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A Fundamental Review of the Relationships between Nanotechnology and Lignocellulosic Biomass

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1.1 Introduction

At first glance, the relationship between nanotechnology and lignocellulosic biomass may seem to be unconnected or at best tenuously connected. It is important to recognize that. at a fundamental level, lignocellulosic biomass is made up of nanometer-size constitutive building block units that provide valuable properties to wood and other types of renewable lignocellulosic and cellulosic biomaterials. Other composite biomaterials, such as bone, teeth, and seashells, have been found to owe their high strength and optical properties to the nanometer dimensions of their building blocks (Sarikaya *et al.* 2003). Similarly, the nanometer dimensions of the cellulose, lignin and other components provide the origin for the unique properties of wood and a host of wood-based products including paper, paperboard, oriented strandboard, glulam beams, etc. (Klemm et al. 2005). For example, paper represents a material produced from fibers that have been 'pulped' and refined to liberate fibrils, microfibrils/nanofibrils, and nanocrystalline cellulose that are responsible for its inherent strength and performance (Brown et al. 1987). While the relative mass of the nanofibrils and nanocrystalline cellulose are small their surface area is large and by number they represent an enormous fraction which has significant consequences.

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Nanotechnology holds great promise of revolutionizing materials use in the 21st century, while lignocellulosic and like-derived biomass provide the key materials platform for the sustainable production of renewable, recyclable, and environmentally preferable goods and products to meet the needs of people in our modern society (Saxton 2007). Nanotechnology can be used to tap the enormous undeveloped potential that trees possess – as photochemical 'factories' that produce rich sources of raw materials using sunlight and water. The merging of nanotechnology and lignocellulosic biomass utilization is vital in sustainably meeting the needs of people for food, clothing, shelter, commerce, and the array of products and goods needed for quality of life considerations both in meeting creature comfort needs but also ecological needs. It is critically important to move forward nanotechnology involving renewable biomaterials by: exploiting wood as an important sustainable and renewable industrial nanomaterial; enabling other nanomaterials to be used in conjunction with lignocellulosic products to impart greater functionality; reducing materials use in producing, for example, wood-based products; and reducing the environmental footprint for producing such materials and products.

The concepts of sustainability and sustainable development provide a convenient contextual framework for examining the importance of the interrelationship of nanotechnology and biomass. Sustainability is many times viewed as a desired goal of development and environmental management. The term 'sustainability' has been used in a variety of disciplines and in numerous contexts, ranging from the concept of maximum sustainable yield in lignocellulosic biomass management to the vision of a sustainable society with a sustainable economy. The meaning of the term is strongly dependent on the context in which it is applied and on whether its use is based on a social, economic, or ecological perspective. Sustainability may be defined broadly or narrowly, but any useful definition must explicitly specify the context as well as the temporal and spatial scales being considered. Although societies differ in their conceptualizations of sustainability, indefinite human survival requires basic support systems which can be maintained only by a healthy environment and a sustainable use of resources. The definition of sustainability is generally that defined by the 1987 Brundtland Commission for sustainable development – meeting the needs of the present without compromising the ability of future generations to meet their own needs (Brundtland 1987). Other definitions include those of the World Business Council for Sustainable Development who defines sustainable development as forms of progress that meet the needs of the present without compromising the ability of future generations to meet their needs. With respect to lignocellulose and lignocellulosic products (e.g. forests and forest products), sustainability can be framed as asking whether those that come after us will be able to enjoy the same or better values and benefits from lignocellulosics as we do today (Society of American Foresters 2003) As we move forward in providing the goods and services needed by the billions of people in our world, we must seek to be good stewards of ecosystems locally, regionally, and globally; minimize the environmental footprint of our modern society; and allow for raising the living standards and quality of life for everyone. We must strive to achieve the preceding without hindering economic and technological growth, development, and progress or hindering the ability of future generations to meet their needs.

1.2 Use of Lignocellulosic-based Materials

Matos and Wagner reported on the use of raw materials in the United States and noted a trend away from renewable materials in the first half of the 20th century (Figure 1.1) as population increased and the US economy moved from an agricultural to an industrial base (Matos 1998). In the latter half of the century there was a large increase in raw materials use as population continued to increase more rapidly and the economy began a shift toward a service-based economy (Figure 1.2) (Matos and Wagner 1998). These trends resulted in significant changes in the mix of raw materials used (Sznopek and Brown 1998, Matthews and Hammond 1999).

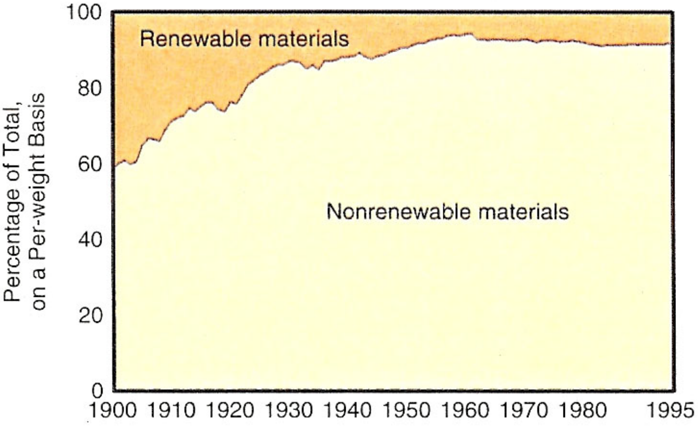

Figure 1.1 *Renewable materials use in the United States, 1900–1995.*

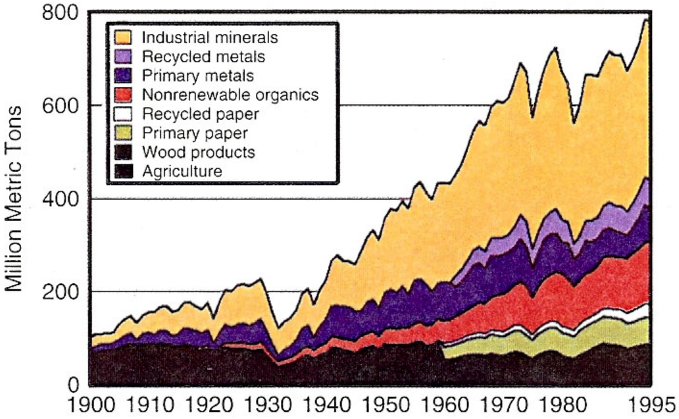

Figure 1.2 *Materials use in the United States, 1900–1995.*

It is noteworthy to observe in Figure 1.2 that the only renewable raw materials used in significance tonnages to be readily visible are lignocellulosic-based materials (i.e. wood products, primary paper and recycled paper). These raw materials represent approximately 20% of the materials consumed. Hence, when it comes to use of renewable raw materials to produce products, lignocellulosic-based materials are extremely important and represent the key renewable raw material link to sustainability. The use of lignocellulosic-based materials provides the opportunity to produce functional materials sustainably for an array of end uses from environmentally preferable or, in the worst case, environmentally benign materials that have been commonly used by mankind for millennia. Carbon dioxide (CO_2) from the atmosphere under the effect of photosynthesis in the tree produces the lignocellulosic materials we recognize as wood. In the US, about 700 million tons (dry basis) of lignocellulosic forest biomass accumulate annually. As a result, the standing stock of timber in the US continues to grow and is currently over 20 billion dry tons. About 300 million tons of this is harvested annually, leaving a very large amount of biomass potentially available for conversion into a variety of new products, energy, or chemicals. Indeed, the rates of current harvest levels are not sufficient to contain the ravages of forest wildfires. Additionally, it has been shown that it will be possible to increase production rate sustainably to levels of 1 billion tons per year through the application of advanced silviculture practices and genetics to wood-based plantations on a portion of the forest lands in the US (Perlack *et al.* 2006).

Worldwide, forests provide a vast timber resource that is geographically and geopolitically dispersed among 150 countries (United Nations 2005). These 150 countries account for 97.5% of the world's forests. Globally, approximately 3.87 billion hectares (ha) are covered by forests; out of a total land mass of 13.06 billion ha. The forests of the world contain over 386 billion m^3 of standing timber with annual use being on the order of approximately 3.8 billion m^3 per year. Globally, the gross value-added by the forestry sector in 2000 (including forestry, logging and related activities, the manufacturing of wood, wood products, paper and paper products) is estimated at about US$354 billion, or about 1.2% of the world's gross domestic product. The importance of wood in the economy of the US and North America can not be understated. With approximately 226 million ha of forestland, the US produces about 25% of the world's industrial roundwood. Together the US and Canada produce approximately 40% of the world's industrial roundwood.

1.3 Green Chemistry and Green Engineering

The use of lignocellulosic-based materials to produce products that meet the needs of people in a sustainable and ecologically preferable manner is (1) based upon the efficient use of solar energy and CO_2 and (2) in keeping with the principles of both Green Chemistry and Green Engineering (Anastas and Warner 1998). Our current industries using lignocellulosic products have evolved over many years. The technologies involved minimize waste and produce safe materials with minimal hazardous by-product generation. After use, spent products can be recycled or will degrade with minimal environmental consequences. The lignocellulosic forest products industry has installed tens of billions of dollars of capital equipment to be in compliance with stringent environmental rules, regulations and quality standards in its role as a responsible and trusted producer of materials for our modem society. Nanotechnology, as it is envisioned for application to lignocellulosic products, is only expected to further enhance industry's ability to produce consumer products from lignocellulosic-based materials in a safe, sustainable manner in harmony with the principles of both Green Chemistry and Green Engineering. As nanotechnology with respect to lignocellulosic-based materials moves forward, it is important to know and adhere to the currently defined principles of both Green Chemistry and Green Engineering (Jenck *et al.* 2004, Schmidt 2007). The Principles of Green Chemistry are as follows:

1. *Prevent waste* – design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. Design safer chemicals and products – design chemical products to be fully effective, yet have little or no toxicity.
3. *Design less hazardous chemical syntheses* – design syntheses to use and generate substances with little or no toxicity to humans and the environment-
4. *Use renewable feedstocks* – use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. *Use catalysts, not stoichiometric reagents* – minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. *Avoid chemical derivatives* – avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. *Maximize atom economy* – design syntheses so that the find product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. *Use safer solvents and reaction conditions:* Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. *Increase energy efficiency* – run chemical reactions at ambient temperature and pressure whenever possible.
10. *Design chemicals and products to degrade after use* – design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. *Analyze in real time to prevent pollution* – include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of by products.
12. *Minimize the potential for accidents* – design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, and releases to the environment.

As mentioned, the principles of Green Engineering are also important in taking advantage of nanotechnology with lignocellulosic products and will lead to more socially acceptable materials and products derived from trees. The Principles of Green Engineering[1] are as follows (Schmidt 2007):

1. Engineer processes and products holistically, use systems analysis, and integrate environmental impact assessment tools.
2. Conserve and improve natural ecosystems while protecting human health and well-being.
3. Use life-cycle thinking in all engineering activities.
4. Ensure that all material and energy inputs and outputs are as inherently safe and benign as possible.
5. Minimize depletion of natural resources.
6. Strive to prevent waste.
7. Develop and apply engineering solutions, while being cognizant of local geography, aspirations, and cultures.
8. Create engineering solutions beyond current or dominant technologies; improve, innovate, and invent (technologies) to achieve sustainability.
9. Actively engage communities and stakeholders in development of engineering solutions.

As we apply nanotechnologies to the lignocellulosic products industry, we will need to be cognizant of how the applications of these new technologies adhere to and advance Green Chemistry and Green Engineering principles.

1.4 Nanotechnology

The ability to see materials at or near atomic dimensions and to measure physical properties at these scales has enabled the emergence of a discipline now known as Nanotechnology. At these scales and up to approximately 100 nm unusual properties are often encountered. In addition many fundamental properties are driven by processes scaled at the 10s of nm dimension. Many 'natural products' with valuable properties such as silk, wool, nacre, wood and clay have building blocks that are 1 to 10s of nm in dimension and owe their valuable properties to these nanometer-scale building blocks (Roco 2003). Table 1.1 shows a short compilation of some of the key physical properties and their dimensional dependencies.

