic Industries Corporation, Riyadh, Saudi Arabia), melt flow index (MFI) 10.5 g/10 min, melting point 160 °C was used as matrix polymer. Maleic anhydride-modified PP (MAPP; Licocene® PP MA 7452, Clariant GmbH, Gersthofen, Germany) was used as coupling agent. MAPP was delivered in granulate form.

COMPOUNDING AND FORMING

Compounding of wood fibers and polymer was done by using a co-rotating twin screw extruder (TSE) (Leistritz ZSE 27 MAXX, Leistritz Extrusionstechnik GmbH, Nürnberg, Deutschland) with two gravimetric feeders. Both materials were fed through the main feed throat of the TSE. The TSE is equipped with 10 heating barrels. The temperature ranged from 180 °C (feed-in unit) to 145 °C at the material outlet. The materials were compounded with a screw speed of 130 rpm and a throughput of 1.3 kg/h, resulting in a specific energy of 0.61 kWh/kg.

The composites were compounded with 20, 30, 40, 50, 60 wt.% wood fiber and with and without the addition of 3 % MAPP, respectively. Test specimens were manufactured according to DIN EN 527:2012-06 and DIN EN 178:2003 using an injection-moulding machine (moulding pressure 1,500 bar at 170 °C) (Arburg Allrounder 420C Golden Edition, Arburg GmbH + Co KG, Loßburg, Germany).

TESTING

Tensile (DIN EN 527:2012-06) and flexural (DIN EN 178:2003) tests were conducted using a universal testing machine (Zwick Roell GmbH & CO.Kg, Ulm, Germany). Unnotched Charpy impact bending (DIN EN ISO 179 1-2 (2005)) was conducted by using an impact testing machine (HIT5.5p Zwick Roell GmbH & CO.Kg, Ulm, Germany) with a 1 and 5 Joule pendulum.

FIBER EXTRACTION

For fiber size measurements, the fibers were separated from the polymer matrix via Soxhlet extraction in hot xylene. Fibers were separated from the compounded granulates and the injection-moulded specimens. Prior to testing, the extracted fibers were conditioned in a climatic chamber at 20°C and 65% relative humidity.

MICROSCOPIC IMAGING

A digital microscope (VHX-5000, Version 1.6.1.0, HDR, Keyence Corporation, Osaka, Japan) was used to reveal the wood fiber characteristics before and after processing.

FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FE-SEM)

Field emission scanning electron microscopy (FE-SEM) was carried out to evaluate the fracture morphology of the composites. Images were taken from the fractured surface of the tested tensile test specimen using a Quanta FEG 250 FE-SEM device (FEI Company, Netherlands). The investigations were performed at a voltage of 5 kV and at 50x and 200x and 400x magnification. The fractured surfaces were sputter coated with gold.

FIBER CHARACTERIZATION

Fibre characterization was done applying the dynamic image analysis system QICPIC combined with vibrating chute VIBRI and dry dispersion unit RODOS (SympatecGmbH, Germany). In the device, the particles are dispersed in an accelerated air jet. A high-speed camera takes pictures of the particle stream. Measuring particle size and shape from the projected particle area of binary pictures and calculating size and shape distributions was done by the software WINDOX (Sympatec GmbH, Germany).

Fiber length was characterized with respect to the median and quartiles of the length-based particle length distribution (q1) (DIN ISO 9276-1) (Teuber et al. 2016b). Fiber length (length of fiber, LEFI) was determined using skeletonization algorithm for the shortest distance between the furthermost endings of the fiber. The fiber diameter (diameter of fiber, DIFI) was determined by the projected area of the respective fiber, divided by their respective total length of all skeleton sections. The elongation value

describes the ratio between length to diameter and represents the inverse of the aspect ratio (Krause et al. 2017b).

4.3 RESULTS AND DISCUSSION

Processing observations

During compounding at higher fiber contents (>40%), difficulties occurred by feeding the fibers into the feed throat of the extruder. The low fiber bulk density led to bridges of fiber material at the feed throat, which was circumvented by forcing the fibers manually into the process. However, a stable compounding process was initiated, without a mechanically induced increase in bulk density of the fibers.

Fiber length

Figure 4.1 gives a visual impression of the influence of the manufacturing processes on the initial fiber geometry (a). The images (b) and (c) are exemplarily shown for the composite with 50 % wood fibers. Before processing the initial wood fibers appear as fiber bundles and single fibers as it is also reported by Wenderdel (2015). From Figure 4.1 it is clearly evident that the processing steps of compounding and injection-molding are noteworthy reducing the fiber length (Teuber 2016a). The determined fiber length, aspect ratio and their respective x_{10}, x_{50} and x_{90} quantiles of the separated fibers are listed in Table 4.1. The fibers were gained from all composites without MAPP (compounds and injection-molded specimens). For the granulated and injection-molded specimens containing MAPP, a separation between the wood fibers and the matrix was not successful. It appeared that even after two up to four days of boiling time in hot xylene the fibers and matrix material were still entangled. Thus, a characterization of fibers originated from MAPP containing composites was not possible.

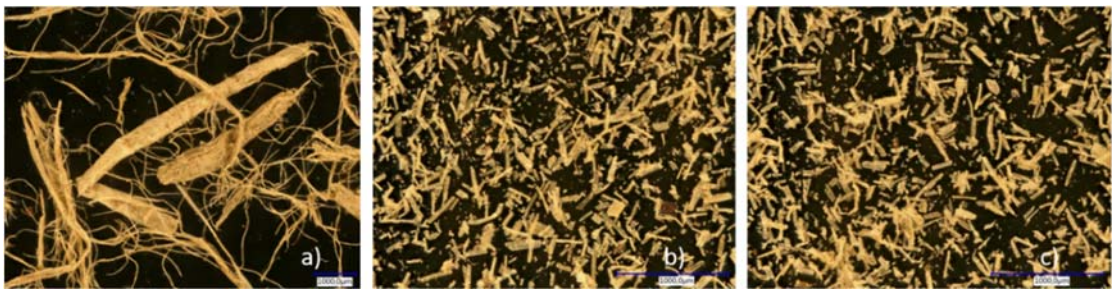

Figure 4.1 Microscopic observations of the native fibers before processing (a) and extracted fibers after compounding (b) and injection-molding (c)

The median of the initial wood fiber length is 1825.9 µm with an L/D ratio of 33.3. The cumulative initial fiber length distribution is displayed in Figure 2a. The graph shown provides a good overview on the distribution of the initial fiber length (x_{10} = 316.3 and x_{90} = 3708.7). Moreover, the notable effect of the process, by means of compounding and injection-molding, on fiber length is displayed. As it is shown, composite processing heavily influences the length of the wood fibers. After compounding, the fiber length is reduced up to 97 % (x_{50} = 60 % fiber content) compared to the initial fiber length. However, the injection-molding causes only a minor additionally reduction in fiber length. In line with Puglia et al. (2008) and Teuber et al. (2016a), fiber length reduction is increasing with increasing fiber content during compounding. With increasing fiber content the chance of higher interactions between the fibers increases. Moreover, the polymer viscosity increases with increasing fiber content resulting in higher shear forces (Peltola et al. 2014).

For co-rotating twin-screw extruders, severe fiber breakage occurs right after feeding the fibers into an extruder (Teuber 2016). With regard to injection-molding, further reduction in fiber length occurs rather at lower fiber contents than at higher fiber contents (Figure 4.2 b). As longer the fibers are after compounding, as higher is the degradation during injection-molding. Similar observations were reported by Peltola et al. (2014). The reduction in fiber length during injection-molding is a result of high shear forces, which occur during the melt transportation at the injection-molding die. Based on the investigation of the fiber length and aspect ratio along the applied process chain, it is evident that the fiber geometry is altered.

Table 4.1 Revealed fiber length and L/D ratio of native wood fibers (WF) and various wood fiber contents for compounds (C) and specimens (IM). Fiber length and L/D ratio are presented as 10% (x_{10}), 50% (x_{50}) and 90% (x_{90}) quantile of the length-based cumulative distribution.

	fibre content		**20%**		**30%**		**40%**		**50%**		**60%**	
		WF	C	IM	C	IM	C	IM	C	IM	C	IM
length [µm]	x_{10}	316,3	28,2	15,1	16,7	16,2	12,2	13,4	12,3	13,1	9,7	9,6
	x_{50}	1825,9	130,1	96,2	89,5	90,2	80,2	86,0	82,1	78,3	62,2	55,8
	x_{90}	3708,7	281,2	247,6	246,8	229,2	222,1	240,1	252,6	226,3	205,5	191,0
L/D	x_{10}	7,7	2,0	1,9	1.8	1,9	1,9	1,9	1,9	1,9	1,2	1,0
	x_{50}	33,3	4,3	3,8	3.3	3,4	3,4	3,3	3,4	2,9	3,0	1,5
	x_{90}	50,0	7,7	7,1	7.1	6,7	6,7	6,7	7,1	6,7	6,3	3,8

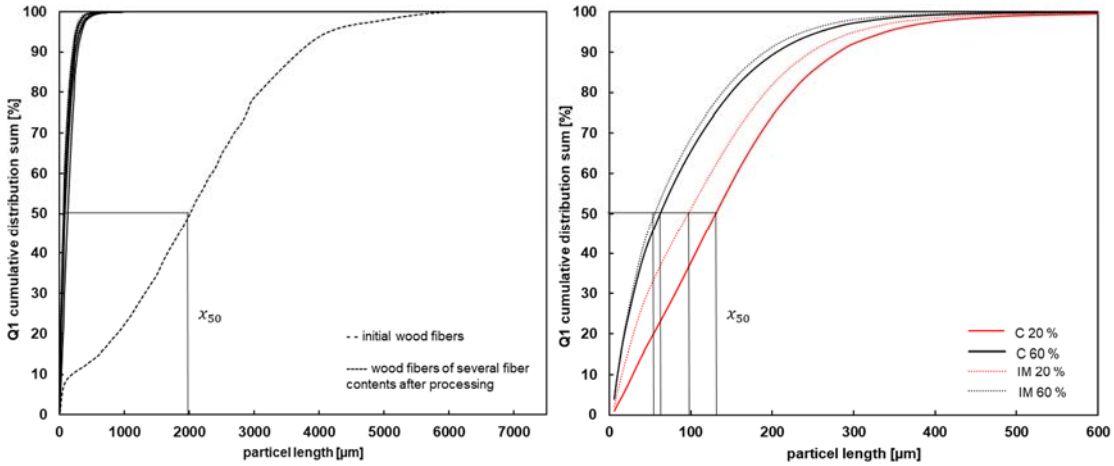

Figure 4.2 Cumulative fiber length distribution (a) for the initial wood fibers and the fibers after processing. Influence of the fiber content and processing step on fiber length (b).

FE-SEM observations

The fracture surface of tensile tested specimens containing 50 wt. % wood is displayed Figure 4.3 and 4.4. It was decided to investigate the fracture surface for a low (20 wt. %) and high (50 wt. %) fiber content for composites with and without MAPP. As apparent from Figure 4.3 and 4.4, the wood fibers are present as single fibers and fiber bundles and they are well distributed in the matrix. Additionally, the cross-section of the fractured surface indicates, a partial alignment of the fibers in the melt flow direction. All fracture surfaces investigated show small holes and fibers that are presumably pulled out of the matrix. The formation of holes are maybe due to inhomogeneous cooling during injection-molding and/or due to fiber pull out during testing. The latter seems to be more likely since intact fiber ends are visible for all investigated specimens. Fiber pull outs indicate a weak interfacial bonding between fiber and polymer or is a result of a fiber length which is below the critical fiber length (Erdmann 2017). The composites without MAPP show consistently clearly gaps between fiber and polymer which underlines the weak interfacial bonding resulting in fiber pull outs. For composites with MAPP and especially at 20 wt.% fiber content both gaps between the polymer and wood fibers and well-bonded fibers are observed (Figure 4.3 d). This is maybe a reason for insufficient distribution or not enough of MAPP used. However, composites with 50 wt.% wood fibers and MAPP (Figure 4.4 c and d) imply a better adhesion between fiber and polymer since some fibers seem to be broken under tension and others are pulled out.

The observed cross-sections of composites show a different fracture morphology along the surface. Composites containing 20 wt.% wood fibers show areas of a plane fractured surface and areas where a more ductile behavior of the polymer matrix appears. Composites containing 50 wt.% wood fibers a ductile polymer matrix does not occur.

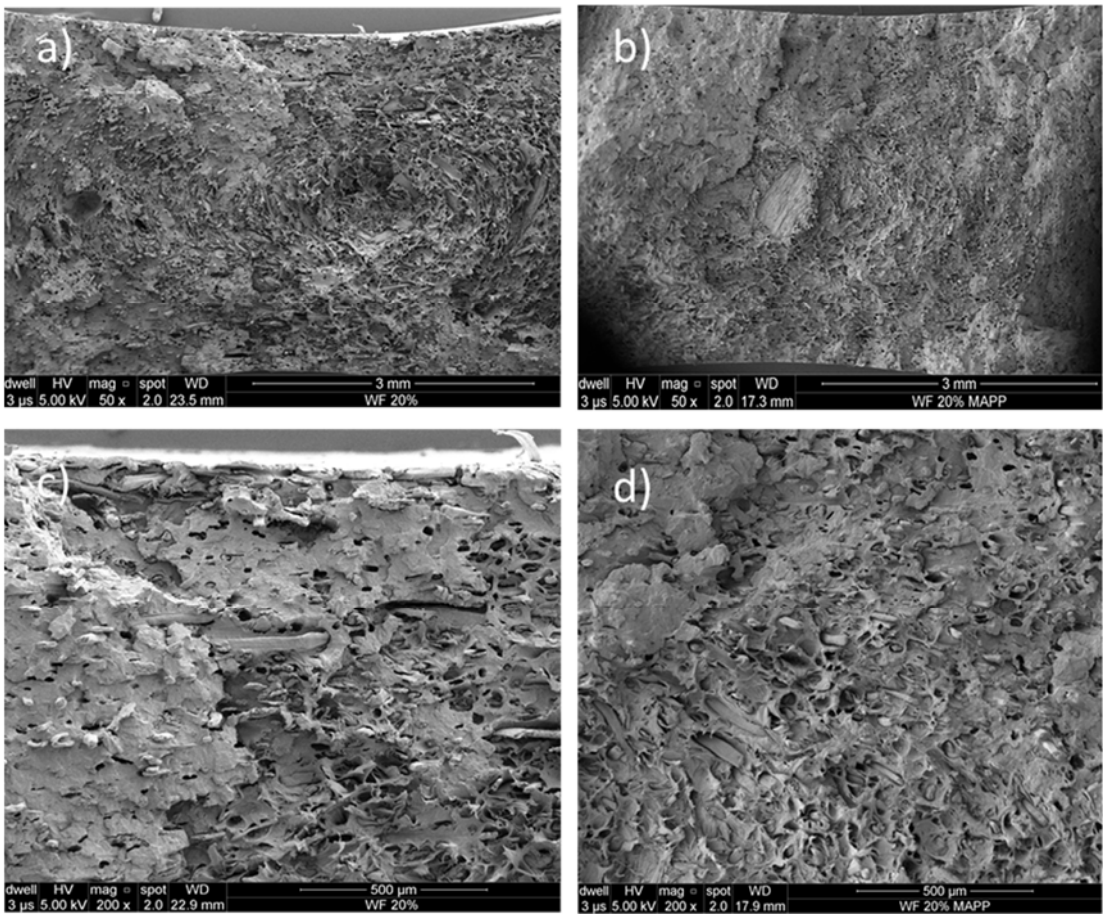

Figure 4.3 FE-SEM images of composites containing 20 wt. % wood fibers without (a and c) and with (b and d) MAPP with a 50x and 200x magnification.

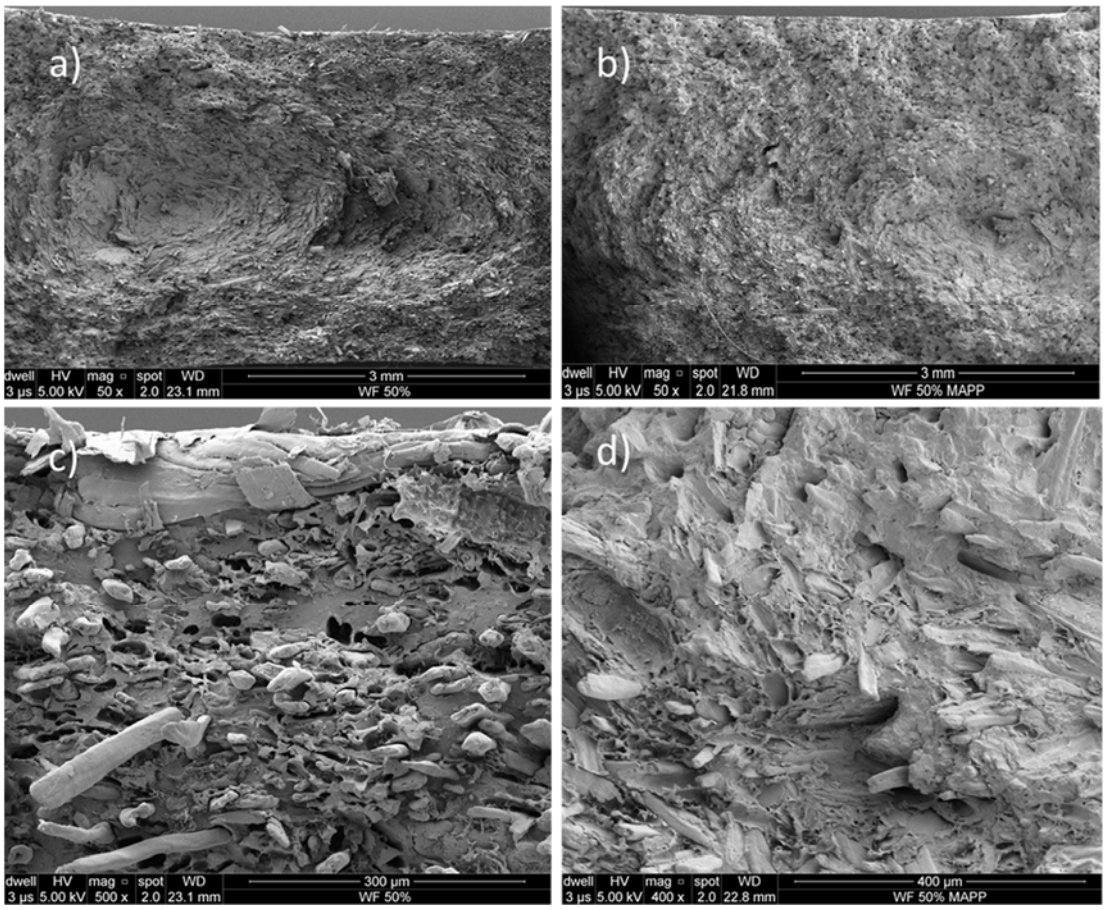

Figure 4.4 FE-SEM images of composites containing 50 wt. % wood fibers without (a and c) and with (b and d) MAPP with a 50x, 400x and 500x magnification

Mechanical Properties

Table 4.2 summarizes the determined mechanical properties of the tested wood fiber/PP composites.

Figure 4.5 shows, that the modulus of elasticity (MOE) is not very different between the tensile and flexural test. With increasing fiber content tensile and flexural MOE increases, which is in agreement with other studies (Radovanovic 2007, Caulfield et al. 2005). Composites with 60 wt.% wood fibers are showing 4.5 times higher MOE than the neat polymer matrix. The addition of MAPP did not affect any significant differences in MOE. Similar results for jute fiber composites are found by Thomason (2009). Of interest is the almost linear slope of the tensile MOE. Using a linear regression, the correlation coefficient amounts R^2= 0.99 for tensile MOE. It is well known that the measurement of strength and MOE values for small wood fibers is difficult

(Thumm and Dickson 2013). However, due to an appropriate correlation, the linear regression equation ($y = ax + b$) can be used to integrate the rule of mixture ($E_c = (E_f - E_m) * f + E_m$). Since the composite ($E_c$) and polymer MOE ($E_m$) as well as the fiber volume fraction (f) is known, the calculation of the fiber MOE is possible. If the known regression variable (a) consists out of the values $a = E_f - E_m$, the wood fiber modulus is calculated with $E_f = a + E_m$. Using the provided data, the wood fiber MOE results in 8.7 GPa, calcultated for tensile MOE without coupling agents. Applying the same approach for composites with MAPP the wood fiber MOE amounts 9.6 GPa. The differences are explained due to use of MAPP, which increases the MOE of the neat polymer (Krause and Krause 2012). Using the reported data for tensile MOE (R^2= 0,98) from Caulfield et al. (2005) for thermomechanical aspen fiber PP comopsites, the wood fiber MOE is calculated with 9.8 GPa. The calculated values are in between the range of the experimental MOE values for thermomechanical wood fibers (4.3 - 15.8 GPa) reported by Wenderdel (2015). The presented approach is enable to give an appropriate estaimate for the calculation of the fiber MOE.

Figure 4.5 b shows the tensile strain of the composites as a function of fiber content. The strain decreases as the fiber content increases. Coupling agents improving the interfacial adhesion between wood fibers and the polymer by forming a covalent bond, a polymer chain entanglement and/or a strong hydrogen bond (Lu et al. 2000). Thus, the lower strain results in higher MOE for MAPP containing composites than for composites without MAPP. The previous mentioned ductile fractured surface of composites containing 20 wt.% wood fibers is maybe explained with the higher strain rate compare to composites containing 50 wt.% wood fibers.

The results of similar MOE values for composites with and without MAPP in this study is in contrast to Krause and Krause (2012), who found that independent from the particle size an increase in MAPP concentration is accompanied with increasing MOE. Moreover, Krause and Krause stated that optimum MAPP concentration for smaller particles is around 4 % and 2 % for larger particles. However, the findings are based on the initial particle size. Fiber size after processing was not observed.

For composites without MAPP, tensile strength steadily decreased with increasing fiber content (Figure 4.6). A reason for the decreasing strength is presumably attributed to the challenging adhesion at the interface between the fibers and the polymer. Thomason (2009) suggested when discussing the strength properties of natural

fiber composites to consider the anisotropy structure of natural fibers and their contribution to the stress-transfer interface of the fiber-matrix system. Due to different thermal expansion coefficients of the fiber and polymer, the cooling process during composite forming induces compressive radial stresses at the interface. The resulting residual stresses improving the coefficient of friction resulting in a higher physical bonding between fiber and polymer (Parlevliet et al. 2006). Thomason (2009) modelled the interface residual stress and showed that for jute fiber PP composites the residual compressive stress is in a great order of magnitude lower compared to glass-, carbon- and aramid-fiber based PP composites.

The addition of 3 % MAPP increases tensile strength for about 1.6 times up to a fiber content of 50 wt. %. No significant differences in tensile strength occur at higher fiber concentrations (60 wt. %). The results of a peaking tensile strength at fiber contents around 50 wt. %, that are found in the previously published literature review (Mertens et al. 2017) are in line with the results found in the present study. These findings are also found for glass fiber composites (Thomason 2005). It is assumed that the wood fiber tip beyond 40-50 wt. % is attributed to several factors. Thomason (2005) stated that, with increasing fiber contents, fiber distribution is getting more inconsistent, the void and agglomeration formation increases and fiber alignment decreases. Also the possibility of areas with fibers which are not fully covered by the polymer increases (Thomason 2005). This is most likely a result of a high viscosity melt which is difficult to mold properly (Woodhams et al. 1984).

