Chapter 7

Production of Nanomaterials from Forest Resources

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Abstract

Renewable resources such as lignocellulose are prospective alternatives for the development of different products in connection with climate change. Cellulose, lignin, and hemicellulose can be extracted from wood and non-wood through a chemical process, subsequently, nanocellulose, nanolignin, and nanohemicellulose can be obtained through mechanical, chemical, and a combination of these two processes. Nanocellulose is suggested for application in improving barrier properties, drug delivery, energy storage, composite film, scaffolds for tissue regeneration, and other smart materials due to its nanoscale dimension, hydrogen bond formation capability, and high surface area. This chapter presents various methods for the extraction of lignin nanoparticles and their applications. Due to the high reactivity, large surface area, and homogeneity, nanolignin is applied in the preparation of nanocomposites, and so far, various thermally stable composites have been suggested. Though very little information is available on nanohemicellulose, it is a very promising nanomaterial from forest resources to show a definite improvement in the tensile strength of biofilm.

Keywords

Lignocellulose, Nanocellulose, Nanolignin, Nanohemicellulose, Barrier Properties, Biofilm

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1. Introduction
The key forest product is wood, which comprises cellulose, hemicellulose, and lignin. These three are the major components of the plant, which represent cellulose 35–50%, hemicellulose 10–25%, and lignin 20–35% of dry mass respectively. The lignin contributes to the strength of the plant through the binding with cellulose and hemicellulose in the cell wall of fiber. Cellulose is the most abundant renewable natural biopolymer in the world that exists generally in plant cell walls as well as a small amount in several marine animals (e.g., tunicates), bacteria, fungi, invertebrates, and algae [1]. Cellulose is a polymer of glucose monomer linked by 1-4 β glucoside linkage (Fig. 1a) and the hydroxyl groups in glucose monomer in the same and adjacent cellulose chains form intra- and inter-molecular hydrogen bonds respectively [2]. The elementary fibrils of cellulose can be 3-4 nm in width and a few micrometers long. The fibrils are interlinked in a regular and irregularly ordered manner that creates a crystalline and amorphous region in the fiber. Cellulose is typically fibrous, structurally rigid, and water-insoluble, which is very important to maintain the structural integrity of plant cells [3]. The hydrogen bonding in the cellulose network (Fig. 1b) gives strength and common solvent insolubility. Xylans and glucomannans are the main components of hemicellulose that makes a branched network with a short chain length. The main constituents of different lignocellulosic biomasses are shown in Table 1.
Fig. 1. a) Chemical structure of cellulose, b) Intramolecular hydrogen bonding network in cellulose. [2]

Table 1. Chemical composition of different lignocellulosic biomasses

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Composition (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cellulose</td>
<td>Pentosan</td>
</tr>
<tr>
<td>Jute</td>
<td>63</td>
<td>14</td>
</tr>
<tr>
<td>Bagasse</td>
<td>39</td>
<td>17</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>35</td>
<td>18</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>37</td>
<td>18</td>
</tr>
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</table>

The wood and other lignocellulosic biomasses are converted to pulp and paper in forest product industry. This industry faces challenges due to document digitalization and is in search of alternative products. The successful production of high-value bio-chemicals and biomaterials from lignocellulosic biomasses would shift the present global economy to a bio-based one, and raise the revenue of the forest product industry. Van Heiningen et al proposed an integrated forest biorefinery concept, where lignocellulosic biomass was pre-
extracted prior to pulping, and the dissolved biomass was modified to biofuel and biochemical along with pulp [10-13]

Nanotechnology is a showcase of demonstrating the ability of science to investigate beyond the molecular level with advantageous results. Nanotechnology is being applied for the development of new materials, systems, and devices at the nano-level. This technology includes a number of disciplines including engineering, biotechnology, electronics, biomechanics, coatings, construction materials, etc. [14,15]. In recent technological advancements in disease control, nanotechnology also plays a crucial role [16].