Already, there are over 700 nanomaterial-containing products available in the market place, including coatings, computers, clothing, cosmetics, sports equipment, and medical devices (Langsner 2006). The estimated global market for nanotechnology enabled products was approximately US$9.4 billion in 2005, over US$10.5 billion in 2006, and projected to grow to over US$25 billion by 2011 (Lux Research Inc. 2004, Hullmann 2006, Technology Transfer Center 2007). Nanomaterials – particularly nanoparticles and nanocomposites – currently account for over 85% of the market. Currently used nanomaterials include carbon nanotubes, carbon black fillers, nanocatalyst thin films, nanodimensional additives, and nanoscale sensors.

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[1] As developed by more than 65 engineers and scientists at the Green Engineering: Defining the Principles Conference, held in Sandestin, Florida in May 2003.

Table 1.1 *Characteristic lengths in solid-state science model.*

Property	Scale length
Mechanics	
Dislocation interaction	1–1000 nm
Grain boundaries	1–10 nm
Crack tip radii	1–100 nm
Nucleation/growth defect	0.1–10 nm
Surface corrugation	1–10 nm
Supramolecules	
Kuhn length	1–100 nm
Secondary structure	1–10 nm
Tertiary structure	10–1000 nm
Electronics	
Electronic wavelength	10–100 nm
inelastic mean free path	1–100 nm
Tunneling	1–10 nm
Magnetics	
Domain wall	10–100 nm
Spin-flip scattering length	1–100 nm
Optics	
Quantum well	1–100 nm
Evanescent wave decay length	10–100 nm
Metallic skin depth	10–100 nm

Source: Murday (2002); Pritkethly (2003).

To date, major national research and development efforts have generally been focused on how nanotechnology can improve efficiency in manufacturing, energy resources and utilization, reduce environmental impacts of industry and transportation, enhance healthcare, produce better pharmaceuticals, improve agriculture and food production, and expand the capabilities of information technologies. Breakthroughs in nanoscale science and engineering are seen as a foundation for systemic economic progress. Nanotechnology is expected to lower raw materials costs in some industries; dramatically improve productivity in others; create some entirely new industries; and increase demand for some goods while lowering demand for others. Over the course of the 21st century we will transition from the relatively crude and unsophisticated technologies society depends upon today to highly efficient and environmentally friendly nanotechnologies. Industries that have been regarded as traditional, with few new scientific challenges, are re-emerging as exciting new areas. The challenges involved with developing and industrially applying nanotechnology are enormous and it is only now that we have the scientific tools to address biomaterials such as wood and paper. Maximizing human benefit will require the development of transformational tools that can be shared across scientific disciplines and industries such as: new scientific instrumentation; overarching theoretical concepts; methods of interdisciplinary communication; and new techniques for production such as those bridging the gap between organic and inorganic materials.

As we move forward, it is vitally important to use common nomenclature and definitions with respect to nanotechnology (American Society for Testing and Materials 2006). The following are the definitions generally used within the nanotechnology community:

- *Nanoparticles* – a particle with one or more dimensions at the nanoscale;
- *Nanoscale* – having one or more dimensions of the order of 100 nm or less;
- *Nanoscience* – the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale;
- *Nanotechnology* – the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanoscale;
- *Nanostructured* – having a structure at the nanoscale;
- Engineered nanoparticles – nanoparticles manufactured to have specific properties or a specific composition;
- *Nanofiber* – nanoparticles with two dimensions at the nanoscale and an aspect ratio of greater than 3:1;
- *Quantum dot* – a nanoscale particle that exhibits size-dependent electronic and optical properties due to quantum confinement;
- *Nanocomposites* – composites in which at least one of the phases has at least one dimension on the nanoscale;
- *Nanophase* – discrete phase, within a material, which is at the nanoscale;
- *Bottom-up processing/manufacturing* – additive processing/manufacturing to create nanostructures from atoms and molecules;
- *Nanowire* – a wire with diameter of the order of nanometers. Alternatively, nanowires can be defined as structures that have lateral size constrained to tens of nanometers or less and an unconstrained longitudinal size. At these scales, quantum mechanical effects are important – hence such wires are also known as quantum wires. Many different types of nanowires exist, including metallic (e.g. Ni, Pt, Au), semi-conducting (e.g. Si, InP, GaN) and insulating (e.g. SiO_2, TiO_2). Molecular nanowires are composed of repeating molecular units either organic (e.g. DNA) or inorganic (e.g. $Mo_6 S_{9-x}I_x$). Nanowires can be coiled and stretched to reach full length.
- *Nanoribbon* – a nanoribbon has a flat profile rather than the cylindrical profile of a nanowire. The thickness is generally of the order of tens of nanometers or less, while the width can be of the order of 10 to 100 nanometers and it has unconstrained longitudinal size. Like a nanowire, nanoribbons may be coiled and stretched to reach full length.

1.5 Nanotechnology-enabled Product Possibilities

By exploiting the full potential of lignocellulosic materials at the nanoscale, nanotechnology can provide benefits that extend well beyond fiber production and new materials development into the areas of energy production, storage, and utilization. For example, nanotechnology may provide new approaches for obtaining and utilizing energy from sunlight – based on the operation of the plant cell. Novel new ways to produce energy and other innovative products and processes from this renewable resource base will help address some major issues facing many nations, including energy security, global climate change, air and water quality, and global industrial competitiveness. Other potential uses for nanotechnology include developing intelligent wood- and paper-based products with an array of nanosensors built in to measure forces, loads, moisture levels, temperature, pressure, chemical emissions, detect attack by wood decay fungi, etc. Building functionality onto lignocellulosic surfaces at the nanoscale could open new opportunities for such things as pharmaceutical products, self-sterilizing surfaces, and electronic lignocellulosic devices (Atalla *et al.* 2005). Use of lignocellulosic biomass nanodimensional building blocks will enable the assembly of functional materials and substrates with substantially higher strength properties, which will allow the production of lighter-weight products from less material and with less energy requirements. Nano-biomaterials could replace a wide range of materials such as metals and petroleum-based plastics in the fabrication of products. Significant improvements in surface properties and functionality will be possible, making existing products much more effective and allowing the development of many more new products. Nanotechnology can be used to improve processing of wood-based materials into a myriad of products by improving water removal and eliminating rewetting; reducing energy usage in drying; and tagging fibers, flakes, and particles to allow customized property enhancement in processing. The exact economic impacts and opportunities for wood as a nanomaterial are unknown, but it is expected that nanomaterials and nano-enabled products will grow to exceed US$ 1 trillion per year as the technology is further developed and is widely applied commercially during the 21st century (National Research Council 2006).

Nanotechnology can also play an important role in the production of liquid biofuels from lignocellulosic biomass. For example, nanoscale cell walls structures within trees could be manipulated so they are more easily disassembled into constitutive materials for liquid fuels production whether through conversion by fermentation, gasification, or catalysis. Another approach would be to use nanocatalysis to break down recalcitrant cellulose. Recalcitrant cellulose is in the order of 15–25% of the carbohydrate fraction of wood and failure to convert this to sugars reduces fermentation ethanol yields. In this approach, nanocatalysts would need to be transported to the reaction sites on the solid substrate recalcitrant cellulose in order to produce water soluble polyol reaction products. In most catalysis schemes, the reactants are brought to the catalyst. In this case the catalyst needs to be brought to the solid substrate reaction sites and water soluble reaction products need to be generated in order to permit recovery of the catalysts. Other possibilities for nanotechnology approaches in biofuel production are through development of engineered nanoscale enzymes or systems of enzymes (including glycol hydrolases, expansins, and lignin degrading enzymes) for improved conversion efficiency. Tree biology could be engineered so that enzymes and enzyme systems are created and stored/sequestered in the living tree until harvest and then be activated for engineered woody biomass self-disassembly. Lastly, another concept would be to create new symbiotic nanoscale biological systems which work together to create ethanol or other biofuels.

Cellulose, while at times referred to as a nanofibril, does not differ much from a coiled nanoribbon. Nanoribbons have been developed specifically as optical waveguides for channeling optical and visible light. Nanodimensional cellulose has already been used as a template to form nanoribbons of Antimony (111) oxide that can then be used as an electrical wire (Ye *et al.* 2006). Nanocomposites for self-cleaning textiles as well as solar cell applications have also been proposed. CdS nanowire has been made using a nanocellulose derivative. Other applications could be possible if one were able to combine other inorganics with cellulose (Venkataramanan and Kawanami 2006). Cellulose has also been used for electrical devices (including artificial muscles), due to its piezoelectric nature (Kim and Yun 2006). Termed smart cellulose, 'electroactive paper' (EAPap) is a chemically treated paper with thin electrodes on both sides. When electrical voltage is applied on the electrodes, the EAPap bends. Natural nanocellulose has also been found to form layer by layer films with antireflective properties. Multiwalled nanoribbon cellulose has also been used for wound dressing (Brown Jr. *et al.* 2007).

1.6 Wood Nanodimensional Structure and Composition

Wood is a cellular hierarchical biocomposite (Figure 1.3) made up of cellulose, hemicellulose, lignin, extractives and trace elements. Wood like many other biological tissues including bones and teeth are hierarchically structured composites in order to provide maximum strength with a minimum of material. At the nanoscale level, wood is a cellulosic fibrillar composite. Wood is approximately 30-40% cellulose by weight with about half of the cellulose in nanocrystalline form and half in amorphous form (Figure 1.3g).

Cellulose (Figure 1.3h) is the most common organic polymer in the world representing about 1.5×10^{12} tons of the total annual biomass production. Cellulose is the major carbohydrate component of wood along with the hemicelluloses (20–35%by weight). Lignin, extractives, and trace amounts of other materials make up the remaining portion of wood. Cellulose is expressed from enzyme rosettes as 3–5nm diameter fibrils that aggregate into larger microfibrils up to 20 nm in diameter (Figure 1.3g and 1.3f; see also Chapter 2 of this book for more information on the cellulose biomachine). These fibrils self-assemble in a manner similar to liquid crystals leading to nanodimensional and larger structures seen in typical plant cell walls (Neville 1993, de Rodriguez et al. 2006). The theoretical modulus of a cellulose molecule is around 250 GPa, but measurements for the stiffness of cellulose in the cell wall are around 130 GPa. This means that cellulose is a high performance material comparable with the best fibers technology can produce (Vincent 2002).

Because wood has a hierarchical structure, advances in separation techniques are goaled at leading to the commercial production and use of multiple nanoscale architectures namely nanocrystalline cellulose, nanofibrils, and nanoscale cell wall architectures (Figure 1.3g and 1.3f) (Cash 2003). Nanofibrils in their simplest form are the elementary cellulosic fibrils shown in Figure 1.3g containing both crystalline and amorphous segments and can be hundreds to a thousand or more nanometers long. Nanoscale cell wall architectures are the larger nanodimensional structures depicted in Figures 1.3g and 1.3f that are composed of multiple elementary nanofibril arrangements. Nanocrystalline cellulose is the liberated crystalline segments of elementary nanofibril crystalline cellulose fibrils after the amorphous segments have been removed – usually via treatment with strong acids at elevated temperature. Nanocrystalline cellulose is in the range

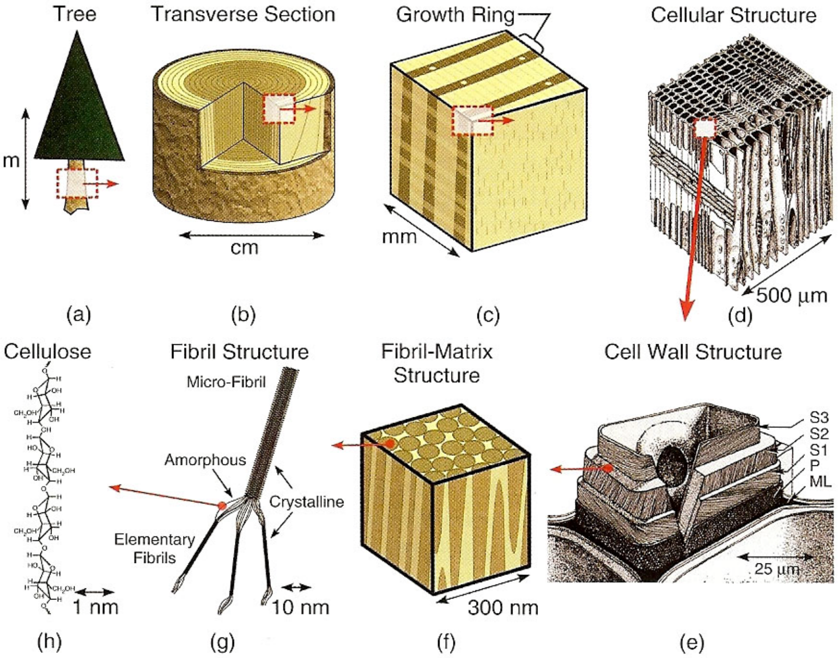

Figure 1.3 *Wood hierarchical structure: from tree to cellulose (Moon 2006).*

of 100–300nm long. Nanocrystalline cellulose is anywhere from a tenth to a quarter of the strength of carbon nanotubes (Xanthos 2005, Samir *et al.* 2005). Nanocrystalline cellulose can also be referred to as nanowhiskers.