Flexural strength increased up to a fiber content of 30 % and started to decrease linearly for wood fiber contents beyond 30 % without MAPP. Increasing flexural strength up to fiber content of 60 wt. % is determined if 3 % MAPP is applied. The maximum strength is 2.2 times higher compared to the neat polymer. The results showed similar strength values than for wood flour based WPC known from the literature (Krause et al. 2017b, Schirp et al. 2014, Stark and Rowlands 2003, Krause et al. 2015).

Figure 4.7 shows that the impact bending strength is decreasing with increasing fiber content. Similar tendencies are found for composites with and without MAPP. The revealed values are the only mechanical properties in this study, in which the utilization of MAPP does not increase the properties. It is proposed to keep the fibers aspect ratio as long as possible, in order to enhance impact bending properties (Ashori 2010).

The fibers aspect ratio determined in this study is rather low for all fiber contents compared to the initial length which may explain the decreasing impact bending strength. Additionally, impact bending strength reacts sensitively on structural defects, like voids, agglomerates and areas of higher and lower fiber concentrations (Erdmann 2017) since it disrupts the efficient energy distribution in the composite during impact bending. Some of these structural defects are partially observed with the FE-SEM analysis and are therefore an indication of the decreasing impact bending strength.

Discussing the mechanical properties with regard to the measured fiber length, the following conclusions can be drawn:

1. Tensile and flexural MOE for composite with and without MAPP increases with increasing fiber content, while for the same composites fiber length and aspect ratio is decreasing.
2. Tensile and flexural strength for MAPP containing composites increases up to a certain fiber content, while fiber length and aspect ratio decreases.
3. Tensile strength for composites without MAPP decreases with increasing fiber content and decreasing fiber length and aspect ratio.
4. Flexural strength for composites without MAPP increases to fiber content of 30 wt.%, while fiber length and aspect ratio decreases.
5. Impact bending strength decreases for all formulations, while fiber length also decreases.

Overall, the mechanical properties of the composites are in line with other studies using similar wood fiber types. The decreasing properties for composites without MAPP is explained with the presumably poor challenging adhesion between fiber and polymer. However, it is shown that fiber length is decreasing with increasing fiber content for all formulations, resulting in aspect ratios between 1 – 7, which is rather in the range of wood flour than wood fibers (Stark and Rowlands 2003). The obtained results of the fiber length analysis are in agreement to Teuber (2016a), Peltola et al. (2014) and Puglia et al. (2008). For our study, it is therefore doubtful that the aspect ratio is the dominating parameter that enhances the mechanical properties. However, it is still unclear whether a rather small amount of retentive fibers might be enough to reinforce the composite. Additionally to the fiber length as important parameter, other

structural fiber properties such as surface chemistry and topography (Schirp et al. 2014) or the residual stress formation (Thomason 2009) might have to be considered.

Table 4.2 Mean values (MV) and standard deviation (SD) of tensile, flexural and impact strength and the corresponding MOE of various wood fiber composites with and without MAPP. Results of the statistical analyses are displayed in groups (HG), whereas measured values assigned with the same letter (differentiation by small and capital letters) are not significantly different from each other at a significance level of α = 0.05.

fiber content	MAPP [%]	tensile strength [MPa]			tensile MOE [GPa]			flexural strength [MPa]			flexural MOE [GPa]			Charpy Impact [kJ/m²]		
		MV	SD	HG	MV	SD	HG	MV	SD	HG	MV	SD	HG	MV	SD	HG
0%	0	29.9	0.2	-	1.7	0.0		34.6	0.2	-	1.5	0.0		-	-	-
20%	0	29.6	0.2	A	2.9	0.1	A	46.9	0.7	A	2.7	0.0	A	18.5	1.2	A
	3	37.0	0.2	a	3.0	0.0	a	56.6	0.4	a	2.8	0.1	a	19.9	1.5	a
30%	0	29.0	0.1	B	3.8	0.1	B	49.0	0.7	B	3.4	0.1	B	14.5	0.8	B
	3	41.3	0.3	b	3.9	0.1	b	67.2	0.5	b	3.5	0.0	b	18.4	1.8	a
40%	0	28.2	0.1	C	4.6	0.1	C	46.4	0.7	A& A_1	4.3	0.1	C	9.5	3.8	C
	3	45.2	0.2	c	4.7	0.0	c	71.3	0.3	c	4.3	0.0	c	16.3	1.3	b
50%	0	27.2	0.3	D	5.1	0.1	D	45.5	0.9	A_1	5.3	0.1	D	7.1	2.8	D
	3	48.1	0.3	d	5.5	0.1	d	76.4	1.0	d	5.2	0.1	d	14.4	0.7	b
60%	0	23.9	0.3	E	5.9	0.1	E	40.8	0.8	C	6.5	0.2	E	4.6	2.0	E
	3	48.1	0.8	d	6.6	0.1	e	77.3	0.8	e	6.8	0.1	e	11.1	4.5	c

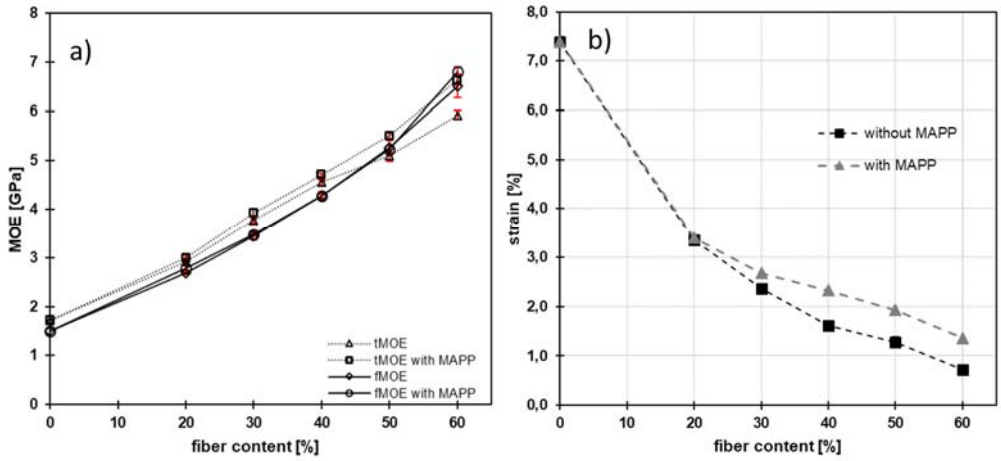

Figure 4.5 Tensile (a) tMOE and flexural (b) fMOE modulus of elasticity at different fiber contents with and without MAPP.

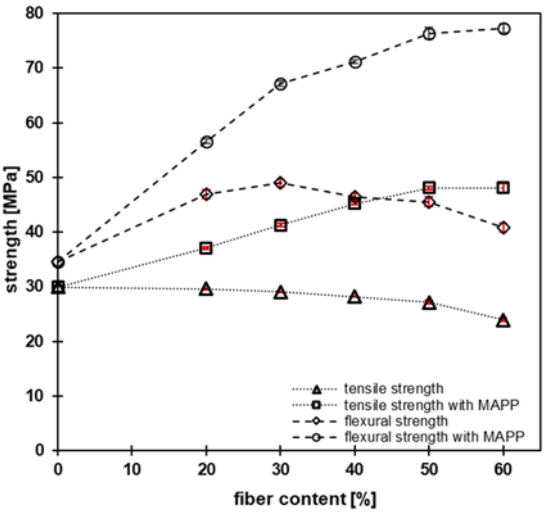

Figure 4.6 Tensile and flexural strength at various wood fiber contents for composites with and without MAPP.

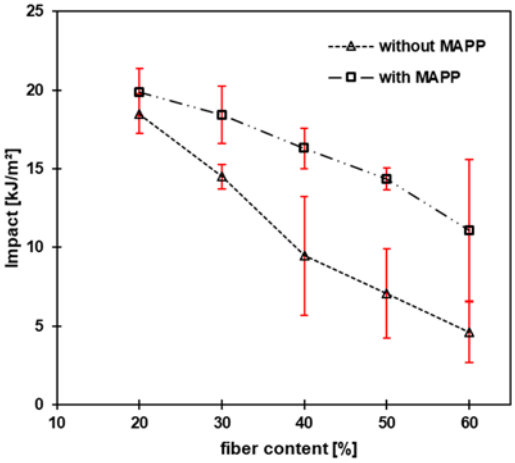

Figure 4.7 Charpy impact strength as a function of wood fiber content for composites with and without MAPP

4.4 CONCLUSIONS

The present study investigates the influence of thermomechanical wood fibers by means of their geometry and fiber content on the mechanical properties of wood-polypropylene composites. The WPC material was compounded using a co-rotating twin screw extruder and subsequently injection moulded to test specimens. The respective fiber loading ranged from 20 wt. % to 60 wt.%, with and without MAPP. For the results found in this study, the following conclusions can be drawn:

1. The processing of thermomechanical wood fibers with conventionally used compounding technologies is still challenging due to the low bulk density of these fibers.
2. The production process applied is resulting in a significant reduction in fiber length. The compounding process was found to be the major lever regarding the fiber degradation. Moreover, it was found that increasing the fiber content is accompanied by an increase of fiber length reduction. It is assumed that this is most likely attributed to an increase in melt viscosity.
3. Adding wood fibers to the polymer matrix results in a steadily increase of MOE, independent of the use of coupling agents.
4. Tensile strength properties increase up to a fiber content of 50 wt.% when 3% MAPP is added to the composite formulation.

Since the fiber length is drastically shortened after composite processing, although, tensile strength and MOE still increase with increasing fiber content, it is assumed that maybe other parameters have to be considered when discussing the mechanical properties of wood fiber thermoplastic composites. In this regard, it was discussed whether a rather small amount of retentive fibers might be enough to reinforce the composite.

CHAPTER 5
EVALUATION OF A SIMULTANEOUS DEFIBRATION AND COMPOUNDING PROCESS

In the previous chapters of the thesis the application and performance of thermomechanical wood fibers as resource in WPC was highlighted. However, it was found that there is a lack of appropriate processes of compounding wood fibers and thermoplastic polymers. Based on the findings an alternative compounding process is developed. The basic idea is, to use the refiner technology, as described in Chapter 1.4, in order to defibrate wood chips together with polymer granulates in a single process step. The process is based on the idea to solve the feed-in problematic of wood fibers and to save production steps of wood preparation, as it usually required for WPC production. Another problem that is caused by traditional compounding methods is that dry fibers tend to agglomerate during compounding. These agglomerates are difficult to dissolve in the process and are weak points, initiating crack propagation in the final product. Thus, the refiner technology aims to defibrate and compound the two different materials simultaneously in a wet and pressurized state in order to avoid any agglomerate formation. Compare to the conventional WPC compounding processes (kg/hours), the production of themomechanical wood fibers with refiner technology is characterized by large production quantities (tons/hour). A successful development of the novel process could therefore presumably lead to cost savings for WPC products. The structure of the present Chapter is based on the evaluation of the development steps of the process, including preliminary studies (5.1) followed by a proof of concept (5.2 and 5.3) and finally an industrial scale-up of the process (5.4).

5.1 PRELIMINARY STUDIES OF A SIMULTANEOUS DEFIBRATION AND COMPOUNDING PROCESS

During the preliminary studies of the simultaneous wood chip defibration and polymer compounding process, an atmospheric Sprout Waldron 12” laboratory refiner was used. The intention of the fist experiments was, to use a simple system to investigate the behavior of the refiner during the process. It was expected that occurring shear forces within the refiner lead to a polymer melting which finally could stop the turning disc. These expectations were not confirmed. For the first experiments a low density polyethylene (LDPE, Sabic Riyadh, Saudi Arabia, melt flow rate 85.0 g/10 min (load

2.16 kg), melting point 104°C) and bleached kraft pulp fibers were used. LDPE was used because of the low melting point. The share of pulp fibers and polymer was 10% to 90%. Mechanical properties were not investigated.

In a further experiment spruce shavings (*picea abies*, no further informations were provided) were mixed with high density polyethylene granulates (HDPE, Sabic Riyadh, Saudi Arabia, melt flow rate 30.0 g/10 min (load 2.16 kg), melting point 132°C). Both components were mixed manually prior to defibration with a share of 50 % to 50 %. In order to provide additionally energy, a steam generator was additionally attached to the refiner body. During defibration water was added to the refiner to provide a material flow. This was done because of to less power of the conveying screw. During defibration the process run stable. The free water was afterwards detached from the fiber-polymer mixture using a conventional spin dryer. To manufacture test specimens, the mixture were pelletized with an pellet press (Type: 14-175, Amandus Kahl GmbH, Reinbek, Germany) to increase the bulk density for further injection-molding. The pellets are further manufactured to dog-bone shaped specimens using an injection-molder (Arburg Allrounder 420C Golden Edition, Arburg GmbH + Co KG, Loßburg, Germany). To investigate the composite performance, which is made out of the novel produced compound, tensile and flexural properties were tested. To classify the properties, the novel produced material was compared to pure HDPE test specimens and to reference wood flour containing composites. Wood flour (Arbocel C100, Rettenmaier & Söhne GmbH + Co KG, Rosenberg-Germany) and HDPE polymer (same as above) were compounded using a co-rotating twin-screw extruder (Leistitz ZSE27iMaxx-400). The extruded compound was directly cut into granulates of 5 mm in diameter using a hot pelletizer. The granulates were injection-molded as described above. All composites were tested according to DIN EN 527:2012-06 (tensile test) and DIN EN 178:2003 (flexural test). The mechanical evaluation was conducted using a universal testing machine (Zwick Roell GmbH & CO.Kg, Ulm, Germany). For each composite, ten specimens were evaluated. The properties are presented in Table 5.1.1.

Table 5.1.1 Mechanical properties of HDPE pure and based wood flour and wood fiber composites.

	tensile test		**flexural test**	
	strength *[MPa]*	tMOE *[GPa]*	strength *[MPa]*	fMOE *[GPa]*
HDPE	19.13	1.04	19.03	0.95
wood flour 50/50	19.21	3.76	32.0	4.0
wood fiber 50/50	19.12	4.1	38.6	3.8

The results obtained, display some interesting facts. Tensile strength is whether improved nor it is deteriorated. Flexural strength is improved by 40% when adding wood flour to the matrix. Wood fibers produced with the novel approach is improving the flexural strength twice compare to the neat polymer strength. The addition of wood to the matrix improves the tensile and flexural modulus. This is a common fact since wood has a much higher stiffness compare to polymers. First of all it could be shown that the novel process is an alternative way to produce a compound with satisfactorily properties. From a resource prospective, adding 50% wood flour or fiber to the polymer matrix can save 50% of polymer by maintaining the properties. Therefore, it is possible to declare, that the properties of the novel produced composite are at least preserved.

The preliminary experiments of the novel process of simultaneous defibration and compounding of wood fibers and polymer led finally to the fact to submit the process as patent. In the following section further developments and other findings are presented.

5.2 EVALUATION OF WOOD FIBER COMPOSITES BASED ON A NOVEL SIMULTANEOUS DEFIBRATION AND COMPOUNDING PROCESS (PAPER III)

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Authors contribution:

	CD	EX	ED
Oliver Mertens	70%	90%	65%
Kim C. Krause	5%	10%	30%
Andreas Krause	15%	0%	5%

CD: Conceptual Design

EX: Conducting experiments

ED: Editing

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ABSTRACT

The distinctive length and morphology characteristics of thermomechanical produced wood fibres make it a promising candidate for the utilization in polymer composites. However, due to the low bulk density of these fibres, the feeding into the compounding process (e.g. extruders) is quite challenging. In this study, a novel simultaneous defibration and compounding process is conducted in order to solve the feed-in problem of thermomechanical fibres. A disc-refiner was used to defibrate wood chips to fibres and compound the fibres with neat polymer granulates in one process step. After the process, the material showed typically thermomechanical fibres with chopped polymer particles which were inseparably attached to the fibre. The observed mechanical properties of the composites were slightly lower than some literature values. With FE-SEM and X-ray microtomography analysis, voids and a polymer enriched surface were found influencing the composites performance.

5.2.1 INTRODUCTION

In the past decade wood-plastic-composites (WPC) have gained great interest in commercial products, such as in construction, automotive, or other consumer good applications (Carus et al. 2015, Ashori 2008). WPC consist of wood particles in different shape and size, a thermoplastic polymer and additives. The most common polymers for WPC are polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). Usually, WPC-manufactures use wood flour as a filler due to its relatively easy processability, its low cost and good availability (Schirp and Stender 2010, Stark and Rowlands 2003, Clemons 2002). The manufacturing of WPC is based on the production technologies of the polymer industry. These technologies (e.g. extruders) require dry material in order to avoid an excessive moisture evaporation during the process.

In recent years, the utilization of wood fibres instead of wood flour as reinforcement in composites is gaining interest (Lerche et al. 2014). Wood fibres differ naturally from wood flour, in that wood fibres consist of the entire cell wall of one former living wood cell. They are rather long compared to their width, but exhibit a wide distribution in size and shape (Lohmann and Blosen 2010, Benthien et al. 2014). The term “wood fibres” in this study is referred to technical produced wood fibres obtained through thermomechanical defibration of wood chips. These fibres are usually used for medium density fibreboards (MDF) or paper (thermomechanical pulp, TMP). Processes for TMP or MDF-fibres differ in that way, that the process for MDF fibres is using a low energy thermomechanical defibration. The TMP process used for paper is much more higher in temperature and shear forces (Walker 2006a). However, both TMP and MDF fibers are produced via a refining process. In this process, steam-heated wood chips are continuously fed into the center of a refiner, consisting of a rotating and a stationary disc. Centrifugal forces and a certain disc pattern provide a defibration (refining) of the wood chips to wood fibers. Due to the thermomechanical processing conditions, most of the lignin remains on the fiber surface. Therefore, it is claimed to enhance the bonding between the fibers and the hydrophobic polyolefin matrices (Schirp et al. 2014). After refining, fiber lengths may vary from 20 µm to 4500 µm and fiber widths from less than 1 µm to 80 µm (Lohmann and Blosen 2010). Thermomechanical fibers have a promising high aspect ratio (length to diameter ratio) which provides the potential to reinforcement the composite (Schirp and Stender 2010). The aspect-ratio of these fibers range from 24 (Gehrmann et al. 2004) to 72 (Nygård et al. 2008, Peltola et al. 2014, Horbens et al. 2012) and tend to increase

tensile strength and elastic modulus (MOE) (Stark and Rowlands 2003). Stark and Rowlands (2003) showed that wood fibers compare to wood flour improve strength and stiffness in WPC. Compared to other fiber composites, composites containing wood fibers have a good price-performance ratio. Furthermore, wood fibers are constantly, readily available at commercial scale, which is a significant advantage over agricultural fibers (Wolodko et al. 2015).

A drawback of wood fibers and other natural fibres, in general, is their low bulk density, the non-free flowing behavior and the tendency to form bridges during feed-in into continuous compounding processes (Thumm et al. 2011). In addition, dissolving fibre agglomerates during compounding is challenging with established technologies such as extruders (Le Baillif and Oksman 2009). To avoid the feed-in problem, scientific investigations (Lerche et al. 2014, Schirp et al. 2014, Nourbakhsh and Ashori 2008, Woodhams et al. 1984) often use laboratory scale batch processes to compound lignocellulosic fibres (Mertens et al. 2017a). Others (Woodhams et al. 1984, Peltola et al. 2011) pelletized the fibres before compounding, resulting in a significant fibre length reduction. Warnes et al. (2006) used the MDF process for producing MDF fibre pellets with a polymer solution which are ready to use for extruders. This product is commercially available under the trade name “Woodforce” supplied by Sonae-Industry. Nevertheless, the industrial utilization of thermomechanical fibers in composites, seems to be limited due to the mentioned drawbacks (Mertens et al. 2017a) given by the compounding process.

In order to solve the feed-in problem of wood fibres into extruders and to avoid fibre drying before compounding, Krause et al.(Krause et al. 2017a) developed a process of simultaneous defibration and compounding process using refiner technology. In this process, fibre production and compounding simultaneously take place within the refiner, resulting in a wood fibre compound. This process is an alternative to the conventional compounding processes and offers several advantages.

- higher throughputs, compared to extruder compounding
- reduction of process steps e.g. wood drying
- convenient process for the application of wood fibres in thermoplastic composites

The objective of this study is, to use this new process in order to evaluate the resulting wood fibre composite properties. In detail, the following objectives are addressed:

- evaluation of the simultaneous defibration and compounding process

- investigation of the mechanical properties and water absorption of the manufactured composites. Mechanical properties are compared with literature values
- visual observation of the composites with field emission scanning electron microscopy (FE-SEM) and X-ray micro-computed tomography (XµCT)

Thermomechanical produced fibres are in the following text termed as “wood fibres” (WF).

5.2.2 MATERIALS AND METHODS

Commercially available wood chips (Räuchergold FS 14, Rettenmaier & Söhne GmbH + Co KG, Rosenberg, Germany) from a mixture of norway spruce (*Picea abies*) and silver fir (*Abies alba*) were defibrated and at once compounded with the thermoplastic polymer, achieving a wood share of 50% and 70% by weight. As polymers were applied:

a) Polypropylene (PP), PP 575p from Sabic (Saudi Basic Industries Corporation, Riyadh, Saudi Arabia), melt flow index 10.5 g/10 min (load 2.16 kg), melting point 160 °C
b) High-density polyethylene (HDPE), CC 3054 (Sabic), melt flow index 30 g/10 min (load 2.16 kg), melting point 130 °C

SIMULTANEOUS DEFIBRATION AND COMPOUNDING PROCESS

For the simultaneous wood chip defibration and wood-polymer compounding, a Sprout-Waldron 12“ (305 mm) pressurized disc refiner with an upstream 55 l boiler was used. Prior to refining the wood chips, the polymer granulates and approximately 12 l of water were mixed manually and filled into the digester of the refiner. In Table 5.2.1 the refining conditions are listed.

Table 5.2.1 Refining parameters applied for compounding

Formulation	boiling time	pre-steaming	Refiner disc gap
WF 50/50 PP	10 min.	145°C	0.4 mm
WF 70/30 PP		145°C	
WF 50/50 HDPE		125°C	
WF 70/30 HDPE		125°C	

After pre-steaming, the mixture was continuously fed into the refiner. After the refining stage, the compound was discharged through a conduit into a cyclone (see Figure 5.2.1). After the refining stage the moisture content of the compound was measured with a moisture measuring device (Satorius M35, Sartorius AG, Göttingen, Germany).

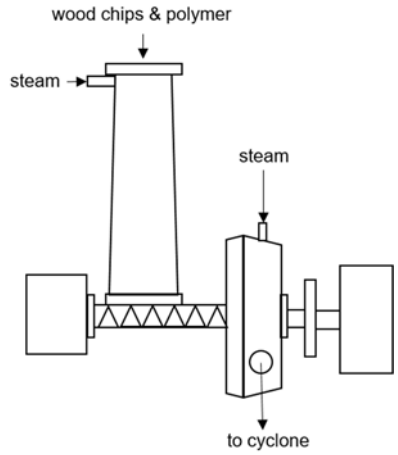

Figure 5.2.1 Schematic view of the refiner.

