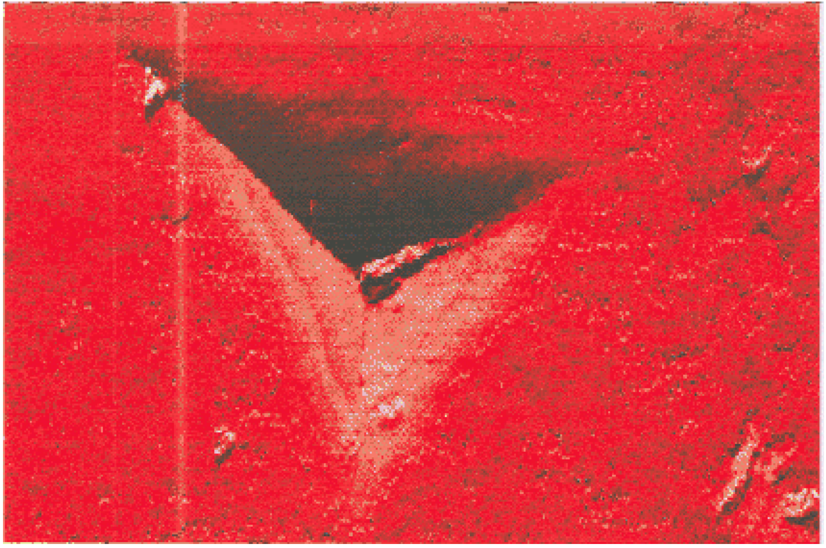

Nanotechnology Applications in the Forest Products Industry

By Robert J. Moon, Charles R. Frihart, and Theodore Wegner

Nanotechnology is the study and engineering of matter at the dimensions of 1 to 100 nanometers, where the physical, chemical, or biological properties are fundamentally different from those of the bulk material. By expanding our understanding and control of matter at such levels, new avenues in product development can be opened. Nanoscale-based science has applications across nearly all economic sectors and allows the development of new technologies with broad commercial potential, such as nanostructured materials, nanoscale-based manufacturing processes, and nanoelectronics. However, to fully achieve these potential applications, investments must be made in the science and engineering that will enable creation of new technologies and enable industry to produce more advanced and cost-competitive products. The necessary basic and applied nanotechnology research and development (R&D) are often too broad, complex, expensive, long-term, and risky for industry to undertake entirely on its own. Therefore, this R&D is best carried out as an integrated partnership and effort involving the federal government, academia, and industry. Figure 1 shows the historical breakdown of overall R&D spending by categorical group, and a similar trend is expected for the specific R&D spending in nanotechnology. This figure demonstrates that federal and university involvement in R&D is highest for basic research, while involvement of U.S. industry is highest in applied research and product development. To best assist industry in the utilization of nanotechnology, the federal government is concentrating its funding on basic research.

The National Nanotechnology Initiative (NNI) was established in 2001 to coordinate the R&D of nanoscale science, engineering, and technology across the federal government. The Nanoscale Science, Engineering and Technology Subcommittee coordinates in the NNI and operates under the auspices of the National Science and Technology Council. In its first year, NNI was composed of six agencies investing in nanotechnology. Since that time, the annual federal investment has more than doubled in nanotechnology R&D to approximately $1.3 billion, while the number of funding and participating federal agencies has grown to 12 and 25, respectively.[1] The vision of the NNI is a future in which the ability to understand and control matter at the nanoscale level leads to a revolution in technology and industry. The four goals of NNI are to 1) maintain a world-class R&D program aimed at realizing the full potential of nanotechnology; 2) facilitate transfer of new technologies into products for economic growth, jobs, and other public benefits; 3) support responsible development of nanotechnology; and 4) develop educational resources, a skilled workforce, and the supporting infrastructure and tools to advance nanotechnology. In addition, the NNI is developing a national infrastructure that will provide access to user centers that house expensive and sophisticated equipment that is necessary but not cost effective for any one group or institution to purchase and maintain. The NNI is also establishing research centers that will each have a specific focus and expertise that can be called upon as needed to solve narrow but complex problems.

Forest Products Nanotechnology Research Agenda

Although wood has unmatched aesthetic qualities, the most important attribute of wood is its mechanical properties. These properties are important whether the forest product is solid wood, a composite, an engineered wood product, a corrugated container, or a sheet of paper. continued R&D on forest products is essential for product property improvements that wiil meet future needs and provide products at reasonable costs. Nanotechnology R&D is critically important to the economical and sustainable production of new generations of forest-based materisal and to help move society toward a biomass-based economy. Nanotechnology offers the potential to transform the forest products industry in virtually all aspects, ranging from production of raw materials, to new approaches for productin engineering wood and wood-based materials, to new applications for composite and paper products, to new generations of functional nanoscale lignocellulosics.[2] 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, and attack by wood decay fungi. 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. Nanotechnology can be used to improve processing of wood-based materials into 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.