The hierarchical structure of wood, based on its elementary nanofibrilar components, leads to the unique strength and high performance properties of different species of wood. While a great deal of valuable study has led to an understanding of many mechanisms relating to the properties of wood and paper, the overall complexity of wood's structure has limited discovery. Today we have the tools used in other areas of nanotechnology to look at structures down to the atomic scale. While this is fueling discovery in a wide range of biomimetic materials, studies on wood are only now beginning. Simpler structures found in seashells, insect cuticles and bones are being understood as relating to their hierarchical structures. (Aizenberg et al. 2005) and we are poised for these techniques to be applied to lignocellulosic-based products.

1.7 Nanomanufacturing

The value chain for lignocellulosic-based nanomaterials (Figure 1.4) is the same as for any other materials – regardless of dimension (Hollman 2007, Langsner 2005). It is based upon being able to profitably produce and sell products in the marketplace. While the focus of nanotechnology-related research may seem to be on nanoscale properties of materials, it is the nanotechnology-enabled macroscale end products that are most

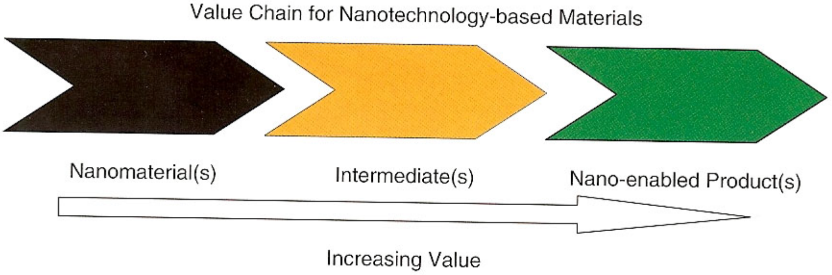

Figure 1.4 *Value chain for nanotechnology-based materials.*

important. Therefore, nanotechnology must be viewed as an enabling technology versus an end in itself (Sixth Framework Programme 2005). To most expeditiously make scientific and technology advancements, the focus for nanotechnology research must always have an end use product application in mind. Examples of nanotechnology enabled end use products include dimensional lumber with built in nanosensors to record and react to static and dynamic loading; multifunctional siding materials that generate electricity, are self-cleaning and self-sterilizing. and never need painting; and smart paper that functions as a digital processor and accepts downloaded information. In the short term, nanotechnologies for lignocellulosic products will likely be in the areas of barrier coatings; architectural coatings; and preservative treatments.

As nanotechnology science and technology develops during the 21st century, the first applications will be use of passive nanostructures where the nanomaterial itself remains static once it is encapsulated into the product. The second generation nanotechnology enabled products will be in the area of active nanostructures where nanostructures change their state during use by responding in predicable ways to the environment around them. Third generation products are expected to be systems of nanosystems where assemblies of nanotools self-assemble and work together to achieve a final goal. Lastly. molecular nanosystems will be developed where through the intelligent design of molecular and atomic devices there will be unprecedented understanding and control over the basic building blocks of all natural and manmade things.

Much of the current research focus in nanotechnology has been on measuring the properties of materials at the nanoscale with much focus on semiconductor materials, carbon nanotubes, and medical applications – especially for diagnostics, cancer treatment, and delivery of pharmaceuticals to targeted locations within the human body. Much less emphasis has been placed upon other materials. Biolohivsl materials (e.g. wood and plant materials) have received much less attention despite their many advantages such as being able to self-assemble, being sustainable, and being ecologically preferable.

The area of nanomanufacturing science and technology has also not received sufficient attention despite its being one of the most critical pathways to applying the benefits of nanotechnology. It is absolutely critical to build the nanomanufacturing science and technology base to the point where nanomaterial (s) exhibiting unique nanoscale properties can: (1) routinely be placed into components or systems, (2) retain and combine their unique nanoscale properties in a matrix of other materials and (3) result in superior and controllable composites performance (NSET 2007, Department of Energy 2007).

The extraordinary properties that make nanotechnology so important often also lead to great difficulties in producing, separating, purifying, consolidating, handling, and measuring nanomaterials. In addition, capturing and retaining nanoscale properties in the final manufactured macroscale products also pose major obstacles to building products from nanomaterials. Overcoming technical barriers to achieving cost-effective manufacture of nanomaterials with unique properties and subsequently efficiently and effectively capturing those properties in producing consumer end use products represent a number of difficult tasks and can best be guided through researchers working with industrial partners who can help guide the research efforts into the most economically viable pathways and relatively quickly determine if the proposed solution makes economic sense. Nanomanufacturing technology development will require overcoming major barriers in materials production and manufacturing and process control as well as predictive modeling. For example, manufacturing products from nanomaterials is challenging because it has been observed that nanopowders, -solids, and -suspensions have a high propensity to agglomerate; have highly reactive surfaces; and have a fundamental tendency to change properties with time, temperature, and handling conditions. Equally challenging is that once nanomaterials are embedded into fibers, sheets, tubes, bars, or other forms, there is limited technology to join these into useful forms without altering the properties at the joint or interface. Additionally, when morphology is important to nano-enabled product performance, it is difficult to obtain this quality throughout the module or body. A listing of generic technical barriers includes the following (NSET 2007, Department of Energy 2007):

- being able to commercially and reproducibly manufacture uniform, high quality, consistent nanomaterials in high volume;
- difficulty in developing economically-viable and scalable unit operations and incorporation of nanomaterials into products make many nanomaterials prohibitively expensive for many applications due to high capital costs and low production volumes;
- difficulty or inability to retain nanomaterial functionality as the material is incorporated into products;
- difficulty in incorporating and controlling admixes of nanomaterials into other bulk materials;
- process-monitoring tools tailored for analyzing the unique characteristics and satisfying the process control needs of producing nanomaterials are lacking; for example, real-time, in-line measurement techniques are needed;
- predictive models of nanomaterials behavior are needed for correlations between nanomaterials properties and end-use performance as a cost-effective aid to design of nanomanufacturing processes.

In developing the needed nanomanufacturing technologies, greater industrial influence and awareness also serves to help guide research into the highest priority and most productive areas. For example, production of nano-enable composites is an area that is a high priority for a number of industry sectors in addition to the forest products industry. Without developing the science and technology for nanomanufacturing and successfully incorporating nanomaterials into macroscale products for consumers, nanotechnology will be primarily a laboratory curiosity. We must be able to reliably, reproducibly, and cost-effectively produce composite matrices of bulk materials and nanomaterials that effectively combine the properties that the individual nanomaterial components and bulk matrix materials possess. This requires developing a whole new array of nanomanufacturing technologies and the fundamental science that underlies them. For example, when nanomaterials are used to produce products, they need to be able to be controllably dispersed or mixed into other materials and retain their functionality in the bulk matrix. Following is a listing of science-based needs with respect to using nanomaterials for commercially producing composite matrices across a number of industries product sectors including the forest products industry and when producing or using lignocellulosic-based nanomaterials.

- Develop the science and technologies needed to control and manipulate dispersion of nanomaterials into a matrix of other materials.
- Develop the tools needed to adequately and easily measure and characterize nanomaterial dispersion and mixing with other materials into a matrix to include degree of nanomaterial dispersion/aggregation.
- Determine how to overcome the deleterious effects of increasing production scale on dispersion/mixing of nanomaterials into a matrix of other materials.
- Develop robust online, real-time, in-situ characterization tools and methodologies to characterize dispersion and mixing of nanomaterials into a bulk matrix of other materials (polar and nonpolar liquids, suspensions, solids and gases).
- Preserve the functionality of nanomaterials (e.g. strength; optical; magnetic, electrical/electronic; thermodynamic, chemical reactivity, catalysis, etc.) when they are incorporated into other materials.
- Develop the science needed to overcome the deleterious effects of high temperature processing on admixed nanomaterial properties.
- Understand the interactions between nanofibrils and bulk matrix materials that are most important to nanofibril reinforcement to include nanofibril morphology (e.g. size, shape aspect ratio, etc.), nanofibril loading level, and surface energies.
- Learn how to control nanofibril orientation in matrices bulk materials.
- Understand how varying composite synthesis methodologies (e.g. extrusion, solvent casting, high shear mixing) impact matrix properties.
- Measure the rheological properties of mixtures of nanomaterials (nano-, micro-, and macroscales) and bulk matrix materials and the effects on dispersion and mixing.
- Determine methodologies to adequately characterize nano-enable composite matrices.
- Determine the impact of aging and storage on nanocomposites properties.
- Develop multiscale (macro-, micro-, nano-) models that allow the prediction of the properties of composite matrices incorporating nanomaterials (to include maximum theoretical nanomaterial influence on matrix properties) and allow use of micro- and macroscale tests to correlate with nanoscale dispersion/mixing.
- Characterize nanoscale architectures of nanomaterials interacting with bulk matrix materials.
- Develop nondestructive quality control testing methods for composites containing nanomaterials.
- Develop a database of standardized nanomaterials/matrices properties.
- l Develop process control tools for producing nanomaterial/bulk matrix composites.

1.8 Nanotechnology Health and Safety Issues

Environmental, health, and safety issues related to nanomaterials and nanotechnology have been under explored but have more recently received much public attention (Davies 2006, Greenwood 2007, National Research Council 2006). Nanomaterials are present in our daily lives (e.g. dust, smoke, ash, soot, etc.) and human exposure to nanodimensional materials has occurred throughout human history. For example, nanomaterials are produced by combustion of fuels and even by volcanic eruptions. The concerns for the environmental, health, and safety aspects of nanotechnology arise from the production of new engineered nanomaterials with unique properties (Friends of the Earth 2008). The aim in using engineered nanomaterials to produce products must be to maximize benefits while guarding against potential harm, based on a realistic assessment of technical facts in the light of human values. Understanding the health risks and risks to the environment or ecosystem that may result from exposure to or introduction of engineered nanoscale materials, nanostructured materials, or nanotechnology-based devices is an extremely important consideration in moving nanotechnology forward (International Risk Governance Council 2007, NSET 2008). This is not only true for wood-based nanomaterials but also for nanomaterials and devices from other industry sectors that are incorporated into forest products. An array of concerns arise with respect the effects of exposure of nanomaterials and nanoproducts on human health and the environment. Included in these concerns are the following items:

- determining the toxicology of nanomaterials and nanoproducts to humans and in the environment;
- determining the mechanisms for uptake and the biokinetics of nanomaterials in organisms and the human body;
- understanding transport, transformation, and the fate of nanomaterials and nanoproducts in air, water, and soil to include mechanisms and routes of exposure;
- understanding dose metrics on humans and animals of nanomaterials and nanoproducts;
- implementing effective protection and long-term exposure safety measures for workers handling and working with nanomaterials and nanoproducts;
  - understanding the properties of nanomaterials as they relate to the effectiveness of personal protective equipment;
  - developing sensors and monitors to sample the workplace environment to determine workers exposure to nanomaterials and nanoproducts;
  - development of methods to control exposure when working with nanoproducts;
- developing life cycle analyses of nanomaterials and nanoproducts;
- measuring and characterizing nanomaterial key properties such as size, surface area, bioactivity, etc.;
- developing scientifically sound in vivo and in vitro protocols and models to understand nanomaterial interactions at the molecular and cellular level.

