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Wood and Paper as Materials for the 21st Century.

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Abstract

Wood and paper are ubiquitous in societies around the world and are largely taken for granted as part of traditional industries with no new science to learn. Many of the technologies used in the forest products industry have been gained empirically through experience. The complexities of wood are now yielding to newer tools and we are beginning to see how the mechanical, optical and other physical properties of wood are related to hierarchical structures based on 2 to 10 nm diameter several hundred nm long fibers of nanocrystalline cellulose (NCC). The liberation of these NCC's is allowing their re-assembly into remarkably strong structures. Examples will be given of the nature of these building blocks and structures assembled from them. Examples will include nanocomposites as well as very high strength "paper". Paper is another example of a process whereby nanofibrils are released and then re-assembled with the use of "retention, drainage and formation aides" to make substrates we call paper with remarkable strength to weight performance. Other disciplines call this process "self-assembly" and the "aids" as necessary surfactants and additives to control structure and performance. Glossy magazine papers, for example, have approximately 10 micron thick coatings of white minerals and latex binders which are increasingly of nano dimensions. The coatings are assembled in structures to provide optical barrier performance (opacity) as well as controlled ink interaction with the necessary strength to survive printing and handling. These coatings are frequently similar in structure to seashells and, from this knowledge, progress has been made in understanding the mechanisms at play in achieving higher strength coatings. More recently kaolin clays have been introduced with mean crystal thicknesses in the range 20 to 40 nm instead of the usual 100 to 140 nm. These clays show useful strength performance and represent what may be called pragmatic nanoclays. Novel chemistries based on biomimetic learnings are emerging to displace the conventional starch or latex binders. Examples will be given of protocols for moving toward higher strength systems.

Introduction

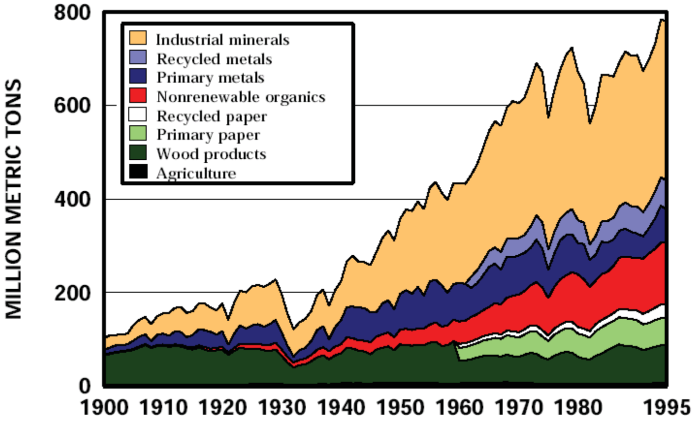
Wood is a cellular hierarchical lignocellulosic biocomposite made up of self-assembled nanometer-sized components. The nanoscale architectures present in wood are complex but are becoming better understood using and adapting the new generations of analytical tools emerging in a variety of science and technology areas. Other composite biomaterials, such as bone, teeth, and seashells have been found to owe their high strength and optical properties to nanoscale architecture [1]. Similarly, the nanoscale architectures of wood provide the origin for its unique properties and a host of wood-based products including paper, paperboard, oriented strandboard, glulam beams, etc. [2]. For example, paper represents a material produced from wood that has been "pulped" and refined to liberate fibrils, (microfibrils/nano-fibrils, and nanocrystalline cellulose) that are responsible for its inherent strength and performance [3]. While the relative mass of the nano-fibrils and nanocrystalline cellulose is small, their surface area is large and by number they represent an enormous fraction which has significant consequences.

Wood provides one of the key materials platforms for the sustainable production of renewable, recyclable, and environmentally-preferable goods and products [4]. Forests can be seen as photochemical “factories” that produce rich sources of raw materials using sunlight, CO_2 and water. It is critically important to move utilization of lignocellulosic biomaterials forward by exploiting wood as an important 21st Century industrial nanomaterial; enabling other nanomaterials to be used in conjunction with wood-based 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.

