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New Products and Product Categories in the Global Forest Sector

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Forests, covering about 30% of the earth’s land area, are a major component in the global ecosystem, influencing the carbon cycle, climate change, habitat protection, clean water supplies, and sustainable economies (FAO 2011). Globally, the vast cellulosic resource found in forests provides about half of all major industrial raw materials for renewable energy, chemical feedstock, and biocomposites (Winandy et al. 2008). Although forests and forest products have been used since the dawn of time, exciting new opportunities are emerging for sustainably meeting global energy needs and simultaneously creating new high-value biobased products from forests.

This chapter is organized into three sections, discussing new products and applications, all of which go beyond traditional solid wood products. The first section of this chapter focuses on forest product-derived nanomaterials and provides a brief description of technologies and applications of nanotechnology for forest-based products. The second section explores research and development trends in wood–plastic composites (WPCs). These products will increasingly penetrate the construction and value-added wood product

markets in the form of siding, fencing, bridge decking, foundation isolation elements, laminate flooring, residential furniture, utility poles, railroad ties, and exterior and interior molding and millwork. The third section covers chemicals derived from wood. It summarizes methods that use distinctive extraction processes that are attractive for new and higher value products and processes such as solvent extraction used to obtain phytosterols and hot water extraction used to obtain arabinogalactans. Books have been written about each of these categories; so in this chapter, we provide a general foundation of knowledge for the reader.

6.1 Nanoproducts

Less than two decades ago, the first reports of cellulose nanocomposites came out of France (Favier et al. 1995a,b), so the field is fairly new and there is still much to be learned, and great potential for the development of new materials with unique properties imparted with the aid of nanotechnology. The use of nanocellulose has been targeted for a number of unique effects, including reinforcement, barrier properties, and stimulus sensitivity.

Nanoparticles, with at least one dimension in the range of 1–100 nm, are materials that have been found to exhibit interesting physical and mechanical properties compared to coarse particles of the same composition (Wegner and Jones 2005). In the last few decades, many industrial and technological sectors have begun researching or adopting nanotechnology. In the forest products industry, nanotechnology is manifested in one of the two forms: nanomaterials derived from forest products or nanotechnology incorporated into traditional forest-based products. The focus of this section will be primarily on forest product—derived nanomaterials, but first a brief description of technologies and applications of nanotechnology into forest-based products is provided.

6.1.1 Incorporation of Nanotechnology into Forest Products

Nanoparticles are currently being added to wood-based products, primarily to enhance durability. Products are currently available on the market that employ nanoparticles to enhance ultraviolet (UV) resistance, scratch resistance, water repellency, fire retardancy, and microbial decay resistance. These nanoparticles are typically composed of inorganic materials, such as metals or clay. Nanoclays can add fire retardancy and barrier properties to materials, while metal nanoparticles are known best as antimicrobial agents. While the methods of incorporating these nanomaterials into products are varied and typically proprietary, they are often applied as thin exterior coatings.

6.1.2 Nanocellulose Introduction

As trees and plants are broken down into nanometer-scale fibers and particles (nanocellulose), the resulting materials begin to exhibit unique and interesting properties, which are resulting in new applications and industries in the twenty-first century. Some of the more unique properties of various nanocelluloses include remarkable strength, liquid crystal behavior in solution, transparency when cast as a film, low thermal expansion, capacity to absorb water, and piezoelectric and electroactive behavior.

Although commercial application of nanocellulose is currently in its infancy, applications are varied, covering many industries. Some applications include food additives (Turbak et al. 1982, 1983; Innami and Fukui 1987), medical and pharmaceutical applications (Innami and Fukui 1987; Pääkkö et al. 2008; Mathew and Oksman 2011), paper applications (Taipale et al. 2010; Klemm et al. 2011), automobile parts (Oksman et al. 2006), substrates for flexible displays (Nakagaito et al. 2010), electronic actuators (Olsson et al. 2010), battery membranes (Nyström et al. 2009), separation membranes (Pääkkö et al. 2008), barrier membranes (Paralakar et al. 2008), paints and coatings (Hoeger et al. 2011; Syverud 2011), and many more. Klemm et al. (2011) provide a good narrative of potential applications and list numerous nonpatents that have been filed.

In recent years, nanoscale cellulosic materials have received a great deal of attention because of their physical and mechanical properties and because of the abundance and renewability of sources of cellulose in forests and agricultural crops. Although numerous thorough reviews of cellulose nanomaterials have been recently compiled (Lima and Borsali 2004; Azizi Samir et al. 2005; Berglund 2005; Kamel 2007; Hubbe et al. 2008; Ioelovich 2008; Eichhorn et al. 2010; Habibi et al. 2010; Siró and Plackett 2010; Klemm et al. 2011; Moon et al. 2011; Peng et al. 2011), this section provides an introduction to the properties and potential applications of nanocellulose.

6.1.3 Nanocellulose Types, Sources, and Preparation Methods

Generally, nanocellulose is considered to be of three different types: cellulose nanocrystals (CNCs) (Figure 6.1), nanofibrillated cellulose (Figure 6.2), and microbial cellulose. CNCs consist of discrete, highly crystalline, rodlike cellulose particles, whereas nanofibrillated cellulose consists of more amorphous, high-aspect-ratio fiber networks. Microbial cellulose is excreted from bacteria (Berglund 2005) and has many similar properties to nanofibrillated cellulose. The source and production method both influence the size range and properties of the nanocellulose.

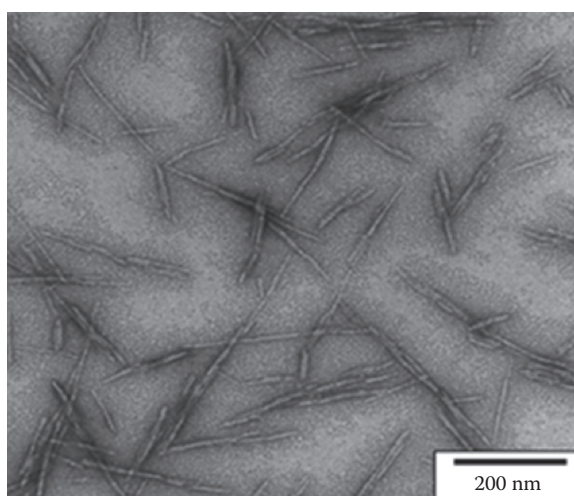
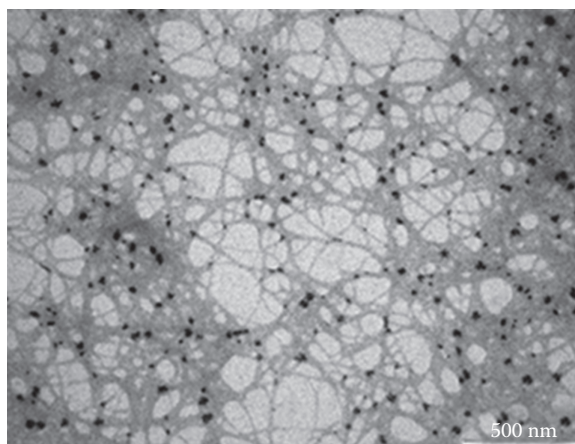


FIGURE 6.1

Transmission electron microscopy image of CNCs from wood. (From Moon, R.J. et al., *Chem. Soc. Rev.*, 40, 3941, 2011.)

**FIGURE 6.2**

Cellulose nanofibers prepared by TEMPO-mediated oxidation of eucalyptus pulp.

Sources for nanocellulose include forests, plants, animals, and microbes, all of which yield somewhat different sizes and types of nanocellulose (Beck-Candanedo et al. 2005). The plant source material for producing nanocellulose is quite varied and includes hardwood (Fukuzumi et al. 2009; Saito et al. 2009; Stelte and Sanadi 2009; Zhu et al. 2011) and softwood (Nakagaito and Yano 2004; Zimmerman et al. 2004; Henriksson et al. 2007; Pääkkö et al. 2007; Stelte and Sanadi 2009; Syverud and Stenius 2009) pulps, potatoes (Dufresne et al. 2000), sugar beet (Azizi Samir et al. 2004), pea hulls (Chen et al. 2009), sisal (Moran et al. 2008), wheat straw (Alemdar and Sain 2008a,b), and banana crop residues (Zuluaga et al. 2007). Most reported studies on nanocellulose production used material processed as nearly pure cellulose (Andresen et al. 2006; Bondeson et al. 2006; Henriksson et al. 2007), such as bleached wood fibers. However, some work has been done on the preparation of nanocellulose from pulps containing significant amounts of lignin and hemicelluloses (Okita et al. 2009).

