

## Reinforcement ability of lignocellulosic components in biocomposites and their 3D printed applications – A review

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### ABSTRACT

Biocomposites based on lignocellulosic components (e.g. pulp fibers, nanocellulose and lignin) are of interest as sustainable replacements for thermoplastic fossil-based materials, which find their application in household items, construction, automotive, 3D-printing, etc. Nanocellulose, a nano-structural component of pulp fibers, is considered having potential as a high-performance reinforcement for bioplastics, due to its high aspect ratio and potentially strong mechanical properties. Lignin, a biodegradable polymer isolated from pulp fibers, can be considered as an essential bioresource for the production of biocomposites, due to the aromatic structure and functional groups. In this review the reinforcing ability of selected lignocellulosic components and their applicability in 3D printing is presented, considering their mechanical properties. At this point, there are challenges in processing nanocellulose that may reduce its attractiveness as a reinforcement in thermoplastic biocomposites. The objective of the review is to identify current challenges and opportunities for the application of 3D printed lignocellulosic biocomposites. Optimization of 3D printing process parameters are considered to be a key to further improve the mechanical properties of the end-product. Importantly, this review revealed that greater efforts in mechanical fatigue research may contribute to assess and improve the potential of lignocellulosic reinforcements for structural applications.

### 1. Introduction

The utilization of lignocellulosic fibers and their nanomaterials has gained major interest during the last years. Lignocellulosic fibers and nanocelluloses have been proposed as reinforcement in bioplastics [1–5]. Particularly, nanocelluloses have been considered as promising candidates for bionanocomposites, based on several characteristics such as mechanical properties (tensile strength and stiffness), low weight and biodegradability [6]. In this review, bioplastics are considered as thermoplastic materials derived from biomass, e.g. poly-lactic acid (PLA), bio-based polyethylene (BioPE), bio-based polypropylene (BioPP), and poly-hydroxyalkanoates (PHA). For a detailed overview of bioplastic production see e.g. Brodin et al. [5].

A composite can be defined as a material composed of two or more components having distinct morphology and chemistry, and giving synergetic effects. Additionally, the term biocomposite also refers to materials having at least one bio-component (e.g. bioplastic, lignocellulosic pulp fibers, lignin or cellulose nanofibrils (CNFs)). One of the reasons for combining nanocellulose and polymers is to improve the

mechanical properties of a given polymer, which strongly depend on the type and fraction of nanocellulose and the dispersion and adhesion between the matrix and the nanocellulose. In this respect, CNFs and cellulose nanocrystals (CNCs) have been proposed as most adequate materials, with excellent mechanical properties [7–9]. However, nanocellulose reinforcements have mostly shown modest improvement of strength in physical tensile tests of biocomposites [8,10–13]. Major challenges are inhomogeneous dispersion, poor interfacial adhesion, low thermal stability, kinking and curling under processing [8,11,13,14]. To overcome these issues, surface modifications and adjustments of melting and mixing processes have been proposed and will be briefly presented in the following sections [11,15,16]. There seems to be a knowledge gap concerning the challenges and benefits of using nanocellulose as reinforcement, compared to lignocellulosic fibers. Long-term investigations regarding mechanical fatigue of biocomposites are also of major importance, if materials are considered for structural applications. However, to the best of our knowledge, such studies are currently lacking in literature about biocomposites reinforced with nanocellulose.

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Three-dimensional (3D) printing as an application for biocomposites has been in focus for some years. Reviews have been written about several techniques for 3D printing, including fused deposition modelling, selective laser sintering, stereo-lithography and bio-plotting [17–20]. Some of the commercially available technologies that seem adequate for biocomposites containing short fibers, nanocelluloses and lignin are briefly described in Table 1. This includes the technology Fused Deposition Modelling (FDM), which will be focused on in the present review. In addition to Table 1, direct ink writing (DIW), inkjet printing, digital light processing (DLP) and laminated object manufacturing (LOM) can also be used to 3D print bio-derived materials [21]. These methods are not considered in this review, since the focus is placed on thermoplastic biocomposites for structural applications. However, further information on several 3D printing techniques, suitable for biocomposites, can be found in [11,20,21].

The present work reviews the latest advances in research and development of biocomposites containing lignocellulosic fibers, lignin and nanocelluloses with a special focus on 3D printing of the corresponding biocomposites. Firstly, a general overview of lignocellulosic pulp fibers, nanocelluloses and lignin will be given. Secondly, the potential of analytical modelling for predicting the mechanical tensile properties of biocomposites will be discussed. Thirdly, the applicability of lignocellulosic materials for reinforcing bioplastics will be explored, with a critical focus on the potential of nanocellulose as reinforcement for bioplastics, compared to lignocellulosic pulp fibers. Finally, mechanical fatigue characteristics of biocomposites will be discussed, considering its importance on structural applications.

## 2. Lignocellulosic components in biocomposites

Exploitation of the full potential of lignocellulosic fibers as reinforcement of bioplastics depends on uniform fiber distribution and sufficient stress transfer between fibers and matrix. These aspects are addressed by modification of the fiber surface, modification of the matrix and development of adequate processing methods. The strength of a biocomposite will always be limited by its weakest point. Hence, care has to be taken not to weaken or damage the reinforcing fibers during modification and processing, as may be the case during thermoplastic processing, such as e.g. melt blending, extruding, pelleting [30].

### 2.1. Lignocellulosic fibers

The interest for lignocellulosic-based biocomposites has increased over the last years due to environmental concerns. In addition, biocomposites could potentially obtain better mechanical strength and stiffness properties if the reinforcement has a greater length-to-diameter

ratio (aspect ratio). Since lignocellulosic fibers have a higher aspect ratio than lignocellulosic particles, these fibers have been extensively studied for their utility as biocomposite components [1,3,31]. They are well implemented as a reinforcement for bioplastics and contribute some beneficial properties, e.g. higher stiffness, strength increment, weight reduction and cost reduction [32–34]. Lignocellulosic fibers can be of various origins including flax, hemp, jute, sisal, bamboo, wood, etc [35–38]. In this review the focus is placed on lignocellulosic wood fibers, as these have been widely used as reinforcement in biocomposite materials for several years. Wood is also the main source of lignin and nanocellulose [39,40].

There are various lignocellulosic pulp fibers that can be used to reinforce thermoplastics, e.g. Thermo-Mechanical Pulp (TMP), Chemi-thermo-mechanical pulp and chemical pulp fibers [1,3,41]. Depending on the pulping process, the pulp fibers differ greatly with respect to the fiber morphology and chemistry (Fig. 1).

TMP fibers are shorter, stiffer, have a lower aspect ratio and contain more lignin compared to chemical pulp fibers [41]. Peltola et al. [41] demonstrated that TMP fibers can offer a greater reinforcing potential for PLA than chemical pulp, due to lignin on the TMP fibers surface that might act as a compatibilizer. For PP and PE matrixes, the addition of TMP or chemi-thermo-mechanical pulp fibers together with maleic anhydride compatibilizers showed promising results regarding the reinforcement of polyolefins [1,43]. The polymeric matrix of biocomposites typically contains about 0–8 wt.% of coupling agent and 10–50 wt.% of fibers [43–45].

### 2.2. Nanocelluloses

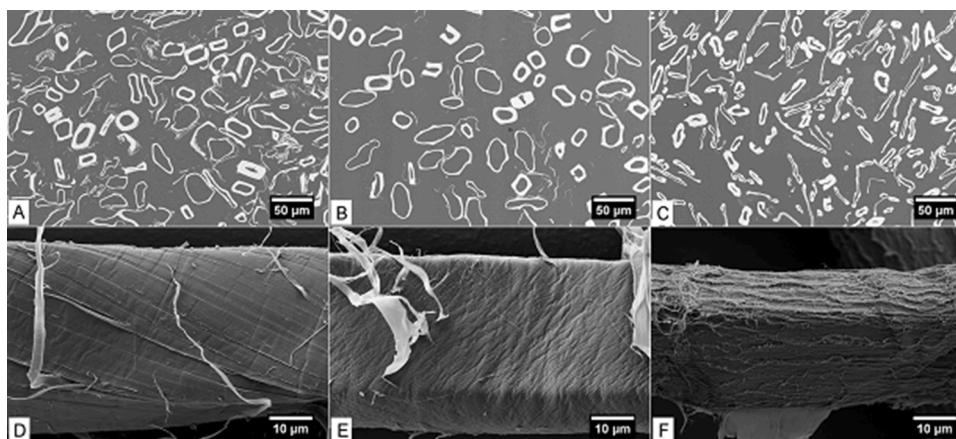
Cellulose is a structural component in plants, embedded in a polymeric matrix of lignin and complex sugars. Cellulose appears as a hierarchical structure of cellulose molecules which are linked to form elementary fibrils (Fig. 2). Fibrils in nanofiber size are named as cellulose nanofibrils (CNF, Fig. 3A and B). CNF are a composition of highly ordered cellulose nanocrystals (CNC, Fig. 3C) and amorphous parts [46].

Chemical pulping includes several processes to extract cellulose fibers by dissolving the lignocellulosic matrix [48]. Chemical pulp fibers have been one of the most used raw materials for production of nanocellulose, mainly based on two types of chemical pulping, i.e. sulphite and kraft pulping. For details on the chemical pulping see [49]. For more information about various methods applied to obtain different nanocelluloses see [50].