SAMPLE MANUFACTURE AND TESTING

The WF compound was first pelletized using an pellet press (Type: 14-175, Amandus Kahl GmbH, Reinbek, Germany). Afterwards, the pellets were dried to a moisture content below 1 % using a granulate dryer (Luxor CA 30 S, Montan GmbH, Isny, Germany). Subsequently, the pellets were injection moulded (Arburg Allrounder 420C Golden Edition, Arburg GmbH + Co KG, Loßburg, Germany) to test specimens.
Tensile properties were determined according to DIN EN 527:2012-06.
Flexural properties were determined according to DIN EN 178:2003. The mechanical evaluation was conducted using a universal testing machine (Zwick Roell GmbH & CO.Kg, Ulm, Germany). For each composite, ten specimens were evaluated. Water absorption of the samples was tested according to DIN EN 15534-1. The water absorption was described by the difference in mass (g) of a dried sample (M_{end}) and a submerged sample (M_i). The water absorption was calculated after 1, 2, 3, 4, 7, 14, 21 and 28 days using the following equation .

$$WA\ [\%] = \frac{M_{end} - M_i}{M_i}\ x\ 100$$

WA = water absorption
M_{end} = mass after end of test
M_i = mass at specific submersion time

Statistical analyses were performed using Origin (OriginLab, Northampton, MA USA). A single factor analysis of variance (ANOVA) at a level of significance of $\alpha = 0.05$ and a Tukey HSD test was conducted for the data from mechanical testing. For the statistical analysis, the PP and HDPE composites were dealt with as a single population for each mechanical test.

VISUAL ANALYSIS

a) Microscopic imaging

Digital microscopy were carried out to evaluate the macro-structure of the obtained WF compound after the refining stage. The digital microscope VHX-5000 (Version 1.6.1.0, Objective: 100x-200x, HDR, Keyence Corporation, Osaka, Japan) was used.

b) Field emission scanning electron microscopy (FE-SEM)

Field emission scanning electron microscopy (FE-SEM) was carried out to evaluate the fracture morphology of the composites. Images were taken from the fractured surface of the tested tensile test specimen using a Quanta FEG 250 FE-SEM device (FEI Company, Netherlands). The investigations were performed at a voltage of 7 kV and at 50x and 100x magnification. The fractured surfaces were sputter coated with gold.

c) X-ray *micro-computed tomography (X*µCT)

X-ray micro-computed tomography was carried out to evaluate non-destructively the internal composite structure. The investigated test samples (4x5x6 mm) were prepared from the middle of a untested WF 50/50 HDPE and WF 50/50 PP tensile test specimens (Figure 2).
The X-ray micro-focus CT system Nanotom® s (phoenix|x-ray, GE Measurement & Contro, Wunsdorf, Germany) was equipped with a cone beam geometry, a transmission molybdenum target, and a CCD detector. The tube voltage was 60 keV, whereby the current was 280 µA. The exposure time per projection was 750 ms. 2000 axial projections were collected over a total angle range of 360° in every tomographic run. The achieved spatial resolution was 4 µm.

The image processing and reconstruction were performed using the software *datos|x reconstruction*© (phoenix|x-ray, GE Sensing & Inspection Technologies GmbH, Wunstorf, Germany). The captured stack of two-dimensional projections was transformed into a three-dimensional data volume. Subsequently, the volume analysis was conducted using the Avizo® Fire 9 software (FEI, Hillsboro, Oregon, USA). The yellow

box in Figure 5.2.2 indicates the investigated sub-volume (ROI: 3472x4640x4016 µm), which was analysed regarding the average grayscale values of X-ray attenuation. Based on the X-ray attenuation, a watershed segmentation was conducted, which led to a binarized data stack. The binarized data contains the segmented volume fractions and their spatial distribution.

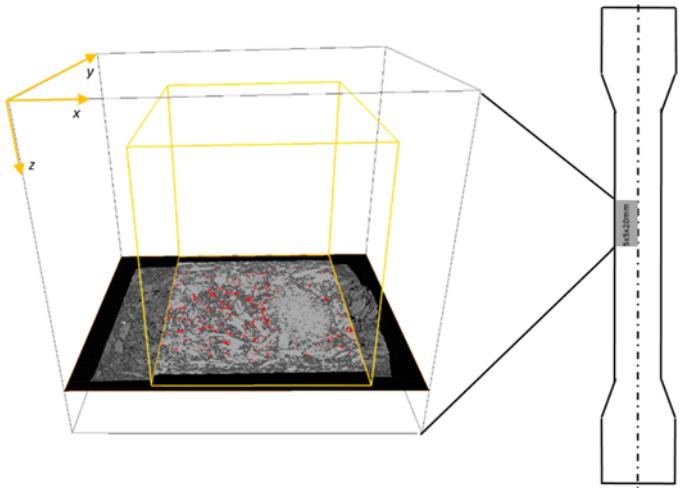

Figure 5.2.2 WF HDPE composite sample volume (grey section; 4x5x6 mm; grey box) scanned via X-ray micro-computed tomography and the analyzed sub-volume (yellow bounding box, ROI: 868x1160x1004 µm).

5.2.3 RESULTS AND DISCUSSION

Process observations

After pre-heating of the wood chip and polymer, this mixture was continuously fed into the refiner for defibration and compounding. During refining the process was stable. The polymer granulates did not exhibit any tendency to get stuck into the refiner plates' patterns. After discharging, the compound showed chopped polymer flakes which were inseparably entangled to the fibres (see 5.2.4). Figure 5.2.4 b displays molten polymer granulates with incorporated fibres. The moisture content of the compound after refining was between 35-40 %. Apparent from Figure 5.2.4 a, a fibrous material was received after the refining stage. Next to the produced fibres, shives, fibre bundles and coarser fibres were visually determined. The fibre geometry is influenced by the refiner disc gap. Increasing the refiner gap leads to increasing fibre lengths and number of shives and coarser particles and decreases the amount of shorter fibre (Ohlmeyer et al. 2015, Wenderdel and Krug 2012). Hence, the visual investigated coarse fibre geometry is probably a result of the applied disc gap distance

of 0.4 mm. Nevertheless, the exact fibre length and width of the obtained WF have to be measured in further studies.

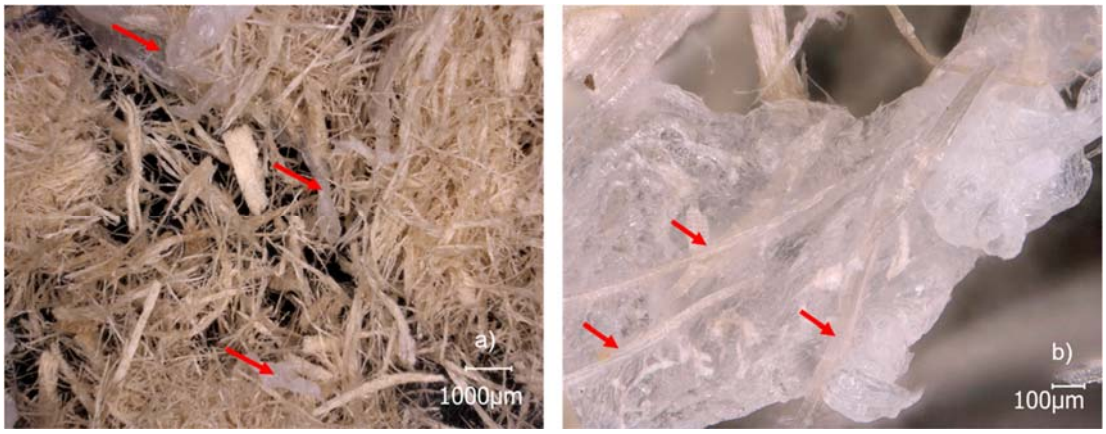

Figure 5.2.3 WF HDPE compound after defibration. Processed polyethylene granulates are inseparably entangled to the fibres. a) 100x magnification, b) 200x magnification.

Image analysis

a) FE-SEM

Figure 5.2.4 displays exemplary FE-SEM images of WF PP 50/50 and WF HDPE 50/50 with different magnifications (50x, 100x). Voids were detected in both composite types (tag 1). In both composites coarser particles (tag 2a) and single fibres (tag 2b) occur, which are embedded in the polymer matrix. This observation was found to be consistent throughout all investigated specimens. With regard to the FE-SEM images, a first conclusion is that the process was consistent over the compounding, pelletizing and injection-moulding processes since the first visual observation shows an adequate material distribution. Nevertheless, the detection of voids and coarser particles presumably influence the composite performance. The FE-SEM image analysis only gives information of the scanned surface structure. For a deeper understanding on how much voids and agglomerates or coarser particles are embedded, is given by the X-ray micro-computed tomography scanned volume. Further conclusions are discussed in the following sections.

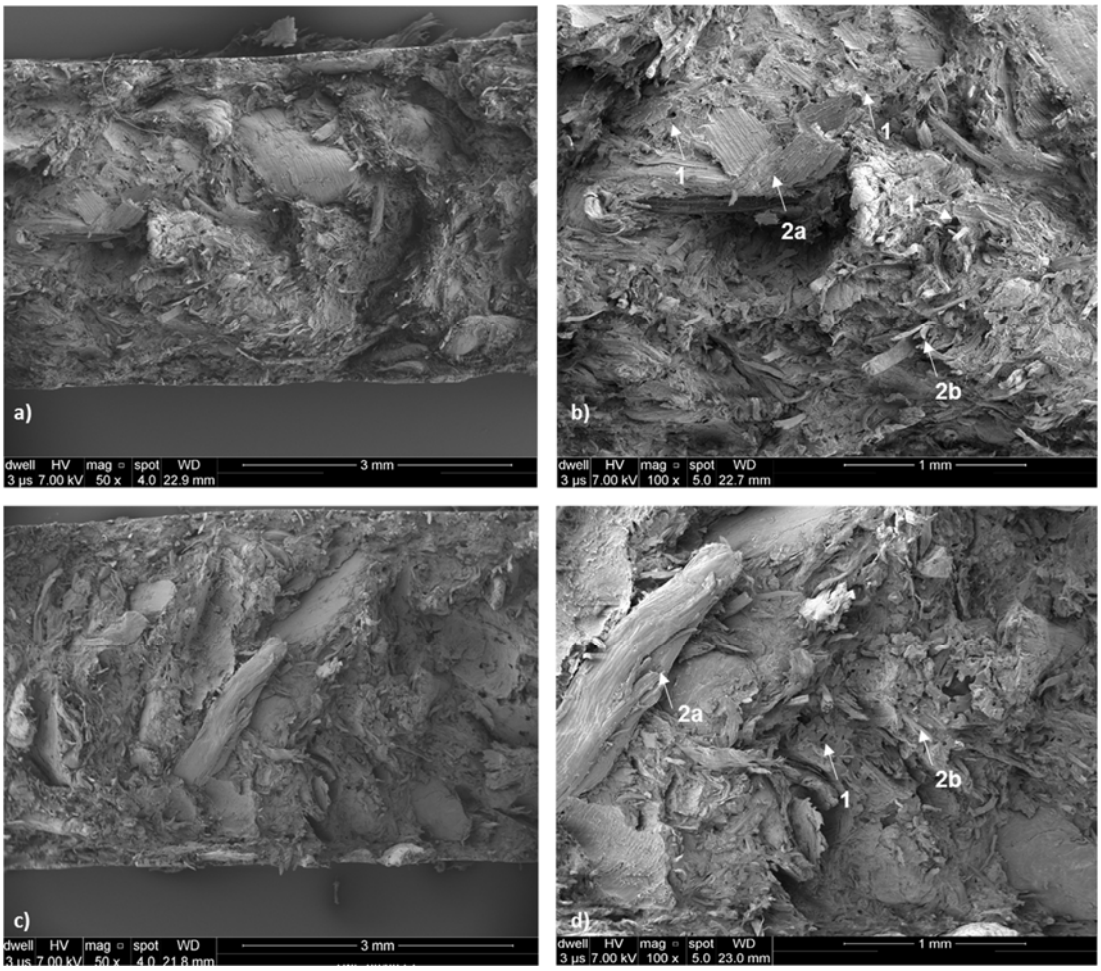

Figure 5.2.4 FE-SEM images of the fractured surface of WF HDPE 50/50 (a - b) and WF PP 50/50 (c - d) composites. Left: 50x magnification, right: 100x magnification. Note the arrows indicate voids (tag 1) within the composites. Tag 2a displays coarser particles and tag 2b single fibres.

b) X-ray micro-computed tomography

Figure 5.2.5 shows the segmented volume fractions within a WF HDPE 50/50 and WF PP 50/50 composite. The presence of segmented fractions and spatial distribution of air is illustrated. The volume fraction distribution displays an inhomogeneous material distribution. For both composites, a notable spatial increase of polymer was revealed near the surface (polymer enriched surface). The increase of polymer near the surface is formed by the mold filling mechanism and the flow pattern during injection-moulding in a manner of a fountain flow (Throne 1998). During injection moulding three microstructural regions are formed: a core, a shear zone and a skin (Bailey and Rzepka 1991). All these regions are created by different shear rates (Toll and Andersson 1993). Within the core layer of the WF composites, coarser particles

and fibre agglomerates are found, which are responsible for the polymer enriched surface. Coarser particles and agglomerates tend to migrate away from planes of higher shear, which occur next to the cavity wall (Throne 1998). Hence, these particles and agglomerates are accumulated in the core layer of the composite. Less and finer fibers are found in the surface layer leading to an enriched polymer surface (Figure 5.2.6)

Between the composites, differences are determined regarding the WF and polymer fraction. In the case of the HDPE composites volume fractions of WF and polymer amounted to 48.4 % and 47.5 %, respectively (Figure 5.2.5 c). However, in the case of the PP composite, the volume fractions of WF and polymer amounted to 42.2 % and 55.2 %, respectively (Figure 5.2.5 d). In both composites, the occurrence of air voids are detected. However, the spatial distribution and amount of air are different between the composites. The PP based composite exhibited a content of 2.6 % air and an accumulation of air near the centre of the composite, whereas the HDPE based composite exhibited a content of 4.0 % air and a broader spatial distribution of the air. Voids in composites have a negative impact on its performance (Graupner et al. 2014). The formation of voids may be caused by a non-uniform temperature profile due to inhomogeneous cooling of the composite during injection-moulding. During this cooling phase and the absence of external forces (low stagnation pressure), residual stresses occur inside the composite. The residual stress distribution shows tensile stresses at the surface and core regions and compressive stress at the intermediate region (Ho et al. 2012). For injection moulded polymers this effect is well known as shrink or sink marks (Jaroschek 2008). In the case of the WF composites in this study, the stagnation pressure was quite low due to feed in difficulties of the pelletized fibres. Shrink marks at the surfaces are not observed. Thus, the residual stresses in combination with the incorporated stiff wood material may have led to a shrinkage in the centre part of the specimens, which in turn led to the formation of voids.
In addition to the detected voids, fibre agglomerates are observed. Agglomerates are a result of strong hydrogen bonding forces between the fibres and indicate lack of fibre dispersion (Gatenholm et al. 1993) and poor interfacial adhesion between fiber and polymer (Qiu et al. 2003). Agglomerates observed within the WF composites are presumed to be the result of fibre compaction during pelletizing. During injection-moulding the agglomerates were not able to dissolve into single fibres. Thus, the problem of agglomeration formulation as it is known for these fiber type could not be solved at the current state of the project. For future experiments regarding the

developed compounding approach, it is suggested to entirely circumvent the pelletizing step.

Furthermore, a volume fraction containing a highly absorbent material was detected within the composites. However, the respective volume content was less than 0.1 % and are may a result of metal abrasion during refing, pelletizing and injection-moulding.

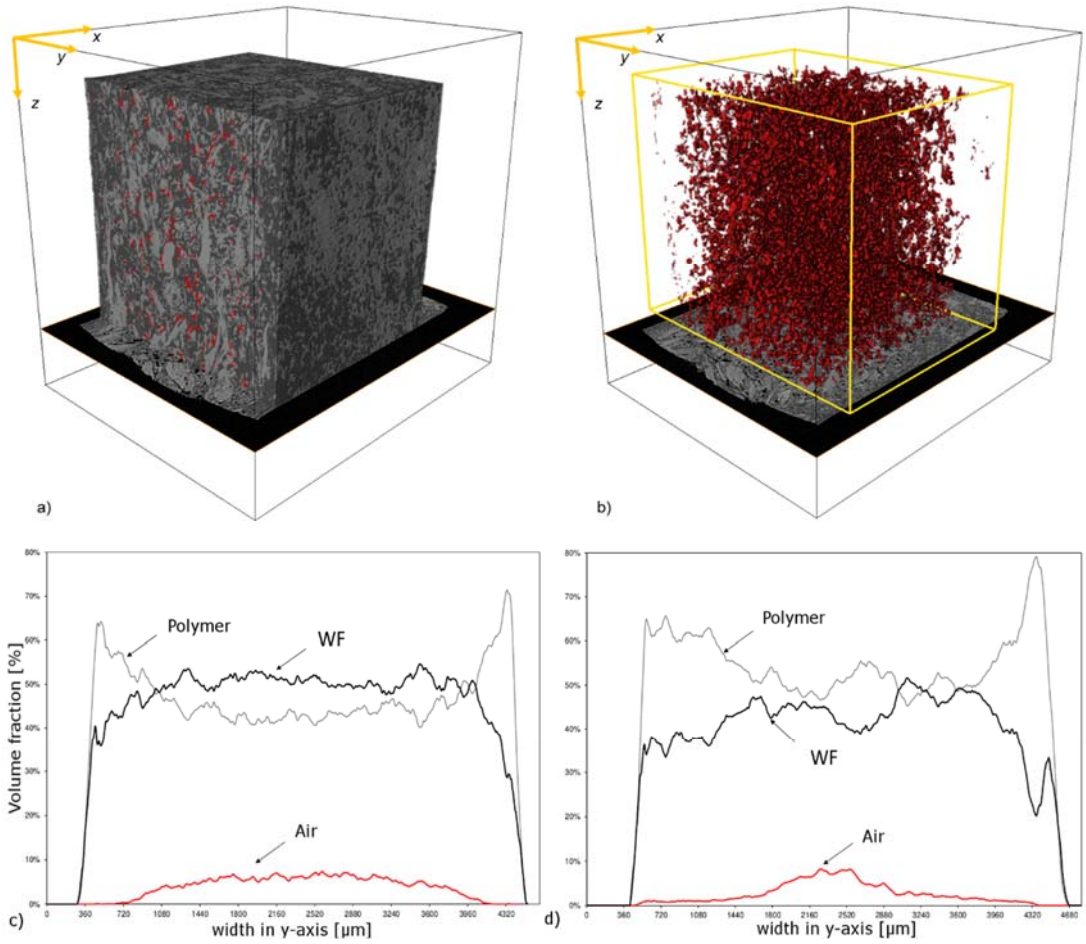

Figure 5.2.5 Depiction of segmented material fractions and their spatial distribution within the refiner-compounded WF thermoplastic composites. (a) Binarized and visually rendered material fractions of WF tissue (light grey), thermoplastic matrix (dark grey) and air (red). (b) Spatial distribution of air voids. Spatial distribution of volume fractions of (c) WF HDPE 50/50 and (d) WF PP 50/50 composites.

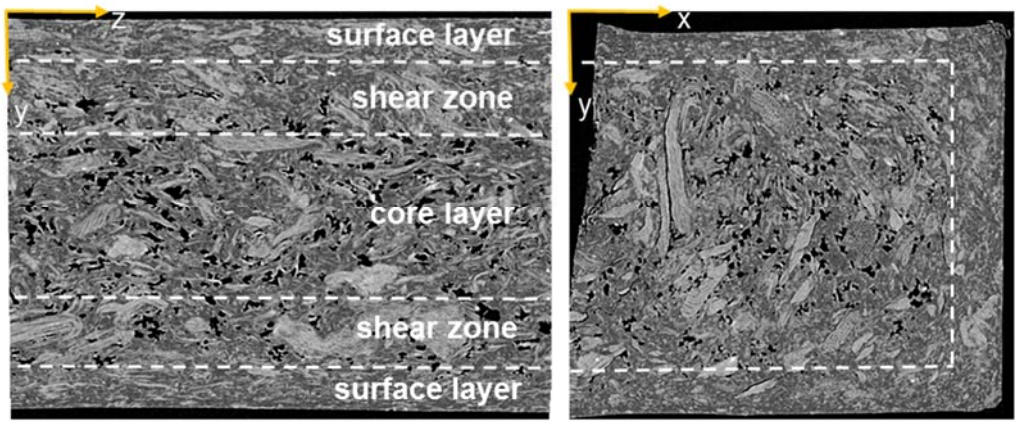

Figure 5.2.6 Hypothetical surface and core layer formation of WF HDPE composite sample scanned via X-ray micro-computed tomography. Left in y-z direction, right in y-x direction. The different layers are referring to the interfaces from the segmented material fractions in Figure 5.2.5.

Mechanical properties

Table 5.2.2 summarizes the values obtained from the tensile and flexural tests. Statistically, differences occurred among the results for the tensile and flexural tests. For both polymer types, tensile strength decreases with increasing fiber content (Figure 5.2.7 a). Both neat polymers show the highest tensile strength values. For PP composites, the addition of WF decreases tensile strength between 1.5 times to 1.8 times. For HDPE composites, a decrease of 1.2 times for WF 50/50 and 1.6 times for WF 70/30 is determined. In general, a comparison of data from former studies is difficult, given by different used resources and technologies. Nevertheless, in contrast to former studies, the addition of wood fibers did not enhance the tensile properties. Improved tensile properties with wood fibers, are reported by Woodhams et al. (1984) and Sean (2010). They achieved tensile strength of 32.5 MPa and 42 MPa respectively for PP based composites with 50%-wt. WF. Composites were compounded with a kneading (batch) mixer and further injection-moulded (Woodhams et al. 1984) or compression moulded (Sean 2010). In contrast to this, Schirp and Stender (2010) manufactured extruded composites with 70%-wt. refiner wood fibers and determined tensile strength of 10.3 MPa. Schirp and Stender (2010) stated that reduced strength is a result of poor fibre dispersion in the polymer matrix. For PP based wood flour composites Radovanovic (2007) found tensile strength values of about 50 MPa (50%-wt.) and 60 MPa (70%-wt.).

Figure 5.2.7 b presents flexural strength of PP and HDPE composites as a function of WF content. Compared to the neat polymers, the addition of WF improved the flexural strength significantly. However, no significant difference between WF 50/50 and WF 70/30 was observed for composites with a PP matrix. For the HDPE composites flexural strength increases to WF content of 50 % and decreases for a WF content of 70 %. With regard to the values achieved in this study, flexural strength of WF and wood flour composites reported in the literature, are higher. For HDPE based WF composites (50%-wt. fibers) Lerche et al. (2014) and Woodhams et al. (1984) reported flexural strength values for of 63 MPa and 65 MPa respectively. For PP composites containing 70%-wt. WF, Schirp and Stender (2010) reported flexural strength of 24 MPa and Stadlbauer (2010) of 32 MPa. For PP based wood flour composites flexural strength of 85 MPa Radovanovic (2007) (50%-wt. wood flour) are reported.

Overall, tensile and flexural strength are lower compared to some reported WF and wood flour composite values. Mechanical properties of composites depend on the

production method (Krause and Krause 2012), fiber-content, polymer properties as well as additives and are difficult to compare to each other. The reduced tensile strength in this study is may a result of the detected voids and agglomerates. Both effectively act as initiators for crack propagation, causing reduced composite performance (Joffre et al. 2014b). Agglomerates or fiber bundles also indicate ineffective dispersion of the fibers in the matrix and provide weak points when aligned perpendicular to the test direction (Spear et al. 2002). Voids may lead to reduced stress transfer from the matrix to the fiber and indicate insufficient fiber-matrix adhesion, resulting in lower strength properties. Thus, the potential benefits of WF leading to improved properties are not fully exploited in this study.