At first glance – for lignocellulosic-based nanomaterials – one would probably expect that such materials being produced by living organisms should not pose an environmental, health or safety problem. The concern about environmental, health and safety issues, however, goes to the heart of the definition of nanotechnology. If nanoscale properties of wood-based nanomaterials exhibit new and unique properties that depend upon size, then the environmental, health and safety impacts cannot necessarily be assumed as known based upon existing information for wood micro- and macroscale particles. For wood-based nanomaterials, we do not have a large body of risk assessment data. The information that is available on the environmental, health, and safety risks for lignocellulosic-based nanomaterials to date does not necessarily mean these lignocellulosic-based nanomaterials pose a risk but there is no clear evidence to rule such concerns out either. Clearly, more information needs to be developed. The best way to obtain reliable data is to work with the larger nanotechnology community dealing with the environmental health and safety of nanomaterials as they develop scientifically sound protocols and procedures. In the meantime, for researchers and others working in the area of nanotechnology, sound chemical laboratory practices should be employed, using nanomaterials in fume hoods or glove boxes, using respirators or at minimum dust masks, and disposing of nanomaterials in a manner equivalent to hazardous materials disposal.

1.9 Instrumentation, Metrology, and Standards for Nanotechnology

Instrumentation, metrology, and standards for nanotechnology are critical components in the chain from discovery of nanomaterials to commercialization of nano-enabled products. Today's array of metrology tools has been developed to meet the current needs of exploratory nanoscale research, primarily for inorganic materials and we are nearing the limits of their resolution and accuracy. While the tools currently available will continue to evolve, they are not expected to meet all the future metrology requirements of nanoscale research, development, and deployment. Instrumentation to probe the nanoscale requires revolutionary developments in addition to evolutionary advances in measurement schemes and instruments (NSET 2006). The immediate tasks at hand are to adapt currently available nanoscale metrology and instrumentation to biological materials and obtain artifact-free property measurements. In addition, it is important to be able to measure the nanoscale properties of wood and wood-based materials in-situ and to relate wood and wood-based material properties within the context of wood's hierarchal composite structure. Instrumentation, metrology, and standards priorities for nanotechnology include development of

- next generation techniques, tools, and instruments that provide a major leap forward with regard to exceeding today's spatial and temporal resolution limits; major emphasis needs to be placed on advancing the state-of-the-art of microscopies and analytical instrumentation such as with scanning probe microscopes, scanning and transmission electron microscopes, and electron, neutron, and photon spectroscopic techniques adapted to biological materials; the effects of electrons, neutrons, and photons on biological materials can be quite different than with inorganic materials such as metals and this can lead to artifacts in the measurements;
- enabling full three-dimensional mapping of biological and nonbiological nanomaterials using instrumentation combining subnanometer spatial resolution with chemical specificity and volumetric detection;

- enhancement of national and international nanometrology infrastructure supporting commercial manufacture of advanced products;
- standardization of measurement techniques, nomenclature, and testing methodologies to facilitate assurance of safety and efficacy of nanoproducts, and their effective regulation and production;
- development and verification of advanced simulation, visualization, and data analysis techniques and supporting standards for biological materials;
- development of nomenclature to define the growing number of nanostructures that is succinctly, precisely, and compatibly related to that of conventional molecular nomenclature.

1.10 A Nanotechnolgy Agenda for the Forest Products Industry

In its first step toward reaching the goals of applying nanotechnology in the forest products industry, a workshop to develop a vision, explore opportunities, and determine research needs was convened in October 2004. The American Forest and Paper Association's (AF&PA) Agenda 2020 Technology Alliance, the Technical Association of the Pulp and Paper Industry. US Department of Energy (DOE) and the US Department of Agriculture (USDA), Forest Service sponsored the conference. AF&PA Agenda 2020 is a special project of the American Forest and Paper Association, the national trade association of the forest products industry. It is an industry-led partnership with government agencies and departments such as the USDA Forest Service, DOE, the National Science Foundation, the National Institute for Standards and Technology, etc. and academia. The overall goal of the AF&PA Agenda 2020 Technology Alliance is to create options to meet industry's competitive challenges while contributing solutions to strategic national needs associated with energy, the environment, and the economy by addressing shared industry and national strategic goals: developing research, development and deployment (RD&D) initiatives; provide the foundation for new technology-driven business models; and leverage collaborative partnerships to drive innovation in the forest products industry's processes, materials, and markets. It is vitally important to remember that close collaboration with the forest products industry is critical for advancing nanotechnology. This is because the range and magnitude of benefits offered by nanotechnology science and engineering research and development can only be realized if the technologies are accepted and implemented (i.e. deployed) by the industry.

Over 110 leading researchers with diverse expertise from industry, government laboratories, and academic institutions from North America and Europe attended the nanotechnology for the forest products industry workshop. Coming out of this workshop was a document entitled *Nanotechnology for the Forest Products Industry-Vision and Technology Roadmap* (Atalla *et al.* 2005). The stated vision for nanotechnology for the forest products industry is as follows:

> To sustainably meet the needs of present and future generations for wood-based materials and products by applying nanotechnology science and engineering to efficiently and effectively capture the entire range of values that lignocellulosic materials are capable of providing.

Workshop participants next identified the unique properties and characteristics of wood lignocellulosic biopolymers that make them an exciting avenue for nanotechnology research, including:

1. lignocellulosic biopolymers are some of the most abundant biological raw materials, have a nanofibrilar structure, have the potential to be made multifunctional, and can be controlled in self-assembly;
2. new analytical techniques adapted to biomaterials are allowing us to see the structure of wood in new ways;
3. lignocelluloses as nanomaterials and their interaction with other nanomaterials are largely unexplored.

Nanotechnology research and development strategies were also discussed and encompassed the following two broad approaches (Atalla *et al.* 2005):

1. Nanotechnologies and nanomaterials developed through nanotechnology research and development (R&D) efforts in other industry sectors will be adopted and deployed into materials, processes and products used in or produced by the current forest products industry. The expected gains of this R&D strategy direction were in improving existing products and processes – with some minor-to-moderate modifications and additions.
2. Nanotechnology R&D will develop completely new materials or product platforms using the improved knowledge of nanoscale structures and properties of the lignocellulosic wood-based materials used in the forest products industry. This direction potentially will lead to radically different products, processing techniques, and material applications as the nanoscale properties of lignocellulose and its nanoscale architecture have not been exploited to any great degree.

The research challenges associated with these two broad strategies were identified and span a range of scientific focus areas to include:

- developing fundamental understanding of nanomaterials and analytical tools for measuring properties at the nanoscale;
- developing new nanoscale building materials;
- developing nanotechnology for manufacturing applications;
- creating nanomaterials by design.

'Nanomaterials by Design' is a uniquely solutions-based research goal. As described in the nanomaterials roadmap developed by the chemicals industry, 'nanomaterials by design' refers to the ability to employ scientific principles in deliberately creating structures (e.g., size, architecture) that deliver unique functionality and utility for target applications (Chemical Industry Vision2020 2003). This research area focuses on the assembly of building blocks to produce nanomaterials in technically useful forms, such as bulk nanostructured materials, dispersions, composites, and spatially resolved, ordered nanostructures. It yields a new set of tools that can provide nearly limitless flexibility for precisely building material functions around end-use applications. Such a powerful, function-based design capability holds the potential to solve critical, unmet needs throughout society. Techniques being developed in the areas of self-assembly and directed self-assembly will allow us to use the building blocks available in the forest products industry to manufacture materials with radically different performance properties.

The following R&D focus areas were initially selected on the basis that they (1) provide the best path forward for a nanotechnology roadmap by identifying the underlying science and technology needed, and (2) foster essential interactions among visionary, interdisciplinary research and technology leaders from industry, academia, research institutions, and government (Atalla *et al.* 2005).

1. *Polymer composites and nano-reinforced materials* – combine wood-based materials with nanoscale materials to develop new or improved composite materials with unique multifunctional properties.
    - Develop and investigate novel materials with enhanced properties (e.g. films, coatings, fillers, matrices, pigments, additives, and fibers – especially lignocellulosic nanofibrils.
    - Develop and investigate novel materials for processing equipment.
    - Develop and understand the interrelationships between nanoscale material characteristics and the resulting product end use property improvements.
    - Determine the best way to implement new materials.
    - Develop economic and life-cycle models for forest-based nanoscale materials and products.
2. *Self-assembly and biomimetics* – use the natural systems of woody plants as either the source of inspiration or the template for developing or manipulating unique nano-, micro-, and macroscale polymer composites via biomimicry and/or direct assembly of molecules.
    - Develop a technical platform enabling self-assembly of paper products and other lignocellulosic materials at the nanoscale.
    - On existing lignocellulosic substrates create novel, functional, self-assembling surfaces.
    - Develop a fundamental understanding of molecular recognition in plant growth and cell wall self-assembly to create new or enhance existing products.
    - Learn to characterize self-assembled natural and synthetic material and to integrate micro- and nanoscale organization in products.
3. *Cell wall nanostructures* – manipulate cell wall nanostructure of woody plants in order to modify or enhance their physical properties and create wood and wood fibers with superior manufacturability or end-use performance.
    - Investigate the process of formation of cellulose nanofibrils, including genetic, biochemical, cellular, and biophysical regulation.
    - Characterize the processes that regulate the formation of the other constituents of the cell wall and the manner in which they are coupled with the deposition of cellulose.
    - Determine the manner in which the processes of assembly and consolidation are guided by the expression of genomic information, the biophysical interactions of the synthesized molecules, and the emerging mechanical properties.
    - Apply new instrumentation methods to study the cell wall native state without significantly altering its structures.
    - Develop cell walls as models and materials for nanoscale assembly.

4. *Nanotechnology in sensors, processing and process control* – use nonobtrusive, nanoscale sensors for monitoring and control during wood and wood-based materials processing to provide data on product performance and environmental conditions during end use service, and to impart multifunctional capabilities to products.
   - Identify microbial species or chemical/optical/physical agents that are unique fingerprints or signatures of food spoilage, medical contamination, or product degradation, and develop methodologies for incorporating these agents into nonobtrusive, low-cost, robust nanosensors for food and medical packaging materials.
   - Investigate genetic and chemical modifications of wood lignocellulose materials to enable basic sensing capabilities and self regulation (e.g. for moisture, temperature, volatile organic compounds (VOCs)).
   - Investigate and develop paper and wood product coating technology and coating materials that can deploy nanosensors to these products through mechanical or chemical means.
   - Study and develop methods to synthesize data from arrays of nanosensors in order to generate useful information for action or process control.
   - Develop cost-effective, efficient, environmentally preferable and highly selective nanostructured catalysts for disassembling wood and lignocellulose.
   - Carry out research on the use of nanomaterials in conjunction with unit operations processing wood and wood-based materials.
5. *Analytical methods for nanostructure characterization* – adapt existing analytical tools or create new tools (e.g. chemical, mechanical, electrical, optical, and magnetic) that accurately and reproducibly measure and characterize the complex nanoscale architecture and composition of wood and wood-based lignocellulosic materials.
   - Create and maintain a compendium of available analysis tools.
   - Develop techniques and tools to measure hemicellulose polymer structure and properties at the nanoscale.
   - Develop techniques and tools to measure lignin structure and properties at the nanoscale.
   - Develop methodologies and instrumentation to determine cell wall morphology and measure properties at the nanoscale.
   - Develop and deploy new collaborative strategies for analysis involving multiple techniques.
6. *R&D collaboration to include the National Nanotechnology Initiative (NNI) and its centers* – this area emphasized the importance of collaboration and cooperation among researchers from various disciplines and organizations, including universities, research institutes, national laboratories, and government agencies and departments. Linkages were needed to be made between research communities of the forest products sector and the broader community of nanotechnology researchers in order to capture synergies, enhance accomplishments, and avoid needless duplication of facilities and efforts. Identified research entities that need to be engaged include:
   - individual researchers;
   - researchers with differing disciplines;
   - basic and applied researchers and research teams;

- research institutions including universities, research institutes, and national laboratories;
- industry, universities, research institutions, and federal agencies and departments;
- all of the previous groups from countries around the world.