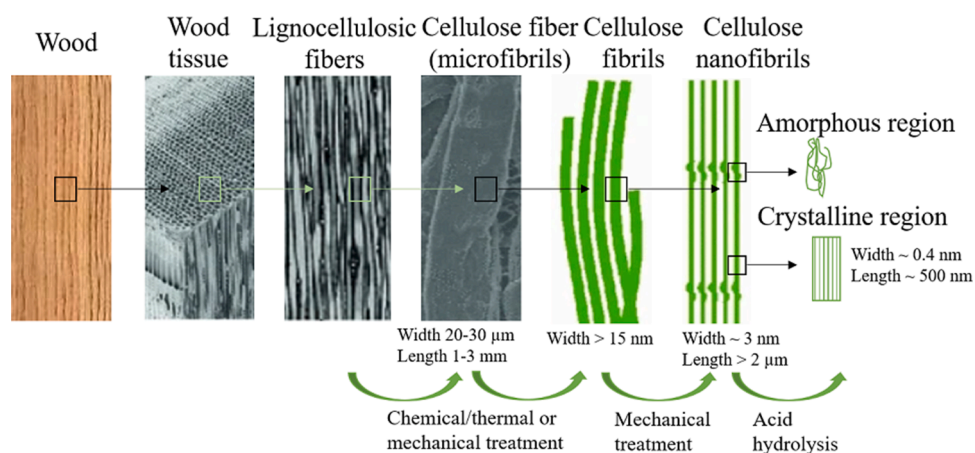
To obtain CNFs, a cellulose suspension can be treated mechanically through high-pressure homogenization, microfluidizers [51], grinding [52], ball milling, ultra-sonication [53] and cryocrushing [54, 55]. Producing mechanical CNFs (Fig. 3A) requires high amounts of energy

**Table 1**  
3D printing techniques for biocomposites

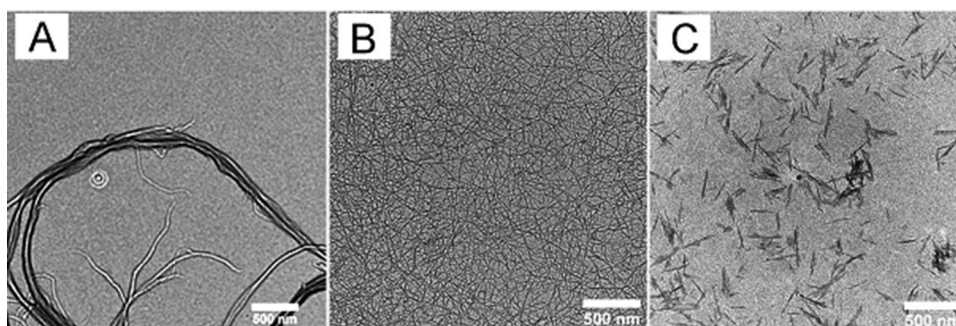
3D printing technique	Materials	Principle	Advantages	Disadvantages
Fused deposition modelling (FDM)	Lignocellulosic fibers and fillers in thermoplastic filaments (10–40 wt.%) [22]	Melted filament is extruded through a nozzle and deposited layer-wise on a heated table [22]	<ul style="list-style-type: none"> <li>- Affordable</li> <li>- Accessible/ simple</li> <li>- Rapid prototyping</li> <li>- Multi material capability [23,24]</li> </ul>	<ul style="list-style-type: none"> <li>- Poor quality/ warping and shrinking</li> <li>- Relatively slow</li> <li>- Limited for large unsupported sections or sharp external corners [20,24,25]</li> </ul>
Selective laser sintering (SLS)	Lignocellulosic fillers blended with thermoplastic powder (5–10 wt.%) [26, 27]	Laser fuses powder particles to impose a selective fused pattern on a powdered surface [26]	<ul style="list-style-type: none"> <li>- Complex geometries possible (no support required)</li> <li>- Ability to process multiple materials in one bed</li> <li>- High accuracy [20,24]</li> <li>- Smooth surface finish</li> <li>- High accuracy</li> <li>- Wide range of materials [24,29]</li> </ul>	<ul style="list-style-type: none"> <li>- Expensive (high machine costs and requires special knowledge)</li> <li>- Requires large amount of material</li> <li>- Slow (long cooling time and cleaning process) [20,24,25]</li> </ul>
Stereolithography (SLA)	UV-resin filled with nanoclay, nanocellulose crystals [28]	- Resin is cured layer by layer via UV-light [28]	<ul style="list-style-type: none"> <li>- High accuracy [20,24]</li> <li>- Smooth surface finish</li> <li>- High accuracy</li> <li>- Wide range of materials [24,29]</li> </ul>	<ul style="list-style-type: none"> <li>- Supports are required</li> <li>- Post-processing to remove supports</li> <li>- Eventually post curing required</li> <li>- Poor mechanical properties [24,25,28]</li> </ul>



**Fig. 1.** Transversal (upper panel) and longitudinal (lower panel) SEM images of lignocellulosic pulp fibers. A) and D) thermo-mechanical pulp fibers. B) and E) chemi-thermomechanical pulp fibers. C) and F) chemical pulp fibers. Reproduced with permission from Jhon Wiley and Sons [[42], P.212], license number: 5006530754958. Copyright (2009) John Wiley & Sons, Inc.



**Fig. 2.** Hierarchical structure from lignocellulose to crystalline nanocellulose. Reproduced and modified from Springer-Verlag ([47], P.450), no permission required. Copyright (2013) The Japan Wood Research Society.



**Fig. 3.** Transmission electron microscopy images of some typical nanocelluloses. (A) Mechanical grade CNF. (B) TEMPO mediated oxidized CNF. (C) CNC. Reproduced and modified with permission from American Chemical Society [65]. Copyright (2014) American Chemical Society.

(over 25 000 kWh per ton of CNFs obtained from high-pressure homogenization) [56,57]. Therefore, enzymatic [51] and chemical [58] pre-treatments (e.g. TEMPO mediated oxidation, (Fig. 3B)) have been implemented to reduce energy consumption. However, the TEMPO process involves chemicals which may be harmful to the environment, if not treated adequately [56,57]. The result after TEMPO mediated oxidation is highly homogeneous CNF (widths of 3.5 nm), which is composed of crystalline and amorphous zones [58]. Alternatively, cellulose fibers can directly be the source of CNC by applying acid

hydrolysis, enzymatic hydrolysis or ion liquid methods to remove the amorphous zones and obtain highly crystalline nano-objects (Fig. 3C) [55–57].

CNFs have typical diameters in the nanometre scale (<100 nm) and lengths in the micrometre scale [58–61]. CNFs produced without chemical pre-treatment are relatively coarse (Fig. 3A). Chemical pre-treatments facilitate the production of structurally homogeneous nanofibrils (Fig. 3B). The morphology and surface chemistry can be widely tailored with chemical and enzymatic pre-treatments, as well as

with processing variables (Fig. 3) [58–64].

As an example, for the mechanical properties of lignocellulosic fibers and nanocellulose, measured and theoretically estimated strength and stiffness values, collected from literature, are presented in Table 2. Additional tensile strength and stiffness values of natural fibers can be found in [31,66].

However, caution has to be taken when interpreting mechanical tensile properties obtained from theoretical estimations and numerical simulations, since these are based on individual nanofibrils with optimum physical characteristics [67,69,70], which seems to be difficult to obtain and use in current processing conditions. In theory, nanofibrils offer a much better reinforcing ability than lignocellulosic fibers (Table 2). This is due to the high aspect ratio of nanofibrils [74]. To make use of these properties in a biocomposite, coupling agents must be added to ensure sufficient interaction between fibrils or fibers and the matrix. Uniform dispersion is equally important for obtaining an entire wetting of each individual fiber with matrix material.

It has been expected, that nanocellulose with a suitable morphology and nanofibrillation degree and an adequate surface chemistry would be beneficial for improving the mechanical properties of a given biocomposite material. However, the full utilization of nanocellulose mechanical properties as reinforcing component in biocomposites has been demanding and is still challenging and uncertain, mainly due to challenges such as dewatering without causing agglomeration of the nanomaterials and the implied production costs [67,74]. The agglomeration of nanofibers due to dewatering/drying may impair the dispersion of the material in the polymer matrix and most probably limit the reinforcing potential.

### 2.3. Lignin

In the last years, research on biomass valorisation has focused on pre-treatment processes that yield fermentable sugars for bioethanol production, while lignin (Fig. 4) has been collected as a low value by-product and used for cogeneration of heat and electricity [75–78]. Each year, over 50 million tons of lignin are produced worldwide as a biorefinery side-product, of which 98% are burned to generate energy. Only 2% is currently used for other purposes, mainly in applications such as dispersants, adhesives, and fillers [75–78].

Recent studies have demonstrated that lignin, a currently underutilized renewable aromatic polymer can be incorporated into biocomposite products, both as a filler or as a polymer matrix [79–81]. However, there are some challenges that require attention in order to facilitate the utilization of lignin in high-value products, e.g. lignin extraction and isolation method and complex lignin structure for given

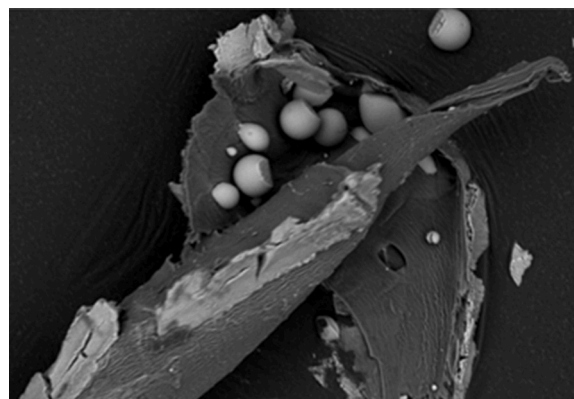


Fig. 4. Lignin particles precipitated on lignocellulosic fibers. The lignin particles appear bright compared to the grey-colored lignocellulosic pulp fiber surface. Image: Per Olav Johnsen, RISE PFI AS.

applications [82]. Attempts to use lignin in thermoplastics have resulted in applying lignin as a filler (up to 40 wt.%), however without providing mechanical improvement [39,78,79]. The adequate and sustainable modification of lignin to be used as thermoplastic matrix seems to remain as an interesting challenge. This could make it possible to produce thermoplastic wood-based biocomposites, i.e. fiber- or nanocellulose-reinforced lignin materials.