Use of Lignocellulosic-based Materials

The importance of wood in the economy of the U.S. cannot be understated (Figure 1 [5]). With approximately 226 million ha of forestland, the U.S. produces about 25 percent of the world’s industrial roundwood. Together the U.S. and Canada produce approximately 40 percent of the world’s industrial roundwood. 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 U.S., about 700 million tons (oven dry basis - o.d.) of woody forest biomass accumulates annually. As a result, the standing stock of timber in the U.S. continues to grow and is currently over 20 billion o.d. tons.

Figure 1 Raw Material Use in the United States



About 260 million o.d. tons of this is harvested annually, leaving a large amount of forest biomass potentially available for conversion into a variety of new products, energy, or chemicals. Additionally, it has been shown that it will be possible to sustainably increase the cumulative production rate of all types of biomass to levels of 1 billion tons per year [6].

The Green Connection and New Materials Opportunities

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) following the principles of both Green Chemistry and Green Engineering [7] Current industries using wood and wood-based materials have evolved over many years and are often written off as traditional industries with no grand scientific challenges. However, this is far from the truth. The problem has been that wood is a very sophisticated and complex material and analytical tools needed to adequately study and understand wood’s hierarchical structure have been lacking.

An array of important new commercial applications for wood and wood-based materials is emerging. For example, forest-based lignocellulosic materials now represents a key raw material source for liquid biofuels production where one can envision an existing pulp mill adding on a bioconversion process to include production of nanocrystalline cellulose. Nanocrystalline cellulose produced from such a reconfigured pulp mill would then be available for an array of new materials developments [8]. Cellulose can also be used for electrical devices (including artificial muscles), due to its piezoelectric nature [9]. Termed smart cellulose, “electroactive paper" (EAPap) is a chemically treated paper with thin electrodes on both sides. When electrical voltage is applied to the electrodes, the EAPap bends [10]. Nanocellulose has also been found to form layer by layer films with antireflective properties and multi-walled nanoribbon cellulose has also been used for wound dressings [11].

Wood Nanodimensional Structure and Composition

Wood is approximately 30 – 40 percent cellulose by weight with about half of the cellulose in nanocrystalline form and half in amorphous form (Figure 2g).

Figure 2 Wood Hierarchical Structure--From Tree to Cellulose [12] (Moon 2008)