CNCs are typically produced by the acid hydrolysis of native crystalline cellulose using hydrochloric, sulfuric, or phosphoric acid. Reports of cellulose crystals from acid hydrolysis date back to work done in the middle of the twentieth century (Battista 1950; Ranby 1951). Processes for producing stable colloidal solutions of crystalline cellulose by hydrolysis with sulfuric acid were later patented (Battista and Smith 1962; Battista 1975). The yield of nanocrystals from natural plant fibers is found to be about 30% (Bondeson et al. 2006).

Nanofibrillated cellulose production generally requires some method of mechanical refining of coarse cellulose fibers, and various chemical and enzymatic pretreatments have been explored to aid in the refinement of cellulose fibers. Mechanical actions through shearing or grinding have been used to produce nanocellulose (Nakagaito and Yano 2004; Andresen et al. 2006; Iwamoto et al. 2007; Alemdar and Sain 2008a).

The method was initially demonstrated through homogenization (Herrick et al. 1983; Turbak et al. 1983). Although cellulose nanofibers (CNFs) were successfully produced using a homogenizer, other mechanical methods, such as stone grinding and disk refining, have also been found to be useful for producing nanofibrillated cellulose (Iwamoto et al. 2007; Okahisa et al. 2009). The purely mechanical method is extremely energy intensive, with the energy consumption as high as 20,000–30,000 kWh/ton (Siró and Plackett 2010). Because the high energy consumption of early techniques was cost prohibitive,

research and development of nanofibrillated cellulose was slow to develop (Siró and Plackett 2010; Klemm et al. 2011). Recent advances in pretreatments and chemical methods for producing CNFs have reduced the energy requirements by more than an order of magnitude with energy consumption as low as 500 KWh/ton (Ankerfors and Lindström 2007, 2009).

6.1.4 Properties and Potential Applications of Nanocellulose and Cellulose Nanocomposites

The crystalline portion of cellulose has been characterized as having excellent mechanical properties. Researchers have both calculated and measured the strength and stiffness of cellulose building blocks to be quite high, making them potentially suitable for various applications, including composite reinforcement (Sakurada et al. 1962; Eichhorn et al. 2001; Azizi Samir et al. 2005; Lahiji et al. 2010; Moon et al. 2011; Postek et al. 2011). Moon et al. (2011) provide an excellent summary of the calculated and experimentally measured moduli of cellulose. A variety of other interesting properties of nanocellulose have been observed. For example, the crystalline portion of cellulose is reported to be piezoelectric and/or electroactive, making nanocellulose potentially suitable for actuators or smart devices (Fukada 2000; Kim and Yun 2006; Yun et al. 2008; Wegner and Jones 2009).

The suspensions of CNCs exhibit birefringence from the anisotropy of the crystals in solution either from their self-ordering at higher concentrations or from induced ordering (Revol et al. 1992; Revol and Marchessault 1993; Dong et al. 1996; Lima et al. 2003; Azizi Samir et al. 2005; Kimura et al. 2005; Beck-Candanedo et al. 2006; Teters et al. 2007). CNCs also align in the presence of an electric field (Lima et al. 2003; Teters et al. 2007). Such ordering properties of CNCs have potential applications in electronics and display devices.

CNF suspensions exhibit gel-like behavior at even low concentrations (Turbak et al. 1983; Pääkkö et al. 2007), and they are known to have shear thinning properties (Klemm et al. 2011). Such rheological properties make CNFs potentially suitable for thickening of foods and as additives in other industrial processes.

Natural fibers have been used extensively as reinforcement for composite materials, and because of their remarkable mechanical properties, nanocellulosic materials are expected to serve as excellent reinforcements. Nanofibrillated cellulose films tend to be transparent or at least translucent, have good mechanical properties, and are often used as a starting point for making composites. Dewatering CNF solutions presents a practical challenge, but CNFs have been commonly cast or filtered into films and evaluated for their properties. These films have been coined “nanopaper” and have been touted as the “strongest cellulose-based material made by man” (Ankerfors and Lindström 2007). A survey of the literature reveals reported tensile strengths of nanofibrillated cellulose films ranging from about 70 MPa to over 300 MPa and tensile moduli ranging from about 3 GPa to nearly 20 GPa. The transparency and flexibility, along with low thermal expansion, of CNF films make them suitable for flexible displays and electronics.

6.1.5 Outlook

Different types of nanocellulose have distinctive properties, so the applications for the various forms are likely to be different. CNCs certainly have some interesting properties and potential for applications such as security printing, scratch-resistant coatings, or liquid crystals. While CNCs from the sea animal have provided good reinforcement for polymer composites, the results have not been as widely successful with CNCs from plants,

especially wood. However, some promising success has been achieved using CNCs from plants such as ramie. Even so, most of the success of reinforcing polymers with CNCs uses solvent evaporation techniques that are not commercially viable. Given that tunicate (and even ramie) are not extremely abundant, it seems the widespread commercial adoption of CNCs as a polymer reinforcement is not likely. Perhaps some breakthrough research or technology will emerge that will change this perspective, but it seems that nanofibrillated cellulose is more likely than CNCs to act as a polymer reinforcement.

CNFs are somewhat analogous to pulp fibers used for producing paper products in that they exhibit entangled networks and can be formed into sheets using similar processes. Agglomeration of nanofibers does not seem to be as worrisome as for CNCs, and the sheets made from CNFs are much less brittle than CNCs and handle similar to paper made from coarse pulp fibers. Strength and other properties of CNF suspensions, sheets, and composites have led to adoption of CNFs in a variety of applications including rheology modification, paint emulsification, polymer reinforcement, coatings, and packaging. Therefore, CNFs are expected by many to prove as a useful material in a broad range of applications and markets in the future.

In the long term, nanotechnology is expected to add significant improvements in the performance and functionality of materials, including forest-based products. Nanomaterials are expected to dramatically enhance both mechanical and barrier properties of papers, packaging composites, and numerous other wood-derived materials. Furthermore, functionalized and tailored nanomaterials are expected to result in stimuli-sensitive products that will offer specific sensing capabilities, including the ability to detect contaminants and food spoilage. The unique properties of wood and other plants refined to the nanometer scale are expected to result in a new generation of renewable, forest-based products, including electronics and composites.

6.2 Trends in Wood–Plastic Composites

The term of WPCs is broad and encompasses the incorporation of wood and/or other lignocellulosic materials into thermoplastics. In the past decade, WPCs have become a widely recognized commercial product in construction, automotive, furniture, and other consumer applications. Commercialization of WPCs in North America has been primarily due to penetration into the construction industry. Current WPC applications include decking, railing, window and door lineals, roofing, picnic tables and benches, fencing, landscape timbers, patios, gazebos, pergolas, auto parts, and playground equipment (Smith and Wolcott 2006). The automotive industry in Europe has been a leader in using WPCs for interior panel parts and is leading the way in developing furniture applications. Manufacturers in Asia are targeting the furniture industry, in addition to interior construction and decorative applications.

Inorganic materials (e.g., glass, clays, and minerals) are used as reinforcements or fillers in the majority of reinforced or filled thermoplastics. Wood and other lignocellulosic materials offer some advantages over inorganic materials: they are lighter, much less abrasive, and renewable. Wood also may reinforce the thermoplastic by stiffening and strengthening and can improve thermal stability of the product compared with that of unfilled material. In typical WPCs, wood content is less than 60% by weight.

The manufacture of WPCs is usually a two-step process. The raw materials are first mixed together, and the composite blend is then formed into a product. The most common types of product-forming methods for WPCs involve forcing molten material through a die (sheet or profile extrusion) or into a cold mold (injection molding), and pressing in calenders (calendering) or between mold halves (thermoforming and compression molding).

Most WPCs in North America are formed using profile extrusion. Products such as decking, railings, and window profiles readily lend themselves to extrusion through a 2D die. Injection-molded applications such as consumer household goods and furniture parts are gaining importance. Thermoforming or compression molding is the forming method of choice for the automotive industry.

6.2.1 New Materials

Thermoplastics selected for WPCs traditionally have melt temperatures below 200°C (392°F) to maintain processing temperatures below the degradation point of the wood component. Higher processing temperatures can result in the release of volatiles, discoloration, odor, and embrittlement of the wood component. Thermoplastics commonly used in WPCs include polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). However, new manufacturing strategies allow for the use of engineering thermoplastics with melting temperatures higher than 230°C (446°F) such as polyethylene terephthalate (PET), polyamide (PA, nylon), and acrylonitrile butadiene styrene (ABS) (Gardner et al. 2008). The use of engineering thermoplastics for WPCs will grow as new applications requiring superior mechanical and thermal properties are introduced.