The raw material and the fractionation method determine the reactivity of lignin, which is represented by the occurrence of hydroxyl and aromatic functional groups. Lignin tends to depolymerize and re-polymerize with itself, leading to formation of additional C-C linkages. As a result, the number of hydroxyl groups is reduced and the molecular weight is increased. The formation of C-C linkages can also reduce the possibilities for further functionalization, which is important to make lignin compatible with other thermoplastics or fibers. Therefore, controlling the condensation and re-polymerization reactions is important in lignin valorisation, e.g. application of lignin in biocomposite products. Moreover, chemical functionalization of lignin is often a necessity to introduce new functional groups compatible with the final material. Different (chemical) reactants have been described in the literature to functionalize lignin towards different properties [76,83]. Modification of the aliphatic and aromatic hydroxyl groups of lignin via esterification is a typical approach [84].

### 3. Dispersion of lignocellulosic components in thermoplastic polymers

Uniform dispersion of fibers, nanofibers and lignin in thermoplastic biopolymers (e.g. PLA, BioPE, Poly-Butylene Succinate (PBS), acrylonitrile-butadiene-styrene (ABS)) is required to ensure sufficient component interaction and desired biocomposite properties. One major challenge in dispersion processes is to avoid agglomeration, caused by e.g. fiber-fiber interaction, fiber entanglement and the non-compatibility between hydrophilic fibers and hydrophobic matrixes [85].

To disperse lignocellulosic fibers in a bioplastic matrix, one common procedure is to mix dry polymer and compatibilizer powder first and then add fibers. Fibers may be pretreated by chemical and/or mechanical procedures to functionalize them. Since lignocellulosic fibers are water absorbents, it can be necessary to dry them before processing. The dried and mixed biocomposite powder can either be fed directly into a melt extruder, or processed into pellets beforehand by melt compounding, pressing and chopping. Through melting and mechanical shearing inside the extruder, the mixture will be further compounded. The steps of pelleting and melt extrusion can be repeated several times, but it should be considered that fiber damage occurs during this procedure [86–88].

The extrusion temperature, speed, mixing elements, repetitions of

Table 2

Theoretically estimated or measured values of tensile strength and stiffness for nanocellulose films, nanofibrils and other lignocellulosic fiber, collected from literature

	Tensile strength [MPa]	Tensile stiffness [GPa]
Nanocellulose films obtained through high-pressure homogenization (measured)	> 200 [67,68]	> 10 [67,68]
Nanofibrils obtained through high-pressure homogenization and acid hydrolysis (estimated)	300–22000 [67]	60 – 300 [2, 67,69,70]
Spruce lignocellulosic fiber obtained through kraft pulping (measured/estimated)	500–1700 [71, 72]	40 [32]
Birch lignocellulosic fiber obtained through sulphite pulping	300–1500	30–80 [35]
Cotton	287–800	6–13 [35, 36]
Flax	344–1500	26–80 [35, 36]
Hemp	389–690	35 [35]
Sisal	287–913	9–28 [35, 36]
Bamboo	450–800	11–35 [73]

compounding and the pretreatment of the raw materials can be varied in order to achieve a given biocomposite quality. Different mixing elements e.g. kneading blocks, conveying elements or tooth mixing elements are connected in series to accomplish certain objectives [89]. Lignocellulosic fibers start degrading above 200°C, whereas lignin has a broader degradation temperature range (200–500°C) [90]. Therefore, it is recommended to maintain a melting temperature that does not exceed this temperature range [88]. In general, the fibers orient according to the flow direction when extruding the biocomposite into a mold. The mold flow can be influenced by temperature, speed and mold geometry [91].

In [86] the authors investigated different dispersion processes for lignocellulosic fibers and polyethylene (PE). Drying the lignocellulosic fibers makes them brittle and fragile. That leads to fiber damage and shortening during the extrusion process. Wet lignocellulosic fibers are not that susceptible to damage development during extrusion, but they agglomerate and cannot be compounded properly. As shown in [86], the agglomeration of wet fibers provides the least increase of the flexural strength and modulus compared to neat PE. The greatest improvement of flexural strength was gained with dried and pelleted fibers. Thus, agglomeration of the fibers affects the mechanical properties of the biocomposite more negatively than fiber shortening.

Boran et al. [92] investigated the effect of different mixing strategies on the mechanical properties of cellulose and high-density polyethylene (HDPE). The authors concluded that the master batch method and extensional flow mixing provided reasonable dispersion [92].

Blending and dispersion of nanocelluloses in a bioplastic matrix is more demanding than for lignocellulosic pulp fibers. That is because the resulting product after deconstructing lignocellulose fibers to nanocellulose is usually a translucent and highly viscous dispersion of more than 95% water and nanocellulose fibrils [42,54]. The nanocellulose fibrils must be separated from water before mixing them with bioplastic polymer, which causes the nanocellulose fibrils to agglomerate, thus forming strong structures that are difficult to disperse in a bioplastic matrix. Dried lignocellulosic pulp fibers on the other side are relatively easy to disperse during melt-compounding in e.g. twin-screw extruders. Water affects a given biocomposite by i) causing fiber swelling, ii) affecting the dimensional stability, iii) disabling the fiber-matrix-interaction and iv) causing voids in the matrix [93–95]. In addition, some polymers (e.g. PLA) degrade in the presence of water [96–98].

Igarashi et al. [99] reported about a process the authors termed the “Pulp Direct-Kneading Method”. The process simultaneously fibrillates dried pulp into nanoscale fibers with a diameter of 10–100 nm and uniformly disperses the resulting CNFs in HDPE. The pulp fibers were previously modified by alkenyl succinic anhydride (ASA), which suppresses the hydrogen bonding between dried CNFs and afterwards kneaded in a melt extruder to fibrillate the fibers and disperse them in HDPE. The authors aim was to increase the attractiveness of CNFs for commercialization by the “Pulp Direct-Kneading Method” [99].

However, Wang et al. [100] pointed out that screw designs still need to be optimized to generate higher shear forces to obtain CNFs that are homogeneously dispersed in thermoplastic matrix and suitable for large-scale production. In addition, better understanding of the relations between extrusion parameters, such as e.g. temperature settings, screw speed, residence time, and dispersion of CNFs is required [100]. Bourmaud et al. [101] investigated the property changes of plant fibers (including lignocellulosic fibers) during processing of biocomposites and presented the importance of selecting suitable processing parameters to take full advantage of lignocellulosic fiber reinforcements.

Tanase et al. (2019) [79] demonstrated that PLA can be compounded with lignin and the biocomposites performed well in 3D printing operations. No sign of phase separation was observed and X-ray analysis revealed that lignin increased the crystallization, indicating that lignin acted as nucleating agent. However, lignin did not improve the mechanical properties of the biocomposite which suggests that an

additional reinforcement (e.g. lignocellulosic fibers) may be adequate for tailoring the mechanical performance [102–104].

#### 4. Compatibilizers and fiber surface treatments

The well-known poor interaction between lignocellulosic fibers and e.g. polyolefins, is related to the highly different polarities of the matrix (hydrophobic) and the lignocellulosic fibers (hydrophilic). Therefore, it is important to include coupling agents and/or fiber sizing, which compensates the polarity difference between fiber and matrix to improve the adhesive strength between the two phases and contribute to an even distribution of the fibers in the matrix.

Fibers can be modified physically to change their surface properties and enhance mechanical adhesion, or chemically to improve adhesion through chemical reactions. Physical treatments include corona, plasma and ultraviolet (UV). Chemical modifications include alkaline, silane [105–109], acetylation, oxidation, maleated coupling agents [110,111], grafting and others. More detailed information on fiber treatments can be found in [15].

Widely used coupling agents for lignocellulosic fibers and thermoplastic polymers are maleated coupling agents, for example maleated polypropylene (MAPP) or maleated polyethylene (MAPE) [112,113]. It is worth to mention that in most cases MAPE and MAPP are based on polyolefins derived from petroleum. However, recent developments have also introduced maleated polyolefins where the PE fraction was derived from biomass resources [114]. In addition, maleic anhydride can also be obtained from carbohydrates, e.g. from 5-hydroxymethylfurfural [115], which makes it possible to produce 100% bio-based compatibilizers.

As an alternative to chemical modifications, Filgueira et al. [116] focused on the enzymatic modification of thermo-mechanical pulp (TMP) fibers by grafting phenolic compounds, which rendered the TMP fibers hydrophobic and with better compatibility with the used PLA matrix. The authors demonstrated that the compatibilization with octyl gallate by enzymatic grafting improved the tensile strength and simultaneously reduced the water uptake of the biocomposite. Although a clear, positive fiber-reinforcing effect was demonstrated, the tensile strength of the 3D printed specimens with reinforcement was low. This was most probably due to the processing parameters selected for 3D printing.

