All-Cellulose Composites

Wood- or plant-based cellulose fibres have shown their potential as a reinforcement in composites for a relatively long time alongside the commonly used glass-fibre and carbon-fibre reinforcements. Whereas regular biocomposites suffer from fibre-matrix adhesion-related challenges, all-cellulose composites (ACCs) can overcome this problem by both matrix and reinforcement having the same or a similar chemical structure, which results in good interfacial compatibility. ACCs can provide an environmentally friendly alternative to conventional petrochemical-based materials since they are a type of single-polymer composites (SPCs) from biomass-derived cellulose, and as such, they are easily recyclable, and they originate from renewable sources.

1. Cellulose

1.1. Characteristics of Cellulose

In nature, cellulose is found in the cell walls of plants, including trees, and it has a vital role in providing mechanical strength and structural support [1]. Plant-based cellulose is accompanied by hemicellulose, lignin, pectin, and other substances [2]. Besides plants, certain bacteria, algae and fungi produce cellulose [3].

Cellulose is a linear homopolysaccharide consisting of β-D-glucopyranose units linked by glycosidic β(1–4) bonds. Each unit contains three hydroxyl groups. The long polymer chain has repeating elements, which have two anhydroglucose units (AGU) that form polymerized chain lengths of several thousand units [3]. Cellulose has an amphiphilic nature: the equatorial direction of a glucopyranose ring is hydrophilic, and the axial direction of the ring has a hydrophobic character (**Figure 1**). These characteristics play a significant role in hydrophilic and hydrophobic interactions between cellulose molecules and other compounds in water [4][5][6].
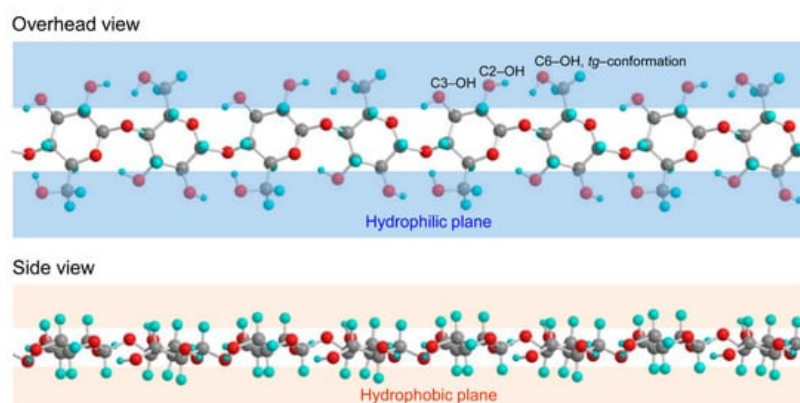

Figure 1. Hydrophilic and hydrophobic planes of cellulose marked with the primary C6-OH (with *tg*-conformation corresponding cellulose I crystalline structure), and secondary C2-OH and C3-OH groups in glucosyl unit. Reprinted with permission from [6].

Cellulose can be considered a semi-crystalline polymer with highly oriented crystalline domains coexisting with non-crystalline amorphous phases, which have a lower degree of order [7][8]. The cellulose crystalline domains have four major allomorphs (I, II, III and IV) based on molecular orientation. The most common allomorph found in nature is cellulose I and the most thermodynamically stable structure is established in cellulose II [3][9]. Cellulose I can have two sub-allomorphs, triclinic I^α and monoclinic I^β, which can be found alongside each other, and the ratio depends on the origin of the cellulose [3]. Cellulose I^α dominates in primitive organisms, such as algae and bacteria, while cellulose I^β is found mainly in higher plants [10] and aquatic animals, such as tunicates [11]. Cellulose II can be modified irreversibly from cellulose I through

alkaline treatment (mercerization) or by the cellulose dissolution process (regeneration) [3]. Cellulose III is obtained through liquid ammonia (NH^3), while cellulose IV is obtained through the heating of small crystallites in glycerol at 260 °C. Cellulose III can be reversibly formed from cellulose I, II or IV, and cellulose IV can be reversibly formed from cellulose I, II or III. The crystalline regions are strong, rigid, and quite inaccessible to water and most chemical reagents, whereas the amorphous regions are weaker and contribute to increased hydrophilicity and accessibility [11]. Physical, chemical, enzymatic or microbiological modifications of cellulose can lead to changes in its crystalline structure and result in new derivatives [12][13].