Nanocellulose (NC) is the most appealing topic in present-day forest products. Mukherjee and Woods isolated NC using sulfuric acid from ramie and cotton fibers [17]. Sulfuric acid hydrolysis of cellulose fibers formed a colloidal suspension [18,19]. Acid-hydrolysed crystalline cellulose is often referred to as nanocrystals, microcrystals, nanoparticles, nanofibers, microcrystallites, or whiskers. The properties of prepared NC depend on the sources and the treatment methods [2]. Lignocellulosic biomass is effectively fractionated into cellulose, lignin, and hemicellulose by organic acids [20,21]. The separated cellulose was subsequently converted to nanocrystalline cellulose (NCCs) by acid hydrolysis by dissolving the amorphous part of the cellulose chain and converted to biofuel [22]. Several commercial and pilot-scale plants for the extraction of cellulose nanofibers (CNFs) and NCCs from wood have been established in Europe and North America [23,24]. CelluForce is the first manufacturing facility of NCCs in the world. The plant was established in 2011 in Quebec, Canada with a production capacity of $3 \times 10^5$ Kg of NCCs per year [25].

Another important fraction of lignocellulosic is lignin, which is a polymeric material that constitutes about 13 – 35% of the total weight, which is an underutilized renewable component and it has the potential in developing green products. At present, lignin is used in generating energy in the pulp mill [26]. In recent years, interest is growing in nanolignin (NL) for potential biobased applications, but the commercialization of NL needs to be developed.

In this chapter, the extraction, and application of NC, NL, and nanohemicellulose in different processes from different sources are discussed. The methods for the production of NC and NL and their characterization and applications are also reviewed. A graphical representation of the of the work is shown in Fig. 2.
2. Nanocellulose

2.1 Types of nanocellulose

NC is isolated from fibers by mechanical, chemical means, or both together. The cellulose which has a width in the nanoscale (<100 nm) is termed NC. The size and properties of the NC highly depend on the methods of isolation [27]. NC is biodegradable, lightweight, is of low-density, and has exceptional strength. Specifically, NC has higher rigidity than Kevlar fiber, with an elastic modulus of up to 220 GPa. In addition, NC has an 8-times better specific strength than stainless steel as well as higher tensile strength than cast iron. NC is also transparent and has a lot of reactive surface hydroxyl functional groups which can be functionalized to various nanomaterials [28,29]. There are three main categories of NC are NCCs, CNFs and bacterial NC (BNCs). The chemical composition of all NCs is similar but differ in particle size, shapes, crystallinity, and morphology according to the sources and extraction methods [28,30]. The different types of NCs, their analogous name, sources, and methods of preparation are given in Table 2.
Table 2. Family of Nanocellulose Material [9]. (Reproduced with permission from John Wiley and Sons, Copyright © 2020)

<table>
<thead>
<tr>
<th>Kinds of nanocellulose</th>
<th>Analogous name</th>
<th>Sources</th>
<th>Preparation method/ size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocellulose and microcellulose</td>
<td>Cellulose nanofiber, microfibrils</td>
<td>Lignocellulose (wood and Nonwoods)</td>
<td>Mechanical fibril width: From 5 to 60 nm Length: Few micrometers</td>
</tr>
<tr>
<td>Cellulose nanocrystal</td>
<td>Whisker nanocellulose, rod-like crystalinestals</td>
<td>Wood, nonwoods (agricultural residue, hemp, cotton etc) plant bark, microbial cellulose</td>
<td>Chemical Fibril width: 5–70 nm Length: From 100 to 250 nm</td>
</tr>
<tr>
<td>Microbial nanocellulose</td>
<td>Microbial cellulose, bio-cellulose</td>
<td>sugar and alcohols</td>
<td>Bacterial synthesis Fibril width: From 20 to 100 nm</td>
</tr>
</tbody>
</table>

2.1.1 Nanocrystalline cellulose

NCCs are rod-like-shaped nanofiber that is highly crystalline and has a large surface area. The morphology of NCC depends not only on the preparation methods but also on the source of cellulose. NCC is mostly produced by dissolving the amorphous portion of cellulose fiber [31]. The length and width of the NCCs varied between 200 and 500 nm, and 3 and 35 nm respectively [27].