Approaches to reduce hydrophilicity of lignocellulosic fiber and CNFs surfaces include the use of relatively simple methods that are usually applied to paper sizing, e.g. hydro-phobization with ASA or alkyl ketene dimers (AKD). Sato et al. (2016) [117] applied ASA to modify the surface of mechanically produced CNFs in order to improve the reinforcement potential of HDPE. The use of unmodified CNFs increased the tensile strength and modulus and the hydrophobized CNFs (18.8 wt.%) potentiated this effect, achieving strength and modulus levels of 43.4 MPa and 1.97 GPa, respectively. Lepetit et al. (2017) [118] confirmed this approach by modifying mechanically produced CNFs with ASA and testing the modified CNFs as reinforcement of low-density PE. The effect of the surface modification led to a significant increase of the tensile strength and modulus. Three main aspects can be drawn from this approach, i) the CNFs grade was a relatively coarse quality which avoid chemical pre-treatment and reduces production costs, ii) the modification can be performed in the wet state of the CNFs which may ease part of the processing and iii) mechanically produced CNFs (Fig.3A) seem to provide an acceptable level of mechanical improvement. However, it remains an open question whether the additional processing steps and energy, to produce the CNFs and compound with PE, are necessary considering that the reported levels of mechanical improvement can be achieved with more reasonable and abundant lignocellulosic pulp fibers, such as thermo-mechanical pulp fibers (see e.g. [119]).

Surface modification through acetylation of CNFs contributed to better dispersion of CNFs in PLA for low fiber loadings up to 0.5 wt.% - 5 wt.% [120]. However, no increment in tensile strength or modulus could

be achieved [121]. For decylamine-modified CNCs in PLA, similar outcomes were reported [122].

According to Olonisakin et al. [109] the currently most used surface modification techniques are silane treatments. Prior maceration of fiber by NaOH causes a rough surface, so that both chemical and mechanical adhesion is promoted. It was stated that a combination of adding compatibilizers to the matrix and treating the fiber with NaOH is an efficient way to compatibilize lignocellulosic fibers and bioplastics.

Lignin has also been proposed as coupling agent in biocomposite filaments [123]. The effect of esterified lignin was comparable to the commercial coupling agent used in these experiments. According to the authors, the lignin esterified with maleic anhydride provided the best specific tensile strength of biocomposite filaments (7.71 MPa), which was comparable to a commercial coupling agent (7.68 MPa). However, the effect of lignin, based on the provided data, has to be taken with care as the significance of the strength effect is small with regard to the scattering of the measurements. In addition, the reported tensile strength values are considerably lower than the expected, considering the commercial PLA used in the study (~4 MPa – value reported in the study vs. 48 MPa – value provided by NatureWorks® Ingeo™ 3051D).

## 5. Analytical modelling for tailoring the mechanical performance of biocomposites

This section shall provide a brief overview about micromechanics of biocomposites, to offer the reader a well-founded background on the mechanical interaction between the previously mentioned components. Analytical methods can be used to estimate and determine the required raw material properties that are necessary for targeted biocomposite tensile properties or to verify the interfacial interaction between fiber and matrix [119]. For predicting tensile strength and modulus of composite materials in general, the rule of mixture is a common assumption [124,125].

Lignocellulosic fibers are not available as endless, continuous filaments. The length of lignocellulosic plant fibers usually ranges between 1–35 mm and their diameter between 15–30  $\mu\text{m}$  [33]. However, the length also depends on the origin [60] and might be reduced during processing, e.g. compounding [30,126,127]. Furthermore, they can be classified, according to their length, as short fibers (1–5 mm) or long fibers (5–50 mm) [30,33,128].

Lignocellulosic-short-fiber biocomposites can be considered as isotropic, if the fiber orientation is completely random [91]. In composites, external loads are applied to the matrix and transferred to the fibers through the fiber ends and the cylindrical surface close to the ends. The critical-fiber-length of a fiber in a matrix can be regarded as the minimum length in which the maximum fiber strength  $\sigma_{f,max}$  can be achieved. The critical-fiber-length  $l_c$  is given by the following equation [91]:

$$\frac{l_c}{d} = \frac{\sigma_{f,max}}{2\tau_y} \quad (5.1)$$

In equation (5.1)  $d$  describes the fiber diameter and  $\tau_y$  is the matrix yield strength in shear, which can be set as equal to the interface shear strength along the fiber length, assuming perfect bonding between fiber and matrix. Through single-fiber pull-out tests the actual interfacial shear strength (IFSS value) can be determined by dividing the load at debonding of fiber and matrix by the shell surface of the fiber [129–131]. Lignocellulosic fibers embedded in a thermoplastic matrix usually result in IFSS values between 3 MPa and 25 MPa [132–136]. Other test methods to determine the interfacial shear strength between fiber and matrix are the single-fiber push-out [137], micro-bonding [133,138] or micro-debonding [139,140] tests. If the fiber length of the lignocellulosic short-fibers is much longer than the load-transfer-length, the biocomposite can be regarded as a continuous-fiber biocomposite [91].

Typical fiber lengths and diameters of lignocellulosic fibers, considered in this review, are presented in Table 3. In addition, a

**Table 3**

Comparison of lignocellulosic fiber types and comparison of a critical-fiber-length for one specific case.

Fiber type	Fiber diameter	Fiber length before compounding	Fiber length after compounding	Theoretically calculated critical-fiber-length
Lignocellulosic fibers	15–30 $\mu\text{m}$ [33]	1–5 mm [47]	~ 500 $\mu\text{m}$ [30, 119, 141]	400–1500 $\mu\text{m}$ (referred to the fiber length after compounding)
Mechanically/enzymatically treated CNF	20–100 nm [142]	> 10 $\mu\text{m}$ [142]	-	0.6–18 $\mu\text{m}$
TEMPO treated CNF	3–5 nm [143]	200–1100 nm [61]	-	282–882 nm
CNC	3–35 nm [143]	200–500 nm [143]	100 nm [144]	529–45300 nm

theoretically calculated critical-fiber-length is given, to compare it to the actual fiber lengths. Equation (5.1) was used to estimate the critical-fiber-length. For each fiber type the maximum fiber strength was taken from literature according to Table 2 [67,71,72]. BioPE was chosen as an exemplary matrix with a tensile strength of 18 MPa according to [119]. The shear strength at yield for BioPE can then be calculated by  $\tau = (\sqrt{2}/3) \cdot \sigma$  and results in  $\tau = 8.5$  MPa.

The calculated load-transfer-length of all fiber types is, in this assumption, equal to or much longer than their actual fiber length. These biocomposites are thus regarded as short-fiber biocomposites. Note that the calculated critical-fiber-length depends on the fiber strength and assumes a perfect bond between fiber and matrix. With weak fiber-matrix bonding, the reinforcement would thus be regarded in the form of particles rather than fibers.

Moreover, it is important to note that the lignocellulosic fiber lengths reported in Table 3 correspond to the lengths of the fibers after compounding. Compounding reduces the fiber length as demonstrated by [30,119,141]. In addition, one may expect that similar damage may apply for CNFs, meaning that they may be structurally modified after compounding [144]. This could be the case in particular with mechanically produced CNFs due to the coarse structure of the material.

Equation (5.1) further indicates, that the critical-fiber-length is proportional to the fiber diameter. Assuming the fiber has a circular profile, its dimensions can be described by the corresponding aspect ratio (fiber length divided by fiber diameter) [41]. According to equation (5.1), a higher fiber aspect ratio leads to more effective strengthening of the biocomposite until a critical value  $l_c/d$  is reached (see equations 5.1 and 5.3). For higher aspect ratios the strength remains approximately constant. However, this assumption does not cover effects of fiber orientation, homogeneous dispersion, fiber shape and interfacial interactions between fiber and matrix.

There are several micromechanical models for short-fiber biocomposites which extend laminate theory [124] by including interfacial adhesion (Hirsch's model), shape fitting factors (Halpin-Tsai model) or the shear-lag parameter (Cox) [145]. Narin [146] modified Cox's shear lag parameter by including the shear modulus of the fibers and an adhesion parameter to create better agreement with experimental values.

Another widely used model to predict the unidirectional tensile modulus  $E_1$  and strength  $\sigma_1$  of biocomposites is the modified rule of mixture (Equation (5.2)). An orientation factor  $x_1$  and a length and interface factor of the fibers  $x_2$  is added to the rule of mixture to cover effects caused by un-oriented short-fiber reinforcements [112, 145]:

$$E_1 = x_1 x_2 E_f V_f + E_m (1 - V_f) \quad (5.2)$$

$$\sigma_1 = x_1 x_2 \sigma_f V_f + \sigma_m (1 - V_f) \quad (5.3)$$

In equation (5.2) and (5.3) the longitudinal fiber tensile modulus and strength are described by  $E_f$  and  $\sigma_f$ . The matrix tensile modulus and strength are described by  $E_m$  and  $\sigma_m$ .  $V_f$  describes the fiber volume fraction in the biocomposite. The length-and-interface factor  $x_2$  is given by  $x_2 = l/(2 \cdot l_c)$  for fiber lengths  $l$  less than the critical fiber length  $l_c$ . If  $l$  is equal or greater than  $l_c$ ,  $x_2 = 1 - l_c/(2 \cdot l)$  [147]. The orientation factor  $x_1$  is assumed to be 0.167 for randomly aligned fibers in three dimensions, 0.334 for a random alignment in plane and 1.0 for unidirectional aligned fibers [148]. However, Sanadi [147] reported difficulties in determining an orientation factor due to the difference between the core- and skin-fiber-orientation, according to the melt flow. Furthermore, the topography of lignocellulosic fibers is quite uneven (Fig. 1) and also the fiber length and strength vary greatly.