A driving force in the development of many new materials is to decrease our use of petroleum. Because the most common plastics used in WPCs, PE, and PP are typically derived from petroleum, there is growing interest in replacing the common WPC thermoplastics with bioplastics. Bioplastics, that is, plastics derived from renewable biomass, may also be biodegradable. Biodegradable bioplastics include polylactic acid (PLA) and starch acetate; nonbiodegradable bioplastics include cellulose acetate and bioderived PE and polyamide (Lampinen 2009). PLA has received the most attention from researchers as it is widely available commercially. Bioplastics will be particularly important in automotive and packaging applications.

The wood and/or lignocellulosics material used in WPCs can be derived from a variety of sources. Geographical location often dictates the material choice. In North America, wood is the most common raw material; in Europe, natural fibers such as jute, hemp, and kenaf are preferred, while rice hull flour and bamboo fiber are typical in Asia. The wood is incorporated as either fiber bundles with low aspect ratio (wood flour) or as single fibers with higher aspect ratio (wood fiber). Wood flour is processed commercially, often from postindustrial materials such as planer shavings, chips, and sawdust. Wood and lignocellulosic fibers are available from virgin and recycled sources. New lignocellulosic sources include paper mill sludge and biorefinery residues. Because wood and lignocellulosic fibers can lead to superior WPC properties by acting more as a reinforcement than a filler, in applications requiring additional strength, a trend is to move toward the use of wood and other lignocellulosic fibers.

The adaptation of nanotechnology in WPCs includes the use of nanofibers derived from wood and other lignocellulosics as a reinforcement for plastics. These new composites are termed cellulose nanocomposites. Cellulose nanocomposites are rapidly expected to open new markets in medicine, packaging, electronics, automotive, construction, and other

sectors (Oksman et al. 2009). The emergence of nontraditional forest products markets is particularly exciting.

Other materials can be added to affect processing and product performance of WPCs. These additives can improve bonding between the thermoplastic and wood components (e.g., coupling agents), product performance (talc, impact modifiers, UV light stabilizers, and flame retardants), and ability to be processed (lubricants). Additives for WPCs are continually evolving, but nanotechnology will drive changes in additive technology as the use of nanomaterials in small amounts in WPCs improves performance. The incorporation of nanomaterials into WPCs is still in its infancy and in the research stage but includes the use of carbon nanotubes (Faruk and Matuana 2008a; Jin and Matuana 2010), nanoclays (Faruk and Matuana 2008b; Hetzer and DeKee 2008), and nanosized titanium dioxide (Stark and Matuana 2009). It is expected that as nano-WPC technology becomes better understood, the use of these and other nanomaterials in WPCs will experience tremendous growth.

6.2.2 New WPC Manufacturing Techniques

Improvements in and changes to manufacturing methods will help pave the way for the next generation of WPCs. New processes under development include coextrusion, foaming during extrusion, and in-line coating technologies. Coextrusion consists of the extrusion of multiple materials through a single die simultaneously. The most common application in WPCs is coextrusion of an opaque, unfilled plastic cap layer over a WPC core. This process became popular for fencing and is quickly becoming the manufacturing method of choice for decking. The unfilled cap layer enhances durability by improving moisture resistance. In addition, coextrusion allows manufacturers to concentrate expensive additives such as biocides, fungicides, and photostabilizers in the cap layer. Coextrusion is also being evaluated as a method to extrude a clear plastic cap layer over a WPC core (Stark and Matuana 2009; Matuana et al. 2011). This method allows for a more natural appearance while still providing enhanced moisture resistance and concentrated stabilization. Others are evaluating coextrusion as a method to extrude an all WPC profile with different additives in different layers as needed (Yao and Wu 2010).

Growth is also expected in the production of foamed WPCs. Creating a microcellular foamed structure in WPCs not only results in weight reduction but also improves impact resistance and allows for better surface definition and sharper contours (Faruk et al. 2007). Chemical and physical foaming agents are typically used to foam WPCs. Chemical foaming agents decompose at processing temperatures into gases, while physical foaming agents liberate gases as a result of evaporation or desorption at elevated temperatures. A new trend in foaming is to meter and dissolve inert gases in the polymer melt during processing. This is termed extrusion foaming when done during extrusion (Diaz and Matuana 2009) or gas-assist injection molding if done during injection molding. Another option is to use moisture in the wood to foam WPCs (Gardner et al. 2008).

Applying a coating to WPCs post processing but before they are made available to the consumer is a growing trend to provide increased durability and enhanced aesthetics. Coatings can include latex paints, polyurethanes, or acrylics. However, surface treatments are required to attain adequate adhesion between the WPC and the coating. Treatments that have been found effective include oxygen plasma, flame, chromic acid, and benzophenone/UV irradiation (Gupta and Laborie 2008). Another treatment being commercialized uses fluorooxidation to modify the surface of WPCs for improved coating adhesion. The advantage of this process is that the rapid chemistry allows for in-line processing. Fluorooxidation also modifies only the outer few molecular layers so

embossed patterns are unaffected (Williams and Bauman 2007). New coatings being evaluated include UV-curable coatings and powder coating. Advantages of a UV-curable coating include virtually unlimited color choice and gloss level; long-term resistance to fading; increased scratch, stain, and mar resistance; and prevention of mold and mildew growth (Burton 2008).

6.2.3 Emerging Applications

Continued research and development will allow each new application to penetrate new global markets. For example, in North America, traditional wood applications that will see increased pressure from emerging technologies include siding, fencing, bridge decking, foundation isolation elements, marine structure (chocks, wales, and pier decking), laminate flooring, residential furniture (bathroom/kitchen cabinets and patio furniture), utility poles, railroad ties, and exterior and interior molding and millwork (Crespell and Vidal 2008). Emerging markets are expected as injection molding becomes more common for WPCs, including applications such as cosmetics packaging and toys. Markets in injection-molded automotive application are poised to grow in Europe and include parts such as glove boxes, fixing hooks, sound systems, and fan boxes (Carus et al. 2008).

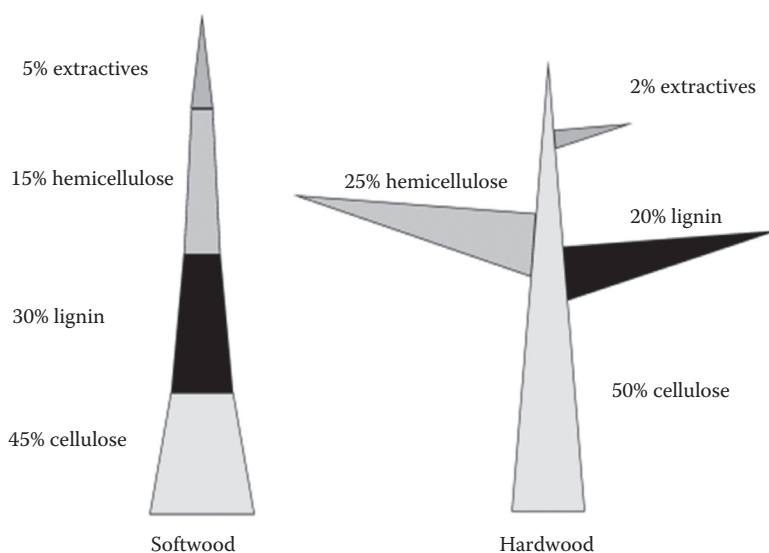
Growth is also expected as improvements to WPCs allow them to be used as structural members. There are various methods being investigated to improve the strength, stiffness, and creep performance of WPCs. Cross-linking the PE polymer matrix in WPCs using silanes in a reactive extrusion process can improve toughness, reduce creep, and improve durability (Bengtsson et al. 2006, 2007). Combining WPCs with other non-WPC materials is also a trend that will allow for more structural composites. Currently, some WPC manufacturers in China are extruding WPCs over solid metal or solid wood. This allows for structural members in applications such as pergolas and gazebos to have WPC surfaces that match the nonstructural members.

6.3 Wood Chemicals

Although there are hundreds of species of trees, the chemical makeup is quite consistent and falls into two broad groups. Softwood trees, also called evergreens or technically conifers, contain 25%–35% lignin, 40%–50% cellulose, and 10%–20% hemicellulose (Figure 6.3).

Hardwoods or deciduous trees contain 15%–25% lignin and 15%–30% hemicellulose. The cellulose content of hardwoods is about 45%–50%. Woods contain a group of small molecules often referred to as extractives. For softwoods, these include volatile chemicals classed as turpentine, fats and fatty acids, resin acids, steroids, and several groups of phenolic compounds. Softwood extractives range from as little as 2% up to as much as 10% of dry wood mass. Hardwood extractives are generally limited to fats and phenols with no or very little turpentine and resin acids. There are exceptions with some tropical species containing as much or more resin than softwoods, but this is not common.