Cellulose has a strong capability to form intra- and intermolecular hydrogen bonds in its establishment network, and these internal hydrogen bonds hinder the free rotation of the glucopyranose rings, which increases the stiffness of the cellulose chains [14][15]. Although cellulose has the same structural motif in each material, its degree of polymerization (DP, the number of monomer units in the polymer) and crystallinity (degree of packing order) can vary greatly [16]. DP and crystallinity depend on the origin and treatment of the raw material [3]. Insights of the physical properties and morphological structure of single polymeric chain, such as chain length or degree of crystallization, can be investigated via X-ray, optical and electron-microscope imaging, or chemical and physical analysis methods [17].

1.2. Nanocellulose

The production of nanoscale cellulose has captured great attention due to its biodegradability, renewability, high mechanical properties and low density [18]. Nanocellulose, as a general term, applies to a wide range of nano- and micro-sized fibrils and crystalline particles (sometimes also referred to as whiskers). Different terminologies have been used for the various types and forms. Because of inconsistency in terminology, the Technical Association of the Pulp and Paper Industry (TAPPI) has proposed standard terms for various types of nanocellulose based on their size and form (**Table 1**). Nanocellulose can be processed from plant-derived cellulose, but it is also found natively in tunicates and bacteria. The feedstock used in nanocellulose manufacture is highly important, as it affects the properties and size of the extracted cellulose [11].

Table 1. Standardize terms for cellulose nanomaterials according (I) TAPPI/W123021 [11], and [II] cellulose nanomaterials review: structure, properties, and nanocomposite [19]. Each abbreviation have two alternatives. e.g., cellulose nanocrystal (CNC) and nanocrystalline cellulose (NCC).

NAME	ABBREVIATION	WIDTH	LENGTH	L/D RATIO
Cellulose nanocrystal	CNC (NCC)	(I) 3–10 nm (II) 3–20 nm	(II) 50–500 nm	(I) > 5
Cellulose nanofibril	CNF (NFC)	(I) 5–30 nm (II) 3–100 nm	(II) 0.5–2 µm	(I) > 50
Cellulose microcrystal	CMC (MCC)	(I) 10–15 µm (II) 10–50 µm	(II) 10–50 µm	(I) < 2
Cellulose microfibril	CMF (MFC)	(I) 10–100 nm (II) 10–100 nm	(I) 0.5–50 µm (II) 0.5–10's µm	

The biosynthesis of cellulose forms continuous microfibrils, which self-organises fibre bundles with crystalline and amorphous domains [20]. The term cellulose microfibrils (MFC) was first introduced in 1983 by Turbak et al. [21] when he and his co-workers developed a new method to prepare highly fibrillated cellulose from wood fibres by high-pressure homogenization treatment in water. The extraction of cellulose microfibrils require great precision in order to minimize damage to the fibrillary structure and to keep the long axial length of the microfibrils to preserve the large aspect ratio. The other native features of the cellulose, such as crystallinity and degree of polymerization, must also be secured [22]. An ideal production method should produce large amounts of high-quality material with low energy consumption. To meet these requirements, a number of pre-treatments can be used to improve the conversion efficiency. Different chemical, mechanical and enzymatic treatments are used for removal of non-cellulosic constituents and loosen the cell wall structure of the cellulose fibres to ease further processing [23].

Cellulose nanofibrils (CNFs), or their microfibril bundles, are typically produced using a variety of mechanical processes, including grinding/refining, high-pressure homogenization, cryocrushing, high-intensity ultrasonic treatments, electrospinning, steam explosion and microfluidization [19][24]. Chemical modification methods such as TEMPO mediated oxidation [25], ammonium persulfate oxidation [26], carboxymethylation [27] and cationization [28] have also emerged as promising methods for CNF production.

'Rod-like' cellulose microcrystals (MCC) and cellulose nanocrystals (CNC) can be obtained from different cellulosic sources such as wood, cotton, bacteria or tunicates with varied dimensions [29][30]. Their dimensions depend on the origin of the cellulose fibre or fibril and the employed conditions. Isolated nanoscale fibres or crystals from natural fibres show much higher strength and stiffness in comparison to the original source [18]. The elastic moduli of solid wood, single pulp fibre, microfibrils and crystallites have been measured at 10, 40, 70 and 250 GPa, respectively [31]. Cellulose nano- and micro-crystals can be produced from nano- and microfibrils by applying chemical treatments (mainly acid) or mechanical processes, which break hydrogen bonds in amorphous regions while crystalline domains remain untouched [32][33].