Furthermore, equation (5.3) is only valid if the fiber strain is similar to the matrix strain. The biocomposites, considered in this review, consist of brittle reinforcing fibers and ductile matrixes. In that case the biocomposite strength  $\sigma_f$  should be lower than the strength of the neat biopolymer, if the fiber volume fraction is below a critical fiber volume fraction  $V_{f,crit} = \frac{\sigma_m - \sigma_m}{\sigma_f + (\sigma_m - \sigma_m)}$  [31,149]:

$$\sigma_1(V_f) = \begin{cases} \sigma_m(1 - V_f) & \text{for } 0 < V_f < V_{f, \min} \\ \sigma_f V_f + \sigma_m(1 - V_f) & \text{for } V_f < V_{f, \min} \end{cases} \quad (5.4)$$

In Equation (5.4),  $\sigma'_m$  is the matrix strength at the fiber failure strain and  $V_{f, \min} = \frac{\sigma_m - \sigma_m}{\sigma_f - \sigma_m}$  is the fiber volume fraction, at which the biocomposite should result in its minimum strength. At a volume fraction below  $V_{f,crit}$  the biocomposite can be regarded as a porous matrix, corresponding to the fiber fraction [149]. According to the Kelly-Tyson equation [150] the fiber strength  $\sigma_f$  is given by  $\sigma_f = (l \cdot \tau)/d$  for fibers shorter than  $l_c$  and  $\sigma'_f = \sigma_{uf}(1 - (\sigma_{uf} \cdot d)/(4 \cdot l \cdot \tau))$  for fibers equal or longer than  $l_c$ , with  $\sigma_{uf}$  is the ultimate tensile strength of the reinforcing fiber [150].

Since  $\sigma_{uf}$  and the orientation factor  $x_1$  are unknown, Bowyer and Bader proposed to assume that  $\sigma_{uf}$  equals the elastic modulus of the fibers times the strain of the composite [148]. They further assume that the orientation factor  $x_1$  is not strain-dependent and equal for all fibers [148]:

$$\sigma_1 = x_1 \cdot \left[ \sum \frac{l_i \cdot \tau}{d} V_{fi} + \sum E_f \cdot \epsilon_c \left(1 - \frac{E_f \cdot \epsilon_c \cdot d}{4 \cdot l_i \cdot \tau}\right) V_{fj} \right] + E_m \cdot \epsilon_c (1 - V_f) \quad (5.5)$$

In equation (5.5) the indices  $i$  are used for fiber fractions with a length less than  $l_c$  and  $j$  for fiber fractions with a length equal or greater than  $l_c$ . The values required to solve equation (5.4) must be obtained from a tensile test and by determining the fiber lengths experimentally. The detailed procedure is described in [148].

Several studies [112,151–153] show good agreements between analytical and experimental results by using the Bowyer-Bader assumption [148]. However, one must be aware of the effect of fiber agglomeration, which is still not considered and can increase the error of the equation (5.4), especially for higher fiber loadings.

Applying analytical models to CNF- or CNC-reinforced thermoplastic polymers turns out to be insufficient for predicting tensile strength and modulus due to inadequate dispersion, poor fiber matrix bonding and fiber agglomeration [4,154]. Further research on how to adjust the known micromechanical models to be applicable for CNF/CNC biocomposites is required.

## 6. Bionanocomposites – challenges and opportunities

Biocomposites containing nanocellulose are commonly referred to as bionanocomposites. There are several articles and reports about the potential of nanocellulose as a reinforcement for bionanocomposites [4, 12,47,155], stating their potentially high tensile stiffness and strength [57,67]. However, there are also some growing concerns as to whether nanocellulose is adequate as thermoplastic reinforcement in large quantities [13], which is understandable when aspects such as energy

consumption during production of nanofibers and the potential nanofiber agglomeration during compounding are taken into account.

Since lignocellulosic fibers exhibit high variations of properties related to disturbances during plant growth, climatic conditions, soil types, etc., the idea is to eliminate the fiber defects by deconstruction [69]. Various grinding and homogenization methods from sectors such as food processing, cosmetics or the pharmaceutical industry were used for the preparation of nanocellulose. The main issues with these methods are still that the fibers tend to entangle which can cause fiber damage, plugging of the processing equipment and a high energy consumption during production [47,69].

As described in Section 2.2, chemical pretreatments are necessary to facilitate the deconstruction of the fibers into homogeneous CNFs (Fig. 3B). When considering lignocellulosic pulp fibers in their largest scale as reinforcement for bioplastics, the previous mentioned chemical pretreatments are omitted. Obviously, this saves time, energy, equipment capacity and human resources.

Lignocellulosic pulp fibers also have a lower outer surface area per unit mass compared to nanocellulose. It thus seems more reasonable to consider surface modification on lignocellulosic pulp fibers than on nanocellulose. Less surface area requires less compatibilizer [13,155]. An extensive overview on how the size of cellulose-based reinforcements affects the mechanical properties of a given biocomposite has been provided by Hubbe and Grigsby [13]. The authors compared multiple recent studies dealing with the mechanical performance of cellulose reinforced HDPE to analyze the effect of fiber size on tensile stiffness and strength. They could not find a statistically significant relation between mechanical strength and fiber size, when considering all their collected data. In contrast they found a statistically significant increase of tensile modulus with increasing fiber length from 0.1 to 10 000  $\mu\text{m}$ . It was also shown that the compatibility between fiber and matrix tend to be a much more important factor, regarding tensile strength, than fiber size.

The use of CNFs in thermoplastic bionanocomposites requires to overcome various limitations. One specific challenge is to dry a CNF dispersion (commonly 1-5% in water) without causing agglomeration of the nanofibrils. Although, the relatively high temperatures applied in compounding and injection molding processes are adequate for lignocellulosic fibers ( $< 210^\circ\text{C}$ ), some CNF grades (e.g. TEMPO CNF) may be more exposed to thermal degradation [64], which may potentially limit the mechanical properties of biocomposites containing CNFs. These conditions lead to significant decrease of tensile strength and stiffness in the resulting bionanocomposite [47]. Such limitations should be a main driver in the development of new compounding processes which may facilitate the potential utilization of nanocellulose in relevant bionanocomposites.

One approach to improve the fiber alignment of CNFs is the so called wet-stretching method [14,156]. The wet-stretching method was developed for wet-spun CNFs for biomedical applications. After spinning a specific wet stretching device is used to increase the fiber alignment [156]. The stretching method was also successfully applied on melt spun poly(butylene succinate) and microfibrillated cellulose [157]. Stretching is generally adopted from classic polymer filament spinning methods, such as wet-, dry- or melt spinning. The filament is stretched by down-drawing to enable orientation of the polymer chains along the fiber axis [158].

An advantage for nanocellulose-based reinforcement may be offered by the use of relatively hydrophilic matrixes like epoxy resin or starch, since there is no need of any coupling agents or surface treatments to gain solid adhesion [13]. Hervy et al. [159] performed a life-cycle-analysis (LCA) for nanocellulose reinforced epoxy resin, neat PLA and 30 wt.% glass fiber reinforced polypropylene (GF/PP). The authors concluded that the production and biocomposite manufacturing of CNFs has a higher global warming potential (GWP) and a higher abiotic depletion potential of fossil fuels (ADf) than producing PLA or GF/PP composites. In terms of use phase and end-of-life it was found that only with a fiber loading of  $> 60$  vol.% the GWP and ADf of

CNF/epoxy can be lower than that of neat PLA [159]. However, it is particular that Hervy et al. [159] compared thermoplastics (PLA, GF/PP) and thermosets (CNF-reinforced epoxy), which are expected to cover different application areas. A relevant study would be to compare e.g. PLA, fiber-reinforced PLA and CNF-reinforced PLA and thus reveal the LCA performance of timely biocomposite materials. Additionally, studies that only take into account the production of CNFs and CNCs have shown that the use of chemicals during the pre-treatment process is the main contributing factor to the environmental impact [160,161].

## 7. 3D printing of lignocellulosic short-fiber reinforced bioplastics

Biocomposites can be produced with several methods, depending on quantity, size, design, application and the material to be processed. In addition to the material composition, the production process also affects the biocomposite properties. Biocomposite products are mainly manufactured through injection molding, compression molding, extrusion or 3D printing. The latter is the main focus of this review and will be explored further in the following.

### 7.1. Fused deposition modelling

For prototyping and/or implementation of challenging designs, 3D printing, such as FDM, is a time and resource saving production method for biocomposite products. FDM applies a heated nozzle to deposit thin threads (approx. diameter  $<400\ \mu\text{m}$ ) to construct 3D structures, layer by layer [162]. The dimensions of the layer height and width depend entirely on parameter selection based on nozzle size, printer and 3D slicer capability. This technique is the most affordable and widespread method within additive manufacturing [18].

The characteristics of FDM printed products depend on processing parameters, layer construction and filament properties. Adjustable processing parameters are the extrusion temperature (nozzle temperature), heating plate temperature, possibly heated enclosure (chamber) temperature, extrusion speed and layer height. The temperature settings are mainly referred to the matrix material, but the degradation temperature of lignocellulosic components (which starts at approx.  $200^\circ\text{C}$ ) is important to consider. The layer construction, including raster width, layer height orientation and gap size between the filament strands, are the main characteristics that affect the mechanical properties of printed parts [18]. The strand shape and gap size are adjustable through extrusion temperature, layer height and speed [163].