2.1.2 Cellulose nanofibers

CNFs are different from NCCs, which are flexible nanofibers. It is literally elementary cellulose microfibrils consisting of alternating amorphous and crystalline regions. By means of mechanical force on cellulose fibers resulting the CNFs with a width of below 100 nm and a length of several micrometers. The difference between NCCs and CNFs is that CNFs show a web-like structure whereas NCCs are rod-like nanomaterials. [1, 32]. CNFs have a high aspect ratio and surface area, and more widespread hydroxyl groups that can be used to modify their surfaces [33]. Applying mechanical force, CNFs can be produced by splitting cellulose fibrils according to the longitudinal axis [27].
2.1.3 Bacterial nanocellulose

BNC is also called microbial cellulose. It is produced from bacterial genera (e.g. Acetobacter, Rhizobium, etc.) [34] and cell-free systems [35]. The production of BNC need not require any further purification process because of the absence of lignin, pectin, and hemicellulose [36]. BNC differs from NCCs and CNFs since NCCs and CNFs are produced from lignocellulosic biomasses by a top-down process but BNC is produced by the bottom-up process where the low molecular weight glucose molecules join each other by bacteria during the biosynthesis process. The shape of BNC looks like twisting ribbons of microfibers with average diameters of 20–100 nm [36,37].

2.2 Preparation of nanocellulose

There are several methods such as mechanical, chemical or a combination of both have been applied for the isolation of highly purified NC from lignocellulosic biomasses. Pretreatments like refining of pulp [38], high-pressure homogenizing [39], enzymatic treatment [40], ultrasonic technique [41,42], and cryocrushing [43,44], microuidization [44], steam explosion [45], etc. facilitated the extraction of NC. A graphical representation of nanocellulose production is shown in Fig. 3.

![Fig. 3. Schematic illustration of nanocellulose extraction pathways from forest resources.](image)

Chemically, cellulose nanocrystals can be produced through acid hydrolysis and cellulose nanofibrils can also be produced mechanically by cleaving the cellulose fibrils. Hairy cellulose nanocrystalloids can be produced by the chemical treatment where the amorphous regions are dissolved but few amorphous chains remain at both ends of crystalline regions.

The NCC is mostly produced by acid hydrolysis of cellulose in which the amorphous parts of cellulose are removed and crystalline parts remain intact [2,46,47]. NCCs are rod-shaped nanomaterials that have similar physical properties to the mother cellulose fibers. The most
extensively used acids for the preparation of NCCs are sulfuric and hydrochloric acids [48-52], but phosphoric [53] and hydrobromic acid [54] were also used for the preparation of NCCs. NCCs produced by hydrochloric acid showed limited dispersibility and a tendency for flocculation in aqueous suspensions [49]. Different protocols for hydrolysis and separation processes have been developed based on cellulose sources. Wood [55,56] and nonwoods [21,22,57-60] are the most common sources of cellulose. The morphology of NCCs is presented in Fig. 4

![Cellulose nanocrystals under transmission electron microscopy (TEM) [48]. (Reproduced with permission from the Royal Society of Chemistry, Copyright © 2011)](image)

CNFs are produced by only mechanical operation without the involvement of any chemical treatment. The mechanical process disintegrated the microfibrils from the interlinkage of the cellulose chain. The cellulose fibrils are isolated along their long axis [61]. Turbak et al. and Herrick et al. introduced CNFs as cellulosic nanomaterial for the first time from the soft-wood pulp by applying a high-pressure homogenization method [62,63]. Mechanical, chemical, enzymatic, or combined methods have been used for production of CNFs. Enzymatic treatments followed by chemical ones and in combination with mechanical treatments were applied to produce nanofiber [64]. A fine network of CNFs can be prepared from wood fiber by applying mechanical and/or enzymatic treatment [65]. Generally, several mechanical methods have been applied for the isolation of CNFs like refining, grinding, high-pressure homogenization, etc. In the chemi-mechanical processing of CNFs, chemical treatment reduces the energy consumption for mechanical defibrillation during the synthesis of CNFs from cellulose [66]. It is mostly employed in moderate climates to modify the hydroxyl groups into carboxyl derivatives. [67]. For example, individual CNFs can be produced by the oxidation with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) from wood under gentle stirring [68]. With this technique, a strong repulsive charge is
created on the surface of CNFs and allows defibrillation with minimum energy input. [69,70]. To produce individual CNFs, both mechanical and chemical techniques can be applied. For instance, carboxymethylation followed by high-pressure homogenization can be used to prepare well-dispersed CNFs [62]. 19.7% CNFs with 1.7 nm diameter with several micrometers in length can be produced from rice straw by the TEMPO-mediated oxidation method [70] TEMPO-oxidation followed by ultrasound treatment was carried out to get NCCs with 6 nm diameter and 122 nm of length from the microcrystalline cellulose. The sono-assistance increased yield and carboxylate content compared to the non-assisted process [71].