Figure 5.2.8 shows the influence of WF on tensile and flexural MOE of PP and HDPE composites as a function of fibre content. The addition of WF increased tensile and flexural MOE of the composites except of WF-HDPE with 70 %-wt. In case of both polymers, the flexural MOE is 1.6 to 1.9 times higher than the corresponding tensile MOE. Both neat polymers, PP and HDPE, show no significant differences in tensile and flexural MOE. The tensile MOE for WF PP composites and flexural MOE of WF HDPE composites are not significantly different. The difference in tensile and flexural MOE are a result of the surface layers properties. More homogenous distributed fibers or particles leading a denser surface with a higher expected MOE (Figure 5.2.7). The expected denser surface for the WF composites would be in agreement to the investigations of Huang et al. (1999) who showed that the surface layer exhibits a higher Young’s modulus than the core layer. For tensile test, the stress distribution is uniform throughout the cross-section during testing, resulting in an overall mean MOE value. However, due to the bending theory there is a maximum stress distribution at the top (compression) and bottom side (-tension) of the specimen and the stress increases with distance from the neutral phase into the middle. Therefore, we conclude that higher local MOE in the surface layers is presumably leading to higher overall MOE value for the flexural test.

Table 5.2.2 Summary of mechanical properties of WF PP and WF HDPE composites MV: mean value; SD: standard deviation; HG: homogenous group (group with no significant differences within the same test indicated by the same letter; α = 0.05 significance level)

	tensile test						flexural test					
	strength (MPa)			tMOE (GPa)			strength (MPa)			fMOE (GPa)		
	MV	SD	HG	MV	SD	HG	MV	SD	HG	MV	SD	HG
PP	29.95	0.19	A	1.72	0.04	A	34.56	0.20	A	1.50	0.02	A
WF PP 50/50	19.21	0.62	B	3.22	0.07	B	40.58	1.21	B	5.50	0.20	B
WF PP 70/30	16.80	0.81	C	3.32	0.06	B	41.08	1.20	B	6.40	0.18	C
HDPE	19.13	0.10	A	1.04	0.03	A	19.03	0.16	A	0.95	0.02	A
WF HDPE 50/50	15.91	0.26	B	3.57	0.07	B	29.34	0.70	B	5.67	0.22	B
WF HDPE 70/30	11.61	0.53	C	3.10	0.29	C	24.86	1.01	C	5.79	0.26	B

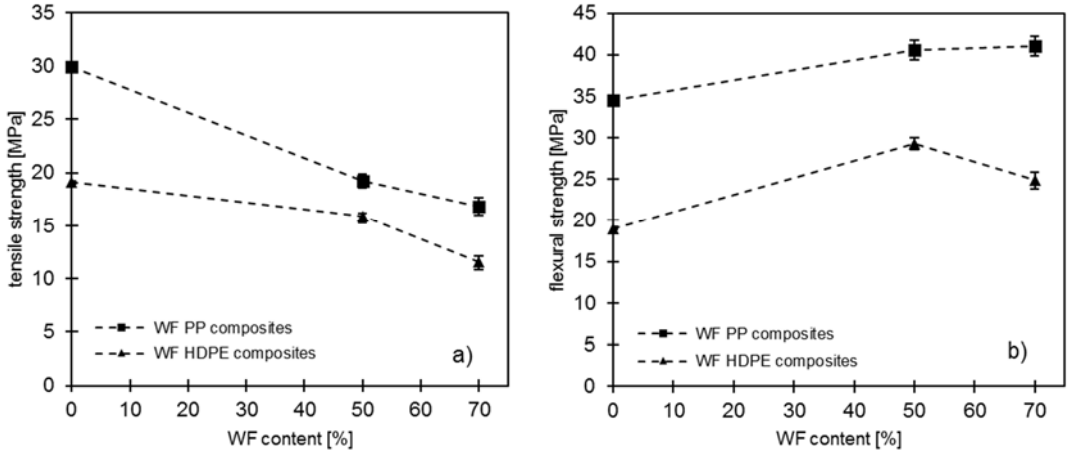

Figure 5.2.7 Tensile strength a) and flexural strength b) of WF PP and WF HDPE composites as a function of fibre content. Data derived from Table 5.2.2

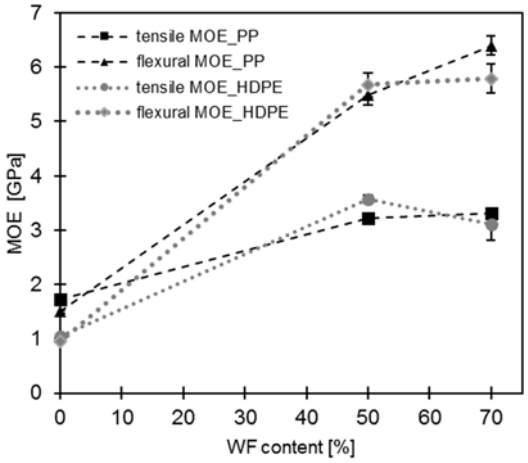

Figure 5.2.8 Tensile and flexural MOE of WF PP (black) and WF HDPE (grey) composites as a function of fibre content. Data derived from Table 5.2.2

Water absorption

Figure 5.2.9 shows the water absorption of WF composites up to 28 d. It appears that water absorption of PP composites is slower than the HDPE composites. HDPE composites with a WF content of 70 % revealed the highest water absorption. Thus, it seems that the WF are better encapsulated with PP than with HDPE. An additionally indication is also given in Figure 5.2.9, were PP composites show a higher share of polymer at the surface than HDPE composites. This, however, can explain the slower water absorption of PP composites. Both neat polymers show no water absorption. The high water absorption is maybe caused by voids and agglomerates. Voids are believed to promote water absorption. During water immersion, the water molecules first enter the free space of microvoids and then diffuse along the interface (Hom et al. 2014). In addition, an incomplete encapsulation of wood particles and the occurrence of agglomerates lead to water absorption (Krause et al. 2017b).

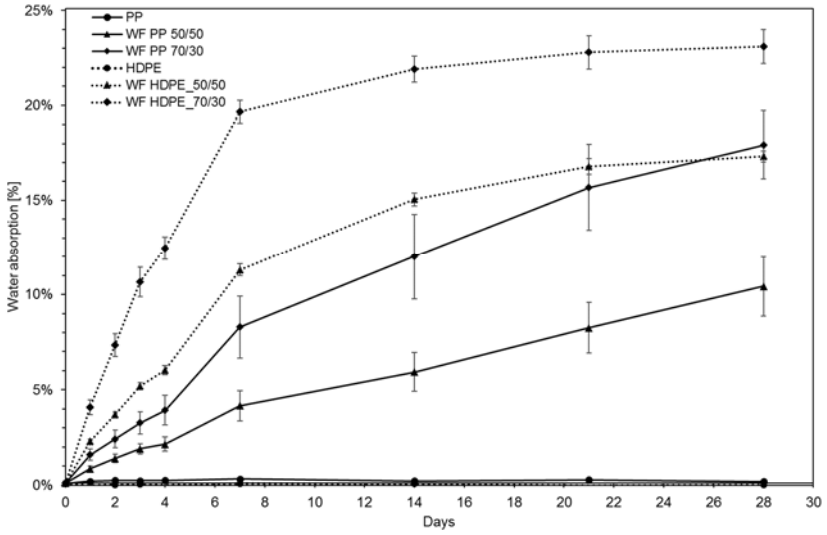

Figure 5.2.9 Water absorption of WF PP and WF HDPE composites.

5.2.4 CONCLUSIONS

A novel developed compounding process for thermoplastic based WF composites is successfully demonstrated in this study. Instead of the established compounding technologies such as extruders, a refiner is used for wood chip defibration and polymer compounding in one process step. Under the given process conditions, the WF based composites showed lower tensile strength values compared to literature val-

ues. The lower performance is attributed to the detected void and agglomerate formation. The occurrence of voids is found to be a result of residual stresses leading to an inner shrinking effect of the polymer.

For further investigations concerning this research, the following issues have to be considered to enhance the composite properties:

- investigation of material treatment between refining and consolidation. As suggested a pelletizing of the compound shall be avoided
- further verification of the composite formulation by means of wood content, processing adjustments, and coupling agents, to enhance the composite performance and to reduce the formation of fibre agglomerates
- upscaling of the process to an industrial level

Nevertheless, for the first conducted experiment it is proved that a composite production is possible. The novel compounding process with the refiner technology offers new usefulness compare to the conventional technologies. However, enhanced composite performance is essential for further product developments. Despite the mentioned advantages the developed process offers alternative markets for MDF or TMP manufactures, if this process is implemented to an MDF or TMP production line. The manufactures would be able to provide an intermediate compound product for composite manufactures or are able to produce composite products by themselves.

Acknowledgement

For the Refiner based compounding approach the refiner plant at Wood K-Plus, Tulln (Austria) was used. At this point we would like to thank Dr. Christian Hansmann, Dr. Stefan Frybort and Stefan Pinkl from Wood K-Plus for their support.

5.3 MONITORING OF FIBER DIMENSIONS AFTER A NOVEL WOOD-PLASTIC COMPOUNDING APPROACH (PAPER IV)

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Authors contribution:

	CD	EX	ED
Oliver Mertens	70%	100%	70%
Jan T. Bentien	25%	0%	30%
Andreas Krause	5%	0%	0%

CD: Conceptual Design

EX: Conducting experiments

ED: Editing

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ABSTRACT

Fibre length and width development was monitored for a novel procedure of combined wood chip defibration and wood-polymer compounding as well as further process steps for the production of wood fibre-based composites by applying an image analysis-based particle size measuring technique. While fibre dimension were maintained at a common level after refiner compounding, pelletizing was found to reduce both fibre length and width to about 50% of its initial dimension after refiner compounding. Subsequent injection moulding led to an additional fibre length reduction.

5.3.1 INTRODUCTION

For the manufacture of wood-plastic composites (WPC), usually wood particles or wood flour is used as wooden component. Technical wood fibres obtained from a thermomechanical defibration process feature the characteristics to increase tensile strength and stiffness of WPC compare to wood flour particles (Stark and Rowlands 2003). However, conventional WPC compounding and shaping processes alter the morphology of the fibres, resulting mostly in a reduction in fibre length (Mertens et al. 2017a). Krause et al. (2017a) developed a process, which combines wood chip defibration and fibre-polymer compounding in a one-step process using the refiner technology. The development of the process aims to solve the problem of fibre feeding of the low bulk density and fluffy fibres into continuously operating extruders. The intention of the present study was to monitor the change in fibre dimension throughout this novel process and additional pelletizing and injection-moulding. Fibre length and width of the different production steps are monitored by applying an image analysis-based particle size measuring technique.

5.3.2 MATERIALS AND METHODS

REFINER COMPOUNDING

Commercially available wood chips (Räuchergold FS 14, Rettenmaier & Söhne GmbH + Co KG, Rosenberg, Germany) from a mixture of Norway spruce (*Picea abies*) and silver fir (*Abies alba*) were disintegrated and at once compounded with thermoplastic polymers, achieving a wood share of 50% by weight. As polymers were applied:

a) Polypropylene (PP), PP 575p from Sabic (Saudi Basic Industries Corporation, Riyadh, Saudi Arabia), melt flow index (MFI) 10.5 g/10 min, melting point 160 °C
b) High-density polyethylene (HDPE), CC 3054 (Sabic), MFI 30 g/10 min, melting point 130 °C

For the combined wood chip defibration and wood-polymer compounding, a Sprout-Waldron 12“ (305 mm) pressurized refiner with an upstream 55 l boiler was used. Prior to defibration the wood chips (5.5 kg,), the polymer granulates (4,4 kg) and 12 l of water were mixed manually in a bin and then filled into the digester of the refiner. The pre-steaming was set by 145 °C (4.2 bar) in the case of the PP mixture and 125°C (2.3 bar) in the case of the HDPE mixture for a time of 10 minutes each. The pre-steaming temperatures were consciously chosen below the polymer melting point in

order to avoid an agglutination of the wood chips and the polymer before the defibration stage. It is assumed that the melting of the polymer takes place between the refiner plates (discs gap 0.2 mm) due to occurring shear energy. During defibration the pressure was kept constant in the digester and decreases after the defibration stage due to the atmospheric discharging unit. After defibration the compound was discharged through a conduit into a cyclone. With an overall temperature below the glass transition temperature of lignin (approximately 170 °C for softwood), the obtained fibres have to be specified as technical fibres (TMP -- short for thermomechanical pulp). Its morphology, thus, differs from medium-density fibreboard (MDF) fibres by its disintegration across the cell lumen instead of disintegration of the wood substance along the fibre's middle lamella. The moisture content after defibration compounding was about 30%.

PELLETIZING

The compounds were pelletized in order to ensure a proper feeding into the injection-moulding machine using a Pelleting Press 14 - 175 from Amandus Kahl GmbH, Reinbek, Germany. Prior to pelletizing, the pellets were dried to a moisture content below 1 % using a granulate dryer (Luxor CA 30 S, Montan GmbH, Isny, Germany).

INJECTION-MOLDING

Test specimens were made according to DIN EN 527:2012-06 and DIN EN 178:2003 using an injection-moulding machine (Arburg Allrounder 420C Golden Edition, Arburg GmbH + Co KG, Loßburg, Germany).

FIBER SEPARATION

For size measurement, fibres were separated from the polymer via Solet extraction (8 hours boiling time in xylene). Fibre samples were separated from the compound, the pellets, and the injection moulded specimens. The revealed fibres are specified in the following text as: "COMPOUND" (here the initial length and width), "PELLET", and "SPECIMEN". Prior to testing, the extracted fibres were conditioned in a climatic chamber at 20 °C and 65% relative humidity.

FIBER CHARACTERIZATION

Image analysis-based fibre size characterization was done applying a measuring system, which was initially developed for the characterization of MDF fibres. Technical details of the system are described by Benthien et al. (2014).

To conduct the measurements, approximately 0.1 g of sample material were transferred into the sample feeding device, automatically spread on the rotating object slide and imaged by a high resolution camera. Length and width of the imaged fibres were determined applying the rectangular model. All elements smaller than 23 µm were omitted from the evaluation. From each of the three fibre types, ten replicates were measured in order to permit statistically backed assertions regarding differences in fibre length and width.

The results from fibre size measurement are presented as the length or width of the fibre, which is in the position of the size-sorted measurement data where 10%, 50% (median), and 90% of the overall cumulated fibre length or width are reached. This procedure corresponds to the 10 %, 50 %, and 90 % quantiles (also referred as x_{10}, x_{50}, and x_{90}) of a length-based cumulative distribution in accordance with DIN ISO 9276-1:2004-09.

STATISTICAL ANALYSIS

Statistical analysis was performed using Origin (OriginLab Corporation, Northampton, Massachusetts, USA). A single factor analysis of variance (ANOVA) was conducted at a level of significance of $\alpha = 0.05$ and a Tukey HSD test. The remaining data analysis was done with Excel (Microsoft Corporation, Redmond, Washington, USA).

5.3.3 RESULTS AND DISCUSSION

The results from fibre size measurements are shown in Table 5.3.1, giving the fibre length and width of the compounds, pellets and specimens as mean values (MV) with standard deviation (SD) of the ten replicates. Fibre length and width are displayed for the 10 %, 50 %, and 90 % quantile of the length-based cumulative distribution Figure 5.3.1 displays the 50 % quantile of fibre length (left) and width (right) with regard to polymer type along the process steps.

Fibre length and width were found to be different across the fibre types for each polymer type (except for the 10 % quantile of fibre length of PP-bonded compounds and

pellets) (Table 5.3.1). The statistical analysis showed neither differences between fibre lengths nor widths at different polymer types at the different fibre types.

The median length (x_{50}) of the fibre type COMPOUND was measured to about 1.3 mm and is in agreement with the fibre length of TMP fibres found by Peltola et al. (2014). It can be concluded from this, that the process step of refiner compounding delivers compounds containing comparably long fibres as would be the case in solely wood chip refining.

Pelletizing and injection moulding were found to reduce fibre length by around 70% in comparison with the initial fibre length after refiner compounding. The median fibre length (x_{50}) decreases during pelletizing from approximately 1.3 mm to about 0.6 mm after pelletizing. Injection moulding leads to a further fibre length reduction of about 30% and is about 0.4 mm. The decrease in fibre length is most likely caused by high shear forces applied to the fibre during pelletizing (Le Baillif and Oksman 2009) and injection moulding.

The decrease in fibre width was found to be in the same proportion as fibre length reduction. This is in contrast to other studies. For pelletized TMP fibre- and cellulose fibre-based compounds produced on a twin-screw extruder, Peltola et al. (2014) and Le Baillif and Oksman (2009) found fibre width to be preserved and only length is decreased. However, fibre length was not measured after injection moulding.

With regard to the measured length and width values, it appears that the fibres are patterned more like shives than fibres. The shive pattern can be expressed with the length to diameter ratio (aspect ratio). The aspect ratio for the x_{50} values is about 3, whereas Peltola et al. (2014) reported a length-to-diameter ratio of 23 after extrusion. Therefore it is questionable if the produced fibres, with their low aspect ratio, provide a reinforcement effect to the composite.

Table 5.3.1 Average fibre length and width as well as standard deviation (in brackets) of the ten replicate measurements as 10%, 50% and 90% quantile of the length-based cumulative distribution in respect to polymer type (differentiation by small and capital letters). Results of the statistical analyses are displayed in groups, whereas measured values assigned with the same letter are not significantly different from each other at a significance level of α = 0.05.

Fibre axis	Polymer type	Fibre origin	10% Quantile (x_{10})		50% Quantile (x_{50})		90% Quantile (x_{90})	
			Measured value (µm)	Statistic Group	Measured value (µm)	Statistic Group	Measured value (µm)	Statistic Group
Length	PP	Compound	213 (28)	a	1263 (479)	a	3615 (724)	a
		Pellet	196 (19)	a	653 (48)	b	1793 (294)	b
		Specimen	152 (7)	b	416 (42)	c	1252 (210)	c
	HDPE	Compound	222 (31)	A	1292 (146)	A	3402 (213)	A
		Pellet	161 (19)	B	602 (43)	B	1789 (153)	B
		Specimen	132 (17)	C	399 (54)	C	1111 (246)	C
Width	PP	Compound	73 (10)	a	409 (124)	a	1501 (257)	a
		Pellet	95 (10)	b	317 (24)	b	970 (88)	b
		Specimen	71 (3)	a	190 (16)	c	622 (118)	c
	HDPE	Compound	87 (4)	A	378 (40)	A	1409 (174)	A
		Pellet	72 (6)	B	208 (21)	B	745 (50)	B
		Specimen	64 (5)	C	161 (13)	C	483 (46)	C

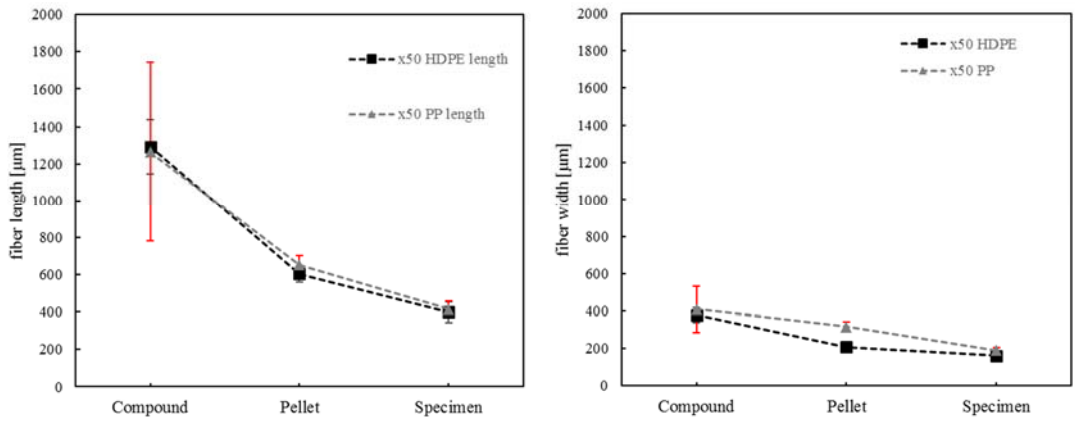

Figure 5.3.1 Averaged fibre length (left) and width (right) as well as standard deviations of the ten replicate measurements as 50% quantile of the length-based cumulative distribution in respect to polymer type for the samples Compound, Pellet and Specimen.

5.3.4 CONCLUSIONS

Fibre length and width were measured throughout the three process steps of (1) refiner compounding, (2) pelletizing, and (3) injection moulding for fibre-based WPC. Fibre length and width were monitored applying an image analysis-based particle size measuring technique. It was the intention to investigate the potential of a combined wood chip defibration and fibre-polymer compounding in a one-step process, to solve current limitations of extruder compounding with respect to fibre degradation during processing and continuous feeding of low bulk density and fluffy technical fibres in the process. As the length of the fibres in the compound were found to be equal to those of conventional thermomechanical fibre manufacturing, it has to be concluded that refiner compounding solves the problems of fibre degradation during compounding and continuous fibre feeding in WPC manufacture. This applies irrespective of the polymer (PP and HDPE) used. Apart from the promising findings regarding fibre length maintenance in refiner compounding, the further process steps, pelletizing and injection moulding lead to a strong decreases of fibre length.

For further investigations regarding the refiner compounding, it is suggested to put effort into the material treatment between refining and consolidation. Pelletizing of the fibres should be avoided as its decreases fibre length by about 50 %. Nevertheless, the approach of refiner compounding provides the possibility for existing refiner capacities to enter the market of WPC compound manufacture.

5.4 SIMULTANEOUS DEFIBRATION AND COMPOUNDING PROCESS OF WOOD FIBER THERMOPLASTIC COMPOSITES USING INDUSTRIAL SCALE DEFIBRATION EQUIPMENT

(unpublished work)

The following study was conducted by *Oliver Mertens, Kim C. Krause, Andreas Krause*

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Authors contribution:

	CD	EX	ED
Oliver Mertens	70%	70%	100%
Kim C. Krause	0%	10%	0%
Andreas Krause	30%	20%	0%

CD: Conceptual Design
EX: Conducting experiments
ED: Editing

5.4.1 INTRODUCTION

The process of simultaneous wood chip and polymer defibration, presented in the previous Chapters, describe an interesting approach for using thermomechanical wood fibers in thermoplastic composites. The process was first experimentally conducted by Mertens et al. (2017b), using a pressurized laboratory batch refiner. In order to further verify the novel approach, the present Chapter aims to up-scale the process to industrial level. A further investigation of the mechanical properties of various produced products made out of the novel produced wood fiber polymer compound is presented. The conducted study was done by using a continuous operating refiner plant, which is able to mimic industrial scale processes. Compared to the previous used batch refiner, the refiner in the present work is able continuously run the process over. Additionally, the received wood fiber polymer compound is further manufactured to different products, using a twin-screw extruder, injection-molder and hot-pressing technologies. Fiber length is analyzed for the received wood fiber compound and for an injection-molded sample. Finally, the mechanical properties of the produced products were tested.

