Chapter 13

Cellulose Nanomaterials and Their Products from Hardwoods

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Cellulose nanomaterials are an emerging class of materials with unique properties that offer promising outlets for undervalued hardwood species. As wood is broken down into nanometer-scale fibers and particles, the resulting materials begin to exhibit unique and interesting properties, including remarkable strength, liquid crystal behavior, transparency when cast as a film, low thermal expansion, high capacity to absorb water, and piezoelectric and electroactive behavior. Potential applications for cellulose nanomaterials include food additives (Turbak et al. 1982, medical and pharmaceutical applications (Innami and Fukui 1987), paper and paperboard additives (Klemm et al. 2011), automotive parts (Kiziltas et al. 2013), substrates for flexible electronics (Sabo et al. 2012, Seo et al. 2015), paints and coatings (Syverud 2011), aerogels (Javadi et al. 2013), and barrier packaging (Lavoine, et al. 2012), among numerous others. Therefore, cellulose nanomaterials may well provide new high-value markets for undervalued and underutilized hardwood species. An overview of these materials, their properties, and potential products is provided here, with an emphasis on undervalued hardwood sources.

Cellulose Nanomaterials

Cellulose nanomaterials, a class of lignocellulosic materials with dimensions below about 100 nm, are typically classified as either cellulose nanocrystals (CNCs) or cellulose nanofibrils (CNFs). CNCs are discrete, rod-shaped cellulose particles with nanometer-scale diameters typically having lengths of hundreds or thousands of nanometers. Typically, CNCs have high crystallinity and are most commonly produced by sulfuric or hydrochloric acid hydrolysis of wood pulp. CNFs usually consist of more network-type structures instead of discrete particles. A countless number of methods are available to produce CNFs, although they almost entirely consist of some combination of chemical or biological pretreatment with mechanical processing to liberate individual or bundles of cellulose microfibrils. A wide range of morphologies and material properties can be attained by processing wood into cellulose nanomaterials, and the application of these materials varies widely with various processing courses.

Cellulose Nanocrystals

CNCs are typically produced by acid hydrolysis of native cellulose using hydrochloric, sulfuric, or phosphoric acid. Cellulose nanocrystals prepared by sulfuric acid hydrolysis have charged surfaces, whereas those prepared using hydrochloric acid are not charged (Azizi Samir et al. 2005). CNCs with charged surfaces can form stable aqueous suspensions, so CNCs are usually produced using sulfuric acid. The yield of CNCs from natural plant fibers is found to be about 30% (Bondeson et al. 2006). Wood-derived CNCs typically have diameters of several nanometers and lengths of hundreds on nanometers (Fig. 13.1).

CNCs have some interesting properties, including exceptional mechanical properties and the ability to self-assemble. Tensile strength and elastic modulus of CNCs are reported to be about 8 GPa and 100–200 GPa, respectively, so they are often targeted as a reinforcement for polymeric materials (Moon et al. 2011). The self-assembly of CNCs in water results in optical activity, which means that they change the orientation of polarized light and behave as liquid crystals (Beck-Candanedo et al. 2005). When dried as a film, this self-assembly can be controlled, resulting in colored films whose colors have the potential to be

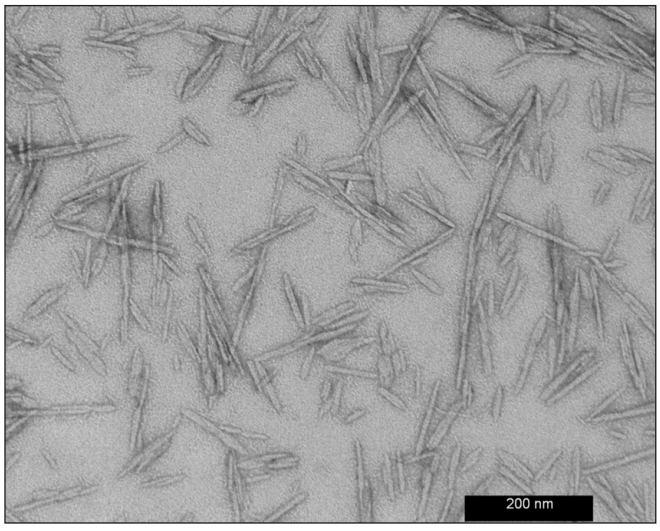

Figure 13.1—Cellulose nanocrystals from Eucalyptus.

manipulated (Cranston and Gray 2006). Because of these interesting properties, CNCs have potential for applications as polymer reinforcements and for use in sensors and security papers.