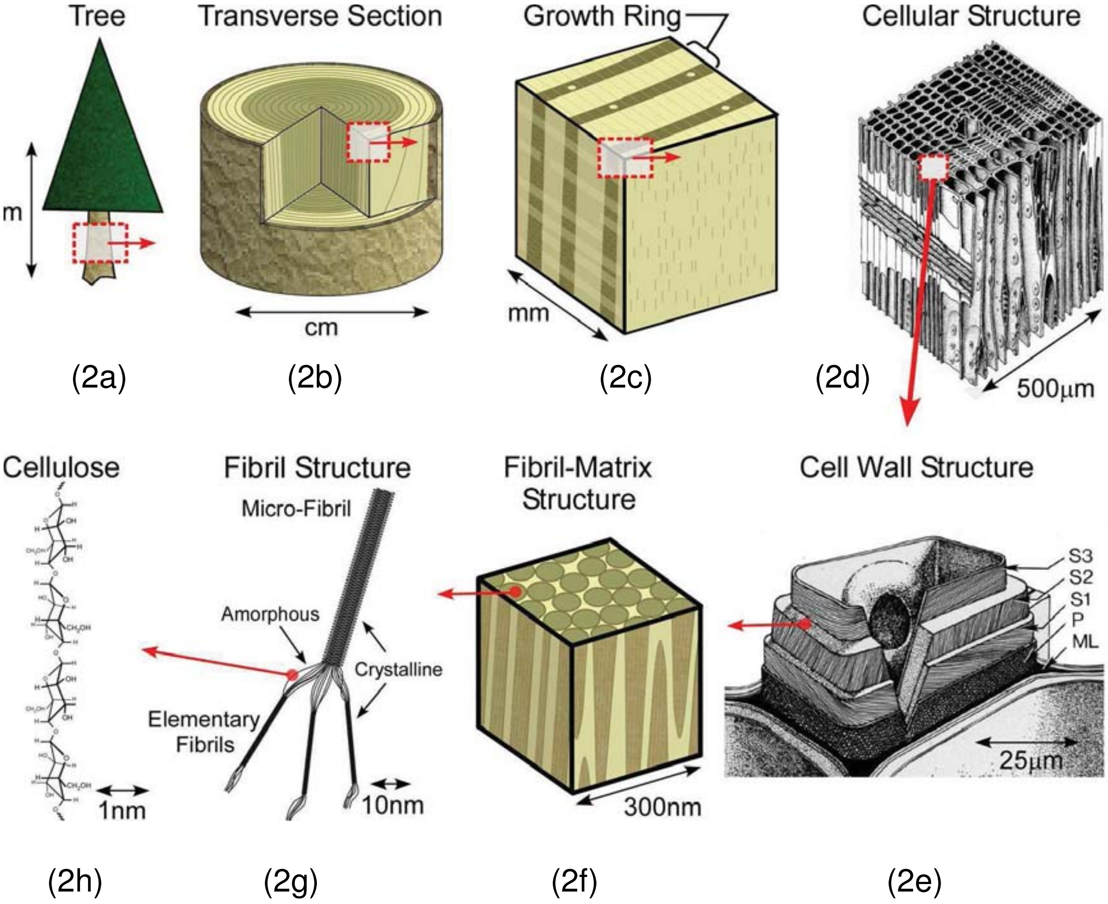


Figure 2e ML = Middle lamellae between tracheids, Tracheid--P = Primary cell wall, S1, S2, S3 + cell wall layers

Cellulose (Figure 2h) is the most common organic polymer in the World representing about 1.5 x 10^{12} tons of the total annual biomass production. Cellulose is the major carbohydrate component of wood along with the hemicelluloses (20 – 35 percent 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 - 5 nm diameter fibrils that aggregate into larger microfibrils up to 20 nm in diameter (Figure 2g and 2f). These fibrils self assemble in a manner similar to liquid crystals leading to nanodimensional and larger structures [13,14]. 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 [15].

Because wood has a hierarchical structure, advances in separation techniques are goaled at leading to the commercial production and use of multiple nanoscale architectures such as nanocrystalline cellulose, nanofibrils, and nanoscale cell wall architectures (Figure 2g and 2f). Nanofibrils (nanowhiskers) in their simplest form are the elementary cellulosic fibrils shown in Figure 2g 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 Figure 2f 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 of 100 to 300 nm long. Nanocrystalline cellulose is any where from a tenth to a quarter of the strength of carbon nanotubes [16 ,17]. 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, overall complexity has limited discovery. Simpler structures found in seashells, insect cuticles and bones are being understood as relating to their hierarchical structures. [18] and we are poised for these techniques to be applied to lignocellulosic-based materials.

In the meanwhile work on using nanocrystalline cellulose in nanocomposite structures is well under way [19].

Paper as a Composite structure

The process of pulping, bleaching and refining of wood to produce pulp essentially liberates an abundance of fibers in the range of 20 to 40 microns in diameter and up to a few millimeters in length, together with an associated large number of fibrils that are 10's of nm in diameter. In forming paper, the suspension of these refined fibers and mineral fillers in water self assemble to form paper at speeds of up to 60 mph (96 kph). Interactions are controlled by the addition of polyelectrolytes such as polyacrylamides and polyethylene imines to control water release and "formation" to give a uniform distribution of components. Figure 3

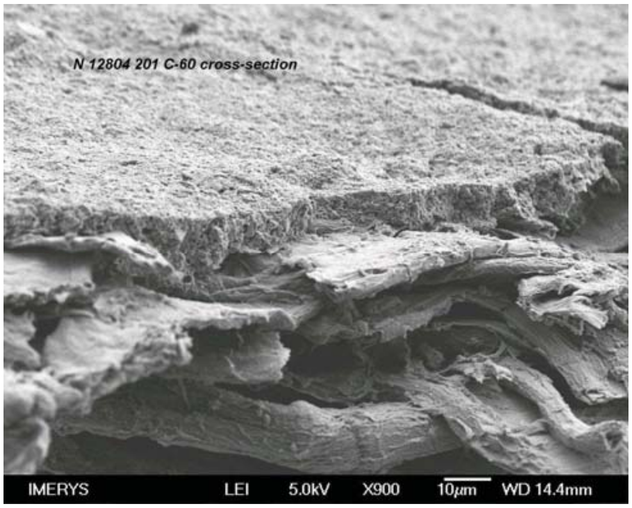


Figure 3.
Freeze fractured coated paper

Coatings, typically 8 to 12 microns thick, of minerals such as kaolin and calcium carbonate are also frequently applied at similar speeds and are used to provide flatter glossy surfaces important to color printing in magazines and catalogs. Control of self assembly is important so as to provide a coating structure that is suitable for controlled receptivity of printing inks as well as developing a uniform and suitable optical appearance.