In moving ahead in the area of nanotechnology, the forest products industry must seize the opportunity to link with larger nanotechnology research and industrial communities such as the ongoing efforts of the National Nanotechnology Initiative (NNI). The NNI is a visionary R&D program that coordinates the activities of 25 Federal departments and agencies and a host of collaborators from academia, industry, and other organizations. The goals of the NNI are to maintain a world class research and development program aimed at realizing the full potential of nanotechnology; facilitate transfer of new technologies into products for economic growth, jobs, and other public benefit; develop educational resources, a skilled workforce, and the supporting infrastructure and tools to advance nanotechnology; and support responsible development of nanotechnology. By linking with communities such as the NNI, the forest products industry would be able to expand its knowledge of nanotechnology, pool its resources with those of others pursuing common R&D goals, and advance its own agenda.

The forest products industry nanotechnology roadmap provides a starting point for focusing the many potential and diverse efforts in nanotechnology for the forest products industry and also serves to further engaging key stakeholders and stakeholder groups in dialogue, consensus building, and partnership building. The following are some of the key stakeholder groups such as primary forest products industry producers, converters, suppliers, and collective industry groups such as AF&PA; Federal departments and agencies (e.g. the USDA Forest Service, USDA Cooperative State Research, Education and Extension Service, Department of Energy and its national laboratories, National Science Foundation, and National Institute of Science and Technology); University and Research Institute/Laboratory Communities (nationally and internationally). A critical step in moving nanotechnology for the forest products sector forward is to gain consensus among stakeholders on what the specific focus should be for the short term, mid term, and long term. It is important that efforts be focused on high-impact, high-priority activities that will be the most critical to commercial producers of nanomaterials and nanoproducts.

1.11 Forest Products Industry Technology Priorities

The AF&PA Agenda 2020 Technology Alliance has now gone further to identify and select six high priority thematic areas for further study that are thought to be the key to re-inventing the forest products industry in the US. The forest products industry has developed a *Forest Products Industry Technology Roadmap*. The Forest Products Industry Technology Roadmap provides a framework for reinvigorating the industry through technological innovations in processes, materials, and markets. These innovations are aimed at three necessary ingredients for creating a healthy future for the US-based forest products industry (American Forest and Paper Association 2006):

1. achieving operational excellence in the production of existing and new products;
2. developing new value streams from wood resources; and

3. assuring an ecologically sustainable, affordable domestic supply of wood and fiber feedstock.

The roadmap's purpose is to provide the research community, and their funding organizations, with information on the technical challenges and research needs that are considered priorities by the US forest products industry. The roadmap's goal is to stimulate collaborative, precompetitive research, development, and deployment that will provide the foundation for new technology-driven business models that enable the industry to meet competitive challenges, while also contributing solutions to strategic national needs. It envisions that the revitalized forest products industry will be built on four cornerstones:

- significantly improved productivity through lower costs and higher yields for raw materials and manufactured products;
- upgraded technical skills of the workforce;
- a stream of new biomass-derived products and materials, including electric power, liquid transportation fuels, polymers and composites, and industrial chemicals;
- adding value to society by reducing emissions and effluents and by providing essential products from renewable and sustainable raw materials.

The industry roadmap also envisions that it will use and rely heavily on emerging technologies, such as biotechnology and nanotechnology, coupled with breakthrough advances in manufacturing process technologies to create and capture value from both new and existing product streams efficiently, cleanly, and economically. Further, the roadmap strategy identifies what the forest products industry sees as its inherent strengths: stewardship of an abundant, renewable, and sustainable raw material base and a manufacturing infrastructure that can process wood resources into a wide variety of consumer products. The industry also views itself as uniquely positioned to move into new, growth markets centered on bio-based 'green' products. The seven industry technology goals or technology platforms for its reinvention are as follows:

- *Advancing the forest 'bio-refinery'* – transform existing manufacturing infrastructure to develop geographically distributed production centers of renewable 'green' bioenergy and bioproducts. Double the return on net assets of existing forest products manufacturing plants by applying technologies that extract new value prior to pulping and produce new, commercially attractive products and power from wood residuals and spent pulping liquors.
- *Sustainable forest productivity* – develop and deploy wood production systems that are ecologically sustainable, socially acceptable, energy-efficient, and economically viable to enhance forest conservation and the global competitiveness of forest product manufacturing and biorefinery operations in the US.
- *Breakthrough manufacturing technologies* – develop and apply 'breakthrough' approaches that can achieve revolutionary changes in the manufacturing process to significantly lower energy and materials costs by reducing raw material, fiber, and energy use and by enhancing fiber functionality.
- *Advancing the wood products revolution* – revolutionize housing and construction by creating superior, low-cost, high-value, sustainable wood products and wood-based building systems.

- *Next generation fiber recovery and utilization* – make recycled fiber interchangeable with virgin fiber with respect to product quality, functionality, and availability by improving the quality and quantity of recovered fiber and improving process technologies at recycling mills.
- *Positively impacting the environment* – develop and deploy an optimum mix of in-process and add-on technologies that will enable continued improvement of the industry's environmental performance.
- *Technologically advanced workforce* – provide training and education needed to ensure that new and existing technologies chosen to create the forest products industry of the future are operated by a technically superior workforce.

It is important to note that the AF&PA Agenda 2020 Technology Alliance views nanotechnology and biotechnology as means to achieving its technological goals and not as ends in themselves. The forest products industry views implementing its technology roadmap will require efforts in all parts of the research, development and deployment (RD&D) continuum, from concept generation to technology deployment. A strong focus on deployment is also a key aspect of the implementation strategy. The range and magnitude of benefits offered by the roadmap's research platforms can only be realized if the technologies are accepted and implemented by the industry. However, the industry views that it is imperative that fundamental scientific research be tapped to explore the rich set of opportunities offered by the rapidly advancing fields of nanotechnology and biotechnology in order to achieve breakthroughs in sustainable forestry, feedstock processing and conversion, and end-product properties.

1.12 Nanotechnology Priority Areas to Meet the Needs of the Forest Products Industry

Building off *The Forest Products Industry Technology Roadmap,* an AF&PA Agenda 2020 task group analyzed where nanotechnology could be expected to make major contributions to achieving the goals in the industry technology platform areas given in the previous section. The following six areas were deemed to be the highest priorities:

- achieving lighter weight, higher strength materials;
- production of nanocrystalline cellulose and nanofibrils from wood;
- controlling water/moisture interactions with cellulose;
- producing hyperperformance nanocomposites from nanocrystalline cellulose;
- capturing the photonic and piezoelectric properties of lignocelluloses;
- reducing energy usage and reducing capital costs in processing wood to products.

Descriptions of these six areas are as follows (http://www.nanotechforest.org).

1.12.1 Achieving Lighter Weight, Higher Strength Materials

The objective is to improve strength/weight performance of paper and paperboard by at least 40% using one or several nanotechnology-based approaches. It was thought that a 40% improvement level was not attainable with any currently known technology and would require one or several breakthroughs in the three key areas of (1) strength,

(2) optical properties and (3) surface enhancement. It was envisioned that nanotechnology could generate these breakthroughs where conventional approaches have been lacking. These enabling and precompetitive technology breakthroughs in the three key areas can then be leveraged separately or in combination by the industry to generate competitive advantage. The solutions would allow radical reduction of raw material use by the industry and its customers; provide opportunities to develop and market new and advanced products with superior performance; and ultimately allow the industry to develop new and unique materials for markets outside the pulp and paper industry. Reduced grammage (basis weight) of paper and paperboard products will substantially reduce wood consumption and the volume of material processed in the pulp and paper industry, with proportional energy reductions and environmental impact. It will also reduce the mass of nonrecoverable paper ending up in landfills. Furthermore, it would provide opportunities to replace nonrenewable materials in a wide range of markets with sustainable materials made from cellulose-based alternatives. The physical and chemical properties of the cellulose fiber network in paper and board have been studied extensively over the past 50 years and vast amounts of information on the subject can be found in the literature. In essence the strength of the network is governed by the bond strength, fiber strength, fiber size and shape, effect of any additives or fillers and uniformity of material distribution. While commercial strength enhancement chemicals are effective to a point, these technologies are not capable of leveraging the inherent strength of cellulose nanofibrillar material, which approaches that of steel. In addition many biologically derived materials of high strength are made up of building blocks that are noncovalently bonded. They rely on the shear large number of points of contact to build strength and provide mechanisms for energy dissipation, i.e. crack termination. Therefore, it is an opportunity in using nanotechnology to diminish or close the gap between actual current network strength, and the orders of magnitude higher strength of the basic cellulose structure building blocks. Both nature and science have accomplished some impressive results in strength development using very small amounts of materials on the nanoscale.

As part of previous research in this area, extensive modeling and theoretical background results have been accomplished, and it is likely that this information can be used as a starting point for developing the theoretical foundation for a nanotechnology-derived strength enhancement. There is a need as part of this priority area to develop tailored modeling capabilities and theory to predict and elucidate strength effects of nanoscale-level modifications to the network structure and effects of nanodimensionally sized additives. This enhanced modeling package should be used as part of a first step to develop a theoretical perspective on the levels and kinds of enhancements to the structure that will be needed to meet research objectives. Such nanotechnology solutions will allow a 40% reduction of basis weight of current products and establish the precompetitive platform for development of new and stronger materials from cellulosic fibers. The preferred solution will allow the industry to continue using current production assets, but this should not be a constraint on the development work. There is a great deal of value in solutions that involve significant modifications to infrastructure as well. Those solutions that allow significant simplifications of the current assets are of special interest. Data are readily available in the literature to understand what the property effects of reduced basis weights will be with the limitations of current technology. It is known that deficiencies will arise in strength, optical properties, and probably surface quality as basis weight is reduced. It is envisioned that solutions would likely be developed to address each of these deficiencies separately but compatibly is necessary as a set of pre-competitive, enabling technologies. The solutions will need to be combined in various ways to generate actual improved products, so adequate coordination will be necessary in order to assure that solutions in strength, optical properties and surface enhancement are compatible. With solutions in place, companies with access to the new technologies can leverage them in order to enter new markets, reduce cost, or in other ways generate competitive advantage. As a secondary objective, the industry is interested in using improved fibers and networks to access opportunities in other markets.

1.12.2 Production of Nanocrystalline Cellulose and Nanofibrils from Wood

The objectives in this area are the liberation and use of nanocrystalline cellulose and nanofibrils derived from lignocellulosic feedstock. Part of nanotechnology-based solutions in this area is the need to identify more commercially attractive methods to liberate nanodimensional materials. Nanotechnologies using noncovalent disassembly and reassembly nanofractionalization is a concept worth pursuing. The entropic effects in the assembly and disassembly of nanomaterials in forest need to be understood. The use of nanocatalysis (e.g. delignification) for separations is a promising concept that should be explored. Once liberated, the nanomaterials must be adequately characterized, stabilized, and the nanomanufacturing and macromanufacturing technologies be developed to allow incorporation of nanocrystalline cellulose and nanofibrils into existing forest products industry allocations as well as new applications. There is a lack of established methods and technology in the Forest Products Industry to do any of the preceding. Success in this area allows the Forest Product Industry the opportunity to become a major supplier of nanoparticles for a wide range of industries. Because of the tonnages of wood available for processing, commercial production would be both sustainable and renewable as well as create an industrially significant supply. Nanocrystalline cellulose and nanofibrils could be extracted from currently underutilized feedstocks, such as forest residuals and sorted wood wastes. In addition, these nanodimensional cellulosic materials would likely not have any deleterious environmental, health and safety issues as cellulose is a biological material that is the world's most abundant polymer and enjoys the label of generally regarded as safe.