BNCs can be produced from *Acetobacter* by using simple culturing methods [72]. Biosynthesized BNCs are partially transparent and resistant to mechanical force but show a property of elasticity and are soft in nature. BNC and plant cellulose are chemically identical, but the purity of bacterial cellulose is very high [73]. BNC is very much biocompatible and has numerous applications in medical science including drug delivery systems, wound healing, tympanic membranes and other. The high-purity BNCs are obtained by culturing microorganisms over the year [74,75]. Static and stirred culture methods are used to extract BNCs. Cowhide-like white BNCs are produced at the air-fluid interface of cultured bacteria in a static culture process. The important factors in selecting this method depend on the surface morphology, properties, and final applications of BNCs [76]. Moreover, several green methods such as deep eutectic solvents, solid acids, ionic liquids, etc. have been used for nanocellulose production [77].

Thus, chemical, mechanical, chemi-mechanical, and microbial processes can be applied for the production of NCCs, CNFs, and BNCs

### 2.3 Application of nanocellulose

NC, is a bio-based nanomaterial that exhibits impressive properties such as high crystallinity, high aspect ratio, large specific surface area, and superior mechanical properties. In addition to that NC is renewable, and biocompatible. Different types of nanomaterials with tunable properties can be produced chemically from NC due to the available hydroxyl groups. NC is a prospective candidate for use in industries like biomedicine, pharmaceuticals, electronics, supercapacitors, barrier films, membranes, nanocomposites, etc. [78-80]. As a sustainable raw material, NC has potential applications in the field of flexible electronics [81,82], sensors [83], energy storage materials [84], food and pharmaceuticals [85], biomedicine [86], packaging [87], and nanocomposite [88], etc. Due to its nanoscale dimensions, NC can easily fill the pores, which improves the superior barrier qualities of films. NC has the capacity to form hydrogen bonds, resulting in a strong network that makes it difficult for the molecules to pass through. The water vapor permeability of carboxymethyl cellulose (CMC) film containing nano-chitosan or nanocellulose at various concentrations improved with increasing nano-chitosan or nanocellulose content [89-91]. NCCs contain only crystalline region while CNFs consist of both crystalline and disordered regions which reflect better barrier properties [92]. CNF film showed excellent oxygen barrier properties with high air resistance capacity. A 21 μm
thick film transmits only $17 \pm 1 \text{ mL/m}^2$ oxygen per day. The oxygen barrier property of CNFs film is highly competitive with the best performed synthetic films. Acetylated CNFs films showed much lower oxygen permeability ($<20 \text{ mL/m}^2 \text{ per day}$), which can be used for packaging under atmospheric conditions [93]. Similarly to that, films made of carboxymethylated CNFs have extremely low oxygen permeabilities [94].

In the biomedical field, NC has many applications, including photodynamic and photothermal therapy of tumors, radical scavenging, healing from microbial infections, drug delivery, biosensors, isolation of different biomolecules, tissue engineering, advanced wound dressing, and engineering of blood vessels [95]. NC–carbon nanotube (CNT) composite can kill cancer cells in absence of anticancer drugs [96].