When producing nanocellulose, the drying process is a critical step. As cellulose is hydrophilic, hydrogen bonds can be formed during drying, leading to an irreversible agglomeration known as hornification [34]. This changes the size of nanocellulose, as well as its unique characteristics. The formation of additional hydrogen bonds correlates with the amount of water removed and does not depend directly on temperature [35][36]. A wide variety of drying methods, such as freeze drying, supercritical drying, atomization drying and spray drying, have been developed to prevent aggregation [24].

2. All-Cellulose Composites

2.1. Raw Materials for the ACC

Natural fibres are divided into three categories: plant fibres, animal fibres and mineral fibres (**Figure 5**). Plant fibres are the most used in conventional composite processing only as a reinforcement. All plant fibres contain cellulose, while animal fibres are made from proteins [37].
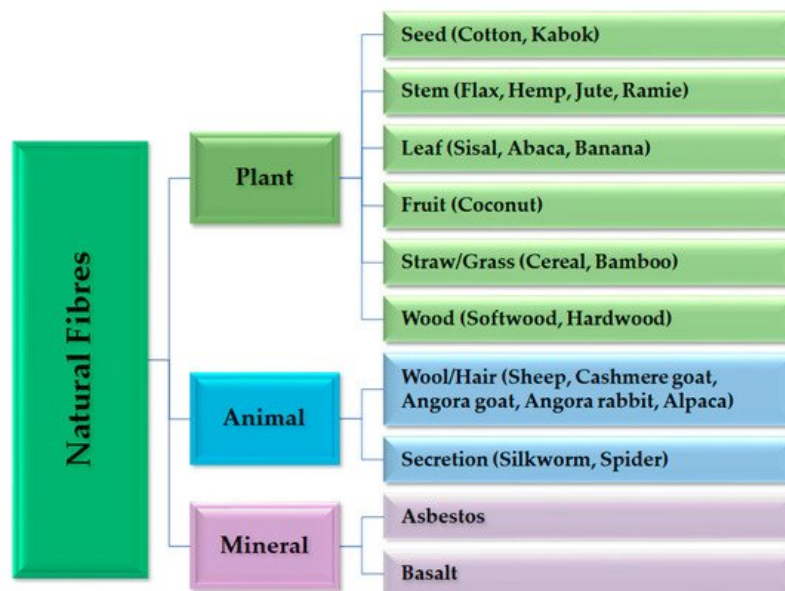

Figure 5. Classification of natural fibres with examples of their origin. This overview excludes nanosized cellulose fibrils and cellulose crystals that are found in bacteria and tunicates.

Plant-based cellulose is considered one of the most promising substitutes for petroleum-based raw materials [38]. The fibre structure and characteristics depend on and vary with the plant species, age, growth location, climate and part of the plant. Therefore, one of the main challenges with plant fibres is the large variation in their properties [11][39]. Fibres are extracted from trees using either chemical or mechanical methods. The characteristics of wood fibre depend somewhat on the processing method used, but mostly on the anatomy of the wood material in the particular tree species. Wood fibres can be divided into softwoods, such as spruce and pine, and hardwoods, such as birch and eucalyptus. Both can be used to create pulp or dissolving pulp. Dissolving pulp has a higher cellulose content and lower hemicellulose content compared to paper-grade pulp, and therefore it is used more commonly in upgraded and high-quality products. Two widely used commercial production methods for dissolving pulp are pre-hydrolysis kraft (PHK) and acid sulphite (AS) [40]. Pulp can also be produced from cellulosic waste with new innovative technologies [41][42].

Man-made cellulose fibres, such as viscose or lyocell, are developed from pulp or dissolving pulp. They are mainly used in the textile industry [43] but are also important materials used in composite manufacturing [44]. Textile-reinforced composites typically have high strength-to-weight and stiffness-to-weight ratios, which can improve the mechanical properties of the composites [45]. Cellulose-based textiles are renewable, but at the same time, textile industry as a whole (including the unsustainable cotton production) are one of the largest contributors to harmful environmental effects on

Earth, and it also generates large amounts of textile waste [46][47]. Therefore, the industry is searching for more sustainable plant-based fibres to meet the demands of current standards, where the focus is on waste reduction, production efficiency, durability, water saving, recycling and closed-loop production [47].