Cellulose is a linear polymer of glucose sugars. The degree of polymerization is about 100,000 monomers and the cellulose regions are of sufficient uniformity and purity that they form highly ordered (crystalline) regions that are very resistant to chemicals and biological degradation. Hemicellulose consists of three polymeric groups of mixed sugars: xylan in which the dominant sugar is xylose, mannans with the dominant sugar being

**FIGURE 6.3**

Typical composition of softwood and hardwood tree species.

mannose, and arabinogalactans where the dominant sugar is galactose (Timell 1957, 1967; McGinnis and Shafizadeh 1980; Pettersen 1984). Xylans contain glucuronic acid as a secondary sugar acid in hardwoods and also contain some arabinose in softwoods. Mannan contains glucose as a secondary sugar in hardwoods and also contains some galactose in softwoods. Arabinogalactan is generally found at low levels in softwoods—about 2% with the exception being larch where it can be 10%–20% of wood mass. Lignin is a cross-linked phenolic polymer that helps to bind the carbohydrate polymers in the tree into a rigid composite structure. Although composed of just one (softwoods) or two (hardwoods) monomers, the bonding pattern is varied resulting in a mixture of reactive and chemically resistant bonds that produces a wide mixture of oligomers and very few pure and useful chemicals when lignin is chemically depolymerized.

Just as wood was the primary construction material and the primary fuel for preindustrial societies, it was also a primary source of organic chemicals. Many early paints and wood finishes were wood derived using a specific group of wood resins that did not remain sticky and did not crystallize. Initially, amber, the fossilized resin of a number of extinct softwoods, was used as the carrier or binder in paints. Later, other wood extrudents including damar (*Dipterocarpaceae* spp.), copals (*Hymenaea* spp.), and kauri (*Agathis australis*) were also used for this purpose. Shellac and tung oil are tree-derived wood finishes still commonly used today. Many fragrances including frankincense, myrrh, sandalwood, and vanillin (Hocking 1997) and some adhesives including Canada balsam and latex are obtained from trees. Some medications were also originally found in trees including quinine (*Cinchona* spp.), salicylic acid (aspirin) from *Betula* and *Salix* spp., and Taxol (Pacific yew) as examples. Tannins from oaks and other wood species were critical for tanning leather, a process used for over 5000 years.

A huge historical use of wood chemicals was and still is Naval stores, so named because pine pitch (pine tar) was critical for waterproofing the hulls and rigging of wooden sailing ships (Zinkel and Russell 1989). Pitch is specifically mentioned in Genesis when describing the construction of Noah's ark and was an item of international commerce during the



FIGURE 6.4
Gum harvesting for naval stores.

Greek and Roman eras. There are a number of methods for collecting and processing pine tar, but large industries (for the times) developed around bleeding resin from pine trees by cutting off strips of bark (Figure 6.4) and recovering resin from pine trees by heating the wood and stumps. The Scandinavian countries became major suppliers for much in Europe, and the British colonies in the Carolinas and Georgia and Florida became the major suppliers for England before the Revolutionary War. Slash pine was the preferred species for pine pitch and is named after the process of cutting the trunk to collect pitch. Wood also provided two of the earliest postindustrial textile fabrics (rayon and acetate), early barrier and clear films (cellophane and cellulose nitrate), and smokeless powder (cellulose nitrate).

Obviously, developments in petroleum, chemical industries, and new synthetic polymers have replaced many of these historic uses for wood chemicals, but the naval stores business continues using turpentine, resin acids, and fatty acids recovered from pulping processes, as well as remnants of the traditional recovery processes using steaming and destructive distillation of pine stumps. Fatty acids are still used to make soap, detergents, and other surfactants. Resin acids are also used for soaps and are modified to improve the properties of paints and varnishes.

Although many of the traditional uses of wood-based chemicals are declining, markets, pharmaceutical, nutraceutical, and specialty chemical product applications are expanding. The litany of known chemicals available in wood extractives and in waste liquor from wood pulping is well beyond the scope of this chapter, with books devoted to the topic (Rowe 1989). There are a number of high-value target compounds that cannot be readily prepared from starting materials found in petroleum. The problem for the forest products and chemical industries has always been the large numbers of similar compounds found in the wood and the high cost of separation processes needed to isolate the more valuable

of these compounds. It is said in the various commercial sectors of the industry that “we can make anything out of lignin or black liquor except money.” As industry moves into other chemical treatment methods, in particular, the biorefinery for fuels and commodity chemicals, the desire to capitalize on other wood chemicals remains high. New markets for wood chemicals are focusing on methods to collect target chemicals without producing a myriad of other compounds that lower yields and increase isolation costs.

The remainder of this section discusses the production of higher-value chemicals in a biorefinery producing wood sugars and current processes and research to obtain higher-value chemicals from the unused parts of the tree. The discussion focuses on phytosterols for nutraceutical use, xylitol as a low-calorie sugar substitute, and hemicelluloses including current use of arabinogalactans and research on new uses for xylans. There are also intense efforts to derive higher value from lignin (Zakzeski et al. 2010), bark (Pietarinen et al. 2006; Liimatainen et al. 2012), and knots (Pietarinen et al. 2006).

6.3.1 Biorefinery

Biorefinery as we understand it today is geared toward replacing petroleum-based fuels or commodity chemicals. There are two broad methods for converting wood in most modern concepts of biorefinery: hydrolysis to sugars (Mosier et al. 2005; Wyman et al. 2005) and partial combustion to produce pyrolysis oil or producer gas. Pyrolysis oil is a very complex mixture, and research today is directed at improving its characteristics to serve directly as a fuel oil or transportation fuel. Research on producer gas (synthesis gas) is focused on Fischer–Tropsch conversion to fuel oil (Anderson et al. 1952), synthetic natural gas (methane), or other stable, high-energy density liquid fuels (Tijmensen 2000). These processes are not well suited to provide high-value chemicals. On the other hand, fermentation methods are capable of producing more complex types of chemicals with higher value. Potential products include alcohols, such as ethanol, propanol, or butanol; diols, such as ethylene, propylene, or butylene diol; polyhydroxyalkanoates; and lactic acid (Hajny 1981; Werpy and Petersen 2004). During World War II, the US Government constructed a dilute acid wood hydrolysis plant with the intention of fermenting the sugars to ethanol for conversion into butadiene for synthetic rubber (Katzen and Schell 2006). Currently, there are industrial-scale processes producing lactic acid (Sreekumar and Thomas 2008), 1,3-propanediol (Kurian 2005), and polyhydroxyalkanoates (Poirier et al. 1995; Sreekumar and Thomas 2008). In all of these cases, the source of sugar is a sugar or starch crop but these are product options for biorefineries using wood as a raw material as well.

6.3.2 Phytosterols

The phytosterols are a group of over a dozen compounds of which sitosterol and campesterol are the most prevalent (Conner 1989). They can be a significant component of crude tall oil, the mixture of fatty acids, resin acids, and sterols that survive the pulping process and can be recovered from the soluble waste products. The sterols present a problem in that they are an impurity that reduces both the yield and value of the resin and fatty acids. Traditionally, crude tall oil is processed by distillation to collect a relatively pure fatty acid fraction, a relatively pure resin acid fraction, and a mixture in the still bottoms referred to as tall oil pitch (Conner 1989). Sterols can end up as contaminants in both the lower and higher boiling fractions (Holmbom and Era 1978; Traitler and Kratzl 1980; Smith 1989). The tall oil pitch fraction is typically 15%–25% of the crude tall oil and the phytosterols can be

as much as 25% of the tall oil pitch (Steiner and Fritz 1959; Holmbom and Era 1978). Again, they dilute the value of this fraction and discolor the product.

Several companies developed processes to remove the sterols before distillation, generally involving either solvent extraction or chemical derivitization followed by extraction (Conner 1989; Rouskova et al. 2011). A second method developed later is able to distill the steroids from the tall oil mixture by adding sodium hydroxide to raise the pH and convert the fatty and resin acids to less volatile salts. By 1980, Oy Kaukas AB in Finland was marketing the tall oil sterols as emulsifiers and viscosity modifiers for use in cosmetics. The ability of phytosterols to inhibit production of serum cholesterol was first reported by Pollak (1953). Sitosterol itself or the esters are used as a food additive to help people lower their cholesterol (Lichtenstein and Deckelbaum 2001; Maki et al. 2001). In addition, lower amounts of other sterols—sitostanol (also called stigmastanol) and campestanol—are available from crude tall oil (Murzin et al. 2007), and these are also used as food additives to inhibit the formation of cholesterol in humans.