Nanocomposites from Nano-dimensional Cellulose

Cellulose is a material which has unique tensile properties and in its pure form can create fibers that are as strong or stronger then Kelvar® (Kevlar = 100 GPa). Cellulose nanocrystals have a Young's modulus of around 140 GPa and a Tensile Strength of around 7.5 GPa. [20]. There are a number of candidate methods to liberate nanodimensional cellulose based on multistage processes involving chemical and mechanical operations. Typical processes involve the use of an acid hydrolysis or enzymatic treatments of bleached kraft pulp followed by intense mechanical liberation of the nanofibers typically using high shear homogenizers [21]. Nanocrystalline cellulose is roughly 3 - 5 nm in diameter and a few hundreds of nanometers in length. It is also desired to either form, or reform cellulose fibers in a variety of matrices in which the cellulose can contribute its full modular strength to the matrix. 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 [14]. 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 non-covalent, 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. Cellulose nanopaper made from cellulose nanofibrils show high toughness (15 MJ/m^3) with a strain to failure as high as 10%. The Young's modulus (13.2 GPa) and tensile strength (214 MPa) are remarkably high despite a porosity around 28%. [22]

Paper Coatings

A kaolin clay based paper coating shows a strong similarity in structure to that seen in many other biomimetic structures such as sea shells and bones. The structure shown in figure 4a is comprised of kaolin bound by styrene butadiene latex and oriented during the blade coating application. The typical latex or starch binder levels of 10 to 20 % allows a significant pore volume to remain in the coating. This is important to scatter light and provide opacity and brightness. In addition the pore shape, pore size distribution and pore number control the ways that printing inks interact with the coating and consequently pore structures are the subject of a lot of investigations. Selection of binder and mineral particle size, particle size distribution and particle shape control particle packing and hence pore structure. The mineral binder interaction is essentially Van der Waals bonding or dipole/dipole interactions and sensitive to water. On-going work with biomimetic structures [23] is lending itself to potential applications in paper coatings and will enable new generations of very high strength coatings based on recently discovered nanodimensional kaolin clays that are 10's of nm thick (figure 4b [24]) that will transform the nature of paper and paperboard packaging. Investigations of ways to increase the strength of paper coatings have emphasized the need to enhance the binder mineral interaction in ways that lend themselves to applications to paper substrates at high speeds [25]. In addition, very high aspect ratio nanodimensional kaolin clays lend themselves to a wide range of assembly and structuring processes. For example it is possible to cause the plates to align both by proper choice of surfactant and electrolyte level as well as via the application technique and have then behave as mineral liquid crystals [26,27]. In addition, disordered bulky structures can be assembled both by method of application to cause turbulence and hence disorder as well as with the use blocky building blocks such as calcium carbonate to provide bulkier lower density coatings.(Figure 4c).

Figure 4a
Cross section of a paper coating showing
Similarity to abalone shell structure