Cellulose Nanofibrils

CNFs are typically produced from wood pulp that has been chemically or enzymatically treated followed by some type of mechanical refining (Lavoine et al. 2012; Qing et al. 2013; Siró and Plackett 2010). Mechanical treatments to produce CNFs can include disk refining, stone grinding, homogenizing, microfluidizing, cryogenic crushing, and ultrasonic processing. Chemical pretreatments of wood often include some type of chemical pulping, such as sulfite or Kraft pulping, and examples in the literature commonly involve CNFs produced from bleached pulps. Additional chemical or enzymatic treatments, or both, are then applied to these pulps. One prominent chemical treatment is an oxidation treatment involving 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)-mediated oxidation of cellulose (Saito et al. 2007, 2009). This TEMPO process dramatically reduces the energy required to produce CNFs and yields uniform nanofibers with diameters around 10 nm and lengths up to micrometers. Other pretreatments, such as endoglucanase hydrolysis, have also been widely demonstrated (Qing et al. 2013; Siró and Plackett 2010). Such enzymatic pretreatments reduce the amount of energy required to produce CNFs but not as effectively as TEMPO-mediated oxidation, and the resulting CNFs are typically not as uniform or long. Figures 13.2 and 13.3 show typical scanning electron micrographs of CNFs created by both of these treatments. Depending on the pretreatment reaction conditions, energy input, and other processing considerations, the morphologies and properties of CNFs can vary quite dramatically.

When elementary fibrils and fibril bundles are liberated from the wood cell wall, the material begins to take on characteristics distinct from coarse wood fibers. For example, CNF suspensions have high viscosities and are shear thinning. A TEMPO-oxidized CNF suspension with about 2% solids will be viscous enough to not flow under the force of gravity, making CNFs candidates for rheology modifiers and colloidal stabilizers. Films made from CNFs are typically highly transparent (Fig. 13.4) and are thus being considered in applications requiring transparency (such as food packaging and electronic displays). These films also exhibit good mechanical properties, especially tensile properties; randomly oriented CNF films are routinely reported as having tensile strengths of 200 MPa or more and moduli of 10-20 GPa (Qing et al. 2013; Saito et al. 2009; Siró and Plackett 2010). Thermal expansion of CNF films has also been measured to be low, with coefficient of thermal expansion values commonly reported as lower than 20 ppm/K and as low as 3 ppm/K, which is lower than most polymers (Iwamoto et al. 2007; Nakagaito et al. 2010).

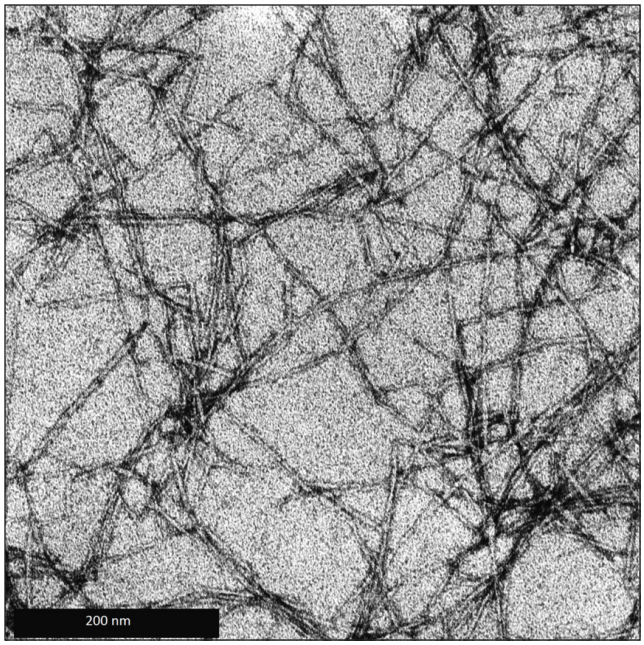

Figure 13.2—Cellulose nanofibrils from TEMPO-mediated oxidation of yellow poplar.

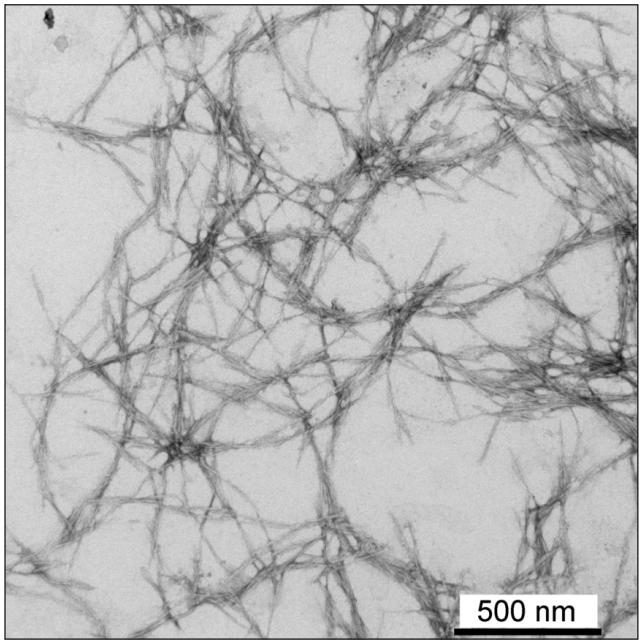

Figure 13.3—Cellulose nanofibrils produced by enzymatic and mechanical treatment of Eucalyptus.