These products have considerable market presence today as food-based sterols that help lower serum cholesterol. The Benecol® line of products originating from the Raisio Group in Finland includes margarine, yogurts, cream cheese, and bread, and the Becel brand of margarine (Promise—Smart Balance® Heart Right™) is produced by Unilever. As wood-based chemicals, they represent a new by-product with high value. The phytosterols also have use as starting chemicals for producing other steroid-based drugs including Rogaine®.

6.3.3 Xylitol

Xylitol is a low-calorie sweetener marketed by Danisco and now several other companies. Xylose, one of the five common sugars in wood (glucose, mannose, galactose, xylose, and arabinose), differs from glucose primarily in that it has just five carbons in the sugar molecule where glucose contains six carbons. Common table sugar produced from sugar cane is usually sucrose, a dimer containing one molecule of glucose and one molecule of a similar six-carbon sugar, fructose. Xylose is about twice the sweetness of sucrose (Robyt 1998) and is poorly adsorbed and metabolized by humans. It is not as chemically stable as glucose and sucrose and was not commonly marketed as a sugar substitute. A reduced form called xylitol is regarded as equally sweet as sucrose, stable, and has been used as a sugar substitute in Europe for many years. Xylitol penetration in the US market has been slower, possibly because it is toxic to dogs. Xylan is quite prominent in hardwoods, typically 20% or more of the dry wood mass.

Sugar is a relatively low-price commodity food product and this sets a price standard for low-calorie substitutes. Direct wood extraction of xylose has not been a suitable process primarily because of yield and cost. However, this option may work well in new wood-processing concepts, as the xylose is readily removed in the pretreatment processes needed to prepare the cellulose for enzyme hydrolysis. Xylan degrades in the kraft pulping process and is not available from this source. A less common pulping process uses acid to neutral pulping conditions with sulfurous acid or sodium sulfite as the active pulping chemical. Xylose is more stable under these conditions (Bryce 1980) and sulfite waste product or pulping liquor is a common source of xylose for xylitol (Heikkilä et al. 2005). The waste pulping liquor from hardwoods is obviously better than the liquor from softwoods. A single sulfite mill can supply 100 T of xylose per day as a valued product. As this market grows, Danisco and competitors may need to look for other sources. Biorefineries are clearly good candidates.

Xylitol represents a modest value use of a wood chemical. The higher concentration in sulfite waste liquors is fortuitous in that this process does not have a good chemical recovery process making the waste product less valuable as process fuel. There are also high concentrations of xylan in corn stover, and this option is equally valid for biorefinery concepts based on agricultural residuals, as it is for wood.

6.3.4 Hemicellulose

Xylitol is a sugar monomer produced from a hemicellulose, but two of the hemicellulose polymers have interesting product applications as polymers and oligomers. Arabinogalactan is a branched chain polymer of galactose monomers with short branches of one or two monomers of galactose or arabinose (Timell 1967). Galactose is a six-carbon sugar-like glucose, but the configuration of atoms around carbon 1 and carbon 4 are different. These seemingly minor changes make the sugar difficult for humans to digest and for microorganisms to ferment. It is not prevalent in most tree species, with Pettersen reporting 0.5%–2.7% arabinose and 1.0%–4.7% galactose in 19 North American softwood species. Because both arabinose and galactose are incorporated into other hemicellulose polymers in softwoods, the sugar analysis is not definitive of the polymer but does cap the maximum levels. Clearly, it cannot exceed about 7%, which Pettersen (1984) reported for Douglas fir. Missing from Pettersen's review is western larch (*Larix occidentalis*), which has an unusually high level of arabinogalactans, generally reported as between 8% and 17%. This is the commercial source of arabinogalactan (Schorger and Smith 1916; Wise and Peterson 1930; White 1941). Unique to arabinogalactan and somewhat to larch, the hemicelluloses can be extracted with water providing a relatively pure polymeric product (Schorger and Smith 1916; White 1941). Arabinogalactan extracted from larch has been an item of commerce for decades, formerly sold under the trade name Stractan by the St. Regis Paper Company and now sold by Lonza under various application specific trade names: ResistAid™ as an antioxidant food additive, LaraFeed™ as an animal nutrition supplement, and LaraCare™ as a cosmetic ingredient.

As stated in the section on xylitol, glucuronoxylan is the most abundant hemicellulose polymer in hardwoods. The polymer and monomer are of interest as by-products of biorefinery, dissolving pulp, and cellulose nanomaterial production processes. The xylan polymers are not really a product of commerce yet, but there is considerable interest in developing uses for this carbohydrate. Xylose is a less valuable sugar in sugar-based biorefinery applications where it is typically removed in the pretreatment and is hard to ferment using traditional organisms (Lee and McCaskey 1983). It is an impurity that must be removed for production of chemical dissolving pulp (Richter 1955; Simmonds et al. 1955; Bernardin 1958) and also is an impurity in the concentrated acid hydrolysis process used to isolate CNCs (Ranby 1952; Bondeson et al. 2006). It is expected that the polymer xylan and monomer sugar xylose are about to become either a valuable by-product or a costly waste product as cellulose-based biorefinery becomes a commercial reality. The current research interest is to find valuable uses.

Polymeric xylan is readily extracted from hardwoods, nearly intact, using 10% sodium hydroxide (Booker and Schuerch 1958; Sixta et al. 2011). This is an expensive process and will require a high-value use, but the residual wood can be used for dissolving pulp or other wood pulp applications (Lyytikäinen et al. 2011). The Finnish-sponsored BioRefine program is evaluating options to integrate this as a pretreatment into kraft pulping where the alkaline extraction liquor can be recovered after separating out the xylan and then used in the pulping process (Sixta et al. 2011).

In addition to xylitol discussed earlier, potential markets for xylan polymers include viscosity modifiers, cosmetics, and dietary fiber, similar to the arabinogalactans. Research groups are also working on modifying the polymer to produce clear barrier films (Gröndahl et al. 2004; Sixta et al. 2011; Escalante et al. 2012). As a packaging film, xylans are renewable and compostable, making them a green alternative for existing petroleum-based polymer films.

6.4 Conclusion

Renewable, recyclable, and compostable products sourced from trees have great potential as low ecological impact products and part of a new sustainable way of life. Wood is a green renewable material that has been accepted mostly as the structural members of choice for residential constructions. However, the potential for an array of wood-based building materials for application in sustainable buildings, both residential and commercial, has not been fully realized. With the incorporation of nanoscale science and engineering into wood-based building materials, new generations of multifunctional, high-performance, ultralow maintenance, and durable building materials and components can be achieved. Globally, the vast lignocellulosic and other wood chemical resources provide about half of all major industrial raw materials for renewable energy, chemical feedstock, and biocomposites. Conversion of woody biomass to biofuels is technically feasible, but this conversion process is marginally economical with the current technology and price of crude petroleum. An integrated utilization of biomass is needed to overcome economic shortcomings by optimizing biomass use and value for a wider array of products.

References

- Alemdar, A. and M. Sain. 2008a. Isolation and characterization of nanofibers from agricultural residues—Wheat straw and soy hulls. *Bioresource Technology*, 99(6):1664–1671, April 2008.
- Alemdar, A. and M. Sain. 2008b. Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties. *Composites Science and Technology*, 68(2):557–565, February 2008.
- Anderson, R.B., B. Seligman, J.F. Shultz, and M.A. Elliott. 1952. Fischer-Tropsch synthesis: Some important variables of the synthesis on iron catalysts. *Industrial and Engineering Chemistry*, 44(2):391–397.
- Andresen, M., L.S. Johansson, B.S. Tanem, and P. Stenius. 2006. Properties and characterization of hydrophobized microfibrillated cellulose. *Cellulose*, 13:665–677.
- Ankerfors, M. and T. Lindström. 2007. On the manufacture and use of nanocellulose. Presented at the *Ninth International Conference on Wood and Biofiber Plastic Composites*, Madison, WI.
- Ankerfors, M. and T. Lindström. 2009. *NanoCellulose Developments in Scandinavia*. A contribution to the *Paper and Coating Chemistry Symposium (PCCS)*, Hamilton, Ontario, Canada, June 2009.
- Azizi Samir, M.A.S., F. Alloin, and A. Dufresne. 2005. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*, 6:612–626.
- Azizi Samir, M.A.S., F. Alloin, M. Paillet, and A. Dufresne. 2004. Tangling effect in fibrillated cellulose reinforced nanocomposites. *Macromolecules*, 37:4313–4316.
- Battista, O.A. 1950. Hydrolysis and crystallization of cellulose. *Industrial and Engineering Chemistry*, 42:502–507.