Fiber reinforcements in filaments can strengthen a 3D printed part but can in cases promote void formation due to inadequate fiber-matrix interphase and rough fiber surface [18]. A high-quality biocomposite-filament needs to be well compounded, can only contain a limited amount of fibers and a limited fiber size. Otherwise the melt viscosity will increase significantly which can lead to nozzle blockage. In addition, the filament may become relatively brittle, the quality of the surface finish gets worse and the dimensional accuracy can be reduced [22]. Commercial biocomposite filaments contain up to 40 wt.% fiber loading [163]. Increasing the fiber loading in FDM-filaments roughens the surface and increases the probability of void formation [164,165] and shape deviation, caused by irregular swelling or shrinking of lignocellulosic fibers [11,166]. Although, a recent study on nanocellulose reinforced PLA [12] revealed a great reduction of voids for CNF reinforced PLA (1 wt.%) compared to neat PLA. The authors attributed this realization to reduced filament swelling at the nozzle outlet.

Shrinkage and warping of FDM-printed parts are especially critical for highly crystalline polymers, such as PP. However, amorphous polymers, such as amorphous PLA and ABS are affected by warping. Warping is the dimensional change of a solidified 3D printed part, due to residual stresses induced through rapid cooling. In order to reduce warping in FDM 3D printing, process parameter optimization is essential. It has been found that warping of PLA-parts can be reduced significantly by

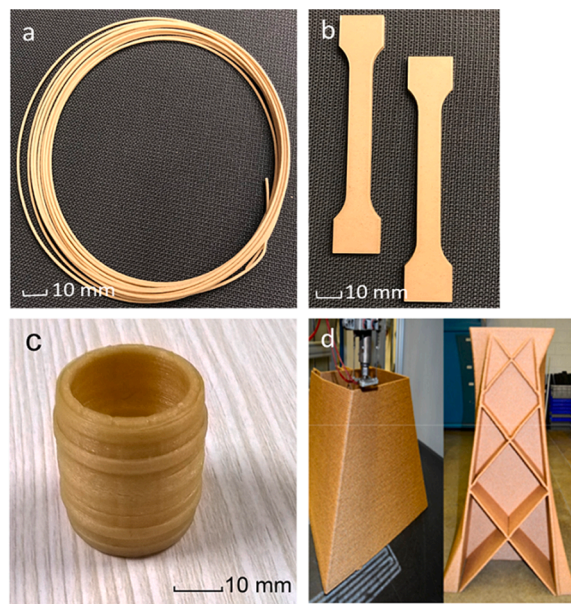
choosing a relatively high nozzle temperature ( $220^\circ\text{C}$ ) and printing speed (15 mm/s) [167]. It was further observed, that it is beneficial to choose a smoother corner geometry over sharp corners [168], a lower length to width ratio of the overall 3D printed part [169] and a greater layer thickness [170,171]. Warpage is also correlated with the thermal expansion coefficient, the difference between glass transition and heat chamber temperature [169]. Lignocellulosic fillers have also been reported to reduce warping [172]. This was attributed to an increase in viscosity [22,66,173,174]. In Fig. 5 an example of lignocellulosic-filled FDM-filament, tensile test specimens and printed structures are shown.

An FDM-part is generally a layout of melted filament strands, which is comparable to a composite made of lamina ply stocks. Due to imperfect bonding between the strands, the material strength is reduced in both building planes, in contrast to an injection or compression molded part [119]. For simple modelling purpose, the filament-material itself can be roughly described as isotropic, assuming fiber lengths less than the critical fiber length. The fibers are mainly oriented according to the extrusion direction [177]. However, the effect of porosity has a greater impact on tensile properties than fiber orientation [178]. The actual FDM-part can then be regarded as orthotropic [179].

### 7.2. Micromechanics of FDM-printed parts

The classical laminate theory [124] considers perfect bonding between each lamina, but FDM specimens are composites of imperfect bonded strands and voids. Therefore, the equations to calculate the elastic constants of a lamina [124] need to be adjusted. Based on the rule of mixture the elastic modulus of a unidirectional FDM-part, printed in flat build orientation [180] can be calculated by the following approaches listed in Table 4 [181]:

The elastic modulus of the filament material and the void densities must be measured experimentally. To calculate the void densities  $\rho_1$  and  $\rho_2$ , microscopic images of the x-y cross section of the unidirectional specimen need to be analyzed. The calculations assume pure geometric shapes (Fig. 6) [181]. The void density  $\rho_{\text{voids}}$  can be modelled based on a

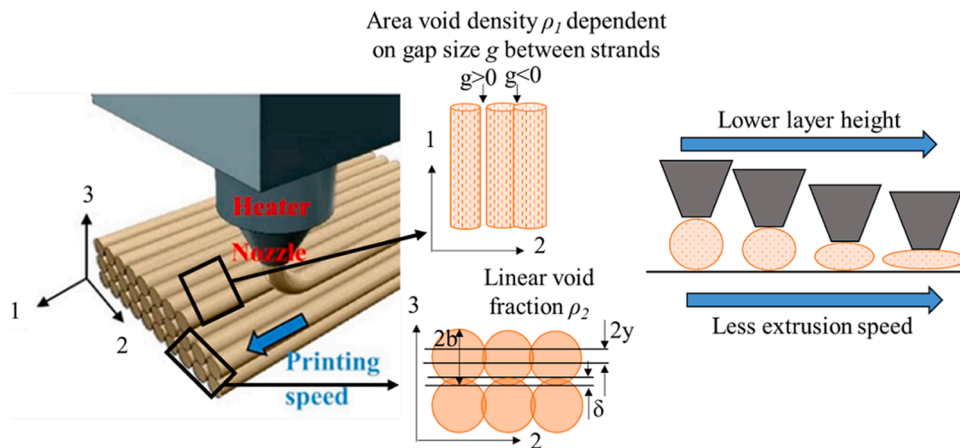


**Fig. 5.** Example of a lignocellulosic-filled FDM-filament. Image: Chiara Zarna, NTNU. (a), FDM-tensile-test-specimens. Image: Chiara Zarna, NTNU. (b), FDM-printed structure from lignocellulosic-filled/PLA-filament Reprinted from MDPI [175], P. 3]. Copyright (2017) by the authors. (c), building structures printed from poplar/PLA composite. Reprinted with permission from American Chemical Society [176], P. 4560]. Copyright (2019) American Chemical Society. (d).



**Table 4**  
Modelling approaches for analytical estimation of the elastic modulus of FDM printed parts

	Elastic modulus	Nomenclature	Deviation to experiment	Filament material
Longitudinal printing direction, applicable for unidirectional printing [0]	$E_{1,p} = (1 - \rho_1)E_F$ [181]	- $E_F$ : Elastic modulus of filament - $\rho_1$ : area void density, depended on gap size $g$ , calculated from experimental measurements (Fig. 6)	4%–16%	ABS
	$E_{long} = E_{01} (e^{(1-\rho_{voids})^{C_E Z}} - \rho_{voids}) + E_{02} \cdot (1 - \rho_{voids})$ ; for an infinite number of layers: $e^{(1-\rho_{voids})^{C_E Z}} = 1$ [182]	- $E_{01,02}$ : Elastic modulus of filament material in longitudinal and transverse direction - $\rho_{voids}$ : area void density - $C_E$ : Sensitivity parameter, needs to be calibrated from experimental results - $Z$ : Number of layers	< 14%	ABS
Transverse printing direction, applicable for unidirectional printing [90]	$E_{2,p} = \xi(1 - \rho_2)E_F$ [181]	- $\xi$ : Empirical factor between 0 and 1 which takes into account the bonding strength between the filaments - $\rho_2$ : Linear void fraction, $\rho_2=1-(2y)/(2b-\delta)$ , compare Fig. 6	~ 5%	ABS
Applicable for multiple printing lay-ups: [0], [0/90], [ $\pm 45$ ]	$E_{trans} = \xi E_{long}$ [182] $E_{Effective} = \frac{A_{11} \cdot A_{22} - A_{12}^2}{A_{22}}$ [183]	- $\xi$ : Empirical factor between 0 and 1 - $A_{ij}$ : Stiffness coefficient of extensional stiffness matrix [183], material parameter obtained from tensile tests on 3D printed parts	< 14 % [0]: 9%–15% [0/90]: 6% - 11% [ $\pm 45$ ]: 1%–20%	ABS PLA, PLA + carbon black
Applicable for multiple printing lay-ups: [0], [0/90], [15/-75], [30/-60] and [45/-45]	$E_{1,\theta} = \frac{1}{[A^{-1}]_{11} \cdot h}$ [181]	- $A$ : Extensional stiffness matrix [124] - $h$ : Thickness of FDM printed part - $\theta$ : printing angle (considered by stiffness matrix)	~ 3–7 %, compare Fig. 7	ABS

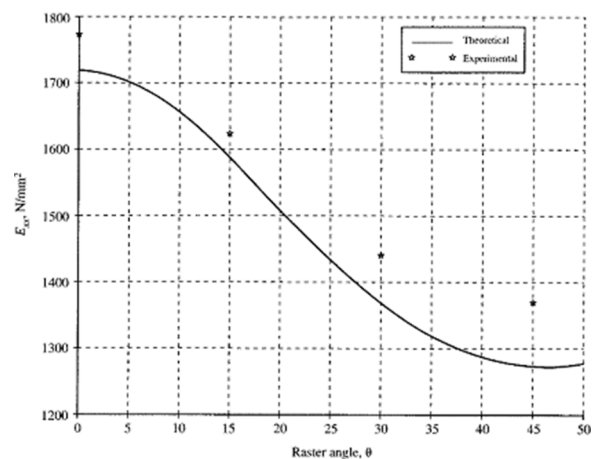


**Fig. 6.** Schematic illustration of an FDM-printed biocomposite part. Reprinted and modified from MDPI [163], P.3], no permission required. Copyright (2020) by the authors.

thermal model to predict the temperature evolution of the filament and a sintering model based on geometrical considerations. The temperature-dependent viscosity and surface tension of the filament material must be measured experimentally. More detailed information can be found in [182].