There are a wide range of cellulose surface modification technologies available and it should be possible to impart multifunctional properties and characteristics to nanocrystalline cellulose and nanofibrils. Additional nanotechnology research needs include (1) identifying and isolating other commercially viable nanomaterials, in addition to nanocrystalline cellulose and nanofibrils, present in biomass; (2) determining the effects of species, age, growth conditions, juvenile wood, mature wood, reaction wood etc., on nanocrystalline cellulose/nanofibril properties and morphology; (3) developing new and modified metrologies to characterize nanomaterials derived from biological materials; and (4) identifying new high-value applications.

In the production of nanocrystalline cellulose or nanofibrils, it is important that a consistent high quality nanomaterial product be able to be produced that does not differ in with respect to important properties such as composition, diameter, aspect ratio, shape, and surface properties. For example, nanocrystalline cellulose is roughly 3–5 nm in diameter and hundreds of nanometers in length. While nanocrystalline cellulose has the potential to be produced in extremely large volumes, the utility of the nanocrystalline cellulose for commercially desirable products will greatly depend upon its uniformity of size, composition, structure, and surface functionality. The properties of nanocrystalline cellulose must not differ from one lot or batch to another. Cost-effective methodologies must be developed to liberate, fractionate, and separate cellulosic nanomaterials into uniform, reproducible cohorts that can be easily dispersed for fabrication of macroscale products. Isolation of nanocrystalline cellulose and nanofibrils is an important area for research and development because current techniques appear to be lacking. For example, hydrolysis of wood with strong acids to liberate nanocrystalline cellulose does not appear to be an environmentally or economically friendly process and ultrasonic disintegration has shown only partial success. In addition, real-time, inline measurement techniques are needed to monitor and provide reproducible control of properties such as particle size and distribution. Predictive models of nanomaterials behavior are also needed in order to correlate nanomaterials' properties and end-use performance requirements. Such predictive models are critically important to cost effectively determine macroscale properties from constitutive bulk matrix and admixed nanomaterials properties without having to do costly and time-consuming trial and error experimentation for product development.

1.12.3 Controlling Water/Moisture Interactions with Cellulose

This nanotechnology priority area is aimed at the very broad area of understanding and controlling lignocellulosic/water interactions. A primary goal is to develop a substantial knowledge base which will enable us to advantageously alter lignocellulosic/water interactions to produce new and improved products and achieve more efficient and effective processes. Because of the almost universal influence of the relationship between water and lignocellulosics, this priority area is closely tied to many of the technology platform areas goals for research, development and demonstration expressed in *The Forest Products Industry Technology Roadmap.* The specific objectives in this nanotechnology area are to (1) develop an extensive knowledge base of the interactions of water and lignocellulosics at the nanoscale and (2) influence and modify these relationships with the goal of producing new as well as improved existing products and processes.

Virtually all aspects of lignocellulosic-based products and the processes by which they are made are impacted by the relationship between water and the lignocellulosic components of the products. The response of cellulose, hemicelluloses and lignin to moisture (both liquid and vapor) is due almost entirely to the super molecular structure of the biopolymers and the nanoscale structures of the lignocellulosic composites that comprise the wood fiber. Factors such as extractives content and location also play a role. However, most of the response to moisture depends on characteristics of the nanoscale structures in the fiber walls. Elementary nanofibrils, which have cross-section dimensions of about 3–5 nm are composed of cellulose polymer chains arranged in ordered (crystalline) and less ordered (amorphous) regions. The nature of these structures greatly influence the way in which the woody plant fiber responds to moisture. Gaining an understanding of these interactions and learning how to manipulate the structures at the nanoscale will enable us not only to decrease the negative impact of moisture on woody materials, but perhaps allow us to turn what is currently perceived as a disadvantage into an advantage. In addition to the size of the nanofibrils, the angle of orientation of the fibrillar bundles of nanofibrils relative to the long axis of the fiber plays a major role in the dimensional stability of the fiber in response to moisture. The degree of crystallinity (i.e. the ratio of the ordered regions to the amorphous regions in the microfibrils) will also impact the response to moisture. Because of inter- and intra-chain hydrogen bonding, crystalline regions are less accessible to moisture. These characteristics, which vary with species, can be genetically manipulated within a given species. Changing the conditions under which the trees are grown and even changing the drying conditions, as moisture is removed from the fiber during processing, can also impact features such as the degree of crystallinity. By studying and understanding the nature of bonding within paper and wood structures at the nanoscale, it may be possible to modify how each composite material responds to moisture. The ability to modify and control mechanosorptive behavior may lead to improvements in existing products and many potential new products based on the lignocellulosic biomass resource, in addition to greatly improving the efficiencies of the processes by which current products are made. Durability of wood and paper products is closely tied to their response to moisture as well. An understanding of the interactions between moisture and woody materials at the nanoscale may permit the development of new and innovative technologies which will decrease or even eliminate degradation.

Control or modification of surfaces of composites based on lignocellulose using nanocoatings or impregnation of nanoparticles could be used to provide physical/ chemical barriers to prevent or control the transfer of moisture. In addition, modification of the topography and surface chemistry could be used to control attractive and repulsive forces between cellulosics and other materials thus enhancing or decreasing wetting and adhesion. For example, this could be used to increase the specific bond strength of an interfiber bond thus permitting a lighter paper sheet with strength and optical properties, equivalent to a heavier weight sheet.

Very large amounts of water must be handled in the making and drying of products made from the forest. Such activities account for a very high percentage of the costs of production. Using nanotechnology, the nature of the interactions between the lignocellulosics and water can be manipulated to improve drainage during formation of the paper and increase the efficiency of drying of both wood and paper. This could take the form of nanomaterials that modify fiber surfaces or change the viscosity of water. Such materials could also be used as coatings on paper machine wires and press felts thus enhancing drainage rates of liquid water. They might also be used on paper machine dryer felts and dryer cans to improve heat transfer, making drying more efficient.

Understanding and manipulating the interactions between water and wood/paper will permit huge reductions in energy and water usage in processes by which products are made from these complex materials. It most likely will result in the more economical use of the raw materials in a broad base of new and existing products. It may also enable the substitution of products based on a sustainable renewable resource for some of the products derived from a more limited and less environmentally friendly material such as petroleum. The relationships between water and lignocellulosic materials have been studied extensively and a great body of literature exists. However, relatively little effort has been directed toward the interactions that occur at the interfaces of the two materials. These interfacial areas can be defined a number of ways. One such interface is the surface of the wood itself. Another would be the wood or wood pulp fiber and a third would be the interfaces that exist between water and the within the fiber walls. The latter can even be broken down to the amorphous areas of the cellulose bundles and the crystalline areas. The arrangement, size and degree of ‘crystallinity’ of the cellulose bundles at the nanoscale can greatly influence the behavior of the materials in response to water and water vapor at the macrolevel. Characterization of the interfaces, and the relationships between water (liquid and vapor) and lignocellulosics at the nanoscale can be achieved utilizing a combination of the newer available tools (e.g. atomic force microscopy (AFM), scanning tunneling electron microscopy (STEM), etc.) and standard technologies (e.g. inverse gas chromatography (IGC), transmission electron microscopy (TEM), scanning electron microscopy (SEM), electron spectroscopy for chemical analysis (ESCA), auger electron spectroscopy (AES), ultraviolet photoemission spectroscopy (UPS) and time-of-flight secondary-ion mass spectroscopy (ToF-SIMS)). Older methods such as electro-kinetic analysis (EKA), water vapor sorption, differential scanning calorimetry (DSC) and microcalorimetry are also very useful, especially when studying the surface charge and thermodynamics in the interfacial regions.

The scope of the proposed research could include the influence of species, location in the tree, site, process conditions, and the response of products in use to water and water vapor. By developing a fundamental knowledge base at this level, tools may be made available to allow companies in the forest products industry to ‘design’ trees for the properties needed in a range of products, to produce them by utilizing processes that are much more efficient in terms of the consumption of energy, water and raw materials; and may even make available a renewable, sustainable resource to the development of products currently made from less environmentally friendly materials. The primary output from work on lignocellulosic/water interactions at the nanoscale will be a knowledge base or ‘toolbox’ from a materials science perspective rather than a wood products or papermaker’s point of view. However, it will provide developers of products and processes in these disciplines the tools needed to improve current products and processes as well as those needed for the development of entirely new products from the forest.

Understanding and characterizing the interfaces in cellulose fibers at the nanoscale are the first step toward modifying the fiber and enhancing its properties as a building block for many products (existing and new). Using the water/lignocellulosic interaction (liquid and vapor) as a probe will enable the understanding of the surface energies of the fiber and permit us to more effectively add coatings (nanolayers), or other surface modifications; as well as derivatize cellulose to meet new and existing product requirements (e.g. strength enhancement, adhesion, and hydrophilic/hydrophobic properties). This knowledge base will be applicable to virtually all products derived from woody and nonwoody plants wherever water and lignocellulosics interact. With the exception of entirely new product streams, the information developed will permit more effective utilization of the current assets in the wood products and paper industries.

Outputs from this nanotechnology priority area would include the following: (1) a package of fundamental knowledge relating to cellulose/water interfacial interactions at the nanoscale; (2) a model based on the fundamental information developed;

and (3) a knowledge base which relates these interactions to more applied areas of adsorption/desorption, drying, dimensional stability strength/weight relationships, surface modification, product durability, and process improvements. The majority of the work considered to be precompetitive would include fundamental studies that relate to fiber/water or other lignocellulose/water interactions. These would relate to areas such as the impact of the nanostructure and properties such as the degree of crystallinity, dimensions of microfibrils and microfibril angle. The surface chemistry and topography of these materials at interfaces between water and the lignocellulosics at the nanoscale will have a big impact on how the materials respond to moisture. Heats of immersion or wetting, energies of adsorption of vapor, and surface free energy of the materials are all impacted by the natural nanostructures. In addition to the cellulose portion itself, hemicelluloses, lignin, extractives and trace minerals etc. will also influence the response of these materials to water or water vapor. Fundamental studies characterizing these materials based on surface science would provide a base to move into applications that take advantage of the properties at the nanoscale.

1.12.4 Producing Hyperperformance Nanocomposites from Nanocrystalline Cellulose

In addition to the wood-based composites, paper and paperboard can be considered to be a form of nanocomposite as they are made up of components that are essentially nanodimensional. Most work, to date, has been the result of empirical formulation where wood or pulp fibers have been mixed together with other components to make useful functional materials. Cellulose is a material which has unique tensile properties. In its pure form it can create fibers that are as strong or stronger then Kelvar® (Cellulose = 70 to 137 GPa, Kevlar = 100 GPa). It is desired to form composites in which cellulose provides its maximum tensile strength. Other properties of interest include formability and geometrical complexity at very small scale, unique physical properties, surface smoothness, biomedical compatibility, and ability to reinforce polymer foams.

It is also desired though the use of nanomaterials, and chemistry to either form or reform cellulose fibers in a variety of matrixes in which the cellulose can contribute its full modular strength to the matrix (Podsiadlo 2007). It has been postulated that the structure of wood is the result of the cellulose nanofibrils forming liquid crystal arrays under the influence of the hemicellulose (Vincent 2002). This represents a form of self-assembly that we would like to capture in order to produce new materials with high strength at lightweight. The interactions are typically noncovalent, such as hydrogen bonding and Van der Waals forces but, because of the extremely small size the interactions add up to provide a high degree of strength.

Other potential avenues can also be investigated to accomplish this. These include: (1) modification of the side chains of inorganic compounds, such as siloxanes, silanes, or sodium silicates to link the cellulose fibers through Si-OH bonds forming an organic/inorganic matrix; (2) growing the cellulose from bacteria; or an enzyme engine such that the cellulose forms in a matrix; (3) a nanostructure template and nanocatalysts could be used to help structure the matrix and increase the rate of formation of the cellulose fibers within the structured matrix; (4) disassembly of plants with enzymes/

chemistries that allows for the separation of cellulose from lignin without mechanical action; (5) development of systems that simulate the growth of cellulose in trees or plants that can be accomplished on a industrial scale; (6) dissolution of cellulose into ionic liquids with precipitation of cellulose into a continuous fiber or incorporation of threads or honeycomb weaves of cellulose into a variety of different material matrixes; (7) reacting wood pulp fibers in a solvent medium that does not fully penetrate the fibers followed by hot-pressing the partially modified pulp fibers at elevated temperature to form a semi-transparent polymer sheet that is a nanocomposite of cellulose esters and unmodified cellulose; (8) use of cellulose nanocrystals for reinforcement of other matrix materials; extreme refining of cellulose fiber resulting in increasing Canadian Standard Freeness (Roman and Winter 2006): and (9) modification of the side chains of cellulose to further enhance self assembly (Gray and Roman 2006).