- Battista, O.A. 1975. *Microcrystal Polymer Science*. McGraw-Hill Inc., New York.
- Battista, O.A. and P.A. Smith. 1962. Microcrystalline cellulose. *Journal of Industrial and Engineering Chemistry*, 54(9):20–29.
- Beck-Candanedo, S., M. Roman, and D.G. Gray. 2005. Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. *Biomacromolecules*, 6(2):1048–1054.
- Beck-Candanedo, S., D. Viet, and D.G. Gray. 2006. Induced phase separation in cellulose nanocrystal suspensions containing ionic dye species. *Cellulose*, 13:629–635.
- Bengtsson, M., K. Oksman, and N.M. Stark. 2006. Profile extrusion and mechanical properties of crosslinked wood-thermoplastic composites. *Polymer Composites*, 27(2):184–194.
- Bengtsson, M., N.M. Stark, and K. Oksman. 2007. Durability and mechanical properties of silane cross-linked wood thermoplastic composites. *Composites Science and Technology*, 67:2728–2738.
- Berglund, L. 2005. Cellulose-based nanocomposites. In A. K. Mohanty, M. Misra, and L. Drzal (eds.), *Natural Fibers, Biopolymers and Biocomposites*. CRC Press, Boca Raton, FL.
- Bernardin, L.J. 1958. The nature of the polysaccharide hydrolysis in black gumwood treated with water at 160°C. *TAPPI*, 41(9):491–499.
- Bondeson, D., A. Mathew, and K. Oksman. 2006. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose*, 13:171–180.
- Booker, E. and C. Schuerch. 1958. Extraction of pentosans from woody tissues, III. *TAPPI*, 41(11):650–654.
- Bryce, J.R.G. 1980. Sulfite pulping. In J.P. Casey (ed.), *Pulp and Paper, Chemistry and Chemical Technology*. Wiley & Sons, New York, pp. 291–376.
- Burton, K. 2008. A cure for wood alternatives: New UV coating technologies can enhance wood plastic composites, fiber cement siding and vinyl substrates used in the construction industry. *Finishing Today*, April 2008:32–35.
- Carus, M., C. Gahle, and H. Korte. 2008. Market and future trends for wood-polymer composites in Europe: The example of Germany. In *Wood-Polymer Composites*. Woodhead Publishing Ltd., Cambridge, U.K. pp. 300–330.
- Chen, Y., C. Liu, P.R. Chang, X. Cao, and D.P. Anderson. 2009. Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: Effect of hydrolysis time. *Carbohydrate Polymers*, 76(4):607–615.
- Conner, A.H. 1989. Chemistry of other components in naval stores. In D.F. Zinkel and J. Russell (eds.), *Naval Stores, Production, Chemistry, Utilization*. Pulp Chemicals Association, New York, pp. 440–475.
- Crespell, P. and M. Vidal. 2008. Market and technology trends and challenges for wood plastic composites in North America. In *Proceedings of the 51st International Convention of Society of Wood Science and Technology*, November 10–12, 2008, Concepción, Chile.
- Diaz, C.A. and L.M. Matuana. 2009. Continuous extrusion production of microcellular rigid PVC. *Journal of Vinyl and Additive Technology*, 15(4):211–208.
- Dong, X.M., T. Kimura, J.F. Revol, and D.G. Gray. 1996. Effects of ionic strength on the isotropic-chiral nematic phase transition of suspensions of cellulose crystallites. *Langmuir*, 12:2076–2082.
- Dufresne, A., D. Dupeyre, and M.P. Vignon. 2000. Cellulose microfibrils from potato tuber cells: Processing and characterization of starch-cellulose microfibril composites. *Journal of Applied Polymer Science*, 76(14):2080–2092.
- Eichhorn, S.J., C.A. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, K.M. Entwistle et al. 2001. Current international research into cellulosic fibres and composites. *Journal of Materials Science*, 36(2001):2107–2131.
- Eichhorn, S.J., A. Dufresne, M. Aranguren, N.E. Marchovich, J.R. Capadona, S.J. Rowan, C. Weder et al. 2010. Review: Current international research into cellulose nanofibres and nanocomposites. *Journal of Materials Science*, 45:1–33.
- Escalante, A., A. Goncalves, A. Bodin, A. Stepan, C. Sandström, G. Toriz, and P. Gatenholm. 2012. Flexible oxygen barrier films from spruce xylan. *Carbohydrate Polymers*, 87:2381–2387.
- Faruk, O., A.K. Bledzki, and L.M. Matuana. 2007. Microcellular foamed wood-plastic composites by different processes: A review. *Macromolecular Materials and Engineering*, 292:113–127.

- Faruk, O. and L.M. Matuana. 2008a. Reinforcement of rigid PVC/wood-flour composites with multi-walled carbon nanotubes. *Journal of Vinyl and Additive Technology*, 14(2):60–64.
- Faruk, O. and L.M. Matuana. 2008b. Nanoclay reinforced HDPE as a matrix for wood-plastic composites. *Composites Science and Technology*, 68(9):2073–2077.
- Favier, V., G.R. Canova, J.Y. Cavaillé, H. Chanzy, A. Dufresne, and C. Gauthier. 1995a. Nanocomposite materials from latex and cellulose whiskers. *Polymer for Advanced Technologies*, 6:351–355.
- Favier, V., H. Chanzy, and J.Y. Cavaillé. 1995b. Polymer nano-composite reinforced by cellulose whiskers. *Macromolecules*, 28:6365–6367.
- Food and Agriculture Organization of the United Nations (FAO). 2011. *State of the World's Forests*. FAO, Rome, Italy.
- Fukada, E. 2000. History and recent progress in piezoelectric polymers. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, 47(6):1277–1290.
- Fukuzumi, H., T. Saito, T. Wata, Y. Kumamoto, and A. Isogai. 2009. Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. *Biomacromolecules*, 10:162–165.
- Gardner, D.J., Y. Han, and W. Song. 2008. Wood plastic composites technology trends. *Proceedings of the 51st International Convention of Society of Wood Science and Technology* 2008. November 10–12, Concepción, Chile.
- Gröndahl, M., L. Erikson, and P. Gatenholm. 2004. Material properties of plasticized hardwood xylans for potential application as oxygen barrier films. *Biomacromolecules*, 5:1528–1535.
- Gupta, B.S. and M.P. Laborie. 2008. Surface activation and adhesion properties of wood-fiber reinforced thermoplastic composites. *The Journal of Adhesion*, 83(11):939–955.
- Habibi, Y., L.A. Lucia, and O.J. Rojas. 2010. Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chemical Reviews*, 110:3479–3500.
- Hajny, G.J. 1981. *Biological Utilization of Wood for Production of Chemicals and Foodstuffs*. USDA Forest Service, Research Paper: FPL 385. Available on-line: Forest Products Laboratory, Madison, WI.
- Heikkilä, H., M. Mänttari, M. Lindroos, and M. Nyström. 2005. Recovery of Xylose. U.S. Patent 6872316B2.
- Henriksson, M., G. Henriksson, L.A. Berglund, and T. Lindström. 2007. An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer Journal*, 43:3434–3441.
- Herrick, F.W., R.L. Casebier, J.K. Hamilton, and K.R. Sandberg. 1983. Microfibrillated cellulose: Morphology and accessibility. *Journal of Applied Polymer Science*, 37:797–813.
- Hetzer, M. and D. DeKee. 2008. Wood/polymer/nanoclay composites, environmentally friendly sustainable technology: A review. *Chemical Engineering Research and Design*, 86(10):1083–1093.
- Hocking, M.B. 1997. Vanillin: Synthetic flavoring from spent sulfite liquor. *Journal of Chemical Education*, 74(9):1055–1059.
- Hoeger, I., O.J. Rojas, K. Efimenko, O.D. Velez, and S.S. Kelley. 2011. Ultrathin film coatings of aligned cellulose nanocrystals from a convective-shear assembly system and their surface mechanical properties. *Soft Matter*, 7:1957–1967.
- Holmbom, B. and E. Era. 1978. Composition of tall oil pitch. *Journal of the American Oil Chemists' Society*, 55(3):342–344.
- Hubbe, M.A., O.J. Rojas, L.A. Lucia, and M. Sain. 2008. Cellulose nanocomposites: A review. *Bioresources*, 3(3):929–980.
- Innami, S. and Y. Fukui. 1987. Additive composition for food or drugs. U.S. Patent 4,659,388.
- Ioelovich, M. 2008. Cellulose as a nanostructured polymer: A short review. *Bioresources*, 3(4):1403–1418.
- Iwamoto, S., A.N. Nakagaito, and H. Yano. 2007. Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites. *Applied Physics A: Materials Science and Processing*, 89:461–466.
- Jin, S. and L.M. Matuana. 2010. Wood/plastic composites co-extruded with multi-walled carbon nanotube-filled rigid poly(vinyl chloride) cap layer. *Polymer International*, 59(5):648–657.
- Kamel, S. 2007. Nanotechnology and its applications in lignocellulosic composites, a mini review. *Express Polymer Letters*, 1(9):546–575. doi: 10.3144/expresspolymlett.2007.78.