Neural interfaces are important for restoring the neural functions of paralysis patients. The most commonly used materials for conventional neural interfaces are platinum, titanium, gold, iridium oxide, and silicon. Recently, scientists have developed biocompatible materials based on NC as substrates for brain implants to reduce inflammatory response through softening neural interfaces [97-99]. These softening neural interfaces can be implanted into the brain. NC-incorporated scaffold showed improved mechanical properties [100]. In tissue engineering scaffolds, BNCs and NCCs are naturally suited [101]. NC based materials are successfully used for drug delivery, membranes technology, and as coating material for tablets [100,102,103]. Additionally, surface-modified NC-based materials provide superior stability and controlled drug release [104, 105].

NC-based materials have been used for fabricating flexible solar cells, sensors triboelectric nanogenerators (TENGs), and field-effect transistors (FET) [106]. The nanofibers ensure the improved mechanical performance of the devices. Good thermal stability and good wettability in various electrolytes along with a high aspect ratio of NC-based materials, is conducive to a wide potential window. These exceptional properties make it a highly desirable dielectric material for flexible organic light-emitting diodes (OLEDs), foldable batteries, organic thin-film transistors (OTFTs), and printed photovoltaic cells [74]. CNFs are fabricated by complex “bottom-up” nanostructures which make them perfect electrode components for piezoresistive sensors [107]. A conductive CNF/Ag nanowires-coated polyurethane (CA@PU) sensor was used to detect and record tiny sounds [108].

NC can be used to fabricate components of portable electrochemical energy storage (EES) devices. The NC-based EES has large absorptive bodies, hydrophilic surfaces, and hierarchical pores for charge storage which is good for the transportation and absorption of electrolytes [109]. NC reinforced multiwalled carbon nanotube forms a hybrid film with poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate) mixture in a ionic liquid of 1-butyl-3-methylimidazolium chloride by in situ polymerization process. The presence of NC provided higher flexibility and mechanical strength. The hybrid film was characterized as excellent supercapacitor with energy density and capacitance of $13.2 \text{ Wh kg}^{-1}$ and $380 \text{ F g}^{-1}$ respectively [110].
Thus, NC has versatile potential applications in energy storage devices, food, pharmaceuticals, biomedicine, flexible electronics, sensors, packaging, and nanocomposite materials, etc.

3. Nanolignin

3.1 Lignin

Lignin is the second most abundant natural polymer after cellulose in the flora world. It consists of 15-40% of mass fraction in the terrestrial plant and provides structural integrity [32]. It is a cross-linked biopolymer that consists of three phenylpropane units: guaiacyl (G), \( p \)-hydroxyphenyl (H), and syringyl (S). The quantitative presence of monomer units varied from plant species to species as well as their interlinkage attachment of monomers [111]. The lignin present in plant cells without any type of modification either chemical or mechanical is called native lignin. [112, 113]. On average about one-third of the plant biomass is made up of lignin. The forest product industry especially the pulp and paper industry and plant-based biorefinery industry produce sixty percent surplus lignin after meeting their need for energy production [114, 115]. High heterogeneity of chemical structure, molecular weight, and low free active group limit its downstream processing and valorization [116]. The lignin obtained as a byproduct from pulping and biorefineries by the chemical, mechanical, or biochemical process is recognized as technical lignin. Technical lignins are highly heterogeneous with regard to molecular structure, molecular weight, particle size depending on wood species, separation technique, growth rate, pulping method, and process intensity. Lignin has active hydroxyl, carbonyl, methoxyl, and carboxyl functional groups but their quantity and composition depend on the source and extraction processes [117]. The interlinkage of lignin is highly complex and there is no nondestructive method of isolation of native lignin from plants. Homogeneity of lignin fraction is crucial for its value-added applications. In recent years, interest is growing on green material development from technical lignin [118-120]. Lignin can be modified to nanoparticle as one of the high value applications of it.

3.1.1 Preparation of lignin nanoparticles

Lignins are soluble in alkaline aqueous medium, which limits their industrial applications, but the limitation could be overcome by dispersing lignin nanoparticles (LNPs) in water. Moreover, materials with nanostructures have many unique properties because of their large surface area. Various processes of LNPs production are described below.