Cellulose nanofiber films have also been demonstrated to act as good barriers to oxygen and other gases, especially at low humidity (Fukuzumi et al. 2009; Lavoine et al. 2012). The rheological, mechanical, optical, barrier, and thermal properties of CNFs make them a unique biobased material with numerous potential applications.

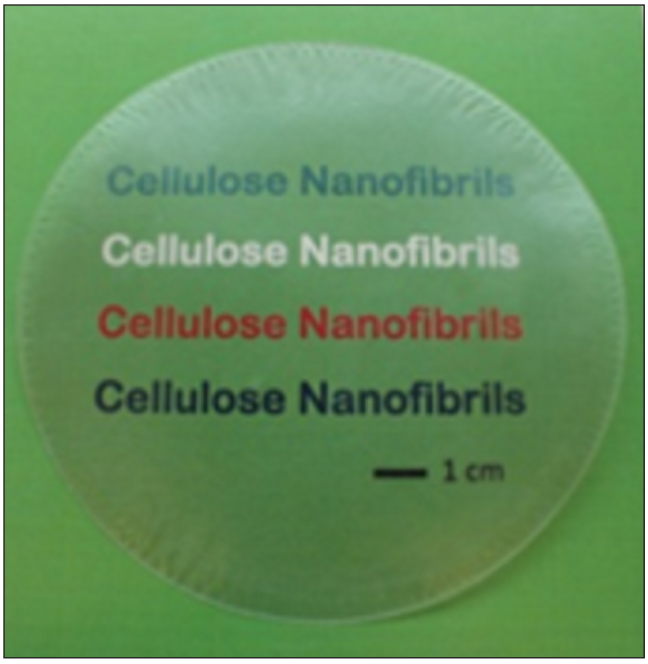

Figure 13.4—Cellulose nanofibril film from hardwood pulp.

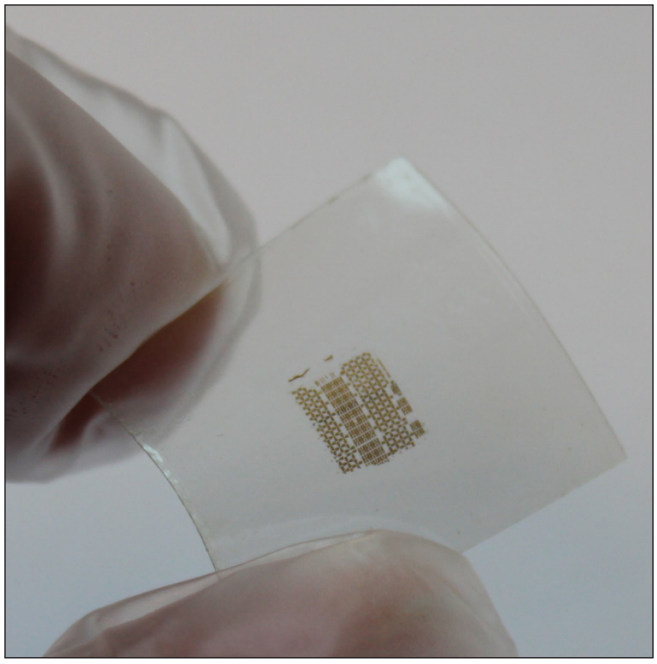

Figure 13.5—Electronic circuit on flexible cellulose nanofibril substrate from hardwoods.

Preparing Cellulose Nanomaterials from Hardwoods

Cellulose nanomaterials can be produced from virtually any lignocellulosic plant, and the limited comparisons among various species indicate that CNCs and CNFs from hardwoods are comparable to those from other species. For example, Fukuzumi et al. (2009) compared the differences of CNFs produced by TEMPO-mediated oxidation of bleached Kraft hardwood and softwood pulps (of unnamed species), and they found nearly identical mechanical properties of films made from both species (Fukuzumi et al. 2009). The hardwood films exhibited somewhat lower transparency than the softwood films, a phenomenon attributed to the hardwood xylan content, which is affected by pulping and other pretreatment processes. Although there may be slight differences in the morphologies and properties of cellulose nanomaterials from bleached pulp derived from various wood species, these differences are minor compared with differences due to manufacturing variabilities and differences between wood and nonwoody sources. For example, differences between chemical and enzymatic pretreatments on CNF properties are far greater than differences between wood species. Therefore, although the effects of varying constituent components of different wood species for producing cellulose nanomaterials has not been thoroughly studied, undervalued hardwood species are expected to yield high-quality cellulose nanomaterials based on numerous examples of these hardwoods being used to create CNCs and CNFs.