According to [182], the tensile strength of an FDM-part can be estimated in the same way as for the elastic modulus, using experimentally obtained material strength data and calibrated sensitivity parameters.

In [181] experiments and theoretical calculations were accomplished with FDM-parts printed in a [0], [0/90], [15/-75], [30/-60] and [45/-45] layup. Laminate theory was used to calculate the tensile modulus in longitudinal loading direction as a function of the printing angle  $\theta$ . In Fig. 7 the dependency of print direction on elastic modulus of 3D printed parts is shown. Laminate theory was also used in [183] to calculate the elastic modulus for different printing layups. In this study the lowest deviation, of ~1 % between model and experiment was found for a [45/-45] layup, using a PLA- or PLA + carbon black-filament. The highest deviation of ~11 % resulted from the unidirectional [0] layup. Additionally, a bi-material part, printed out of PLA and PLA+carbon black, showed an even higher deviation (< 20 %) between analytical model and experiment in a [45/-45] layup. This was attributed to



**Fig. 7.** Comparison between theoretical and experimental values of the elastic modulus at different angled FDM-specimens. Reprinted with permission from Elsevier [181], p. 139], license number: 4965541406639. Copyright (2002), Society of Manufacturing Engineers.

improper adhesion between PLA and PLA + carbon black.

No studies about analytical modeling of 3D printed lignocellulosic fiber reinforced biocomposites could be found, indicating a lack of research in this area. The models presented in Table 4, showed reasonable agreement with experimental results for pure polymer and PLA/carbon black composite FDM-filaments. Since void formation and irregular surface appearance is even more present in filaments containing lignocellulosic reinforcements [11,164,165], the error of the models might be comparatively greater.

### 7.3. Influence of printing parameters on tensile strength and modulus of lignocellulosic short-fiber biocomposites printed via FDM

Le Duigou et al. [162] presented the influence of gap size between the printing strands and set it in relation to the raster width. The authors showed that printing with less horizontal space between the strands, leads to a greater overlapping area and thus to higher tensile strength and modulus for both, a 0° and 90° printing layout.

Yang and Yeh [163] investigated the effect of extrusion speed on mechanical properties of FDM-printed wood fiber reinforced PLA. Lower extrusion speed with same layer height results in wider layer width. The smoothest surface and greatest overlapping between strands could be produced with the lowest investigated speed of 30 mm/s compared to 50 mm/s and 70 mm/s. The samples were all printed with a 0° layout which means the filament strands were aligned longitudinal to the test direction. This setup did not result in any significant change of tensile strength or modulus for different extrusion speed parameters. Showing, that in a 0° layout the porosity or void formation between the strands has almost no effect on tensile properties longitudinal to the printing direction. In contrast, compressive strength was significantly reduced (~34%) for samples printed with an extrusion speed of 70 mm/s, compared to 30 mm/s. This indicated the improved interaction between the printing strands at lower extrusion speed [163].

Several studies have shown that the overlapping or porosity of printing strands is the main influence parameter with respect to mechanical properties, apart from the layout construction. The porosity can be minimized through optimized extrusion temperature adapted to matrix and filler material [10,184,185], low extrusion speed [163], low raster width [162] and low layer height, resulting in greater layer width [66,185,186] (Fig. 6). Garzon-Hernandez et al. [182] identified the layer height as the main influencing factor on tensile properties. Through adjusting the layer height from 0.3 to 0.1 mm the void density decreased by more than 97 %.

Selected tensile properties of FDM-printed specimens made of different types of lignocellulosic biocomposites are presented in Table 5. Extensive overviews of filament types and tensile properties, including lignocellulosic fiber types for 3D printing have been presented in [21, 165,187,188].

Comparing the mechanical properties of 3D printed specimens for neat and reinforced PLA (presented in Table 5) it appears that neither tensile strength nor modulus have been improved when using fibrillated poplar [189] or lignin [79], as fillers. Using CNF to reinforce PLA increased the strength by ~24% [190] or even ~45% [10]. TMP fibers (20 wt.%) more than doubled the tensile strength and modulus of BioPE [119]. This seems to confirm the ability of wood fibers to reinforce bioplastics for 3D printing applications, compared to wood powder and lignin. Similar conclusions have been drawn by [165].

It can also be observed, that the improvement of almost 45% in tensile strength after adding 30 wt.% freeze-dried CNF to a PLA matrix, is strongly related to adjustments of the FDM-printing parameters. With the first printing setup, almost no tensile strength increment could be gained by increasing the CNF loading. After lowering the extrusion temperature from 215°C to 180°C, increasing the bed temperature from 93°C to 120°C and lowering the speed from 15 mm/s to 7.5 mm/s, a clear strength increment was achieved [10]. The influence of an optimized printing setup becomes obvious and leads to the assumption that

**Table 5**  
Examples of tensile properties of 3D printed biocomposites

Thermoplastic polymer	Biocomposite	Strength [MPa]	Stiffness [GPa]	Elong. at break [%]
PLA [189]	Neat PLA	60	2.9	6.3
	PLA/poplar wood powder (80/20) wt. %	50	3.6	1.6
	PLA/fibrillated poplar fiber (85/15) wt. %	32	2.6	1.5
PLA [190]	Neat PLA	~46	-	~3
	PLA/PEG/CNF (91/4/5) wt.%	~57	-	~4.5
PLA [10]	Neat PLA	~55	~3	~3
	PLA/CNF (70/30) wt.%	~80	~7	~1.5
PLA [79]	Neat PLA	58.5	2.9	2.5
	PLA/Lignin (60/40) wt.%	45.7	2.7	1.9
BioPE [119]	Neat BioPE	10	0.7	10
	BioPE/ lignocellulosic fiber (80/20) wt. %	30	1.5	5.5

important effects can be overlaid due to insufficient parameter configurations.

### 7.4. Stereolithography

Stereo-lithography (SLA) is a 3D printing technology based on photo-polymerization. A stereo-lithography resin was reinforced with CNC (0.5–10% w/w) for the prototyping of 3D objects [191]. The mechanical properties (e.g. tensile strength, young's modulus and flexural modulus) of the biocomposites increased modestly as the CNC content increased from 0.5 to 2%. Increasing the CNC content to 5% reduced the tensile strength and flexural modulus, potentially due to the formation of CNC aggregates that act as stress concentrators. Photo-polymerization is an attractive 3D printing technology that may be adequate for nanofibers and lignin. Potentially these components may be valuable reinforcement and filler candidates provided that the materials can be mixed with the photo-curable ink components.

### 7.5. Selective laser sintering

In Selective Laser Sintering (SLS) polymer powder is spread in a bed and a selected cross-sectional area is sintered or melted through a laser and forms a solid layer.

Lignocellulosic fiber – thermoplastic SLS parts have low mechanical strength, up to 5 MPa in tensile strength without post-processing and 6–11 MPa with wax-, or epoxy-infiltration [192-194]. To address this issue, a prosopis chilensis wood powder/poly-ethersulfone biocomposite formulation was proposed by [194]. An addition of 10% wood powder to poly-ethersulfone powder was found to be the optimum, regarding bending and tensile strength. In addition, the dimensional accuracy was improved through the filler material.

Lignin has also been introduced as a filler material in SLS to safe costs while maintaining or improving processability [195]. Including lignin in a polyamide (PA) matrix resulted in higher porosity and accordingly a higher elastic modulus and lower tensile strength compared to neat PA. The effect of lignin on the tensile strength and modulus was related to differences in surface roughness and surface energy. However, lignin also enhanced the thermal stability and wettability (for 90° print orientation) of the structure. The wettability was attributed to higher surface roughness, caused by the addition of lignin.

### 7.6. Applications for 3D printed lignocellulosic biocomposites

Biocomposites are widely applied for structural and nonstructural products, for example in building industry, automotive industry and household items [34,196–198]. As applications for CNF-based bionanocomposites the paper industry, packaging industry and medical applications are often mentioned in literature [46,47,155,199].

Presently, there are no known structural applications for bionanocomposites in which CNFs have proven major advantages over lignocellulosic fibers. However, there are some interesting approaches for potential future applications like wind turbine blades [200] or car components [99]. An overview of recent studies on FDM and SLA polymeric input materials containing lignocellulosic components and their applications is provided in [187]. As mentioned above, processing of a given CNF reinforced bionanocomposite is limited by the high polarity and water content of the CNF dispersion. Therefore, water-soluble polymers are the most favorable systems for CNF-based bionanocomposites, so far [199].

However, the use of biocomposites, primarily composed of PLA as the bioplastic matrix, has gained attention as a filament for FDM, because of its degradability and ease of printing [165]. Advances on the manufacturing of PLA- biocomposite filaments for FDM have been reported, focusing on the appropriate fiber modification for increasing the adhesion to the PLA matrix [116]. Gauss et al. [21] stated in a recent review, that continues efforts have been taken to improve the mechanical and physical performance of PLA as matrix material for biocomposite FDM-filaments, since it is widely applicable and the best tensile performance of cellulose-reinforced biocomposites has been achieved by using PLA as a matrix.

As mentioned above, lignocellulosic material covers lignocellulosic powders, fibers, nanofibrils and lignin. These materials have varying properties, enabling a wide range of different type of 3D printed applications. There exist several published studies about the mechanical properties of 3D printed lignocellulosic biocomposites [11,22,79,116,119,189,201], but there are only a few about CNF [10,11,190,202] or CNC reinforced filaments for FDM [9,11,203]. Suggesting that structural applications for these nanomaterials are still uncertain. In addition, research on long-term behaviour, is currently missing. To assess the suitability of 3D printed lignocellulosic biocomposites for structural applications, studies on durability, fatigue and reproducibility could play a major role.