The frontrunner in the field of sustainable fibre production, Lensing AG, produces wood pulp-based fibres called EcoVero[TM], the production of which consumes less water and releases less emissions than generic viscose production, and their Tencel[TM] x Refibra[TM] fibre contributes to the circular economy by using an efficient closed-loop process [48][49]. Kuura-fiber is another new pulp-based wood fibre, which shares similar sustainable values, and it is currently on pilot scale production by Metsä Fibre in Äänekoski bioproduct mill, Finland [50]. Recycled textiles and agriculture waste are used in a fibre technology called Infinna[TM], created by the Infinited Fiber company [51], and recycled cotton fibres have been transformed into sustainable yarn by Haksa Textiles [52]. More recently, new types of wood fibre have been mechanically produced without using harmful chemicals or solvent systems. In Spinnova's innovative fibre process, the pulp is mechanically refined and transformed into spinning-ready fibre suspension without dissolution or regeneration [53].

These novel textile fibres offer versatile reinforcement choices for a more sustainable composite industry. Recently, biocomposites [54] and all-cellulose composites [55] have also been created using denim waste.

2.2. Biocomposites

Biocomposites have at least one of their constituents (either reinforcement or matrix) derived from biomass [56]. Already in the early 1940s Henry Ford created natural fibre reinforcement biocomposites using soy-based plastics to reduce the weight of the cars [57]. However, it was not until recently that bio-based automotive parts caught popularity among the car manufacturers due to increasing emission control and sustainability concerns [58].

The most commercially important biocomposites are made by combining man-made and biobased sources. Commonly, matrices are petrochemically derived thermoplastic polymers, such as polypropylene or polyamide, or thermoset polymers, such as unsaturated polyester or epoxy resins; meanwhile, the reinforcement is formed using a variety of biobased sources, such as natural cellulosic plant-based fibres or wood pulp [59][60]. The use of wood and plant fibres in composites is motivated not only by their sustainability characteristics, but also their good performance, low cost, low density, safe handling, high electrical resistance, good acoustic insulation and the fact that they do not require moulding equipment [61][62]. A major drawback of natural plant-based fibres compared to man-made fibres is the hydrophilic nature of cellulose. Water absorption by cellulose fibres can result in aging, poor mechanical properties and reduced dimensional stability of the composite. Plant fibres also naturally have poor fire resistance, and they degrade when heated to over 200 °C. They are also easily susceptible to biological degradation [39][62].

Nanocellulose, which is used as a raw material especially for ACNC, can be obtained by two approaches (i) top-down and (ii) bottom up. The top-down approach involves the disintegration of lignocellulosic biomass into nanoscale cellulose. In the bottom-up approach nanoscale cellulose can be produced via fermentation of low weight sugars by cellulose-producing bacteria, such as from the Acetobacter species. This type of nanoscale bacteria (BC) is pure cellulose and does not include hemicellulose, lignin, or pectin [63]. When cellulose-based composites are produced from less purified sources, such as wood pulps or other plant fibres, hemicellulose and lignin are always present to some degree, and these can act as impurities which often results impairing properties of the composite [64].

2.3. Matrix-Reinforcement Compatibility

Two main components forming a composite are the reinforcement and the matrix, where reinforcement gives strength and stiffness to the composite [65], and the matrix acts as a binder for the reinforcement and transfer external loads along the reinforcing fibres [39][66]. Compatibility between reinforcement and matrix depends on fibre dimensions, microstructure, and morphology; as well as the mechanical, physical, chemical, and thermal characteristics of the different constituents present in the interfacial zone. During composite manufacturing the changes in the constituent's properties or structure also influence interfacial interactions. For instance, if the fabrication process involves cooling from high temperatures to ambient temperature, the difference in the expansion coefficients of two components might lead to thermal stress and can be the cause of plastic deformation and impaired matrix-reinforcement compatibility [67].

The main performance challenge when using conventional biocomposites is the poor interfacial adhesion between the hydrophilic plant-based reinforcement and the hydrophobic matrix phases, which can lead to weakened mechanical performance, as well as problems in recycling due to the heterogeneous mixture [61][68]. One way to overcome weak compatibility and recyclability challenges in conventional composites and biocomposites is to create single-polymer composite (SPC), where similar or identical polymers are used for both the reinforcement and the matrix [69]. The

polymers can be of renewable or non-renewable origin [70]. Non-renewable SPCs are, e.g., all-polyethylene composites [71] and all-propylene composites [68], whereas renewable fully cellulosic SPCs are bio-based. Basically, all-cellulose composites are reviving old vulcanized fibre technology where a cellulosic material is converted into a unique SPC laminate product [72][73].

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