There are numerous examples of using hardwoods as a source material for both CNCs and CNFs. In one example, CNFs were produced from southern hardwood pulp containing gum, maple, oak, eucalyptus, poplar, or beech or a mixture (Stelte and Sanadi 2009). Processes for producing cellulose nanomaterials from hardwoods as a bioenergy co-product have also been described (Song et al. 2014; Zhu et al. 2011). Zhu et al. (2011) produced CNFs from bleached Kraft Eucalyptus pulp fibers using a combination of enzymatic hydrolysis and mechanical treatments, and they separated the sugar streams to create ethanol. Song et al. (2014) later performed similar experiments using northern maple hardwood. Poplar has also been used to produce both CNCs (Yang et al. 2014) and CNFs (Chen et al. 2013; Hassanzadeh et al., 2017). Birch is another hardwood that was used to produce cellulose nanomaterials (Vartiainen et al. 2011). Clearly, a wide variety of hardwood species can be used to produce cellulose nanomaterials.

Applications and Products

A number of applications containing cellulose nanomaterials derived from hardwoods have been demonstrated. Researchers at the University of Wisconsin and the USDA Forest Service, Forest Products Laboratory, demonstrated that cellulose nanofibril films from Eucalyptus can be used as substrates for high-speed flexible electronics (Fig. 13.5) (Sabo et al. 2012; Seo et al. 2015). These substrates were demonstrated to be biodegradable, offering possible solutions for growing electronic waste issues. Another example of using cellulose nanomaterials to improve the environmental impact of electronics includes recyclable solar cells that were constructed on substrates made of CNCs from hardwoods (Zhou et al. 2014). Modified cellulose nanofibril aerogels from Eucalyptus were demonstrated to be excellent candidates for cleaning oil spills because they preferentially absorbed oils and

other organic liquids in quantities up to nearly 100 times their own weight (Zheng et al. 2014). CNCs and CNFs have also been demonstrated to facilitate void structure in foamed polymers to yield plastic parts with better strength-to-weight properties, which has enormous potential, for example, to reduce the weight of interior automotive parts and thus improve fuel efficiency (Peng et al. 2016; Srithep et al. 2012). CNCs from Eucalyptus were found to be a potential reinforcement in concrete and to result in increased hydration (Cao et al. 2015). Coatings made from CNCs have also been demonstrated to improve abrasion resistance, potentially offering more durable paints and coatings. Cellulose nanomaterials from hardwoods clearly have a wide range of applications and products, and those applications continue to expand.

Many demonstrated applications of cellulose nanomaterials derived from sources other than hardwoods can also be extended to CNCs and CNFs derived from hardwoods, so some of these applications merit discussion in this context. CNFs can potentially be used in food applications as thickeners and to improve consistency and texture of foods (Turbak et al. 1982). CNFs have been demonstrated to improve the properties of paper and to facilitate the addition of inexpensive fillers (Phipps et al. 2015; Taipale et al. 2010). A variety of cellulose nanomaterials have been demonstrated to act as barriers to moisture and oxygen and to improve the barrier properties of polymers, so both CNCs and CNFs from hardwoods have the potential to be incorporated into packaging materials (Lavoine et al. 2012). CNFs have also been shown to act as a stabilizing agent for paints and other colloidal systems (Syverud 2011). The number of potential and demonstrated applications for cellulose nanomaterials is quite substantial and continues to grow. As the field matures, more of these applications are expected to become commercialized.

Outlook

Research and development of cellulose nanomaterials and their use in products is rapidly growing, and numerous efforts to advance commercialization are underway. Many see these biobased materials as potentially revolutionary for their unique properties, and market projections for cellulose nanomaterials are in the tens of millions of tons per year (Cowie et al. 2014; Shatkin et al. 2014). Cellulose nanomaterials are currently being produced at numerous demonstration- and pilot-scale facilities, many of which are operating at a scale on the order of a ton per day (Walker 2012). Cellulose nanomaterials are beginning to be incorporated into products, but manufacturers are reluctant to advertise the use of nanomaterials because of regulatory and public perception uncertainties. As the economics and health and safety impacts are better understood, the production and adoption of cellulose nanomaterials is expected to dramatically rise, and these materials have the potential to improve the value of hardwoods and offer partial solutions to forest management issues.

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Undervalued Hardwoods for Engineered Materials and Components

Second Edition

Forest Service
Forest Products Laboratory
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Abstract

This report summarizes information on the use of wood from hardwood species in engineered materials, components, and structures. It includes information on use in a wide variety of engineering products and applications.

Keywords: Wood; hardwoods; engineered products

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Undervalued Hardwoods for Engineered Materials and Components

Second Edition

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