5.4.2 MATERIALS AND METHODS

MATERIALS

Wood fibers were derived from industrial pine wood chips (moisture content 80 wt-%). Polypropylene, PP 575p from Sabic (Saudi Basic Industries Corporation, Riyadh, Saudi Arabia), melt flow index 10.5 g/10 min (load 2.16 kg), melting point 160°C were used as matrix polymer. The share of wood fibers for the produced composites were 70%, 60% and 50%. The mixture and the manufactured samples are specified as:

70% wood fiber and 30% PP → WF 70/30

60% wood fiber and 40% PP → WF 60/40

50% wood fiber and 50% PP → WF 50/50

SIMULTANEOUS DEFIBRATION AND COMPOUNDING PROCESS

Before processing, the wood chips and polymer granulates were mixed manually in bins. Principally, the procedure is used as described by Krause et al. (2017a) and Mertens et al. (2017b). For the simultaneous defibration and compounding process

the refiner plant at Fraunhofer Institute for Wood Research (WKI, Braunschweig, Germany) was used. A schematic draw of the plant and the process-flow is given in Figure 5.4.1. The in advance mixed wood chips and polymer granulates were placed into the hopper. After material feed-in the material is compressed via a plug screw feeder (MSD, multiple screw device) and then fed into pressurized pre-steaming unit. The plug screw feeder ensures that the following system is pressurized. A screw conveyor inside the angled digester moves the material upwards and drops the material after a certain retention time into the defibration (refining) zone. After passing the defibration zone the material is forwarded to the cyclone due to a pressure gradient. The refiner plant used is equipped with a 12” pressurized Andritz Sprout-Bauer defibrator. The process conditions are summarized in Table 5.4.1.

Table 5.4.1 Parameter and settings used for the defibration process.

parameter	**settings**
MSD rotation	3.5 rpm
pre-steaming	140°C (3,3 bar)
retention time	5 min.
refiner rotation	3000 rpm
gap distance	0.1 mm
disc pattern	Andritz 12XY802
through put	40 kg/h

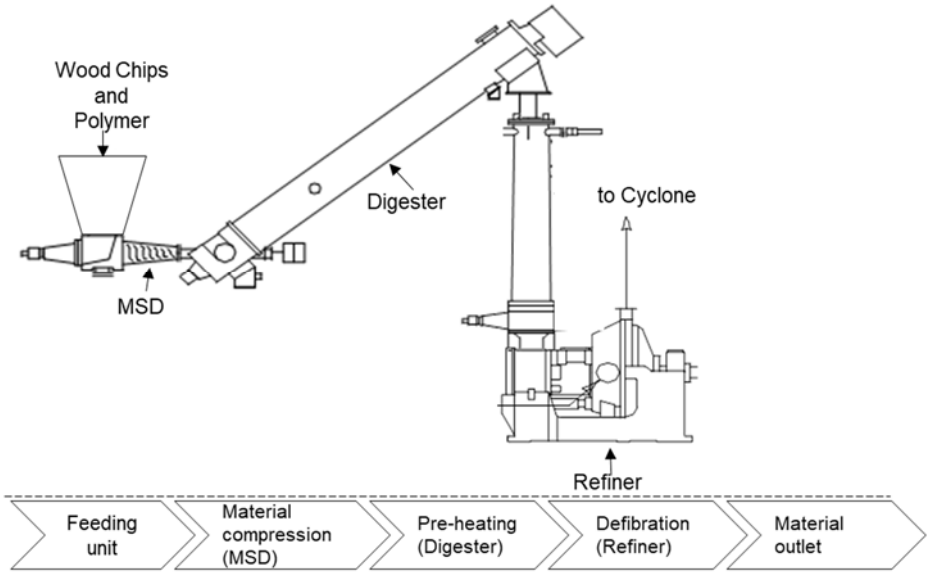

Figure 5.4.1 Scheme of the refiner plant and the process-flow used for the conducted test.

SAMPLE MANUFACTURE AND PREPARATION

The received wood fiber polymer compound (WFC) was dried to moisture content of 3 wt.%. In order to demonstrate possible fields of application, the material was further manufactured in different ways.

Compounding

The WFC (60/40 and 50/50) was further manufactured to injection-moldable granulates by using a co-rotating twin screw extruder (TSE) (Leistritz ZSE 27 MAXX, Leistritz Extrusionstechnik GmbH, Nürnberg, Deutschland). The TSE is equipped with 12 heating barrels. The temperature was set from 180°C (feed-in unit) to 145°C at the material outlet. The WFC was fed into the TSE with a gravimetric feeder. The TSE was run with 120 rpm and a throughput of 1.5 kg/h resulting in a specific energy of 0.37 kWh/kg.

THE WFC 70/30 was used as “Masterbatch” material. The same procedure as mentioned above was used, whereby the WFC was mixed up with PP to achieve a wood fiber/polymer content of 50% to 50%. Additionally, a coupling agent (3% of Maleic anhydride-modified PP (MAPP); Licocene® PP MA 7452, Clariant GmbH, Gersthofen, Germany) and color pigments (RAL1550) were added.

Hot-pressing

The WFC (50/50 and 60/40) was pressed to thin panels (170 x 250 x 4 mm) using a laboratory hot-press (Siempelkamp Labor-Heißpresse Typ2, Siempelkamp GmbH, Krefeld, Germany).

Injection-molding

Test specimens were manufactured according to DIN EN 527:2012-06 and DIN EN 178:2003 using an injection-moulding machine (Arburg Allrounder 420C Golden Edition, Arburg GmbH + Co KG, Loßburg, Germany).

In addition to the manufactured wood fiber polymer granulates, a panel (50/50) was milled to approximately 10 x 10 mm pieces using a Retsch cutting-mill for the injection-molding process.

TESTING

Tensile (DIN EN 527:2012-06) and flexural (DIN EN 178:2003) tests were conducted using a universal testing machine (Zwick Roell GmbH & CO. Kg, Ulm, Germany).

Charpy impact bending (DIN EN ISO 179 1-2 (2005)) was conducted by using an impact testing machine (HIT5.5p Zwick Roell GmbH & CO. Kg, Ulm, Germany) with a 1 and 5 Joule pendulum. The tensile and flexural test specimens from the hot-pressed panels were cut and shaped according to the standards. For all formulations and tests 10 specimens were tested.

FIBER CHARACTERIZATION

The fibers of the WFC (50/50) were analyzed after defibration and injection-molding. Prior to the analyzation, the fibers of the compound and an injection-molded specimen were separated from the matrix with a Soxhlet extraction in hot xylene. Arbocell C100 wood flour (Rettenmaier & Söhne GmbH + Co KG, Rosenberg, Germany) was used as a reference to compare the particle geometry to conventional used flour materials. The wood flour was not separated from a polymer and therefore analyzed in a native state. Fiber characterization was done applying the dynamic image analysis system QICPIC. In the device, the particles are dispersed in an accelerated air jet. A high-speed camera takes pictures of the particle stream. Measuring particle size and shape from the projected particle area of binary pictures and calculating size and shape distributions was done by the software WINDOX (Sympatec GmbH, Germany). Fiber length was characterized with respect to the median and quartiles of the length-based particle length distribution (Q1) (DIN ISO 9276-1) (Teuber et al. 2016b).

X-RAY MICRO-COMPUTED TOMOGRAPHY

X-ray micro-computed tomography was carried out to evaluate non-destructively the internal composite structure. The investigated test samples (4x10x6 mm) were prepared from the middle of a untested WF 50/50 PP tensile test specimens.
The X-ray micro-focus CT system Nanotom® s (phoenix|x-ray, GE Measurement & Contro, Wunsdorf, Germany) was equipped with a cone beam geometry, a transmission molybdenum target, and a CCD detector. The tube voltage was 60 keV, whereby the current was 280 µA. The exposure time per projection was 750 ms. 2000 axial projections were collected over a total angle range of 360° in every tomographic run. The achieved spatial resolution was 6 µm.
The image processing and reconstruction were performed using the software *datos|x reconstruction*© (phoenix|x-ray, GE Sensing & Inspection Technologies GmbH, Wunstorf, Germany). The captured stack of two-dimensional projections was transformed

into a three-dimensional data volume. Subsequently, the volume analysis was conducted using the Avizo® Fire 9 software (FEI, Hillsboro, Oregon, USA).

5.4.4 RESULTS AND DISCUSSION

Process observations

The conducted study carried out, that the process of simultaneous wood chip and polymer defibration as described by Krause et al. (2017a) is able to run continuously under industrial conditions. It was found, that the pre-steaming temperature is a crucial factor in the process. The polymer granulates tend to agglomerate when the processing temperature is close the polymer melting point. This results in an inhomogeneous distribution of wood and polymer during defibration. It is assumed, and in accordance with the theoretical principals of defibration, that the temperature during mechanical and thermal treatment between the refiner discs is higher than in the rest of the pressurized system. Hence, the polymer becomes molten between the narrow disc gap because of higher temperature, pressure and friction. In addition to the conducted experiments by Mertens et al. (2017b), it could be shown that the process is stable over a longer period of processing time independent of the wood fiber polymer ratio. For each formulation the process was conducted for about 1.5 hours. No significant increase in power consumption was found in relation to the polymer content. The mechanical power consumption ranged between 18 – 21 kW/h. The received wood fiber polymer compound showed typical thermomechanical produced wood fibers with chopped polymer flakes which are visually entangled to the wood fibers. Compare to the results reported by Mertens et al. (2017b) the wood fibers are obviously finer due to the narrower gap distance (0.1 mm).

X-ray micro-computed tomography (µ-CT)

µ-CT was carried out to evaluate non-destructively the composite structure. Figure 5.4.2 shows ortho-slices of the scanned volume. The shown grey-scale image (a) is taken close to the composite surface. Figure 5.4.2 a, displays that the wood fibers are present as fine and coarser particles. The wood fibers near the surface area are predominately orientated in the flow direction of the melt during injected-molding. However, near the center, the wood fibers are more randomly orientated. The different orientated fiber are a result of different shear rates during forming (Bourmaud et al. 2013, Mertens et al. 2017b). Figure 5.4.2 b shows the spatial wood fiber fraction distribution within the region of interest (ROI). The wood fiber fraction was analyzed with

the mentioned software while using different separation and analyzing algorithms. For the ROI a spatial distribution of wood fiber and polymer is calculated to 54.0% and 45.0% respectively. Additionally, around 0.05% of air is detected (Figure 1 c)). Thus and as expected, twin-screw extrusion leads to a satisfactorily material distribution within the composite. With the non-destructive image analysis it is proved, that the volume fraction of wood fiber polymer is close to the ratio (50/50) that has been determined before the simultaneous defibration and compounding process. Thus, it seems that after defibration the polymer is entangled or attached to the wood fiber, even it is obviously difficult to see. However, possible errors during these quantitative analysis (scanning duration and software adjustments) must be taken into account, which may can falsify the result.

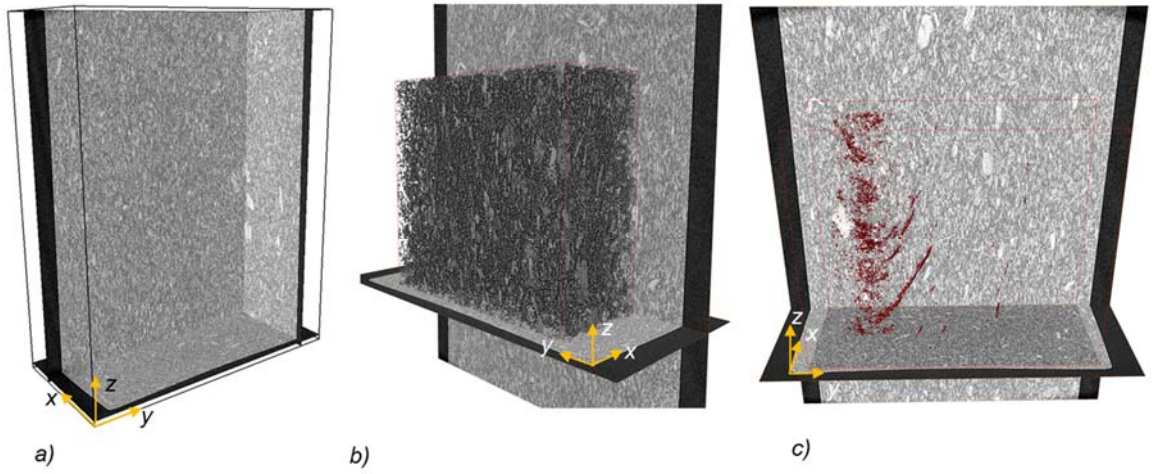

Figure 5.4.2 Ortho-slices of the XµCT scanned volume. A) displays the slices in x-z-y direction. B) shows the spatial distribution of wood fibers within the volume of the ROI. C) shows the separated air within the ROI.

Fiber length

Fiber length was investigated for the fiber polymer compound after defibration and injection-molding. The revealed length and the respective aspect ratio is displayed in Table 5.4.2. Figure 5.4.3 shows the cumulative distribution (q1) and the fibers elongation after defibration and injection-molding. Additionally, the length and the length distribution of conventional used wood flour is shown. The mean length (x_{50}) of the initial wood fibers after simultaneous defibration and compounding is around 880 µm with an aspect ratio of 16. Compare to the wood fibers used in Chapter 4, the mean

length in this study is about 1000 µm shorter. Injection-molding causes a fiber length reduction of 85% and has therefore roughly the same length as untreated wood flour. Also the aspect ratio after injection-molding shows similar values as the wood flour. However, the mean length fiber after injection-molding is about 40% longer compare to the mean fiber length revealed after injection-molding in the experimental study in Chapter 4. Nevertheless, the low aspect ratio of the wood fibers appears more particle like. Schirp and Stender (2010) found that the aspect ratio of wood flour is not significantly changed after compounding and extrusion. Teuber et al. (2013) stated that, wood particles might have a threshold particle size, at which a further reduction of the particle geometry is unlikely due to the intrinsic structural and mechanical properties of wood. Additionally, Teuber et al. (2013) found that the strongest effect on particle reduction was found during compounding. This would be also in agreement to the findings in Chapter 4, and can also be accepted in current case.

Finally the investigation of the fiber length revealed that the process of simultaneous defibration and compounding generates high aspect ratio wood fibers, however the subsequent processes applied leading to an severe fiber length reduction.

Table 5.4.2 Revealed fiber length and aspect ratio of initial wood fibers (length after defibration) and after injection-molding. Arbocell C100 is presented as wood flour reference without any composite processing step. Fiber length and aspect ratio are presented as 10% (x_{10}), 50% (x_{50}) and 90% (x_{90}) quantiles of the length-based cumulative distribution q1.

q1		initial wood fibers (50/50)	injection molded sample (50/50)	Arbocell reference
length [µm]	x_{10}	123.93	34.53	29.39
	x_{50}	884.12	126.42	96.67
	x_{90}	2352.29	297.94	297.05
aspect ratio	x_{10}	2.8	1.5	1.3
	x_{50}	16.6	2.7	2.4
	x_{90}	33.3	5.8	5

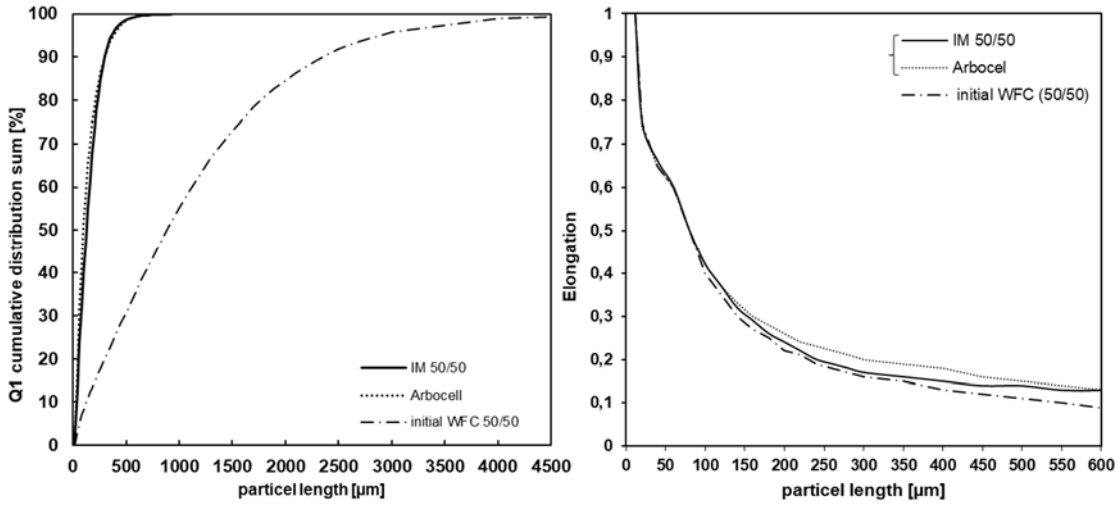

Figure 5.4.3 Cumulative fiber length distribution (left) for the initial wood fibers, the fibers after injection-molding and the reference wood flour. Elongation to particle length for the analyzed fibers and flour (right).

Mechanical properties

Table 5.4.3 summarizes the mechanical properties. The formulation with highest wood fiber content (IM-WFC 60/40) also reveal the highest modulus of elasticity (MOE). Comparing the overall MOE, the formulations that are further processed to granulates by twin-screw extrusion show higher MOE values than the other further processing technologies used. Thus it is concluded that twin-screw extrusion leads to a satisfactorily material distribution.

Table 5.4.3 Summary of mechanical properties for the manufactured composites.

Formulation	**tensile strength**	**tensile MOE**	**flexural strength**	**flexural MOE**	**charpy impact**
	[MPa]	*[GPa]*	*[MPa]*	*[GPa]*	*[kJ/m²]*
Masterbatch (50/50)	53.50	5.3	88.35	5.6	-
IM-WFC 50/50	32.50	4.8	54.96	5.4	9.5
IM-WFC 60/40	28.31	5.7	50.82	6.5	6.1
IM-Panel (50/50)	19.80	3.5	45.64	4.8	-
Panel (50/50)	9.10	2.2	20.00	2.1	-
Panel (60/40)	11.0	2.6	18.46	2.1	-

Tensile and flexural strength of the tested composite are displayed in Figure 5.4.4. The Masterbatch (50/50) formulation shows the overall highest strength values. The higher strength properites compare to the other formulations is owed to the addition of MAPP. It is found, that the addition of MAPP increases the strength properties for about 1.6 times. Compared to the strength values of pure PP, the Masterbatch formulation revealed a significant fiber reinforcement effect. Similar results were found in the experimental study in Chapter 4 were the performance of thermomechanical wood fibers was generally investigated. The achieved strength properties of the formulations IM-WFC 50/50 and 60/40 (both without coupling agent) in this study, are higher than those obtained for similar wood fiber contents in Chapter 4, despite the fact that they are produced in the same way. Compare to other studies (Caulfield et al.), the strength properties are higher.

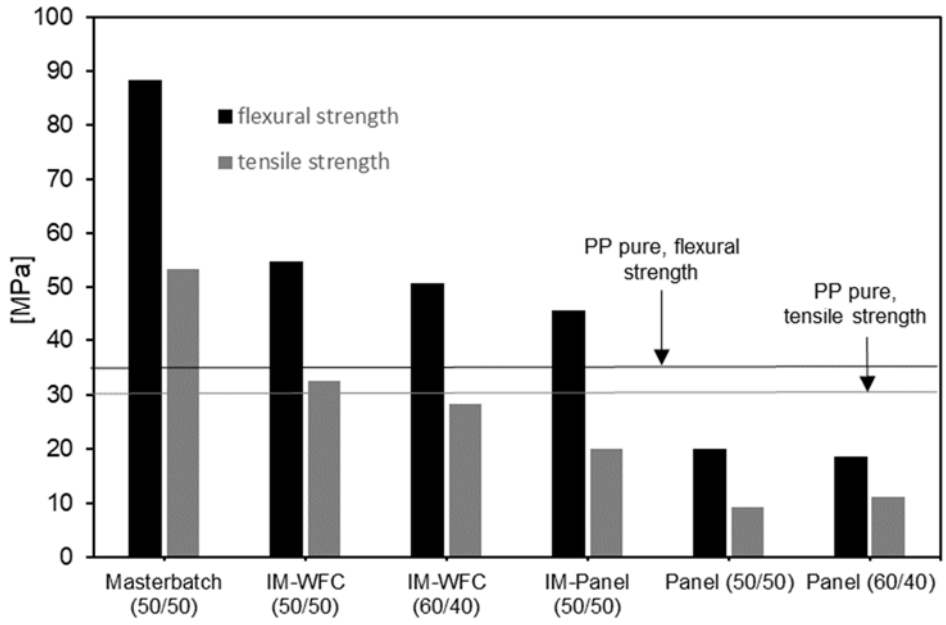

Figure 5.4.4 Tensile and flexural properties of the tested composites. The number in brackets refer to the wood fiber / polymer ratio.

Significant lower strength are observed for the injection-molded panel (IM-Panel (50/50)) and the tested panel formulations 50/50 and 60/40. The IM-WFC (50/50) show similar strength properties as found in the previous study by Mertens et al. (2017b). In the previous study, the poor strength are attributed to the pelletizing step and the low stagnation pressure during injection-molding. Additionally it is believed, that the injection-molding conveying screw is not able to dissolve the compressed structure of the panels. The insoluble structure results in a formation of agglomerates,

which significantly influence the mechanical properties of the composite. This findings are in accordance to other studies (Joffre et al. 2014a, Spear et al. 2002). The hot-pressed panels show for both formulations the overall lowest strength properties. This is attributed to two factors. One is owed to the insufficient manually scattering of the WFC mat before hot-pressing, which is difficult to do manually. Due to imperfections during scattering the resulting panel show different densities. On the other hand, the hot-pressing process did not lead to effective flow of the molten polymer. Thus, the wood fibers are only partially in contact with polymer. The effect on the resulting panel is displayed in Figure 5.4.4. It is therefore evident, that an insufficient polymer distribution and flow behavior during pressing results in poorer strength properties.

Figure 5.4.5 Wood fiber compound (50/50) manufactured to panels. Here view on the cross section.

5.4.4 CONCLUSIONS

From a processing prospective, the conducted study of simultaneous defibration and compounding could generally confirm that:

- an industrial scale-up of simultaneous wood chip and polymer defibration using continues operating refiner equipment is possible.
- the process is stable over a period of time. No significant change in power consumption was recognized, while changing the wood chip / polymer ratio.
- the novel produced compound, that is further processed with an twin-screw extruder and injection-molder to test specimens, show quite sophisticated strength properites
- the analysis of fiber length, revealed that the fibers are considerable degraded in their length after injection-molding.

CHAPTER 6
RESULTS AND DISCUSSION OF THE CONDUCTED RESEARCH

6.1 IDENTIFICATION OF THE POTENTIALS OF THERMOMECHANICAL WOOD FIBERS IN THERMOPLASTIC COMPOSITES

Overall, the potentials of thermomechanical wood fibers in thermoplastic composites are identified in Chapter 3 (literature review) and 4 (experimental performance evaluation). Based on the findings, it can be stated that thermomechanical wood fibers can provide reinforcement to the polymer matrix. However, generally it is found that the composite properties depend on:

a) Compounding and forming technology
b) Scale of the compounding and forming technology
c) Fiber content and additives
d) Defibration conditions

6.1.1 PROCESSING EFFECTS ON MECHANICAL PROPERTIES AND FIBER CHARACTERISTICS

For industrial produced composites, the mechanical properties, achieved in the conducted study described in Chapter 4, are in agreement with the findings of the literature review (compare Figure 6.1). Although the matrix properties from the data in the literature review are often unknown and may differ from each other, it is evident that with industrial scale equipment higher tensile strengths and MOEs are achievable than with laboratory scale equipment. This leads to the assumption that full exploitation of fiber reinforcement depends on the production method. To achieve appropriate composites properties, wood fibers have to be properly mixed in the polymer matrix. Laboratory scale processes differ to industrial scale processes in feed-rates (Teuber 2016a), operating conditions such as heat transfer and shear (Kohlgrüber 2007) as well as processing effects (Inceoglu et al. 2011) such as distributive and dispersive mixing. Stresses in in twin-screw extruders are more diverse than in internal mixers (Teuber 2016a), since the process length and design of the mixing and shear elements is different compared to e.g. internal mixers. In the literature review it was found that, in extruders a different pressure formation and a better dispersion takes place, leading to overall higher MOE.