## 8. Fatigue of lignocellulosic biocomposites

When studying mechanical properties, the short-term quasi static strength and elastic properties tend to get most attention. However, for many applications the long-term performance is no less important and may be the critical design parameter. Many parameters can influence long-term performance, such as cyclic loading (fatigue), long-term static loads (stress rupture), swelling due to the absorption of fluids and chemical degradation. This paper will just describe one of these aspects, mechanical fatigue.

Fatigue of thermoplastics generally depends on loading rate and temperature as well as on the concentration of absorbed liquids such as water [204,205].

S-N curves (stress – number of fatigue cycle curves) are used to characterize fatigue test results and to predict the remaining fatigue life of a material. Originally S-N curves were presented as Woehler curves in the log-log scale as [206]:

$$\log \Delta \sigma = \log \Delta \sigma_0 + \alpha \cdot \log N_f \quad (8.1)$$

$\Delta \sigma$  is the stress amplitude and  $\Delta \sigma_0$  and  $\alpha$  are fit parameters. This presentation of fatigue data is used also today in many design codes. However, polymer and composite fatigue material data are often published as in the linear-log scale. A widely used model in composite fatigue is the following fatigue-life-relation [207]:

$$\sigma_{max} = \beta + \alpha \cdot \log N_f \quad (8.2)$$

In equation (8.2)  $\sigma_{max}$  describes the maximum applied stress,  $\beta$  and  $\alpha$  are curve fitting parameters and  $N_f$  is the number of cycles to failure. The S-N curve is only valid below the yield strength.

This model was used by Haque et al. [208] to analyze the fatigue behavior of PP reinforced with 50 wt.% lignocellulosic flour, 2.5 wt.% CNF and 2.5 wt.% maleic anhydride and peroxide (MAPO). The authors presented a S-N curve for a 95% survivability of neat PP and PP/lignocellulosic flour composites, as seen in Fig. 8.

In general, fiber-reinforced bio-composites offer higher fatigue strength than unreinforced plastics, because the reinforcement hinders the crack propagation in the matrix [208,209]. However, in Fig. 8 the slope of PP/lignocellulosic flour is steeper compared to neat PP. The graphs A-G refer to different temperatures ((120, 140, 160, 180)°C) and mixing time ((5, 10, 20) min.) during twin-screw extrusion of the PP/lignocellulosic flour/CNF/MAPP biocomposite. Furthermore, sample A was composed without MAPP. However, neither mixing temperature nor time variation showed a significant influence on the fatigue properties of the composites. It was also concluded that the effect of molecular degradation of PP, due to the addition of MAPP, had a higher influence on the fatigue properties of the composites compared with the compatibilizing effect of MAPP [208].

Due to the hygroscopic nature of lignocellulosic pulp fibers, the environmental conditions affect its dimensional stability and thus the fatigue behavior [210]. Several recent studies on fatigue behavior of lignocellulosic fiber-reinforced thermoplastic biocomposites can be found in the literature, comparing neat thermoplastics to biocomposites and studying the influence of coupling agents on the corresponding fatigue properties [208,211,212]. Fotouh [212] observed that after water absorption the S-N curve was shifted down on the fatigue-strength-axis about 4–7% compared to the dry composite.

In a recent study from Travieso-Rodriguez, et al. [213] the fatigue behavior of 3D printed lignocellulosic fiber reinforced PLA was investigated. The authors showed an experimental investigation of the influences of different manufacturing parameters. They concluded that the addition of lignocellulosic fibers increases voids between the filament layers and thus decreases their fatigue behavior. The mechanical fatigue properties of 3D printed parts are influenced by the same factors like under static loading: Printing parameters, material and reinforcement and layer construction [214].

Shanmugam et al. [214] presented a review about fatigue behavior

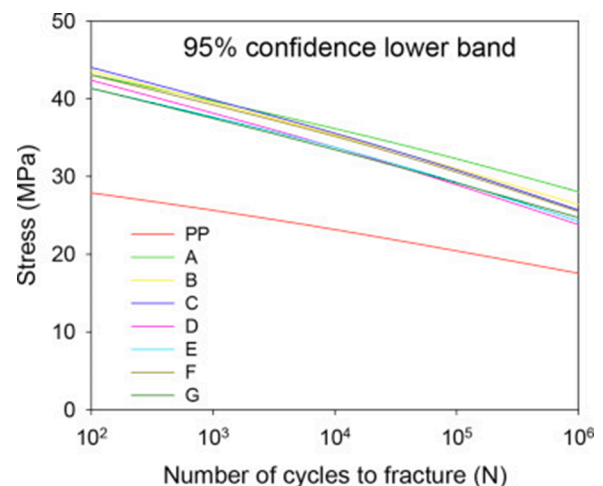


Fig. 8. S-N curve of 95% confidence band of experimental data of neat PP and PP/lignocellulosic flour composites (A-G), prepared under different mixing conditions. Reproduced with permission from Elsevier [[208], P.140], under creative commons license: <https://creativecommons.org/licenses/by-nc-nd/4.0/>. Copyright (2019), Kingfa SCI. & TECH. CO., LTD.

of FDM-3D printed polymeric composites. The authors aim was to evaluate 3D printed polymeric materials' fatigue properties and they emphasize that mechanical fatigue investigations play a major role for enabling the use of FDM-printed products in various structural and load-bearing applications. They further concluded that a  $+45^\circ/-45^\circ$  print layout yields to longer fatigue life for PLA-based materials and that process parameter optimizations (regarding void reduction and ink material characteristics) are of high importance for fatigue properties. When it comes to fiber reinforcements the authors indicated the fiber wettability, fiber fraction in the matrix, fiber dimension and properties as crucial factors for determining fatigue life. But also mentioned the lack of such investigations in literature [214]. This seems to apply to biocomposites in general [215].

Studies on the fatigue properties of CNF bionanocomposite materials also lack in literature, so far. Nonetheless, analyzing the fatigue properties are important to evaluate if there are feasible applications for thermoplastic CNF-based bionanocomposites. Since the fatigue properties of biocomposite are strongly dependent on the water absorbing ability of the lignocellulosic reinforcements [210,212] and the interfacial coupling between fiber and matrix, these dependencies might apply for CNF-based bionanocomposites as well.

An investigation of lignocellulosic fiber/PP biocomposites with different aspect ratios of fibers [216] showed, that a higher aspect ratio can lead to a slight improvement of the fatigue performance of the biocomposite. But the effect of aspect ratio on fatigue strength appeared to be quite low ( $< 5\%$  increased strength with  $\sim 44\%$  increased aspect ratio) [216]. However, water absorption of lignocellulosic fibers is a known issue regarding to their fatigue performance due to swelling and fiber-matrix de-bonding [212,217].

A deeper understanding of failure mechanism behind the static and dynamic loading condition of 3D printed lignocellulosic biocomposites can help to improve the durability and reliability of such products [214, 215]. Greater research effort is required in this field to drive forward the implementation of (3D printed) lignocellulosic biocomposites in structural applications. Liber-Kneć et al. [218] found accelerated fatigue testing to be a useful tool to recognize basics of fatigue behavior of lignocellulosic fiber reinforced thermoplastic biocomposites or for comparative studies.

## 9. Conclusions

This review focused on the reinforcing ability of lignocellulosic materials as a component of biocomposites and attempted to shed light on several perspectives in terms of applicability and production challenges. Furthermore, important background information about micro-mechanics of biocomposites was presented to contribute a wider perspective for the reader.

Lignocellulosic fibers are well implemented as a reinforcement for bioplastics and contribute with beneficial properties, such as e.g. higher stiffness and strength increment. Additionally, lignin has shown potential in combination with thermoplastics and may be a plausible addition to fiber and nanocellulose-based biocomposites. However, a main challenge remains to extract and isolate lignin with high purity and reactivity. Moreover, one must find adequate chemical and enzymatic functionalization method for lignin to be further used as a polymeric matrix in thermoplastic wood-based biocomposite materials.

Optimally shaped, individual cellulose nanofibers seem to offer great mechanical properties, according to theoretical estimations. However, the reinforcing ability of nanofibers undergoes a strong reduction during biocomposite production. The most critical factors in this context are agglomeration of the nanofibers and in some cases poor compatibility between nanofiber and matrix. Presently, both of these factors suggest that nanofibers have a limited reinforcing effect in bioplastics and are not well controllable and reproduceable, yet.

In 3D printing, inadequate parameter setups may greatly detract the reinforcing ability of lignocellulosic components. This review draws

attention to the deviation between theoretical estimations and physical test results, mainly caused by the poor consideration of fiber-matrix-interaction and strong impact through biocomposite processing on the resulting mechanical properties of the end-product.

Concluding, this review indicates that presently lignocellulosic pulp fibers may be more adequate as component of thermoplastic biocomposites than the corresponding cellulose nanofibers. In addition to their reinforcing properties, they require less production efforts and may perform better in LCA analysis compared to the corresponding nanofibers. This is expected to extend their applicability in a wide variety of industries such as construction, household items, interior design, and automotive. Further, investigations on durability and fatigue of lignocellulosic biocomposites are required. Understanding of production processes and their influence on the mechanical properties of biocomposites, appear to be of high importance to apply biocomposites in conversion processes such as extrusion, injection molding and 3D printing. In addition, a stronger focus on the development of energy-saving production processes could support the attractiveness of biocomposites for large-scale productions.

## Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

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