A variety of understanding and characterization techniques would need to be established to accomplish the above. These include: (a) understanding cell wall formation in tree and plants; (b) development of the appropriate inorganic chemistry for linking cellulose; (c) understanding of cellulose chemistry and the sheet layering of cellulose to establish pathways by which cellulose could be modified to enhance self assembly; (d) understanding and modeling the formation of cellulose from glucose or other simple sugars by bacteria; (e) understanding of the effect of a variety of enzymes on the structure and tensile strength of cellulose; (f) understanding of the chemistry of cellulose and manipulation of its precipitation based on its solubility in various liquids and subsequent processing; and (g) effects of enzymes and extreme refining conditions on cellulose and cellulose composites.

Use of cellulose in a variety of different matrixes will be dependent on the interactivity of the matrix material with cellulose and lignocellulose surface chemistry. Wetting and surface area play key roles in the formation of high-strength interfaces between the matrix, matrix components and cellulose. Nanomaterials can provide unique levels of surface area for the formation of chemical bridges between the cellulose, the matrix and other fillers used. The strength of cellulose composites is influenced by the chemical interface and cellulose particle geometry. Interfacial interactions are governed by adhesion, water sorption, durability, and processing of the material. Cellulose derivatives can also be combined with nanomaterials and used in conjunction with cellulose fibers, or other fibers to form nanocomposites (Choi and Simonsen 2006).

1.12.5 Capturing the Photonic and Piezoelectric Properties of Lignocelluloses

Many grades of paper require using higher grammage (basis weights) than needed, not because of strength property end use requirement but because of the need to achieve sufficient opacity. Our target to use nanotechnology to help overcome this technical barrier and allow lower grammage sheets to be used in printing and writing allocations will result in paper with lower opacity and the likelihood of it not being fit for use. While this would allow savings by permitting raw material reductions in both fiber and coating, we need to avoid the loss of optical performance of the paper by building ‘optical band gap’ coatings to enhance opacity. Nanotechnology could also provide the ability to produce high sheet brightness with no fluorescence and could eliminate the requirement to bleach pulp to make white paper. The color gamut in the final printed image could be greatly improved by allowing for 'pure' pastel shades.

Currently the Kubelka-Munk approach of deriving apparent light scatter and absorption coefficients is useful for characterizing materials (Jones 2004). In addition, Mie theory uses fundamental Maxwell equations to describe the way light is scattered from particles and is useful for predictions of optimal sizes for light scattering units. Regular arrangement of these units can give rise to reinforcement of light interactions and is called a 'photonic effect'. For example, photonic band-gaps are structures that prevent the passage of light. Photonic properties have been shown to be possible using 'standard' materials and producing structures with regularities that provide photonic effects. Natural materials such as butterfly wings, seashells (abalone) and insect cuticles demonstrate effective optical barriers with minimal materials (Vukusic, Hallam and Noyes 2007). These are effects different from those described by Kubelka-Munk, Mie or Raleigh scattering.

It has been demonstrated that it is possible to make photonic structures that stop narrow wavelength band (e.g. latexes, Stober Silica – Synthetic Opals, and block co-polymers). The challenge is to make a structure with a range of sizes that has an effect over a very broad bandwidth and therefore, appears white. We are looking for high (close to 100%) opacity with high whiteness/brightness with minimal amounts of materials. More efficient optical performance with minimal weight is required at all grade levels but especially at the ultra-light grade where opacity decreases rapidly with weight. If we can make coated paper in the same weight range as tissue paper we can gain the benefits of high distribution costs and consequently limit competition from far afield. This will revitalize production units serving local areas. As a subgoal we expect to achieve:

1. a range of colors through unique structures (permanently stable unlike dyes);
2. improved gloss and appearance through control of unique structures;
3. pearlescent/iridescent effects;
4. control of ink interactions;
5. applications for security/ticket stock;
6. brightness unachievable today without using optical brightening agents (OBA) for enhanced image quality.

Electromechanical coupling effects in wood date back to 1950 when Bazhenov reported a piezoelectric response in wood (Bazhenov 1961). In 1955, Fukada also showed how the piezoelectric coefficients of wood were related to oriented cellulose crystallites (Fukada 2000). Piezoelectricity, a linear coupling between electrical and mechanical properties, is displayed by crystal structures that lack a center of symmetry (noncentric symmetric). Cellulose in wood is piezoelectric due to the internal rotation of polar atomic groups associated with asymmetric carbon atoms providing the noncentric symmetry. Shear piezoelectricity in wood varies depending on the type of wood, orientation of wood samples, moisture, and temperature and is comparable to that of quartz. Despite these early studies the potential of cellulose as smart lightweight material that can be used as a sensor and an actuator has not been investigated. Kim *et al.* have shown that it is possible to take advantage of this noncentric symmetry feature of cellulose to develop electro-active devices (Kim 2006). It is envisaged that, as we develop self-assembling cellulosic materials, we will be able to take advantage of these piezoelectric properties to build in greater functional performance.

Smart paper and packaging materials including radio frequency identification (RFID) and integrated moisture, impact and biological/chemical sensors, require paper substrates with new physical and chemical specifications. Moreover, advanced devices may require the ability to print much smaller and more uniform features onto paper substrates. However, several areas of advancement are needed. For example, printed electronics on paper will place new constraints on paper substrate frequency response and conductivity. The complex dielectric constant and dielectric loss tangent performance will need to be addressed to accommodate different frequency regimes. Radio frequency identification (RFID), for example, operates in the ~1–50MHz range, but development of systems operating in the 300–500MHz range is also underway. The specific application will drive the final specifications, but process, material and coating technologies capable of supporting device operation in the 1–50 MHz and 50–500MHz should be explored.

Electronic devices such as printed interconnects, resistors, reactive components and even active electronic and optoelectronic devices operating at high frequencies will require small printed feature dimensions and film thicknesses produced with better uniformity and reproducibility than is currently achievable, thus placing an additional constraint on the surface morphology of the paper substrate. Printed features, such as interconnect lines, may exhibit feature dimensions ranging from <10 to 100 microns in width and from <1 to 10 microns in thickness. The roughness and porosity of the paper substrate may be limiting in these applications, creating opportunities for new fillers, fiber materials, and fiber assembly or coatings to improve the structure of the substrate. We expect to improve the particle size and shape distributions of selected building blocks. This may be the extension of the engineered mineral pigments emerging currently or the development of new synthetic materials from wood fiber.

In order to achieve the most benefit from the opportunities to modify optical and electrical properties, we need to be able to select with precision the needed building blocks and then control their assembly into useful structures. This is probably the most challenging area. Paper coatings currently use additives and components that are applied in shear fields and dried under precise conditions to control the migration and positioning of the components to best advantage. Much of this has been derived empirically with information inferred from bulk measurements. Similarly in papermaking, pulp refining has been tuned to select the most useful building blocks and drainage, retention, and formation aids are used to control the structure development in the shear and compressive fields that occur on the paper machine in papermaking. Again many of these developments have been empirical but have benefited from recent microcopy developments.

The new disciplines of soft matter physics and nanotechnology are leading people to the study of self-assembling systems and offer the opportunity to leverage the findings into the world of forest products. Some of the areas that should be of value are:

1. block copolymer reactions;
2. drying moderated assembly;
3. hydrophobic/hydrophilic assembly;

4. mineral based liquid crystal assemblies;
5. layer by layer assemblies of polyelectrolyte coatings.

The forest products industry will also be able to take advantage of the substantial application equipment industry that has developed a number of novel machines for making paper and applying coatings at very high speeds such as:

1. metered size press;
2. spray applicator;
3. multilayer curtain coater;
4. new applications devices yet to be determined.

1.12.6 Reducing Energy Usage and Reducing Capital Costs in Processing Wood to Products

Priority goals for the application of nanotechnology in the forest products industry are the reduction of energy consumption as well as reducing capital costs. These are priority goals because conversion of wood into lignocellulosic products – lumber, engineered wood, composites, pulp, and paper – uses considerable amounts of energy and is quite capital intensive. This is because of (1) the large tonnage of forest product used annually in the US – over 205 million metric tons; (2) variability of wood as a raw material; (3) the need for water removal from the final product; (4) many sequential processing steps, (5) the amounts of water used in processing, (6) the need to deal with byproduct waste streams, and (7) the fact that many of the conversion technologies have their origins dating back from many decades to even centuries ago.

Overall energy consumption is between 2.891 EJ (2,740 trillion BTUs) and 3.511 EJ (3,272 trillion BTUs). This level of consumption represents 12–16% of US manufacturing energy demand – depending upon the literature source cited. Energy use is the second or third largest cost factor for the industry, especially as fuel and electricity prices continue to rise. Although the industry as a whole self-generates almost 50% of its energy needs from on-site combustion of biomass and pulping by-products, the industry still ranks as the country's fourth largest consumer of fossil energy (American Forest and Paper Association 2006). Paper and paperboard production accounts for the largest share of energy use (approximately 78%) in the industry, mainly due to the amount of energy required to evaporate the large quantities of water used to form the pulp slurry and the paper web. Pulping (7%), engineered wood products/composites (7%), sawn lumber (5%), and preservative treated and other lumber production (3%) uses comparatively less energy. However, because of the large tonnages of materials involved, the amount of energy used is substantial.

Capital costs are also a major problem for the forest products industry. For example, the pulp and paper industry ranks as one of the most capital-intensive industries in the nation. Paper machines are by far the largest and most expensive capital component. Pulping and bleaching equipment and chemical recovery plants also represent a large share of installed capital due to their size and complexity. By-product waste stream abatement and control are also a significant and recurring capital expense industry-wide.

The objectives for applying nanotechnology in reducing energy and capital costs are to employ nanomaterials in forest products processing in order to reduce manufacturing costs by both reducing the amount of energy consumed during processing and capital equipment required. Nanotechnology applications can take the forms of nanocatalysts to reduce the temperatures and time needed to delignify wood in pulping; low corrosion nanocoatings and nanomaterials to prolong the life of capital equipment; nanodimensional tags/markers for fiber separations; nano-inspired products that help with water removal on paper machines (drainage wires, vacuum boxes, wet presses, and dryers), kilns, and hot presses; and robust nanodimensional sensors (temperature, pressure, tensile/compressive forces, etc.) that can be used to monitor and optimize processing conditions as well as reduce/eliminate off specification product productions; etc.

Fiber, energy, and chemicals rank as the highest nonlabor operating cost items or categories at most pulp and paper mills. The ratio of costs will vary among different types of mills, but a typical integrated mill producing 1500 tons of kraft pulp per day will spend about US$45–60million for wood, US$30 million for chemicals, and US$15–20million for purchased energy each year. Energy reduction goals for pulping and papermaking are to reduce pulping process energy consumption by at least 33% and produce the same or better quality fiber at 5–10% higher yield; reduce energy consumed in the process of increasing black liquor solids (kraft pulping) by at least 50%; develop lower-cost technology to replace the current (energy and capital intensive) causticizing process; reduce energy consumed in the paper machine wet end by at least 33%; reduce the energy consumed in paper dewatering, pressing, and drying by at least 50%; and reduce energy and produce same or better-quality paper products by using: (a) nanocoating pigments and (b) three times the nonfiber filler content.