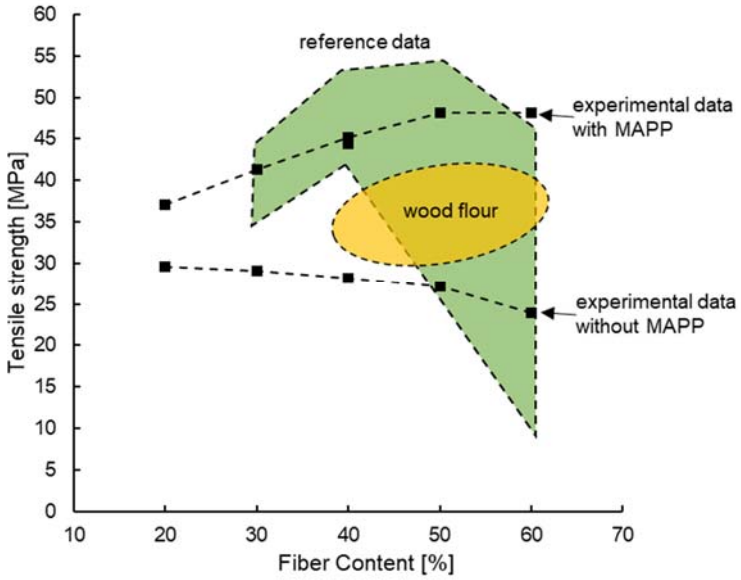

Figure 6.1 Influence of fiber content on tensile strength. The black dots display the tensile strength values obtained in Chapter 4 for MDF fiber polypropylene composites with (upper line) and without (lower line) coupling agent. The green area displays the range of tensile strength values for industrial-scale produced wood fiber composites gathered from the literature review conducted in Chapter 3. Values for various wood flour composites are taken from Gehrmann et al. (2003) (60 wt. %). Krause et al. (2017b) (60 wt. %). Nygård et al. (2008) (50 wt. %). Stark and Rowlands (2003) (40 wt. %). All wood flour composites were produced with industrial-scale technologies.

On the other hand the literature review (Chapter 3) and the experimental performance evaluation (Chapter 4) found, that during twin-screw extrusion, the fiber length considerably reduced. The experimental study (Chapter 4) confirmed, that fiber degradation increases with increasing fiber content. The resultant aspect ratio after twin-screw extrusion was found to be between 1.8 and 7 which is a reduction of about 80-90 % compared to the initial fiber aspect ratio. In part, this may be caused by the increasing fiber-fiber interaction with increasing fiber content. In this regard Schirp and Stender (2010) stated, that a heating-cooling mixer is economically way to process wood fiber based composites with minor fiber damage compared to twin-screw-extrusion due to a larger free volume.

Moreover, fiber length reduction also occurs during injection-molding. The longer the fibers are prior to injection-molding, the more their length is reduction during that process. The promising fiber lengths could not be maintained with the processing equipment and conditions used. Hence, the preservation of the promising fiber length is a question of the applied processes.

In addition to compounding, the technology of composite forming is highly influential on the mechanical properties of the composite. Many of the publications cited in the reviewed literature found lower mechanical properties for compression molded composites compared to injection molded ones. In the literature review it is therefore concluded, that the processing technology is a major factor in discovering the full reinforcement potential of thermomechanical wood fibers. Krause and Krause (2012) stated that with injection molding higher strength values are achievable compared to compression molding. They argued that during compression molding a relatively low polymer melt flow and a lack in degassing lead to lower strength properties. This statement is in agreement with many of the reviewed literature. However, it is in contrast to the results of Graupner et al. (2016), who found higher tensile strength for compression molded Lyocell/PLA (40 wt. % with 92 - 118 MPa) composites than for injection-molded (40 wt. % with 45 - 66 MPa) composites. They argued, that injection-molding leads to better compaction and fiber/matrix adhesion than compression molding. However, by injection molding the fibers aspect ratios are reduced below the critical aspect ratio and thus influencing the strength properties negatively (Graupner et al. 2016).

It has to be noted that Graupner et al. (2016) used pre-manufactured multilayer webs in their study. These webs have a predefined fiber alignment, which significantly influences the mechanical properties. Due to the process, fibers are shortened more extensively during injection-molding than in compression molding (Graupner et al. 2016). Thus, fiber alignment and fiber length are more maintained during compression molding than injection molding.

6.1.2 INFLUENCE OF FIBER CONTENT ON COMPOSITE PROPERTIES

For most common fiber or particle based composites it is well known, that MOE increases with increasing fiber or particle content. Wood in general is stiffer than most common thermoplastic polymers. Thus, the addition of a stiff material such as wood yields improved potential stiffness to the composite. In material science the composite modulus ($\mathrm{E_c}$) is expressed by the rule of mixture as given with the following equation

$$\mathrm{E_c} = \mathrm{f}E_f + (1 - \mathrm{f})\ \mathrm{E_m})$$

where f is the volume fraction of the fiber and E_f is the modulus of the fiber and $\mathrm{E_m}$ is the modulus of the matrix. In Chapter 4 it was shown, that the MOE is almost linearly increasing with increasing fiber content independent of the utilization of MAPP. For composites without MAPP it is of interest, that the mechanical properties, except the MOE, decrease with increasing fiber content. Strength properties of the composite are very dependent on the inherent parameters of the fiber and the polymer matrix. Furthermore strength properties are controlled by critical defects, which are statistically distributed in the composite (Wisnom 1992). Tensile strength for example is the maximum force in tension before failure for a given cross-section. The determination of the MOE during testing takes place in the range of linear-elasticity with little elongation and only low stress concentrations, which would promote fracture propagation (Erdmann 2017). Thus, it becomes more understandable why the MOE increases while other values of the composite properties decrease.

In Chapter 3 and 4 it is found, that for coupling agent containing composites (Figure 6.1) at fiber contents between 45 - 50 wt.% a tensile strength threshold is reached. At a fiber content of 50 wt.% the tensile strength reaches its maximum and no significant further increase is observed. Thomason (2005) stated, that with increasing fiber content, the formation of fiber agglomerates increases. This leads to areas with fibers, which are not fully covered by the polymer. Thus, an increasing fiber content is likely to contribute to void formation by the mentioned structural formations during processing. From a processing perspective, high fiber contents are difficult to mold properly due to an increase in melt viscosity (Woodhams et al. 1984). The difficult processing with high fiber contents is confirmed in the experimental performance evaluation in Chapter 4.

The lower reinforcement effect at higher fiber contents is presumably explained with a decreasing interfacial shear strength (ISS) (Erdmann 2017). Thomason (2007) analyzed the effect of decreasing ISS as a function of increasing fiber content for glass fiber composites. It was shown that the ISS from the matrix to the fiber, depends on the residual radial compressive stresses their action on the fiber surface. During the cooling phase in the mold, the polymer shrinks on the fiber surface and therefore generating radial compressive stress. Residual stresses improve the coefficient of friction, which results in a higher physical bonding between fiber and polymer (Parlevliet et al. 2006). However, the decrease of residual radial compressive stresses with increasing fiber content, yields finally in a lower reinforcement effect. Thomason (2009) showed, that the radial compressive stress is even lower for natural fiber composites compared to glass fiber composites.

Although the wood fiber based composites without coupling agent (Chapter 4) show decreasing tensile strength with increasing fiber content, it is assumed that some reinforcement occurs. The statement is based on the following assumptions:

- tensile strength is a value that refers to the cross-section of the tested material and is calculated with $\sigma = \frac{F}{A}$, with F the applied force and A the cross-section of the material.
- the volume and respectively the cross-section of a polymer matrix is reduced by the addition of any fiber volume
- no load transmission between the fiber and the polymer matrix occurs (some indications are given by the FE-SEM images in Chapter 4)

With these assumptions, the tensile strength of a filled composite would be lower compared to the tensile strength of the neat polymer matrix, since the cross-section is reduced. However, it is found that a composite containing 20 wt.% wood fibers has the same tensile strength as neat PP. Further is has to be noted that the addition of 60 wt.% wood fibers, reduces the tensile strength just by 10 % compare to the strength of the PP matrix. Thus, it is concluded, that some kind of reinforcement occurs even when the strength is not significantly improved. Maybe only a small volume of fibers with an aspect ratio above the critical aspect ratio is responsible to provide a reinforcement to the composite.

As mentioned by Thomason (2005), understanding the structure-property relationship (especially for injection-molded composites) is one of the toughest challenges for composite scientists, due to the complex material and processing parameters.

A deeper understanding of the results obtained here, and of wood fiber polymer composites in general, maybe gained by applying analytical or numerical models, in order to investigate the impact of different influencing variables. There are several approaches available for modelling different composite properties. For example, one can calculate the critical fiber length to get an information about the reinforcement effect. Or the model of Kelly and Tyson (1965), can be used for predicting the strength of short fiber reinforced composites. The rule of mixtures for calculating the composite stiffness, was developed and adjusted to different parameters over time. It is reported that for natural fiber composites the rule of mixtures is able to predict acceptable properties. Most of the models available today though were developed to analyze conventional composites (glass-fiber, carbon-fiber, etc.) rather than WPC. These approaches all have in common, that at least one input value is required to be constant (e.g. fiber diameter, perfect bonded interfaces or fiber alignment). These assumptions usually do not meet the real properties of wood fiber based composites, because of inhomogeneous geometries and properties inherent to these fibers. The difficulties for calculating natural fiber based composites properties are summarized by Nystrom et al. (2007), who attributed the complexity to the single constituents, which are in detail:

- *“ fiber/matrix interfacial shear strength between wood particles and PP is not easy to measure since these fibers are very short;*
- *for the same reason as above, direct measurements of fiber strength are also rather complicated;*
- *fiber orientation measurements are not the simplest task either ”.*

6.1.3 CONCLUSION

In Chapter 3 and 4 of the present thesis, the potential of thermomechanical wood fibers as reinforcement material in thermoplastic composites is presented. Thermomechanical wood fibers, as received after the defibration process, show characteristics (e.g. the aspect ratio) to provide a reinforcement effect to thermoplastic composites. The mechanical properties of thermomechanical wood fiber based composites are influenced by the production process. Industrial scale produced composites perform better than laboratory scale produced composites. However, as shown in the conducted experiment in Chapter 4, the use of industrial scale production technologies, e.g. extruders and injection-molding equipment are leading to severe fiber degradation. The resulting aspect ratio is between wood flour and wood fibers. Though the fiber length is reduced, it is shown that the performance of the composites properties are comparable to reported literature values or even better. Finally, it is concluded that with the current technologies utilized in the composite manufacturing industry, is difficult to appropriately process thermomechanical wood fibers to fully reach their mentioned potential as reinforcement.

6.2 EVALUATION OF THE SIMULTANEOUS DEFIBRATION AND COMPOUNDING PROCESS

In the present thesis it is pointed out, that there is a lack of appropriate processes to fully exploit the potential of thermomechanical wood fibers in thermoplastic based composites. In Chapter 5 the development of an novel process of compounding wood fibers and polymer is presented.
The development of the process was carried out in three stages. The objectives and results of the conducted study, are summarized as follows:

1. *Preliminary Studies (Chapter 5.1)*

Objective: General process observations. How does the wood fiber and polymer mixture influence the refiner system?
Result: Generally, it was found that the idea of simultaneous defibration and compounding using refiner equipment is realizable. However, the atmospheric refiner system was not able to generate enough energy for fiber defibration and optimal polymer melting.

2. *Proof of Concept (Chapter 5.2)*

Objective: General process observations, using a pressurized batch refiner system. How does the refiner perform when wood chips and polymer is preheated prior to defibration?
Results: The conducted study demonstrated, that the process of simultaneous defibration of wood chips and polymer granulates did not influence the refiner system. A stable process within the utilized system was realized. After the process typical thermomechanical wood fibers and chopped polymer particles, which were inseparably attached to the fiber, were received. It was found that with the given conditions, the polymer does not influence the defibration process.

3. *Up-scaling process to industrial level (Chapter 5.4)*

Objective: General process observations. Is the process able to run continuously over a long period of time (hours) while using an industrial scale refiner? Further, it was intended to use industrial wood chips (as usually used in industrial processes) to investigate their influence on the defibration performance while changing the wood chip and polymer ratio.

Results: Generally, it has been proven, that the simultaneous defibration of industrial wood chips and polymer granulates over long periods of time, using industrial scale refiner equipment, is feasible. The process was found to be stable and no significant increase in power consumption was noticed even with changing wood chip and polymer ratios.

In addition to the successful evaluation of the developed process, the idea of simultaneous defibration and polymer compounding with refiner equipment was patented (WO2017/045676 A1). A successful international evaluation was reported to the inventors by the European Patent Office (EPO) and therefore confirms the novelty of this approach.

According to the conducted studies, it is believed, that the developed process can save production steps compared to the traditional way of wood flour or fiber production and compounding. Schematically both processes are illustrated in Figure 6.2. It is believed, that the developed process results in a less expensive product compared to the conventional WPC-process. This statement is based on the following assumptions:

- the milling process for wood flour production and the following particle fractioning is expected to be more energy intensive with respect to the final product.
- the developed process can save production steps (e.g. drying).
- refiner units have usually much higher capacities (tons/hour) than the traditionally milling units and compounding extruders (kg/hour).

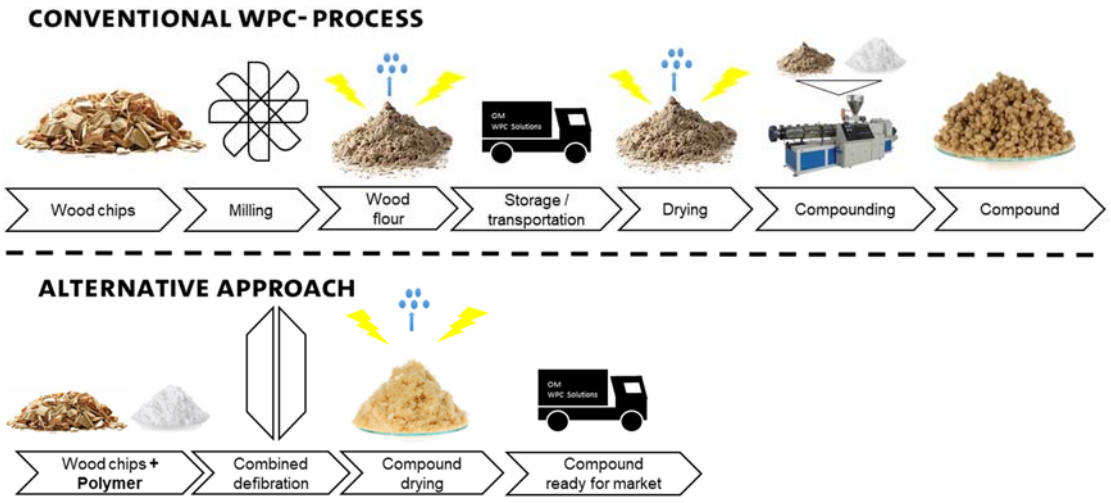

Figure 6.2 Conventional way of WPC processing compared to the novel approach of simultaneous defibration and compounding.

Unresolved process issues

A successful development of a novel process approach for wood fiber based thermoplastic compounds is presented. However, at the current state of the process development, some issues are unresolved and are discussed in the following:

Polymer agglomeration

During the up-scaling process, it was noticed, that the polymer granulates have the tendency to form agglomerates and stacked together in the pre-heating stage and consequently entered the defibration zone. However, the polymer agglomerates obviously did not affect the material distribution within the final composite. This may be attributed to the subsequent processing steps (see following discussion Chapter 6.2.3).

Compound composition

The wood fiber / polymer compound, as received after defibration consists of typical thermomechanical wood fibers and partly larger polymer fragments (see exemplary Figure 6.3). During the process the wood chips and polymer granulates have to pass a narrow gap (for instance 0.1 mm during the up-scaling process) of a stationary and opposing rotating disc. Thus, it is astounding that the polymer granulate was partially in their initial grain size after the defibration process. Hence, the following considerations are made:

Figure 6.3 Obtained compound after simultaneous defibration and compounding (Chapter 5.4). The red circles show larger polymer fragments.

1. Considering that the stator and rotor discs may not be absolutely parallel to each other and may have changed their adjusted position during the process, the possibility, that some of the polymer granulates or fragments moved undamaged out of the defibration zone, arises.
2. It is assumed, that, due to the plasticized wood structure, lower shear forces are needed for their defibration than, for polymer granulate defibration. Hence, the possibility of only partially molten polymer granulates or larger fragments increases.
3. It is reported that the temperature and pressure between the disc gap can be higher than in the refiner system (Chapman 2006) (was in both experiments below the polymer melting point). Hence, it is assumed that the polymer becomes molten and starts to flow while passing the defibration zone. Due to the high disc rotation (3000 rpm) it is believed that the polymer melt forms threads while leaving the defibration zone, which then agglomerate to larger particles.

To avoid the mentioned larger polymer fragments, the following suggestions are made:

a) Utilization of polymer powder for the following experiments: With the utilization of polymer powder, the previous mentioned consideration 1) is at least is avoided. However, if consideration 3) still come up, the taken assumption is confirmed.

b) Improvement of refiner disc pattern: A specific tailored disc pattern for wood chip and polymer defibration may help produce homogenous fiber and polymer morphologies.

c) Two step defibration: To avoid larger polymer particles, a series of two connected refiner units may help to homogenize the material morphology.

6.2.1 FURTHER PROCESSING OF THE NOVEL PRODUCED COMPOUND

After the simultaneous wood fiber and polymer defibration, the received compound has to be further processed to generate the final composite. In principal, three measures need be implemented:

1. Compound drying.
2. Processing the compound to bulk material (intermediate product).
3. Forming / consolidation of the bulk material to a final product.

In the present study, exemplary three different approaches were used to process the received compounds into bulk materials. Schematically, the used processes and the received intermediate products of each conducted study are displayed in Figure 6.5. It can be stated, that each applied further process is suitable to manufacture the compound into a bulk material as intermediate product, which can be used for composite forming. However, some issues have to be discussed regarding the further processes and the respective intermediate product.

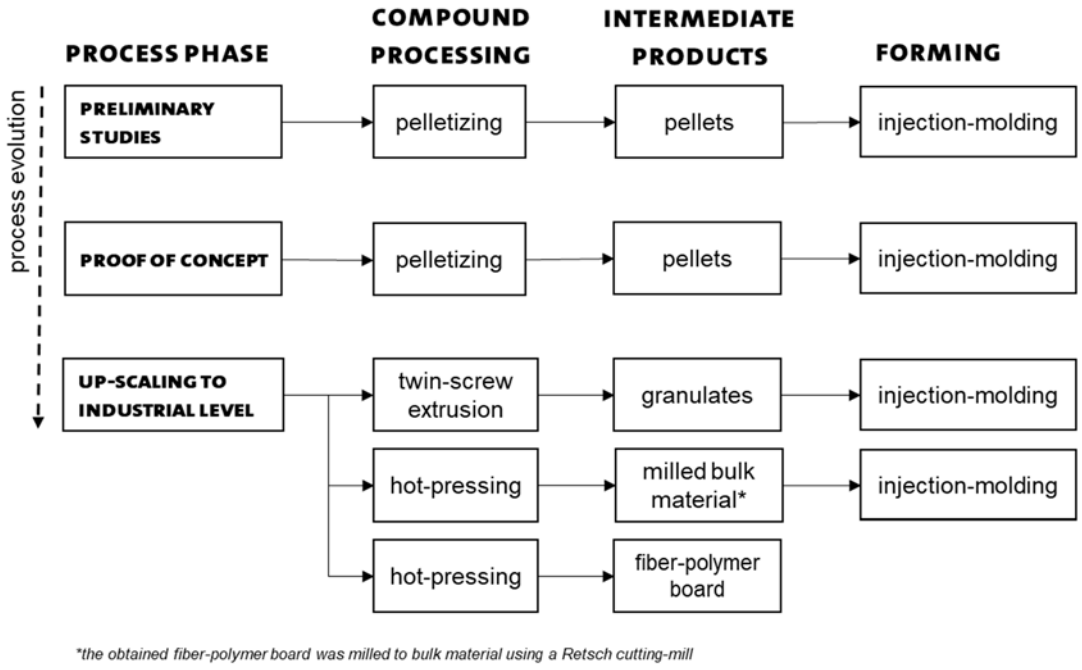

Figure 6.4 Conducted experiments and their respective production processes.

Unresolved process issues for the further processes

Pelletizing

Pelletizing was used as further process in two studies (Chapter 5.1 and 5.2). It was found, that drying the compound to a moisture content of about 12 % is needed to receive an appropriate pellet. After leaving the matrices channel the compressed compound expands and breaks apart, if the moisture content is not adjusted appropriately.

Nevertheless, even after drying many pellets broke apart into smaller pieces. It was obvious, that the polymer and in particular polymer fragments acted as fracture initiators. The induced mechanical energy was probably insufficient to produce a malleable fiber-polymer mass, which may result in a solid bulk material.

The monitoring of the fiber dimensions after pelletizing (Chapter 5.3) revealed that pelletizing leads to severe fiber length degradation. Similar observations during fiber pelletizing are reported by Nygård et al. (2008), Le Baillif and Oksman (2009) and Bengtsson et al. (2007). It s therefore suggested, to avoid fiber pelletizing in order to preserve fiber dimensions.

During the study of the proof of concept, fiber agglomerates and voids were present in the final composite after injection-molding. The observations are attributed to:

- the poor dispersion ability of the injection-molding screw.
- a low back pressure during injection-molding.

Usually the injection-molding screw is not designed for the dispersion of particle or fiber based granulates. Rather the screw is designed to realize the material feed-in, polymer plasticization, melt transportation and material compression. The pelletized material is difficult to disperse properly, because of hydrogen bonds between the fibers (Felix and Gatenholm 1991, Le Baillif and Oksman 2009), which have been formed during the process. Thus, fiber agglomerates are still present in the final composite.

The back pressure is an adjustable process parameter which ensures material compression and the elimination of remaining air that is previously transported into the screw channel. A low screw back pressure was chosen, because of feed-in difficulties of the pelletized material. It is assumed, that some remaining air was not driven out of the melt and thus trapped in the final composite.

Hot-pressing

Hot-pressing was used to manufacture fiber based panels made out of the compound (Chapter 5.4). Exemplary the cross section of a manufactured panel (thickness 4mm) is displayed in Figure 6.6. As seen here the material distribution over the panel thickness is highly inhomogeneous. This is most likely due to:

- inhomogeneous manual scattering of fibers and polymer prior to ho-pressing.
- polymer impregnation through of the entire panel thickness was not achieved because larger polymer particles were only molten locally.

Figure 6.5 Panel cross section manufactured from a compound produced by the up-scaling process containing a 50/50 ratio of wood fibers to polymer.