- Katzen, R. and D.J. Schell. 2006. *Lignocellulosic Feedstock Biorefinery: History and Plant Development for Biomass Hydrolysis in Biorefineries—Industrial Processes and Products*. Vol. 1, Kamm, B., Gruber, P.R. and Kamm, M. (eds.). Wiley-Vch, Weinheim, Germany, pp. 129–138.
- Kim, J. and S. Yun. 2006. Discovery of cellulose as a smart material. *Macromolecules*, 39:4202–4206.
- Kimura, F., T. Kimura, M. Tamura, A. Hirai, M. Ikuno, and F. Horii. 2005. Magnetic alignment of the chiral nematic phase of a cellulose microfibril suspension. *Langmuir*, 21:2034–2037.
- Klemm, D., F. Kramer, S. Moritz, T. Lindstrom, M. Ankerfors, D. Gray, and A. Dorris. 2011. Nanocelluloses: A new family of nature-based materials. *Angewandte Chemie International Edition*, 50:5438–5466.
- Kurian, J. 2005. A new polymer platform for the future—Sonora from corn derived 1,3-propanediol. *Journal of Polymers and the Environment*, 13(2):159–167.
- Lahiji, R.R., X. Xu, R. Reifengerger, A. Raman, A. Rudie, and R.J. Moon. 2010. Atomic force microscopy characterization of cellulose nanocrystals. *Langmuir*, 26:4480–4488.
- Lampinen, J. 2009. Biocomposite research as a way to add value and sustainability to composites. *Proceedings 4th Wood Fibre Polymer Composites International Symposium*. March 30–31, 2009, Bordeaux, France.
- Lee, Y.Y. and T.A. McCaskey. 1983. Hemicellulose hydrolysis and fermentation of resulting pentoses to ethanol. *Tappi Journal*, 66(5):102–107.
- Lichtenstein, A.H. and R.J. Deckelbaum. 2001. Stanol/Sterol ester—Containing foods and blood cholesterol levels. *Circulation*, 103:1177–1179.
- Liimatainen, J., M. Karonen, J. Sinkkonen, M. Helander, and J.P. Salminen. 2012. Characterization of phenolic compounds from inner bark of *Betula pendula*. *Holzforschung*, 66:171–181.
- Lima, M.M.D.S. and R. Borsali. 2004. Rodlike cellulose microcrystals: Structure, properties, and applications. *Macromolecular Rapid Communications*, 25:771–787.
- Lima, M.M.D.S., J.T. Wong, M. Paillet, R. Borsali, and R. Pecora. 2003. Translational and rotational dynamics of rodlike cellulose whiskers. *Langmuir*, 19:24–29.
- Lyytikäinen, K., E. Saukkonen, I. Kajanto, and J. Käyhkö. 2011. The effect of hemicelluloses extraction on fiber charge properties and retention behavior of kraft pulp fibers. *Bioresources*, 6(1):219–231.
- Maki, K.C., M.H. Davidson, D.M. Umporowicz, E.J. Schaefer, M.R. Dicklin, K.A. Ingram, S. Chen et al. 2001. Lipid response to plant-sterol-enriched reduced fat spreads incorporated into a national cholesterol education program step 1 diet. *The American Journal of Clinical Nutrition*, 74:33–43.
- Mathew, A.P. and K. Oksman Niska. 2011. Artificial ligaments/tendons based on cellulose nanofibers. *11th International Conference on Wood & Biofiber Plastic Composites and Nanotechnology in Wood Composites Symposium*, May 18, Madison, WI.
- Matuana, L.M., S. Jin, and N.M. Stark. 2011. Ultraviolet weathering of HDPE/wood-flour composites coextruded with a clear HDE cap layer. *Polymer Degradation and Stability*, 96(1):97–106.
- McGinnis, G.D. and F. Shafizadeh. 1980. *Cellulose and Hemicellulose in Pulp and Paper, Chemistry and Chemical Technology*, Casey, J.P. (ed.). Wiley & Sons, New York, Chapter 1: pp. 1–38.
- Moon, R.J., A. Martini, J. Nairn, J. Simonsen, and J. Youngblood. 2011. Cellulose nanomaterials review: Structure, properties and nanocomposites. *Chemical Society Reviews*, 40:3941–3994.
- Moran, J.L., V.A. Alvarez, V.P. Cyas, and A. Vazquez. 2008. Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose*, 15:149–159.
- Mosier, N., C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, and M. Ladisch. 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, 96:673–686.
- Murzin, D.Y., P. Mäki-Arvela, T. Salmi, and B. Holmbom. 2007. Catalytic transformation for production of fine chemicals and pharmaceuticals from wood-derived raw materials. *Chemical Engineering and Technology*, 30(5):569–576.
- Nakagaito, A.N., M. Nogi, and H. Yano. 2010. Displays from transparent films of natural nanofibers. *MRS Bulletin*, 35:214–218.

- Nakagaito, A.N. and H. Yano. 2004. The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Applied Physics A: Materials Science and Processing*, 78:547–552.
- Nyström, G., A. Razaq, M. Strømme, L. Nyholm, and A. Mihranyan. 2009. Ultrafast all-polymer paper-based batteries. *Nano Letters*, 9(10):3635–3639.
- Okahisa, Y., A. Yoshida, S. Miyaguchi, and H. Yano. 2009. Optically transparent wood–cellulose nanocomposite as a base substrate for flexible organic light-emitting diode displays. *Composites Science and Technology*, 69:1958–1961.
- Okita, Y., T. Saito, and A. Isogai. 2009. TEMPO-mediated oxidation of softwood thermomechanical pulp. *Holzforschung*, 63:529–535.
- Oksman, K., A.P. Mathew, D. Bondeson, and I. Kvien. 2006. Manufacturing process of cellulose whiskers/poly(lactic acid) nanocomposites. *Composites Science and Technology*, 66:2776–2784.
- Oksman, K., A.P. Mathew, and M. Sain. 2009. Novel bioanocomposites: Processing, properties and potential applications. *Plastics, Rubber and Composites*, 38(9–10):396–405.
- Olsson, R.T., M.A. Azizi Samir, G. Salazar-Alvarez, L. Belova, V. Ström, L.A. Berglund, O. Ikkala, J. Nogués, and U.W. Gedde. 2010. Making flexible magnetic aerogels and stiff magnetic nanopaper using cellulose nanofibrils as templates. *Nature Nanotechnology*, 5:584–588.
- Pääkkö, M., M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen et al. 2007. Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*, 8(6):1934–1941.
- Pääkkö, M., J. Vapaavuori, R. Silvennoinen, H. Kosonen, M. Ankerfors, T. Lindström, L.A. Berglund, and O. Ikkala. 2008. Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically porous templates for functionalities. *Soft Matter*, 4:2492–2499.
- Paralikar, S.A., J. Simonsen, and J. Lombardi. 2008. Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes. *Journal of Membrane Science*, 320:248–258.
- Peng, B.L., N. Dhar, H.L. Liu, and K.C. Tam. 2011. Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective. *The Canadian Journal of Chemical Engineering*, 89:1191–1206.
- Pettersen, R.C. 1984. The chemical composition of wood. In R.M. Rowell (ed.), *The Chemistry of Solid Wood*. American Chemical Society, Washington, DC, Chapter 2: pp. 57–126.
- Pietarinen, S.P., S.M. Willför, M.O. Ahotupa, J.E. Hemming, and B.R. Holmbom. 2006. Knotwood and bark extracts: Strong antioxidants from waste materials. *Journal of Wood Science*, 52:436–444.
- Poirier, Y., C. Nawrath, and C. Somerville. 1995. Production of polyhydroxyalkanoates, a family of biodegradable plastics and elastomers, in bacteria and plants. *Biotechnology*, 13:142–150.
- Pollak, O.J. 1953. Successful prevention of experimental hypercholesterolemia and cholesterol atherosclerosis in rabbit. *Circulation*, 7:696–701; Reduction of blood cholesterol in man. *Circulation*, 7:702–706.
- Postek, M., A. András Vladár, J. Dagata, N. Farkas, B. Ming, R. Wagner, A. Raman et al. 2011. Development of the metrology and imaging of cellulose nanocrystals. *Measurement Science and Technology*, 22:024005.
- Ranby, B.G. 1951. The colloidal properties of cellulose micelles. *Discussions of the Faraday Society*, 11:158–164.
- Ranby, B.G. 1952. The cellulose micelles. *Tappi*, 35(2):53–58.
- Revol, J.F., H. Bradford, J. Giasson, R.H. Marchessault, and D.G. Gray. 1992. Helicoidal self-ordering of cellulose microfibrils in aqueous suspension. *International Journal of Biological Macromolecules*, 14:170–172.
- Revol, J.F. and R.H. Marchessault. 1993. In vitro chiral nematic ordering of chitin crystallites. *International Journal of Biological Macromolecules*, 15:329–335.
- Richter, G.A. 1955. Production of high alpha-cellulose wood pulps and their properties. *Tappi*, 38(3):129–150.
- Robyt, J.F. 1998. *Essentials of Carbohydrate Chemistry*. Springer-Verlag, New York, p. 143.