**Chemical process**

Jiang et al. [121] used sulphate lignin to produce LNPs and natural rubber composite. The nanoparticle was co-precipitated with rubber. Lignin was dissolved in distilled water at the mass concentration of 0.5% and the pH was adjusted to 12 using sodium hydroxide. A 2% alkaline solution of poly(diallyldimethylammonium chloride) (PDAMAC) was prepared in water with pH 12. The two solutions were mixed with vigorous stirring to form a lignin-
PDAMAC (LPC). Finally, the colloidal solution was prepared by dropping the pH to 2 with sulfuric acid. It produced the LNPs of 90 – 100 nm.

Wang et al. [122] prepared LNPs by a solvent shifting method combined with sonication. A dilute solution (1 to 4 mg/mL) of acetylated lignin (AcL) in tetrahydrofuran (THF) was sonicated in an ultrasonic bath with various intensities (0, 100 kHz, and 200 W). LNPs were separated as distilled water was added drop by drop into the lignin/THF solution. The nanoparticles were separated immediately by centrifugation for 10 min at 10000 rpm under cool conditions. The lower the concentration of AcL and higher the sonication intensity, the lower was the particle size produced [122- 123]. Lievonen et al. prepared LNPs from the solution of softwood kraft lignin in THF (1-10 g/L) by precipitating in distilled water [124]. The THF solution of lignin in the dialysis bag of 6-8 kDA was placed in deionized water and kept for 24 h. This process produced colloidal LNPs of size between 200 and 500 nm. The particle size depends on the concentration of THF solution. The lower concentration provided smaller sized nanoparticle. Figueiredo et al. [125] produced LNPs of 221 ± 10 nm following the same method as described by Lievonen et al [124]. Xiong et al. [126] studied the LNPs form the organosolv lignin using the solvent shift method. However, the solution concentration was 10 – 100 g/L and the antisolvent ratio was 1:20 and 1:10. Lower lignin solution concentration and higher antisolvent ratio results in lower particle size. Lignin concentrations in THF of 10–20 g/L and antisolvent ration 1:20 produced an average nanoparticle size of 151 nm. Wang et al. [122] produced LNPs using a simple and green process. Initially, lignin was acetylated by microwave-assisted acetylation process in absence of any solvent or catalyst except the main reagent acetic anhydride. Acetic anhydride works as both reagent and solvent. Later, the acetylated lignin was converted to nanoparticles by applying solvent shifting and ultrasonication process.

Acetone-water solvent system was used to produce LNPs from commercial alkali lignin [127] and hardwood acidic dioxane lignin [128]. The lignin was dissolved in 9:1 (vol/vol) acetone: water mixture at a concentration of 10 g/L, the solution was added in a double volume of deionized water to separate lignin as nanoparticle. The average sizes of dioxane LNPs and alkali LNPs were 80 ± 27 nm and 82 ± 33 nm respectively [129]. Li et al. [130] prepared LNPs from the kraft lignin obtained from the pulp industry. A solution of kraft lignin in ethanol was subjected to the production of the nanoparticle. To precipitate lignin as nanoparticles, distilled water was added dropwise to the lignin solution in ethanol. It produced capsule-shaped nanoparticles in 10–100 nm range. Juikar and Vigneshwaraan produced LNPs from coconut fiber through two different mechanical processes-homogenization and ultrasonication. The lignin was first extracted by digesting coconut fiber with soda at 170 °C. The soluble lignin was precipitated by reducing the pH to 2 by adding acid. In one process, the bulk lignin was diluted to a 7% mass fraction with distilled water. The aqueous suspension was homogenized at 10,000 rpm for 60 min. The mixture was allowed to settle down for 60 min. The large particles were precipitated and the nanoparticles remain suspended in the supernatant. In the ultrasonication process, the diluted lignin suspension was subjected to sonication in an ultrasonic water bath with 30 W power and 37 kHz frequency for 60 min. Later the mixture was allowed for
sedimentation for 60 min. The supernatant contained the nanoparticle only. To avoid agglomeration, the supernatants were stored in an ice bath. The homogenization and sonication process produced particle sizes of $31.8 \pm 11.2$ and $58.6 \pm 13.5$ nm respectively [131].