In addition to panel manufacture, in a second step the panels were milled in a cutting-mill in order to produce a bulk material for further injection-molding. The specimens produced, show fiber agglomerates, as previously discussed for the produced pellets. It is also here assumed, that the poor mixing ability of the injection-molding screw could not release the compressed material, which results in agglomerates within the composite.

Suggestion for further process improvements

It can be stated, that in general a composite production was achieved. However, at the current state of the project, the processes have to be further optimized to improve the composite quality. The following improvements are suggested:

1. The application of dispersion aids, as reported by Le Baillif and Oksman (2009) may release the hydrogen bonds between the fibers and thus, the mixing ability of the injection-molding screw may improve.
2. Instead of using polymer granulates it is suggested to evaluate the influence of polymer powder on the different process behaviors and composite characteristics. It is assumed, that powder may disperse better between the fibers due to the very small grain size. For polymer powders only localized flow of melt is required, resulting in better impregnation (Thomason and Vlug 1996)

of hot-pressed panels. This presumably results in an enhanced fiber-polymer network and appropriate composites.

6.2.2 CHARACTERISTICS AND PROPERTIES OF THE WOOD FIBER BASED COMPOSITES

Fiber characteristics

The fiber characteristics of the novel wood fiber-polymer compound were determined after defibration, further processing and composite forming. Table 6.1 summarizes the fiber length and aspect ratio of various investigated fibers. All listed values are obtained from composites containing 50 wt.% wood fibers.

Table 6.1 Average fiber length l [µm] and corresponding aspect ratio AR as 10 %, 50 % and 90 % quantile of the length-based cumulative distribution for composites containing 50 wt.% wood fibers. Values are presented for "initial" fibers (as received after defibration) and fibers after injection-molding. Further information is listed in the respective chapters.

		"initial" fibers			fibers after injection-molding			method
		x_{10}	x_{50}	x_{90}	x_{10}	x_{50}	x_{90}	
MDF WOOD FIBERS (CHAPTER 4)	*l*	316.3	1825.9	3708.7	12.3	82.1	252.6	Quickpic
	AR	7.7	33.3	50	1.9	3.4	7.1	
PROOF OF CONCEPT (CHAPTER 5.3)	*l*	213.0	1262.0	3615.0	152.0	416.0	1552.0	Fiber-Cube
	AR	2.9	3.0	2.4	2.1	2.2	2.0	
UP-SCALING (CHAPTER 5.4)	*l*	123.9	884.1	2352.3	34.53	126.4	297.9	Quickpic
	AR	2.8	16.6	33.3	1.5	2.7	5.8	

Initial wood fiber characteristics

Table 6.1 shows that different initial fiber length in each study are obtained after defibration. The fiber characteristics after defibration are influenced by the intensity of pre-steaming (pressure and temperature), disc gap (Wenderdel and Krug 2012, Ohlmeyer et al. 2015, Benthien et al. 2016) and disc pattern. The longest fibers with the highest aspect ratio are used in the experimental study in Chapter 4, in which the potentials of thermomechanical wood fibers in thermoplastic composites were identified. Regarding the fiber length that is obtained after the novel process of simultaneous wood chip and polymer defibration, the fibers in the proof of concept are obviously longer than those obtained in the up-scaling process. However, difference occur if the aspect ratios between the fibers from the proof of concept and the up-scaling process are compared. The "initial" fibers received after defibration in the proof of concept

(Chapter 5.3) show the overall lowest aspect ratio. From this it is concluded, that the fibers are quite coarse and maybe consisting out of fiber bundles and fiber agglomerates, which is presumably a result of the adjusted disc gap (0.4 mm).

Fiber characteristics after composite processing

It is previously shown that the initial fiber length and aspect ratio after defibration are different. However, after composite processing (compounding and forming) the values are overall almost similar. All investigated wood fibers are severely degraded during composite processing. Based on this, the composite processing technology used, did not preserve the former promising fiber lengths and aspect ratios. The resulting geometry is more similar to that of wood flour than of fibers. The results of the investigated final fiber lengths and aspect ratios are summarized as follows:

- the investigation of the fiber geometry in the proof of concept revealed, that pelletizing and injection-molding reduced the fiber length to some extent by the half. However, the aspect ratio is found to be nearly the same compare to the initial aspect ratio. Thus, it is concluded that particle with a larger volume (agglomerates and fiber bundles) were present in the final composite. A further investigation concerning that issue is discussed in the following section.
- the fibers investigated in the up-scaling process and in the experimental study in Chapter 4 show nearly the same order of magnitude in their length reduction. Twin-screw extrusion and injection-molding which were used as processes lead to severe fiber length reduction. The presented values revealed, that as longer the initial fiber length is, as higher is the length reduction.

The results found in this concern, are similar and in agreement to the results found by Teuber (2016a). Teuber (2016a) stated that changes towards a gentle compounding process are needed, to fully exploit the reinforcement potential of fibers.

Investigation of fiber geometry using µ-CT imaging

In addition to the dynamic image analysis for fiber characterization, an alternative approach was applied by investigating the scanned µ-CT volumes which were analyzed in Chapter 5.2 and 5.4.

The final aspect ratio (after injection-molding) of the fibers obtained from the proof of concept and the up-scaling study are quite similar. However, notable differences occur when considering the final fiber length. Thus, greater fiber length with a low aspect ratio should result in a larger particle geometry or agglomerates and therefore in a total higher particle volume and vice versa.

To proof the hypotheses, the scanned µ-CT volumes of each composite were further investigated. The particle geometry was analyzed applying a Watershed algorithm and different separation and labeling tools by using the software Avizo® Fire 9. Figure 6.7 presents the obtained data, shown as cumulative frequency of the particle volume. The algorithms applied, separated in total 9643 particles, for the proof of concept composite, and 54102 particles from the up-scaling process composite. The data supports the previous found results and statements that:

a) Twin-screw extrusion and injection-molding (both used in the up-scaling process) causes small particles resulting in volume of smaller single particles
b) Injection-molding is not able to dissolve fiber agglomerates that have been formed during pelletizing (used in the proof of concept)

Thus, it is stated here, that µ-CT-analysis is an appropriate technique to investigate non-destructively the particle geometry. However, the approach presented can be subjected to errors such as set threshold parameters when applying the algorithm or different scan quality or duration.

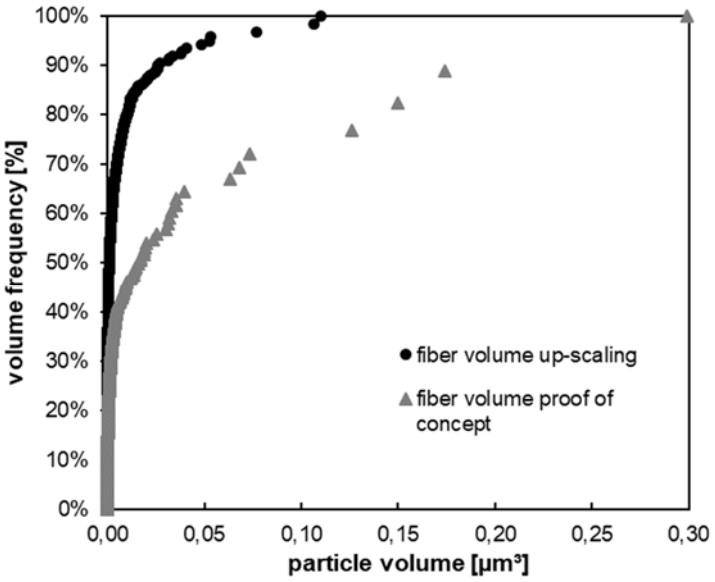

Figure 6.6 Particle volume and their respective frequency for composites investigated in Chapter 5.2 (proof of concept) and 5.4 (up-scaling process). Data is based on µ-CT volume image analysis and manipulated with Avizo® Fire 9.

Mechanical properties

Table 6.2 summarizes the mechanical properties of the composites made out of the novel produced compound. As a point of reference, the values obtained from the wood fiber composites revealed in the experimental study (Chapter 4), are also listed. All presented composites have a fiber content of 50 wt.% and the same polymer matrix, except the composites produced in the preliminary studies. Additionally, all composites are formed with the same injection-molder machine.

With regard to the mechanical properties, generally it can be stated, that,:

1. An improvement of the mechanical properties has been achieved in the order of each conducted study.
2. The composite properties are depending on the production technology used.

The highest strength properties are achieved with the Masterbatch formulation that was used in the up-scaling study. From Table 6.2 it is also evident, that composites which are further processed with a twin-screw extruder show reveal higher strength values than composite which are not processed with extrusion technology (see IM-WFC, Masterbatch and References).

The lower mechanical properties that are revealed in the preliminary studies, the proof of concept and the up-scaling process (only IM-Panel), confirm the previous discussed statements. If the fiber / polymer compound as received after defibration is processed to bulk material with pelletizing or hot-pressing technology, the injection-molding screw is not able to release and distribute the former compressed material. As a result of the unsolved hydrogen bonds between the fiber, agglomerates and voids occur in the composite and thus affecting the properties.

Table 6.2 Mechanical properties of several produced wood fiber based composites. All presented composites have a wood fiber / polymer ratio of 50-50%. The reference values are taken from Chapter 4. Further information can be found in the respective chapters.

formulations	polymer	tensile strength	tMOE	flexural strength	fMOE
		[MPa]	*[GPa]*	*[MPa]*	*[GPa]*
PRELIMINARY STUDIES*	HDPE	19.12	4.1	38.6	3.8
PROOF OF CONCEPT*	PP	19.21	3.22	40.58	5.5
UP-SCALING					
IM-Panel*	PP	19.80	3.5	45.64	4.8
IM-WFC		28.31	5.7	50.82	6.5
Masterbatch (incl. MAPP)		**53.50**	**5.3**	**88.35**	**5.6**
REFERENCES (Chapter4)					
wood fibers	PP	27.2	5.1	45.5	5.3
wood fibers (incl.MAAP)		48.1	5.5	76.4	5.2

** not further processed with extrusion technology*

In order to classify the performance of the composite made out of the novel process, the tensile strength of the composites are implemented in Figure 6.8. The red dot (1) presents the Masterbatch composite, red dot (2) the composite IM-WFC and red dot (3) comprises values obtained from the preliminary studies, the proof of concept and the up-scaling process (here IM-Panel). As can be seen from the graph, the values obtained from composite made out the novel produced compound fit well to the already discussed composite performance, which are found and determined in the present thesis. From Figure 6.8 it is evident, that thermomechanical wood fibers have potentials to reinforce a thermoplastic matrix. It was previously discussed, that the further processes for composite production lead to severe fiber length reduction.
However, fiber length should not be overestimated, since other aspects like fiber dispersion fiber orientation and fiber matrix adhesion are also influencing the composite performance (Le Baillif and Echtermeyer 2010, Thumm and Dickson 2013). Since for example the performance of the Masterbatch (1) composite is much better than wood flour composites, maybe some fibers are left that are above the critical fiber length and thus are responsible to provide a reinforcement effect (Teuber 2016a).

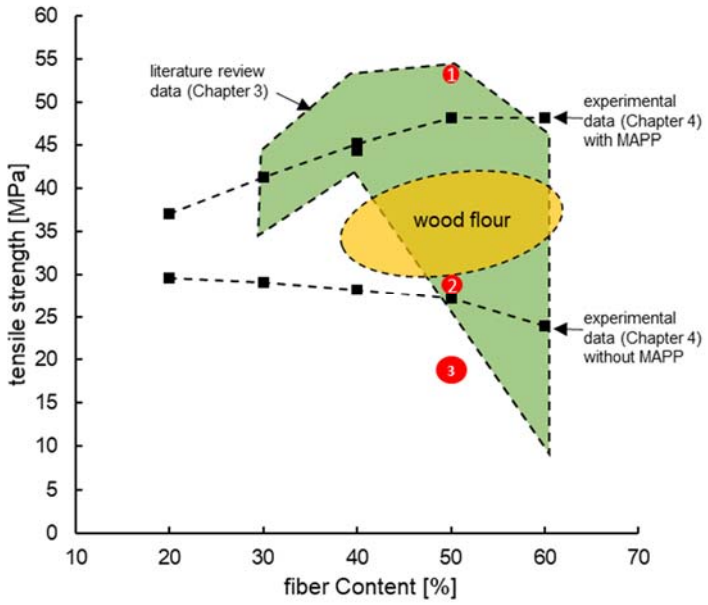

Figure 6.7 Influence of fiber contents on tensile strength. Red marked dots indicate tensile strength of the composites made out of material obtained from the novel compounding process. The black dots display the tensile strength values obtained in Chapter 4 for MDF fiber polypropylene composites. The green area displays the range of tensile strength values for industrial-scale produced wood fiber composites found in the literature review (Chapter 3). Tensile strength for various filler loadings of wood flour composites are taken from Gehrmann et al. (2003) (60 wt. %). Krause et al. (2017b) (60 wt. %). Nygård et al. (2008) (50 wt. %). Stark and Rowlands (2003) (40 wt. %). All wood flour composites are produced with industrial-scale technologies.

6.2.3 CONCLUSIONS

The previous chapter evaluated the development of a novel process of simultaneous wood chip and polymer defibration as well as the respective composite properties.

The process of simultaneous wood chip and polymer defibration to a novel kind of compound is successfully established and the process is principally feasible. The refiner technology, which is usually used for wood fiber production, is able to simultaneously process wood chips and polymer. The process, including material preheating and defibration, runs continuously over a longer period. An implementation in existing industrial processes for MDF or TMP fiber production is supposed to be possible. It is believed that production steps can be saved compared to the conventional WPC compounding process. Hence a less expensive product is expected. However, the polymer behavior during defibration is an open issue and has to be investigated in further studies.

The received wood fiber / polymer compound was further processed using different approaches. Generally, it was shown that a further processing to intermediate products is possible. For further studies it is suggested to investigate the application of processing aids to avoid fiber agglomeration in order to manufacture appropriate composite properties. Severe fiber length reduction was revealed after pelletizing and injection-molding.

The mechanical properties of the produced composite are depending on the further process applied. The obtained mechanical properties are in the range of the wood fiber composites that have been previously evaluated.

CHAPTER 7
GENERAL CONCLUSIONS

For the production of WPC, different raw materials and polymers are suitable. Usually, wood flour with a low aspect ratio is used as a filler in thermoplastic composites. Thermomechanical produced wood fibers show characteristics, such as a high aspect ratio, that make these fibers to a promising candidate for the utilization in thermoplastic composites. The fiber morphology is presumed to be important and influenced by the fiber defibration process. The performance of the final composite depends on the WPC processing technology used. However, the industrial application of thermomechanical wood fibers in WPC seems to be limited, due to the low bulk density of the fibers. Thus, the processing with traditional continuously operating technologies, such as extruders, is quite challenging. Additionally, these fibers tend to form agglomerates after drying, which are difficult to disperse in the final composite. The experimental performance evaluation showed that these fibers can reinforce the polymer matrix. A reinforcement to the matrix can be achieved up to a fiber content of 40 - 50 wt.%, if coupling agents are used. However, the processing with extruders and injection-molding leads to a severe fiber length reduction. In addition, it is confirmed that the processing with extruders is challenging.

The novel process of simultaneous wood chip and polymer defibration with refiner technology was developed to solve the fiber feed-in challenge and fiber agglomeration, which occurs with traditional compounding equipment. It is successfully demonstrated, that the refiner technology is able to produce a wood fiber polymer compound. The received compound consists of typical high aspect ratio thermomechanical wood fibers and chopped polymer granulates, which are inseparably attached to the fiber. It is believed that the developed process saves production steps compared to the traditional procedures of WPC compounding. Regarding the novel process, further investigations are needed for a better understanding of the material behavior within the refiner. According to the current state of the project, an industrial application in existing thermomechanical wood fiber production lines is expected to be possible.

Pelletizing, hot-pressing and twin-screw extrusion were used to further process the received novel wood fiber polymer compound to intermediate products. The properties of the injection-molded test specimens revealed different results. It is concluded that the properties are depending on the production technology used. The applied

further processes have to be improved in following studies to obtain appropriate composites.

Finally it can be stated, that according to the presented results and conclusions, the drafted working hypotheses is confirmed. A successful demonstration of the novel process is presented. The refiner technology is able to solve the previously discussed fiber feed-in and agglomeration problem.

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

°C	Celsius
µ-CT	Micro computed tomography
µm	Micro meter
EMDI	Emulsifiable methylene diphenyl diisocyanate
FE-SEM	Field emission scanning electron microscopy
g	Gramm
GPa	Giga pascal
h	Hour
HDF	High density fiberboard
HDPE	High density polyethylene
kg	Kilogram
kg/h	Kilogram per hour
kWh	Kilo watt hours
L/D	Length to diameter ratio
LDPE	Low density polyethylene
MAPP	Maleic anhydride modified polypropylene
MDF	Medium density fiberboard
MFI	Melt flow index
mm	Millimeter
MOE	Modulus of elasticity
MPa	Mega pascal
NFC	Natural fiber composites
OSB	Oriented strand board
PE	Polyethylene
PLA	Polylactide
PP	Polypropylene
PVC	Polyvinylchloride
ROI	Region of interest
rpm	Rounds per minute
SME	Specific mechanical energy
TMP	Thermomechanical pulp
TSE	Twin screw extruder
WBC	Wood based composites
WFC	Wood fiber compound
WPC	Wood plastic composites
wt.%	Weight content

REFERENCES

Ashori A (2008) Wood-plastic composites as promising green-composites for automotive industries. Bioresource technology 99(11):4661–4667. doi: 10.1016/j.biortech.2007.09.043

Ashori A (2010) Study on mechanical properties of wood fiber/polypropylene composites. AMR 123-125:1195–1198. doi: 10.4028/www.scientific.net/AMR.123-125.1195

Bailey R, Rzepka B (1991) Fibre orientation mechanisms for injection molding of long fibre composites. IPP 6(1):35–41. doi: 10.3139/217.910035

Bengtsson M, Le Baillif M, Oksman K (2007) Extrusion and mechanical properties of highly filled cellulose fibre–polypropylene composites. Composites Part A: Applied Science and Manufacturing 38(8):1922–1931. doi: 10.1016/j.compositesa.2007.03.004

Benthien JT, Bähnisch C, Heldner S, Ohlmeyer M (2014) Effect of fiber size distribution on medium-density fiberboard properties caused by varied steaming time and temperature of defibration process. Wood and Fiber Science 46(2):175–185

Benthien JT, Heldner S, Ohlmeyer M (2016) Investigation of the interrelations between defibration conditions, fiber size and medium-density fiberboard (MDF) properties. Eur. J. Wood Prod. doi: 10.1007/s00107-016-1094-2

Bourmaud A, Ausias G, Lebrun G, Tachon M-L, Baley C (2013) Observation of the structure of a composite polypropylene/flax and damage mechanisms under stress. Industrial Crops and Products 43:225–236. doi: 10.1016/j.indcrop.2012.07.030

Buerkle E, Sieverding M, Mitzler J (2003) Spritzgießverarbeitung von langfaserverstärkten PP. Kunststoffe 3:47–50

Burgert I, Frühmann K, Keckes J, Fratzl P, Stanzl-Tschegg SE (2003) Microtensile testing of wood fibers combined with video extensometry for efficient strain detection. Holzforschung 57(6):14. doi: 10.1515/HF.2003.099

Callister WD (2001) Fundamentals of material science and engineering. An interactive e.text, 5. ed. Wiley, New York

Carus M, Eder A, Scholz L (2015) Bioverbundwerkstoffe: Naturfaserverstärkte Kunststoffe (NFK) und Holz-Polymer-Werkstoffe (WPC), Gülzow

Carus M, Partanen A (2017) Natural fiber-reinforced plastics: established and growth in niche markets. 7th Conference on Wood and Natural Fiber Composites: Biocomposites Cologne

Caulfield D, Clemons C, Jacobson R, Rowell RM Wood thermoplastic composites. In: Rowell (Hg.) 2005 – Handbook of Wood Chemistry

Chapman KM (2006) Wood based panels: Particleboard, Fiberboard and orianted Strand Boards. In: Walker JCF (ed) Primary wood processing: principles and practice. Pulp and Paper Manufacture. Springer Netherlands, pp 427–476

Clemons C (2002) Wood-Plastic Composites in the United States. The interfacing of two industries. Forest products journal 52(6)

EN 15534-1: 2014 Verbundwerkstoffe aus cellulosehaltigen Materialien und Thermoplasten (üblicherweise Holz-Polymer-Werkstoffe (WPC) oder Naturfaserverbundwerkstoffe (NFC) genannt) –Teil 1: Prüfverfahren zur Beschreibung von Compounds und Erzeugnissen. Deutsches Institut für Normung e. V., Berlin

Dickson AR, Even D, Warnes JM, Fernyhough A (2014) The effect of reprocessing on the mechanical properties of polypropylene reinforced with wood pulp, flax or glass fibre. Composites Part A: Applied Science and Manufacturing 61:258–267. doi: 10.1016/j.compositesa.2014.03.010

Diniz JMB, Gil MH, Castro, J. A. A. M. (2004) Hornification - Its origin and interpretation in wood pulps. Wood Science and Technology 37(6):489–494. doi: 10.1007/s00226-003-0216-2

Eder M, Stanzl-Tschegg S, Burgert I (2008) The fracture behaviour of single wood fibres is governed by geometrical constraints. In situ ESEM studies on three fibre types. Wood Science and Technology 42(8):679–689. doi: 10.1007/s00226-008-0214-5

Ehrenstein GW (2006) Faserverbund-Kunststoffe. Werkstoffe - Verarbeitung - Eigenschaften, 2., völlig überarb. Aufl. Hanser, München

Ehrenstein GW, Wurmb R (1977) Verstärkte Thermoplaste - Theorie und Praxis. Die angewandte Makromolekulare Chemie 60/61(851):157–214

Erdmann J (2017) Biobasierte Kunststoffe mit Cellulosefaserverstärkung – Zusammenhänge zwischen Struktur, Haftung und mechanischen Eigenschaften. Doctoral Thesis, Martin-Luther-Universität Halle-Wittenberg

Felix JM, Gatenholm P (1991) The nature of adhesion in composites of modified cellulose fibers and polypropylene. J. Appl. Polym. Sci. 42(3):609–620. doi: 10.1002/app.1991.070420307

Gatenholm P, Bertilsson H, Mathiasson A (1993) The effect of chemical composition of interphase on dispersion of cellulose fibers in polymers. I. PVC-coated cellulose in polystyrene. J. Appl. Polym. Sci. 49(2):197–208. doi: 10.1002/app.1993.070490202

Gehrmann K, Busch M, Meinicke S, Starke R, Krombholz A (eds) (2004) Der Einfluss der Fasergeometrie unterschiedlicher Naturfasern und unterschiedlicher Polypropylentypen auf Schlüsselkennwerte von Composites und extrudierten Hohlkammerprofilen

Gehrmann K, Starke R, Wilczek G, Nagel F, Morawietz K, Meinicke S, Busch M (2003) Perspektiven mit Profilextrusion. Erste Ergebnisse über den Einfluss unterschiedlicher Holzfaserstoffe und Polypropylen-Typen auf mechansiche Kennwerte und Composites. Holz und Kunststoffbearbeitung(4):50–52

Godavarti S, Karwe MV (1997) Determination of specific mechanical energy distribution on a twin-screw extruder. Journal of Agricultural Engineering Research 67(4):277–287. doi: 10.1006/jaer.1997.0172