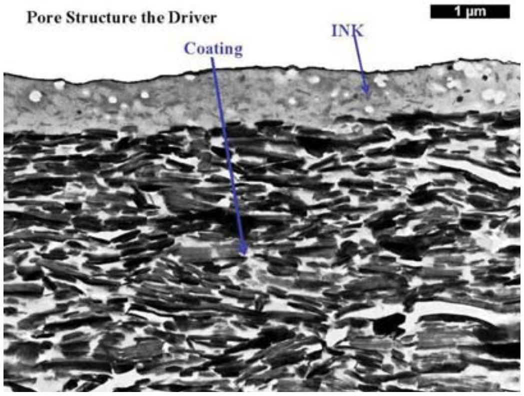


Figure 4b
New class of nanokaolin clays 10’s nm

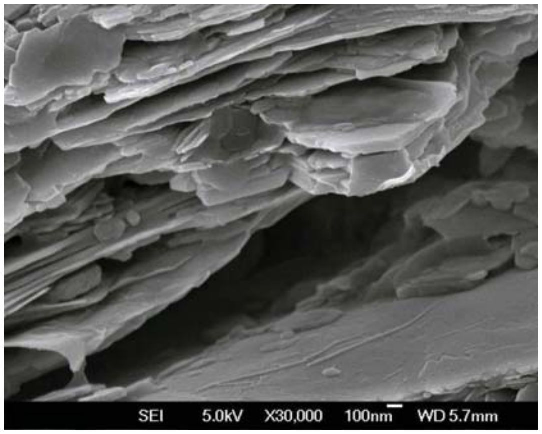
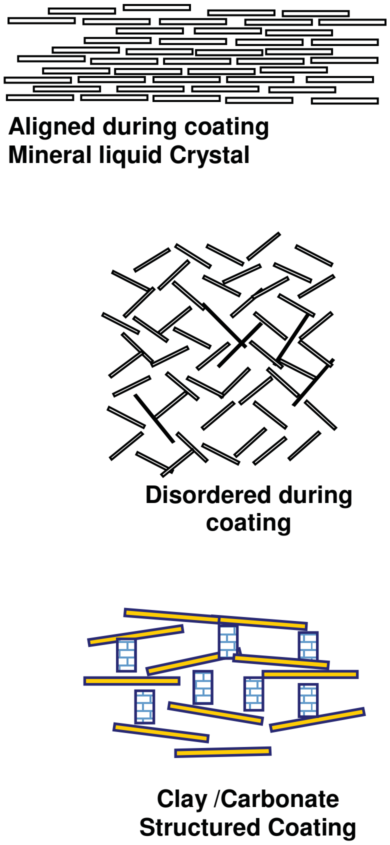


Figure 4c
Thin crystal nanokaolin clays
can be assembled in many ways


Aligned during coating
Mineral liquid Crystal

Disordered during coating

Clay /Carbonate Structured Coating

Many kaolin and calcium carbonate processing plants are now being operated more like petroleum refineries, where selection of the crude mineral ore is vital and the processing involves grinding (cracking) followed by mineral separations and by magnetic separation, froth flotation, selective flocculation and finally by a wide arrange of centrifuges to “distil” off a range of size and shape fractions.

In addition the work underway on photonic structures in nature such as the color of butterfly wings and white beetles is laying the groundwork to build coatings with improved optical barrier and opacity [28]. The ability to both make very high cellulose based substrates using additions of nano crystalline cellulose to a kraft pulp together with the ability to make very high toughness coatings with nanokaolin clays will open substantial opportunities for new products based on abundant material resources.

Forest Products Industry Focus

Working through the American Forest & Paper Association and the Agenda 2020 program the U.S. Forest Products Industry has identified priority nanotechnology application areas[29] to include:

- achieving lighter weight, higher strength materials;
- producing nanocrystalline fibrils from wood;
- controlling water interactions with cellulose;
- producing hyper-performance nanocomposites using nanocrystalline cellulose fibrils;
- capturing the photonic and piezo-electric properties of lignocelluloses; and
- reducing energy usage and capital costs in processing wood to products.

Understanding and taking appropriate actions to mitigate health and safety risks and dangers to the environment that may result from exposure or introduction for engineered nanoscale and nanostructures materials and devices is a serious consideration in responsively moving technology forward. This applies to both wood-based materials and materials and devices that are produced by other sectors that are incorporated into forest-based products.

Conclusions

For the forest products industrial sector, the understanding of biomimetic mechanisms 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. Wood provides a key materials platform for the sustainable production of renewable, recyclable, and environmentally-preferable raw materials for producing goods and products. Lignocellulosics provide a vast material resource and are geographically dispersed but often concentrated near population concentrations in the United States. An excellent job has been done in capturing the values that wood can provide at the macro- to micro-scales, but the values of wood and wood-based materials at the nanoscale are virtually untapped. The forest products industry sees its inherent strengths to include (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. Expanding efforts in biomimetic work on lignocellulosic material will further enhance the industry's ability to produce new high performance consumer products from trees in a safe and sustainable manner.

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