**Mechanical process**

Nano-sized particles can be produced by various mechanical treatments; dry and wet milling is a widely used treatment. One of the obvious limitations is the uniformity of particle size. Many researchers produced LNPs by applying mechanical processes [132-135]. Nair et al. [136] prepared nano-sized lignin from softwood kraft lignin dispersed in water with a concentration of 5 g/L which was treated with a high shear homogenizer at 15000 rpm for up to 4 h. A shorter shearing time left larger particles. Approximately 75% of particles had diameters smaller than 100 nm after 2 h of shearing. However, after 4 h shearing, 100% of particles had diameters less than 100 nm.

Gilca et al. [137] reduced the wheat straw and Sarkanda grass macro sized lignin particle to nano size by applying the ultrasound technique. Lignin suspended in water at a concentration of 0.7% was sonicated with the intensity of 20000 kHz and 600W power. This technique successfully reduced the micro-sized lignin particle to 10–20 nm. Ball milling is another well recognized mechanical treatment for reducing particle size. Shawn et al. [138] and Beisi et al. [139] produced LNPs of around 10 nm size by ball milling treatment at 18 °C.

Zimniewska et al. [140] prepared nanolignin from the kraft lignin by high intensity of ultrasound treatment. The LNPs were impregnated on the linen fabric structure lignin. The distribution of the nanoparticle was around 170 nm to 5 nm however, the particle size was mostly below 40 nm.

A water-miscible organic solvent is used to dissolve an organic compound. The organic compound is mixed with an excess of water, resulting in the formation of nanoparticles [141]. This process has been applied by many researchers to produce LNPs.

**Microbial process**

Juikar and Vigneshwaran [131] produced LNPs from the soda lignin of coconut fiber by a microbial process using Aspergillus sp. fungus. Aspergillus sp. was cultured on lignin as the only carbon source at 31 °C for 15 days with shaking at 110 rpm. The unhydrolyzed lignin was separated by filtration through a 1 μm filter. The filtrate contains the LNPs. The size of 25.8 LNPs was ± 8.9 nm.

Most of the LNPs were so far prepared by the solvent shifting system. The mechanical process was also widely applied to prepare LNPs. The size of the particles depends on processes, applied conditions, and sources.
3.1.2 Application of lignin nanoparticles

Nanomaterial has great importance for their target application efficiency, quality of product, and diversity of applicability. LNPs have been successfully applied for the applications in the fields of medicine, agriculture, and various engineering.

Bulk lignin and LNPs are incorporated into the phenol–formaldehyde resol resin for the production of biobased adhesive. The binding strength of the LNPs showed superior quality [142]. A nanocomposite from natural rubber and LNPs were also produced. The rubber-NL composite showed superior mechanical and thermal properties and oxidative stability to the rubber-carbon black composite. The nanolignin dispersed homogeneously in the nanocomposite matrix [121].

Lignin has antioxidant, UV absorbent, and antimicrobial properties and potential for use as a reinforcing agent [143]. A composite film was produced from polyvinyl alcohol, chitosan, and LNPs for biobased packaging. The film showed excellent thermal, optical, antioxidant, and antibacterial activities with high mechanical properties. The surface analysis showed a homogeneous distribution of nanoparticles which provided excellent mechanical properties. The film inhibited Gram-negative bacterial growth such as Erwinia carotovora subsp. Carotovora and Xanthomonas arboricola pv. pruni offers a novel way to control harmful bacterial plant/fruit pathogens [144].

Chitin nanofibrils-NL and chitin nanofibrils–NL–glycyrrhetinic acid were used to produce two composites for skin regeneration. The investigation showed that the complexes were cytocompatible with HaCaT cells and hMSCs. The complexes were capable to downregulate the expression of anti-inflammatory cytokines in human keratinocytes without altering their proliferative or osteogenic capabilities. In biomedical, personal care, and cosmetic applications, these materials are very promising. [145].

LNPs have been widely used for reinforcement in various polymer composites. Saz-Orozco et al. reinforced the phenolic foam with nano-sized lignin to improve the mechanical properties. The reinforced foam showed up to 128% and 174% higher compressive modulus and compressive strength in comparison to unreinforced foam [146]. LNPs were used to produce soy oil-based polyurethane biofoams. The foams showed higher thermal stability composite with improved mechanical properties in comparison to unreinforced foam. [147].