- Rouskova, M., A. Heyberger, J. Triska, and M. Krticka. 2011. Extraction of phytosterols from tall oil soap using selected organic solvents. *Chemical Papers*, 65(6):805–812.
- Rowe, J.W. 1989. *Natural Products of Woody Plants*, 2 vols. Springer-Verlag, Berlin, Germany.
- Saito, T., M. Hirota, N. Tamura, S. Kimura, H. Fukuzumi, L. Heux, and A. Isogai A. 2009. Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using tempo catalyst under neutral conditions. *Biomacromolecules*, 10:1992–1996.
- Sakurada, I., Y. Nukushina, and T. Ito. 1962. Experimental determination of the elastic modulus of crystalline regions in oriented polymers. *Journal of Polymer Science*, 57:651–659.
- Schorger, A.W. and D.F. Smith. 1916. The galactan of *Larix occidentalis*. *Industrial and Engineering Chemistry*, 8(6):494–499.
- Simmonds, F.A., R.M. Kingsbury, and J.S. Martin. 1955. Purified hardwood pulps for chemical conversion. *Tappi*, 38(3):178–186.
- Siró, I. and D. Plackett. 2010. Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose*, 17:459–494.
- Sixta, H., L. Testova, M. Alekhina, A. Roselli, O. Ershova, M. Tenkanen, H. Komu et al. 2011. Raw material pretreatment, fractionation and extraction. In *Bio Refine Yearbook 2011*, Tekes Review. Helsinki, Finland. pp. 17–29.
- Smith, K.T. 1989. Vinsol resin and tall oil pitch, in naval stores. In D.F. Zinkel and J. Russell (eds.), *Naval Stores, Production, Chemistry, Utilization*. Pulp Chemicals Association, New York, pp. 715–737.
- Smith, P.M. and M. Wolcott. 2006. Opportunities for wood/natural fiber-plastic composites in residential and industrial applications. *Forest Products Journal*, 56(3):4–11.
- Sreekumar, P.A. and S. Thomas. 2008. Matrices for natural-fiber reinforced composites. In K.M. Pickering (ed.), *Properties and Performance of Natural-Fiber Composites*. Woodbridge Publishing Ltd., Cambridge, U.K. Chapter 2: pp. 67–126.
- Stark, N.M. and L.M. Matuana. 2009. Co-extrusion of WPCs with a clear cap layer to improve color stability. *Proceedings of 4th Wood Fiber Polymer Composites International Symposium*, March 30–31, 2009, Bordeaux, France.
- Steiner, C.S. and E. Fritz. 1959. Pharmaceutical-grade sterols from tall oil. *Journal of the American Oil Chemists Society*, 36(8):354–357.
- Stelte, W. and A.R. Sanadi. 2009. Preparation and characterization of cellulose nanofibers from two commercial hardwood and softwood pulps. *Industrial and Engineering Chemistry Research*, 48:11211–11219.
- Syverud, K. 2011. A novel application of cellulose nanofibrils for improving the water resistance of commercial paints. Presented at the *11th International Conference on Wood & Biofiber Plastic Composites and Nanotechnology in Wood Composites Symposium*, May 18, 2011, Madison, WI.
- Syverud, K. and P. Stenius. 2009. Strength and barrier properties of MFC films. *Cellulose*, 16:75–85.
- Taipale, T., M. Österberg, A. Nykänen, J. Ruokolainen, and L. Janne. 2010. Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. *Cellulose*, 17:1005–1020.
- Teters, C., W. Kong, M. Taylor, J. Simonsen, M. Lerner, T. Plant, and G. Evans. 2007. The cellulose nanocrystal electro-optic effect. Presented at the *International Conference on Nanotechnology for the Forest Products Industry*, June 13–15, Knoxville, TN.
- Tijmensen, M.J.A. 2000. *The Production of Fischer-Tropsch Liquids and Power Through Biomass Gasification*. University of Utrecht, Utrecht, The Netherlands. NWS-E-2000-29, ISBN 90-73958-62-8. Doctoral thesis.
- Timell, T.E. 1957. Carbohydrate composition of ten North American species of wood. *Tappi*, 40(7):568–572.
- Timell, T.E. 1967. Recent progress in the chemistry of wood hemicelluloses. *Wood Science and Technology*, 1:45–70.
- Traitler, H. and K. Kratzl. 1980. Investigations on tall oil of southern pine wood. Part 2: Tall oil pitch. *Wood Science and Technology*, 14:101–106.
- Turbak, A.F., F.W. Snyder, and K.R. Sandberg. 1982. Food products containing microfibrillated cellulose. U.S. Patent 4,341,807.

- Turbak, A.F., F.W. Snyder, and K.R. Sandberg. 1983. Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential. *Journal of Applied Polymer Science, Applied Polymer Symposium*, 37:815–827.
- Wegner, T. and P. Jones. 2005. Nanotechnology for the forest products industry. *Wood and Fiber Science*, 37(4):549–551.
- Wegner, T. and P. Jones. 2009. A fundamental review of the relationships between nanotechnology and lignocellulosic biomass. In Lucian, A.L. and Orlando, J.R. (eds.), *The Nanoscience and Technology of Renewable Biomaterials*. John Wiley & Sons Ltd, West Essex, U.K.
- Werpy, T. and G. Petersen. 2004. *Top Value Added Chemicals from Biomass*. Vol. 1. US Department of Energy, National Renewable Energy Laboratory, Golden, CO, DOE/GO-102044-1992.
- White, E.V. 1941. The constitution of arabo-galactan. I. The components and position linkage. *Journal of the American Chemical Society*, 63:2871–2875.
- Williams, K. and B. Bauman. 2007. New technology for enhancing wood-plastic composites. *JCT CoatingsTech*, 4(8):52–57.
- Winandy, J.E., A.W. Rudie, R.S. Williams, and T.H. Wegner. 2008. Integrated biomass technology: A future vision for optimally using. *Forest Products Journal*, 58(6):6–16.
- Wise, L.E. and F.C. Peterson. 1930. The chemistry of wood, II—Water-soluble polysaccharide of western larch wood. *Industrial and Engineering Chemistry*, 22(4):362–365.
- Wyman C.E., B.E. Dale, R.T. Elander, M. Holtzapple, M.P. Ladisch, and Y.Y. Lee. 2005. Coordinated development of leading biomass pretreatment technologies. *Bioresource Technology*, 96:1959–1966.
- Yao, F. and Q. Wu. 2010. Coextruded polyethylene and wood-flour composite: Effect of shell thickness, wood loading, and core quality. *Journal of Applied Polymer Science*, 118:3594–3601.
- Yun, G.Y., H.S. Kim, J. Kim, K. Kim, and C. Yang. 2008. Effect of aligned cellulose film to the performance of electro-active paper actuator. *Sensors and Actuators A*, 141(2008):530–535.
- Zakzeski, J., P.C.A. Bruijninx, A.L. Jongerius, and B.M. Weckhuysen. 2010. The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*, 110:3552–3599.
- Zhu, J.Y., R. Sabo, and X.L. Luo. 2011. Integrated production of nano-fibrillated cellulose and biofuel (ethanol) by enzymatic fractionation of wood fibers. *Green Chemistry*, 13(5):1339–1344.
- Zimmermann, T., E. Pohler and T. Geiger. 2004. Cellulose fibrils for polymer reinforcement. *Advanced Engineering Materials*, 6(9):754–761.
- Zinkel, D.F. and J. Russell. 1989. *Naval Stores*. Pulp Chemicals Association, New York.
- Zuluaga, R., J.L. Putaux, A. Restrepo, I. Mondragon, and P. Ganan. 2007. Cellulose microfibrils from banana farming residues: Isolation and characterization. *Cellulose*, 14:585–592.