Drying is the most energy-intensive process employed in most pulp and paper mills, consuming between 4.6 to 9.2 GJ/metric ton (4 to 8 million BTU/ton) of pulp, depending on the paper grade. The amount of water removed by drying is determined by the efficiency of the nonthermal water removal processes (i.e., drainage, vacuum dewatering and wet pressing). As an approximation, every 1% increase in sheet solids as the sheet passes to the dryer section effects a 4% savings in dryer energy use. Papermaking is a complex operation requiring tight control to produce the expected level of quality. The huge quantity of water that must be removed and the required level of precision drive capital and operating costs. Nanotechnology needs for paper and paperboard drying are to develop cost-effective nano-inspired technologies that reduce the energy consumed in web/paper/paperboard dewatering, pressing, and drying by at least 50% via (1) developing next generation one-way water removal wet presses that employ felts that prevent/eliminate sheet rewetting, allow higher press nip forces, and extended nip lengths/dwell times to achieve significantly higher solids content of the paper/paperboard web entering the dryer section and (2) developing next-generation technologies that improve energy transfer to the web/sheet and water/water vapor removal for drying.

Energy and chemical usage varies with the pulping processing used. In the US, kraft pulping (both bleached and unbleached) is by far the largest pulping process used with over 45 million metric tons (50 million tons) of pulp produced annually. Semi-chemical, chemi-thermomechanical, Thermomechanical, and refiner mechanical pulps are employed but the tonnages produced are much, much less. In kraft chemical pulping, wood chips are heated to 160–180°C (320-356 °F) at a liquor to wood ratio of about 3.5 to 1 using sodium hydroxide and sodium sulfide and held for a period of time ranging from about 30 to 45 minutes depending upon the degree of delignification desired. The resulting pulp exiting the digesters is diluted and washed with water to remove the black liquor (spent pulping chemicals and dissolved wood solids). Large quantities of water are used, resulting in dilute black liquor – typically between 12 and 18% solids. The diluted black liquor must be concentrated before it can be efficiently burned in a recovery boiler to produce energy and recover the chemicals for reuse in the pulping process. The recovery of chemicals to form fresh pulping liquors is a vital part of the pulping operation. The energy generated by burning the black liquor in the recovery boiler is used in pulping and papermaking operations and significantly reduces purchased energy requirements. The black liquor is concentrated to 70−78% solids in steam-heated, multiple-effect evaporators. The evaporators are typically the second largest energy users in pulp mills and the largest source of steam consumption, at around 4.4 GJ (4.2 million BTU) of steam per metric ton of pulp.

Causticizing is a multistep process in chemical recovery process chain aimed at regenerating the original pulping liquor ('white' liquor) from the molten smelt of inorganic chemicals (sodium sulfide and carbonate) exiting the chemical recovery boiler. The process starts by dissolving the molten salts in water to form an aqueous solution called 'green liquor.' Lime (calcium oxide) is then mixed with the green liquor in a slaker to form sodium hydroxide and calcium carbonate. The chemical reactions that form the white liquor are completed in a series of reactors called 'causticizers'. The spent carbonate sludge ('lime mud') from the slaker and causticizers is removed in a clarification step, thickened, washed, and calcined in a lime kiln to recover calcium oxide for reuse in the slaking process. Causticizing is an old technology that has not benefited from innovation in many years. It is extremely capital intensive and suffers from very high operating and maintenance costs. The lime kiln in particular is a high-energy user and prone to maintenance problems. Lime kilns are typically fueled by oil or natural gas and represent one of the largest consumers of purchased energy in the pulp mill. Lime kilns and causticizers can also be a production bottleneck, limiting the mill's production capacity.

Nanotechnology opportunities/needs in pulping are to: (1) use nanotechnology to reduce steam use for black liquor evaporation to achieve energy savings; (2) develop low corrosion nanocoatings and nanomaterials to prolong the life of capital equipment especially in bleach plants; (3) develop cost-effective alternative nanocatalyzed, simpler means of regenerating white liquor, that regenerates sodium hydroxide in the recovery boiler and smelt-dissolving tank; (4) develop new nanocatalysis techniques to rapidly delignify wood (e.g. in 10 minutes or less) at lower temperatures (i.e. below the boiling point of water so as to not require pressurized vessels) that would also allow for easier separation of spent pulping liquor components, easier solids concentration, and easier; and (5) develop new nanocatalysis techniques for separating wood cell wall constituents without altering native structures of wood constitutive components (i.e. hemicellulose, cellulose, and lignin).

The kraft pulp industry has traditionally been a source of odorous emissions (primarily methylmercaptans) that, although not a health risk, are regarded as a nuisance in nearby communities. In recent years, the industry has made great progress by installing state-of-the art systems to reduce in-mill sources of the odors. However, odors from wastewater treatment operations continue to be a cause for community concern in many locations. Nanotechnology needs in this area are to develop cost-effective methods to reduce or eliminate odorous kraft emissions beyond the mill property.

The US pulp and paper industry discharges about 45 m^3/ton (12,000 gallons/ton) of wastewater. Although this is a significant improvement over decades past, the industry is still among the largest industrial water consumers. Developing ways to reduce water use in the mill and/or to recycle the process water within the mill for reuse would significantly lower wastewater treatment costs. Low-quality thermal energy in the wastewater could potentially be captured in the water recycling process and the industry's water use and effluent discharges would be greatly reduced. Almost all of the wastewater generated from the pulp and paper industry is treated in wastewater treatment plants made up of settling ponds (primary treatment) and biological purification (secondary treatment). The treatment process involves multiple steps and generally requires significant amounts of electrical power, adding to manufacturing costs and resulting in emissions from power production. In addition, many of these systems are reaching the ends of their useful lifetime and will need to be renovated or replaced at significant capital expense to the industry. Nanotechnology needs in wastewater treatment are to (1) develop alternative methods for wastewater treatment that are less energy- and capital-intensive than current biological effluent treatment systems and (2) develop low corrosion nanocoatings and nanomaterials to prolong the life of capital equipment.

Current recycling mills are complex, require numerous separate unit operations, and are energy inefficient and costly to operate. These operations need to be streamlined to improve operating efficiency, lower capital costs, and reduce energy and water consumption. Technologies to improve yield, recover all on-grade fibers, and tolerate or remove contaminants are also needed. Because of the variability in recovered paper collection and sorting systems across the US, gross contaminants and out-of-spec fiber continues to reach the recycle mill. Moreover, lower quality and rejected fibers – including shorter, inferior fibers from recycled paperboard imported from Asia – are also generating an increased volume of solid waste in US recycled fiber mills. Overall recycling goals focus on sorting and recycling mill wet-end equipment and processes such as pulpers, screens, cleaners, and flotation devices to significantly improve paper fiber recovery, fiber utilization, and energy efficiency in order to reduce fiber yield loss by 50%; improve contaminant removal by two-thirds; reduce overall costs by as much as US$40 per ton; reduce energy use by 50%; and reduce water use by 50%. Nanotechnology needs are to: (1) develop functional nanomaterials to enable paper and fiber tagging; (2) use nanomaterials to facilitate ink removal (i.e. de-inking) and contaminant removal; (3) develop low corrosion nanocoatings and nanomaterials to prolong the life of capital equipment; and (4) develop nanomaterials to improve recyclability of paper and paperboard products.

Processing wood products requires large amounts of energy, and represents the single highest wood processing cost. Drying processes account for the largest share of energy consumption. Energy used to cure wood composites and to dry lumber and other wood products in kilns accounts for 50–80% of the manufacturing energy consumed in these operations. More efficient wood drying and curing processes, better technologies for utilizing sawmill residues for energy, and methods for utilizing low-grade energy from available engines and motors could significantly reduce the purchased energy-intensity of wood products mills. A large amount of energy is also used in pollution control devices to control emissions of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). New regulations may require increased use of energy-intensive regenerative thermal oxidizers to further control releases of VOCs and HAPs from mill operations. The use of fossil fuels to power thermal oxidizers for VOC and HAP emissions control has significantly increased natural gas consumption. Development of energy-efficient and cost-effective technologies to reduce VOC and HAP emissions is needed. Advances could include more energy-efficient pollution control technologies, methods to reduce VOC and HAP precursors in the wood itself, or technologies to trap and purify specific VOCs suitable for sale as byproduct chemicals. Overall goals for wood products are to reduce capital and operating costs for wood products manufacturing by improving energy efficiency and reducing emissions control costs while providing greater flexibility to customize products for end-users. Nanotechnology needs are to: (1) reduce VOC and HAP emissions from manufacturing wood-based products by 90%; (2) use nanoscale materials and technology to improve conversion efficiencies of wood products; (3) use nanocoatings and nanocatalysis to decrease emissions to indoor air from wood-based products by 50%; (4) investigate ways to use nanotechnology and nanomaterials to enhance and increase the efficiency of drying wood and wood-based materials in kilns and presses; (5) increase marketable chemical byproducts of wood by 10%; and (6) employ robust nanodimensional sensors (temperature, pressure, tensile/compressive forces, etc.) to monitor and optimize processing conditions and improve conversion yields as well as reduce/eliminate off-specification product productions; etc.

1.13 Summary

Nanotechnology is an emerging area of science and technology that will revolutionize materials use in the 21st century. Over the course of this century, we will move from many of the relatively crude and unsophisticated technologies on which we currently depend and replace them with highly efficient and environmentally friendly nanotechnologies that meet the desired goals, guidelines, and principles of sustainability, sustainable development, green chemistry, and green engineering. For the forest (lignocellulosic) products industrial sector, nanotechnology will be used to tap the enormous undeveloped potential that tree's possess – as photochemical 'factories' that produce rich sources of raw materials using sunlight and water. Lignocellulosic biomass resources provide a key materials platform for the sustainable production of renewable, recyclable, and environmentally preferable raw materials for producing goods and products to meet the needs of people. Lignocellulosics provide a vast material resource and are geographically dispersed. Humankind has done an excellent job of capturing the values that wood can provide at the macro- to microscales, but the values of wood and wood-based materials at the nanoscale are virtually untapped. The vision for nanotechnology in the forest products is to sustainably meet the needs of present and future generations for wood-based materials and products by applying nanotechnology science and engineering to efficiently and effectively capture the entire range of values that wood-based lignocellulosic materials are capable of providing. In addition, the lignocellulosic products industry sees its inherent strengths as including: (1) stewardship of an abundant, renewable, and sustainable raw material base; (2) a manufacturing infrastructure that can process wood resources into a wide variety of consumer products; and (3) being uniquely positioned to move into new, growth markets centered on bio-based environmentally preferable products. Nanotechnology, as it is envisioned, will further enhance the industry's ability to produce new high performance consumer products from lignocellulosic-based materials in a safe and sustainable manner.

While the focus of nanotechnology research may seem to be on determining the nanoscale properties of materials, it is really achieving nanotechnology-enabled macroscale end products that are most important. Nanotechnology must be viewed as an enabling technology versus an end in itself. To most rapidly make scientific and technology advancement, the focus for nanotechnology research must have an end use application or product in mind. The range and magnitude of benefits offered by nanotechnology science and engineering research and development can only be realized if the technologies are accepted and deployed by industry to produce economically-viable products that consumers want and need. Therefore, it is important that research efforts be focused on high-impact, high-priority activities that will be the most critical to commercial producers of nanomaterials and nanoproducts. It is absolutely critical to build our nanomanufacturing science and technology knowledge base so nanomaterials exhibiting unique nanoscale properties can be controllably placed into components or systems, retain and combine their unique nanoscale properties in a matrix of other materials, and result in superior products. Industrial input and influence on nanotechnology science and engineering serves to help guide activities into the highest priority and most productive areas. The US forest products industry has identified six priority nanotechnology application areas. These six areas are to use nanotechnology to (1) achieve lighter weight, higher strength materials; (2) produce nanocrystalline fibrils from wood; (3) control water interactions with cellulose; (4) produce hyperperformance nanocomposites using nanocrystalline cellulose fibrils; (5) capture the photonic and piezoelectric properties of lignocelluloses; and (6) reduce energy usage and capital costs in processing wood to products. Lastly, understanding the health risks and taking appropriate action to mitigate risks to health, safety, and the environment that result from exposure to or introduction of engineered nanoscale materials, nanostructured materials, and nanotechnology-based devices is an extremely important consideration in responsibly moving nanotechnology forward – for both wood-based nanomaterials and nanomaterials and devices that are produced by other industry sectors that are incorporated into forest products.

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