A transparent film was made through solvent casting process from LNPs and polyvinyl alcohol (LNS/PVA) for cutting the UV light penetration. The composite film showed excellent properties of UV light absorption with nice mechanical properties compared with lignin-PVA film. No phase separation occurred like macro particle rather evenly distributed nanoparticle transparent film was obtained. The UV radiation absorption and transparent property of the film makes it an excellent material for medicine bottle and food packaging [148].

Poly(L-lactide) based nanocomposite was produced with LNPs and various metal oxide nanoparticles (0.5% wt., Ag2O, TiO2, WO3, Fe2O3 and ZnFe2O4). The synergistic effect of
LNPs and metal oxide was excellent in term of mechanical property, thermal stability, surface smoothness, UV absorption, antioxidant, and antibacterial properties. The LNPs played pivotal role in the mechanical property, surface wettability, and smoothness of the film as well as UV light absorption. LNPs show excellent protection against UV light while allowing visible light to pass. These wonderful properties make the composite film an attractive renewable additive for the fields of food, drug packaging, and biomedical applications [149].

LNPs can be used in the development of biomaterials, in biobased food packaging, in introducing antibacterial, antifungal, and UV light absorption properties of different consumer products, and in biomedical applications. NL helps in improving the mechanical properties of films/composites in all cases.

4. Nanohemicellulose

Hemicellulose is mainly present in the primary and secondary walls of plant cells. It acts as a crosslinker between cellulose and lignin as well as cellulose microfibrils. Hemicellulose is composed of multiple sugar monomers with a short polymer chain and it contributes 20 to 30 % of dry mass of plants [150]. Composition of sugar units in the hemicelluloses depends on the type of plants. Hemicellulose extracted from rice straw is composed mainly of xylose and arabinose which contribute about 97% of total mass [151]. Although hemicelluloses are one of the important lignocellulosic biomasses, the research on their utilization is limited. Recently interest is growing in nanohemicellulose extraction. A biofilm produced from nanocellulose and reinforced with nanohemicellulose showed 18% higher tensile strength and 78% higher Young’s modulus than the unreinforced biofilm [152]. In addition, the water vapor permeability (WVP) of the biofilm reduced remarkably. Louis et al [153] prepared starch nanocomposites using nanocellulose and nanohemicellulose, which improved mechanical properties and reduced WVP value. Hemicellulose from corn husk was extracted by sonication-assisted mild alkaline treatment followed by the treatment with deep eutectic solvent [154]. Nanohemicellulose was produced for the extracted hemicelluloses by mechanical homogenization. The properties of the marine calcium alginate film were improved using nanohemicellulose and nanocellulose. Small amounts of nanohemicellulose and nanocellulose synergistically improved the strength and gas barrier properties of the film.

The nanohemicellulose is the most recent topic for biomass chemists. Nanohemicellulose has rendered itself as a good reinforcing agent for improving the mechanical and barrier properties of biofilm.

Conclusion

This chapter provides an overview of nanomaterials from lignocellulosics (cellulose, hemicellulose, and lignin) and their applications. Cellulose fibers are composed of nano-sized fibrils which entangle together to form a cellulose fiber. Many chemical, mechanical, and microbial operations have been applied to separate the entangled fibrils to produce
different types of NC. The aspect ratio of the NC is very high and applied to produce nanocomposites with special characteristics such as lightweight and high mechanical strength. Lignin and hemicellulose are nonfibrous macrostructure biopolymers. Various methods mostly chemical-mechanical methods are used to produce nanoparticles. LNPs have been used for producing lignin nanocomposites with improved special characteristics. LNPs enhance the strength and thermal stability of composite matrix materials, act as an antibacterial agent, flame retardant, and UV light adsorbent and exhibit a number of other properties. Lignin nanocomposites have many applications in engineering, agriculture, biomedical, drug delivery, and many others. Hemicellulose nanoparticles have been used for producing high strength biobased film materials. The research today is directed to the efficient synthesis of nanomaterials from lignocellulosic materials from natural forests with ease and exploitation of the advantageous features of the nanostructures for a range of applications.

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