Graupner N, Beckmann F, Wilde F, Müssig J (2014) Using synchroton radiation-based micro-computer tomography (SR µ-CT) for the measurement of fibre orientations in cellulose fibre-reinforced polylactide (PLA) composites. J Mater Sci 49(1):450–460. doi: 10.1007/s10853-013-7724-8

Graupner N, Muessig J (2016) Influence of fibre loading, fibre length, fibre orientation and voids on the characteristics of compression and injection moulded cellulose fibre-reinforced polylactide (PLA) composites. ECCM17 - 17th European Conference on Composite Materials Munich, Germany, 26-30th June 2016

Graupner N, Ziegmann G, Wilde F, Beckmann F, Müssig J (2016) Procedural influences on compression and injection moulded cellulose fibre-reinforced polylactide (PLA) composites. Influence of fibre loading, fibre length, fibre orientation

and voids. Composites Part A: Applied Science and Manufacturing 81:158–171. doi: 10.1016/j.compositesa.2015.10.040

Groom L, Mott L, Shaler S (2002) Mechanical properties of individual southern pine fibers. Part I. Determination and variability of stress-strain curves with respect to tree heigth and juvenility. Wood and Fiber Science 34(1):14–27

Groom LH, So CL, Elder T, Pesacreta T, Rials TG (2006) Effects of refiner pressure on the properties of individual wood fibers. In: Stokke DD, Groom LH (eds) Characterization of the cellulosic cell wall, 1st ed. Blackwell Pub, Ames, Iowa, pp 227–240

Groom L, So CL, Rials T, Neese J, Alexander J (2002) Relationships between wood quality, refiner pressure, and resin distribution and their influence on MDF panel properties. 6th European Panel Products Symposium 2002, Llandudno, Wales, UK

Ho M, Wang H, Lee J-H, Ho C-k, Lau K-t, Leng J, Hui D (2012) Critical factors on manufacturing processes of natural fibre composites. Composites Part B: Engineering 43(8):3549–3562. doi: 10.1016/j.compositesb.2011.10.001

Hom N, Dhakal Z, Zhang Y (2014) Properties and characterization of natural fiber-reinforced polymeric composites. In: Thakur VK (ed) Green composites from natural resources. CRC Press, Boca Raton, pp 335–389

Horbens M, Pfriem A, Ganster J, Wagenführ A (2012) Holzfasern als Verstärkungsfasern in Holz-Polypropylen-Verbundwerkstoffen. Holztechnologie 53(6):21–24

Huang C, Li RKY, Wu CML, Duan Z (1999) Stiffness behaviour of injection moulded short glass fibre/impact modifier/polypropylene hybrid composites. Journal of Materials Processing Technology 96(1-3):48–52. doi: 10.1016/S0924-0136(99)00251-4

Hull D, Clyne TW (1996) An introduction to composite materials. Cambridge University Press, Cambridge

Inceoglu F, Ville J, Ghamri N, Pradel JL, Durin A, Valette R, Vergnes B (2011) Correlation between processing conditions and fiber breakage during compounding of glass fiber-reinforced polyamide. Polym Compos 32(11):1842–1850. doi: 10.1002/pc.21217

Jaroschek C (2008) Spritzgießen für Praktiker, 2. Aufl. Hanser, München

Joffre T, Miettinen A, Berthold F, Gamstedt EK (2014a) X-ray micro-computed tomography investigation of fibre length degradation during the processing steps of short-fibre composites. Composites Science and Technology 105:127–133. doi: 10.1016/j.compscitech.2014.10.011

Joffre T, Miettinen A, Wernersson ELG, Isaksson P, Gamstedt EK (2014b) Effects of defects on the tensile strength of short-fibre composite materials. Mechanics of Materials 75:125–134. doi: 10.1016/j.mechmat.2014.04.003

Kazayawoko M, Balatinecz JJ, Matuana LM (1999) Surface modification and adhesion mechanisms in wood-fiber-polypropylene composites. Journal of Material Science 34(24):6189–6199. doi: 10.1023/A:1004790409158

Kelly A, Tyson WR (1965) Tensile properties of fiber-reinforced Metals: Copper/Tungsten and Copper/Molybdenum. Journal of the mechanics and physics of solids 13(6):329–350

Kelly S, Elder T, Groom L (2015) Changes in the chemical composition and spectroscopy of loblolly pine medium density fiberboard furnish as a function of age and refining pressure. Wood and Fiber Science 37(1):14–22

Klyosov A (2007) Wood-plastic composites. Wiley-Interscience, Hoboken, N.J.

Kohlgrüber K (ed) (2007) Der gleichläufige Doppelschneckenextruder. Grundlagen, Technologie, Anwendungen. Hanser, München

Kokta BV, Chen R, Daneault C, Valade JL (1983) Use of wood fibers in thermoplastic composites. Polym. Compos. 4(4):229–232. doi: 10.1002/pc.750040407

Krause A, Krause KC (2012) Proceedings of 11th Pacific Rim Bio-Based Composites Conference: Relation between surface area and optimal concentration of coupling agent in WPC.:176–185

Krause A, Mertens O, Kordsachia O (2017a) Method for producing a lignocellulose plastic composite material. 2017 WO/2017/045676 UNIVERSITÄT HAMBURG

Krause KC, Mueller M, Krause A (2015) Converting wood from short rotation coppice and low-value beech wood into thermoplastic composites. In: Bemman A, Ammer C, Butler-Manning D, Bredemier M, Lamersdorf N (eds) Bioenergy from dendromass for the sustainable development of rural areas. Wiley-VCH, Weinheim, pp 483–496

Krause KC, Mueller M, Militz H, Krause A (2017b) Enhanced water resistance of extruded wood? Polypropylene composites based on alternative wood sources. Eur. J. Wood Prod. 75(1):125–134. doi: 10.1007/s00107-016-1091-5

Krug D (2010) Einfluss der Faserstoff-Aufschlussbedingungen und des Bindemittels auf die Eigenschaften von mitteldichten Faserplatten (MDF) für eine Verwendung im Feucht- und Außenbereich. Dissertation, Universität Hamburg

Krug D, Mäbert M (2008) Verwendung von Laubholz als Rohstoffalternative zur MDF-Herstellung. Forschungsbericht, Dresden

Le Baillif M, Echtermeyer A (2010) Effect of the preparation of cellulose pellets on the dispersion of cellulose fibers into polypropylene matrix during extrusion. J. Appl. Polym. Sci. 115(5):2794–2805. doi: 10.1002/app.30421

Le Baillif M, Oksman K (2009) The effect of processing on fiber dispersion, fiber length, and thermal degradation of bleached sulfite cellulose fiber polypropylene composites. Journal of Thermoplastic Composite Materials 22(2):115–133. doi: 10.1177/0892705708091608

Lee BJ, McDonald AG, James B (2001) Influence of fiber length on the mechanical properties of wood-fiber/polypropylene prepreg sheets. Mat Res Innovat 4(2-3):97–103. doi: 10.1007/PL00010786

Lerche H, Benthien JT, Schwarz K, Ohlmeyer M (2014) Effects of defibration conditions on mechanical and physical properties of wood fiber/high-density polyethylene composites. Journal of Wood Chemistry and Technology 34(2):98–110. doi: 10.1080/02773813.2013.838269

Li H, Sain MM (2003) High Stiffness Natural Fiber-Reinforced Hybrid Polypropylene Composites. Polymer-Plastics Technology and Engineering 42(5):853–862. doi: 10.1081/PPT-120024999

Lohmann U, Blosen M (2010) Holzlexikon. 1.448 Seiten, 15.700 Stichwörter, 2.050 Abbildungen, 4. Aufl. Nikol, Hamburg

Lu JZ, Wu Q, McNabb Jr. H (2000) Chemical coupling in wood fiber and polymer composites: A review of coupling agents and treatments. Wood and Fiber Science 32(1):88–104

Lu JZ, Wu Q, Negulescu II (2004) Wood-fiber/high-density-polyethylene composites. Compounding process. J. Appl. Polym. Sci. 93(6):2570–2578. doi: 10.1002/app.20707

Madsen B, Gamstedt EK (2013) Wood versus Plant Fibers. Similarities and Differences in Composite Applications. Advances in Materials Science and Engineering 2013(2):1–14. doi: 10.1155/2013/564346

Marutzky R, Thole V (2005) Fibre-based WPC with enhanced mechanical properties: New manufacturing processes and first results. 2nd Wood Fibre Polymer Composites Symposium, Bordeaux

Mertens O, Gurr J, Krause A (2017a) The utilization of thermomechanical pulp fibers in WPC. A review. J. Appl. Polym. Sci. 52:10. doi: 10.1002/app.45161

Mertens O, Krause KC, Krause A (2017b) Evaluation of wood fiber composites based on a novel simultaneous defibration and compounding process. J. Appl. Polym. Sci. 99:45859. doi: 10.1002/app.45859

Michaud F, Riedl B, Castéra P (2005) Improving wood/polypropylene fiberboards properties with an original MAPP coating process. Holz Roh Werkst 63(5):380–387. doi: 10.1007/s00107-005-0004-9

Migneault S, Koubaa A, Erchiqui F, Chaala A, Englund K, Krause C, Wolcott M (2008) Effect of fiber length on processing and properties of extruded wood-fiber/HDPE composites. J. Appl. Polym. Sci. 110(2):1085–1092. doi: 10.1002/app.28720

Mott L, Groom L, Shaler S (2002) Mechanical properties of individual southern pine fibers Part II. Comparison of earlywood and latewood fibers with respect to tree height and juvenility. Wood and Fiber Science 34(2):221–237

Nourbakhsh A, Ashori A (2008) Fundamental studies on wood–plastic composites. Effects of fiber concentration and mixing temperature on the mechanical properties of poplar/PP composite. Polym. Compos. 29(5):569–573. doi: 10.1002/pc.20578

Nygård P, Tanem BS, Karlsen T, Brachet P, Leinsvang B (2008) Extrusion-based wood fibre–PP composites. Wood powder and pelletized wood fibres – a comparative study. Composites Science and Technology 68(15-16):3418–3424. doi: 10.1016/j.compscitech.2008.09.029

Nystrom B, Joffe R, Langstrom R (2007) Microstructure and strength of injection molded natural fiber composites. Journal of Reinforced Plastics and Composites 26(6):579–599. doi: 10.1177/0731684407075536

Ohlmeyer M, Helder S, Benthien JT, Seppke B. (2015) Effects of refining parameters on fibre quality measured by fibre cube. International Panel Products Symposium 2015. COST Action FP1303 Performance of bio-based building materials:17–25

Oksman K, Sain M (eds) (2008) Wood-polymer-composites. Woodhead Publishing and Maney Publishing, Boca Raton

Parlevliet PP, Bersee HEN, Beukers A (2006) Residual stresses in thermoplastic composites. A study of the literature. Part I. Formation of residual stresses. Composites Part A: Applied Science and Manufacturing 37(11):1847–1857. doi: 10.1016/j.compositesa.2005.12.025

Partanen A, Carus M (2016) Wood and natural fiber composites current trend in consumer goods and automotive parts. Reinforced Plastics 60(3):170–173. doi: 10.1016/j.repl.2016.01.004

Paulitsch M, Barbu MC (2015) Holzwerkstoffe der Moderne, 1. Aufl. DRW-Verlag, Leinfelden-Echterdingen

Peltola H, Laatikainen E, Jetsu P (2011) Effects of physical treatment of wood fibres on fibre morphology and biocomposite properties. Plastics, Rubber and Composites 40(2):86–92. doi: 10.1179/174328911X12988622801016

Peltola H, Pääkkönen E, Jetsu P, Heinemann S (2014) Wood based PLA and PP composites. Effect of fibre type and matrix polymer on fibre morphology, dispersion and composite properties. Composites Part A: Applied Science and Manufacturing 61:13–22. doi: 10.1016/j.compositesa.2014.02.002

Pritchard G (2004) Two technologies merge. Wood plastic composites. Plastics, Additives and Compounding 6(4):18–21. doi: 10.1016/S1464-391X(04)00234-X

Puglia D, Terenzi A, Barbosa SE, Kenny JM (2008) Polypropylene-natural fibre composites. Analysis of fibre structure modification during compounding and its influence on the final properties. Composite Interfaces 15(2-3):111–129. doi: 10.1163/156855408783810849

Qiu W, Zhang F, Endo T, Hirotsu T (2003) Preparation and characteristics of composites of high-crystalline cellulose with polypropylene. Effects of maleated polypropylene and cellulose content. J. Appl. Polym. Sci. 87(2):337–345. doi: 10.1002/app.11446

Radovanovic I (2007) Verarbeitung und Optimierung der Rezeptur von wood plastic composites (WPC). Dissertation, Universität Osnabrück

Ren S, Hon DN-S (1993) Newspaper Fiber-Reinforced Polypropylene Composite. Journal of Reinforced Plastics and Composites 12(12):1311–1322. doi: 10.1177/073168449301201205

Rowell RM (ed) (2005) Handbook of wood chemistry and wood composites. CRC Press, Boca Raton, Fla.

Sain M, Pervaiz M (2008) Mechanical properties of wood-polymer composites. In: Oksman K, Sain M (eds) Wood-polymer-composites. Woodhead Publishing and Maney Publishing, Boca Raton, pp 101–117

Schirp A, Mannheim M, Plinke. B. (2014) Influence of refiner fibre quality and fibre modification treatments on properties of injection-moulded beech wood–plastic composites. Composites Part A: Applied Science and Manufacturing 61:245–257. doi: 10.1016/j.compositesa.2014.03.003

Schirp A, Plinke B, Napolow D (2015) Effectiveness of organic and inorganic pigments for mass colouration of thermo-mechanical pulp used in wood–plastic composites. Eur. J. Wood Prod. 73(1):5–16. doi: 10.1007/s00107-014-0839-z

Schirp A, Stender J (2009) Herstellung und Eigenschaften von extrudierten Wood-Plastic Composites mit Refinerfasern (Thermomechanical Pulp-Fasern). Chemie Ingenieur Technik 81(11):1773–1781. doi: 10.1002/cite.200900070

Schirp A, Stender J (2010) Properties of extruded wood-plastic composites based on refiner wood fibres (TMP fibres) and hemp fibres. Eur. J. Wood Prod. 68(2):219–231. doi: 10.1007/s00107-009-0372-7

Schwarzkopf M, Muszynski L (2015) Strain distribution and load transfer in the polymer-wood particle bond in wood plastic composites. Holzforschung 69(1). doi: 10.1515/hf-2013-0243

Schwarzkopf MJ, Burnard MD (2016) Wood-Plastic Composites - Performance and environmental impacts. In: Kutnar A, Muthu SS (eds) Environmental Impacts of

Traditional and Innovative Forest-based Bioproducts. Springer Singapore, Singapore, pp 19–43

Schwendemann D (2008) Manufacturing technologies for wood-polymer composites. In: Oksman K, Sain M (eds) Wood-polymer-composites. Woodhead Publishing and Maney Publishing, Boca Raton, pp 72–100

Sean ST (2010) MDF Fiber Reinforced polypropylene composites. In: Ngo AD (ed) Design, manufacturing and applications of composites. Proceedings of the Eighth Joint Canada-Japan Workshop on Composites ; École de Technologie Supérieure, Montréal, Québec, Canada [and] Industrial Materials Institute, Boucherville, Québec, Canada ; July 26-29, 2010. DEStech Publ, Lancaster, Pa., pp 68–77

Shahi P, Behravesh AH, Daryabari SY, Lotfi M (2012) Experimental investigation on reprocessing of extruded wood flour/HDPE composites. Polym Compos 33(5):753–763. doi: 10.1002/pc.22201

Solala I, Antikainen T, Reza M, Johansson L-S, Hughes M, Vuorinen T (2014) Spruce fiber properties after high-temperature thermomechanical pulping (HT-TMP). Holzforschung 68(2). doi: 10.1515/hf-2013-0083

Solala I, Koistinen A, Siljander S, Vuorinen J, Vuorinen T (2016) Composites of high-temperature thermomechanical pulps and polylactic acid. bioresources 11(1):1125–1140

Spear M, Hill C, Tomkinson J (2002) Natural fibre reinforced polypropylene composites: Assessing the potential of Hemp and TMP fibre. Proceedings of the 6th European Panel Product Symposium:118–129

Stadlbauer W (2010) Wood Plastic Composites – Neues Eigenschaftsprofil durch Refinerfasern (New property profile by using refiner fibres). Projektreport for "Fabrik der Zukunft". Berichte aus Energie und Umweltfoschung, Wien

Stark N, Rowlands RE (2003) Effects of wood fiber characteristics on mechanical properties of wood/polypropylene composites. Wood and Fiber Science 35(2):167–174

Stark NM, Cai Z, Carll C (2010) Wood-based Composites and Panel Products. In: Wood handbook. Wood as an engineering material. Forest Products Society, Madison, Wis.

Stokke DD, Han G, Wu Q (2014) Introduction to wood and natural fiber composites. Wiley series in renewable resource. Wiley, Chichester, West Sussex, United Kingdom

Sundholm J, Gullichsen J, Paulapuro H (eds) (1999) Papermaking science and technology. A series of 19 books covering the latest technology and future trends. Fapet Oy, Helsinki

Teuber L (2016a) Evaluation of particle and fibre degradation during processing of wood plastic composites (WPC) using dynamic image analysis. PhD.-Thesis, University Göttingen

Teuber L (2016b) Evaluation of particle and fibre degradation during processing of wood plastic composites (WPC) using dynamic image analysis. Mimicking industrial scale twin-screw compounding of wood and glass fibres: effect of process conditions on fibre length. PhD. Thesis, Georg-August-University Göttingen

Teuber L, Militz H, Krause A (2013) Characterization of wood particle change during processing. Proceedings of 6th International Wood Fibre Polymer Composites Symposium - Bio-based Composites Improving the Environment. Biarritz, France

Teuber L, Militz H, Krause A (2016a) Dynamic particle analysis for the evaluation of particle degradation during compounding of wood plastic composites. Composites Part A: Applied Science and Manufacturing 84:464–471. doi: 10.1016/j.compositesa.2016.02.028

Teuber L, Militz H, Krause A (2016b) Processing of wood plastic composites. The influence of feeding method and polymer melt flow rate on particle degradation. J. Appl. Polym. Sci. 133(13):n/a-n/a. doi: 10.1002/app.43231

Thomason JL (2005) The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene. Part 6. The properties of injection moulded long fibre PP at high fibre content. Composites Part A: Applied Science and Manufacturing 36(7):995–1003. doi: 10.1016/j.compositesa.2004.11.004

Thomason JL (2007) The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene. 7. Interface strength and fibre strain

in injection moulded long fibre PP at high fibre content. Composites Part A: Applied Science and Manufacturing 38(1):210–216. doi: 10.1016/j.compositesa.2006.01.007

Thomason JL (2009) Why are natural fibres failing to deliver on composite perfomance? In: 17th International Conference on Composite Materials, ICCM17

Thomason JL, Vlug MA (1996) Influence of fibre length and concentration on the properties of glass fibre-reinforced polypropylene. 1. Tensile and flexural modulus. Composites Part A: Applied Science and Manufacturing 27(6):477–484. doi: 10.1016/1359-835X(95)00065-A

Throne JL (1998) Processing Thermoplastic Composites. In: Peters ST (ed) Handbook of Composites. Springer US, Boston, MA, pp 525–555

Thumm A, Dickson A, Vuorinen J, Even D, Fernyhough A, Markotsis M (2011) The use of pulp fibres for the production of wood/plastic composites. In: Appita (ed) 65th Appita Annual Conference and Exhibition, pp 105–108

Thumm A, Dickson AR (2013) The influence of fibre length and damage on the mechanical performance of polypropylene/wood pulp composites. Composites Part A: Applied Science and Manufacturing 46:45–52. doi: 10.1016/j.compositesa.2012.10.009

Toll S, Andersson P-O (1993) Microstructure of long- and short-fiber reinforced injection molded polyamide. Polym. Compos. 14(2):116–125. doi: 10.1002/pc.750140205

Walker JCF (ed) (2006a) Primary wood processing: principles and practice. Pulp and Paper Manufacture. Springer Netherlands

Walker JCF (2006b) Pulp and Paper Manufacture. In: Walker JCF (ed) Primary wood processing: principles and practice. Pulp and Paper Manufacture. Springer Netherlands, pp 477–535

Warnes J, Witt M, Anderson R, Shar S, Fernyhough A Wood Plastic Composites based on MDF Fibre reinforcement. Proceedings of Wood-Plastic Composites Conference 2005. Bordeaux, France

Warnes JM, Fernyhough A, Anderson CR, Lee BJ, Witt MRJ (2006) Method for producing wood fibre pellets. http://www.google.com/patents/WO2006001717A1?cl=en

Wenderdel C (2015) Herstellung mehrschichtiger Faserplatten im Trockenverfahren mit kartonähnlichen Eigenschaften . PhD. Thesis, ETH Zürich

Wenderdel C, Krug D (2012) Untersuchung zum Einfluss der Aufschluss-bedingungen auf die morphologische Ausprägung von aus Kiefernholz hergestelltem TMP-Faserstoff. Eur. J. Wood Prod. 70(1-3):85–89. doi: 10.1007/s00107-010-0487-x

Winandy JE, Stark N, Horn E (2008) Wood-plastic composites using thermome-chanical pulp made from oxalic acid-pretreated red pine chips. Proceedings 7th Global WPC and Natural Fibre Composites Congress and Exhibition, Kassel

Wisnom MR (1992) The relationship between tensile and flexural strength of unidi-rectional composites. Journal of Composite Materials 26(8):1173–1180. doi: 10.1177/002199839202600805

Wolodko J, Alemaskin K, Perras T (2015) An Evaluation of pulped natural fibers in thermoplastic composites. Cancom 2015 Canadian International Conference on Composite Materials

Woodhams RT, Thomas G, Rodgers DK (1984) Wood fibers as reinforcing fillers for polyolefins. Polym. Eng. Sci. 24(15):1166–1171. doi: 10.1002/pen.760241504

Yam KL, Gogoi BK, Lai CC, Selke SE (1990) Composites from compounding wood fibers with recycled high density polyethylene. Polym. Eng. Sci. 30(11):693–699. doi: 10.1002/pen.760301109

Zhang SY, Zhang Y, Bousmina M, Sain M, Choi P (2007) Effects of raw fiber materi-als, fiber content, and coupling agent content on selected properties of polyeth-ylene/wood fiber composites. Polym. Eng. Sci. 47(10):1678–1687. doi: 10.1002/pen.20854

Zierdt P, Theumer T, Kulkarni G, Däumlich V, Klehm J, Hirsch U, Weber A (2015) Sustainable wood-plastic composites from bio-based polyamide 11 and chemi-cally modified beech fibers. Sustainable Materials and Technologies 6:6–14. doi: 10.1016/j.susmat.2015.10.001

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2003 - 2006	Carpenter / timber-framer journeyman
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EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre hiermit. dass ich diese Dissertation selbstständig ohne Hilfe Dritter und ohne Benutzung anderer als der angegebenen Quellen und Hilfsmittel verfasst habe. Alle den benutzten Quellen wörtlich oder sinngemäß entnommenen Stellen sind als solche einzeln kenntlich gemacht.

Diese Arbeit ist bislang keiner anderen Prüfungsbehörde vorgelegt worden und auch nicht veröffentlicht worden.

Ich bin mir bewusst, dass eine falsche Erklärung rechtliche Folgen haben wird.

Hamburg 10.04.2018