Advancing the forest products nanotechnology research agenda requires cooperation between the forest products and nanotechnology research communities, the federal departments and agencies thathave ongoing programs in nanotechnology R&D, and the NNI.[1] The forest products industry has a goal to establish a nanotechnology R&D program under the NNI that would have an annual budget of $40 million to $60 million. To focus the R&D efforts, a consensus on research needs and priorities among forest products industry, academia, and government is needed. The forest prducts iondustry can build upon established and successful programs such as the Americqan Forest & Paper Association's Agenda 2020 Research Alliance. This Alliance is an industry-led partnership with government and academia for collaborative, pre-competitive research, development, and deployment. It has developed an industry-wide research agenda for the entire forest products industry to include paper, composites, and solid-sawn lumber. Specifically, the alliance has identified six major areas of technological needs: 1) advancing the forest biorefinery; 2) positively impacting the environment; 3) developing the next generation fiber recovery and utilization; 4) creating breakthrough manufacturing technologies, 5) advancing the wood products revolution; and 6) developing a technologically advanced workforce. The Alliance recently adopted nanotechnology as a focus area and is developing a technology roadmap for research in this area.

In fiscal year 2006, the USDA Forest Service has initiated the following research programs: 1) use the intrinsic nanoscale properties of wood and similar lignocellulosic materials for developing advanced nanomaterials; 2) use nanoprocesses to modify lignocellulosic materials; and 3) use nanometrology techniques to investigate the fundamental structure of materials, the ways in which they degrade, and methods for inhibiting this degradation. In fiscal year 2007, the USDA Forest Service will place additional emphasis on these programs using internal and external resources. Scientists will investigate areas of fundamental nanoscale phenomena and processes, nanomaterials, nanoscale devices and systems, instrumentation, metrology, and standards for nanotechnology.

Nanotechnology R&D at the USDA Forest Service, Forest Products Laboratory (FPL) has five focus areas for basic research: 1) analytical methods for nanostructure characterization: 2) cell wall nanostructures; 3) nanotechnology in sensors, processing, and processing control; 4) polymer composites nad nanoreinforced materials; and 5) self-assembly and biomimetics. The remainder of this article describes in detail one nanotechnology R&D area of interest as an example of research that FPL will be exploring. This basic research utilizes sub-micrometer mechanical property characterization (via nanoindentation) and structure-property modeling to investigate nanoscale chemical and mechanical interactions between the basic polymers of wood (cellulose, hemicellulose, and lignin). The outcome of such research will assist in the understanding of wood's mechanical and chemical properties and allow for improved mechanical performance of wood, adhesive joints, swelling/shrinking behavior, and other attributes. By understanding how nature works its magic, we may be able to use genetic, biological, or chemical changes to design wood products rather than just using what nature has provided.

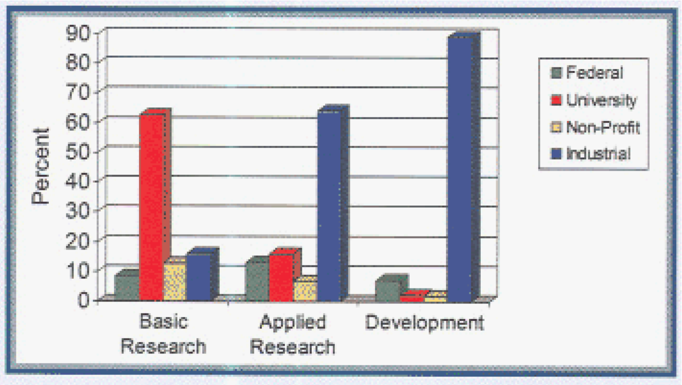

Figure 1. – Research and development activities by categorical group, 2003. Source: National Science Foundation.

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[1] www.nano.gov

[2] www.nanotechforest.org

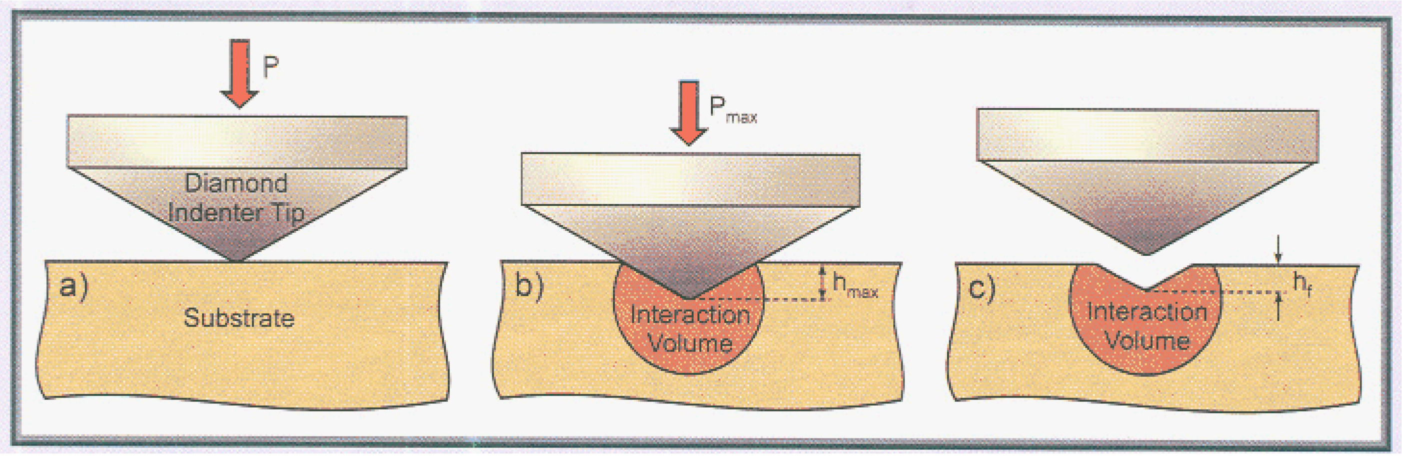


Figure 2. – Schematic showing the general sequence of indentation: a) indenter tip makes contact with sample surface; b) is pressed into the sample surface; and c) is retracted from the surface, having a permanent indent.

Using Nanoindentation for Basic Wood Research

Structure of Wood

The most important attribute of wood is its mechanical properties, in particular its unusual ability to provide high mechanical strength and high strength-to-weight rationwhile allowing for flexibility to counter large dimensional changes due to swelling and shrinking. These unique properties of wood are a direct result of its hierarchical internal structure. The structure of wood spans many length scales (see cover illustration): meters for describing the whole tree, centimeters for describing structures within the tree cross section (pith, heartwood, sapwood, and bark), millimeters for describing growth rings (earlywood, latewood), tens of micrometers for describing the cellular anatomy, micrometers for describing the layer structure within cell walls, tens of nanometers for describing the configuration of cellulose fibrils in a matrix of hemicellulose and lignin, and nanometers for describing the molecular structures of cellulose, hemicellulose, and lignin and their chemical interactions. the bulk properties of wood result from the culmination of interactions within and between each length scale. Thus, to completely understand bulk wood response to an applied load or given environment, the properties and response characteristics must be understood at each length scale.

Although wood has been widely used as an engineering material for thousands of years, its chemical complexity and hierarchical architecture have hindered the efforts of researchers to understand and control its performance. Significant procress has been made in understanding the mechanical properties of bulk wood, isolated fibers, and cellulosic fribrils; however, much remains to be understood about characteristics of intact cell walls, interactions between cell wall layers, and properties of and interactions among the nanoscale domains (cellulose, hemicellulose, and lignin) that provide the basis for properties we observe in the system as a whole.

Technological advances in instrumentation allows us to fill in these knowledge gaps. The atomic force microscope (AFM) has been widely used to understand surface topography and some surface properties (chemistry, reactivity). However, only nanoindentation allows the measurement of mechanical properties. In the following sections we describe what nanoindentation techniques actually determine, how they can be applied to wood, and what we can learn from them.

Nanoindentation Techniques

Mechanical properties of materials have been commonly characterized using indentation techniques because of the ease and speed of conducting the tests. The basic premise of all indentation techniques is that a hard material of specified shape (indenter) is pressed into the surface of a softer material (substrate) with sufficient force that the softer material deforms (Fig. 2). Properties that are measured by indentation describe the deformation of the volume of material beneath the indenter (interaction volume). Deformation can be by several modes: elasticity, viscoealasticity, plasticity, creep, and fracture. These deformation modes are described by the following properties, respectively: elastic modulus, relaxation modulus, hardness, creep rate, and fracture toughness, Characterizing these properties provides a method for describing a material's response to an applied loading condition, which helps predict material performance.

Elastic deformation is nonpermanent deformation that occurs instantaneously after a stress is applied or released and is described by the elastic modulus. Viscoelastic deformation is nonpermanent time-dependent deformation and is described by the relaxation modulus. Plastic deformation is permanent deformation where hardness describes a material's resistance to permanant deformation. Creep is permanent time-dependent deformation and is described by the creep rate. Fracture occurs when a material can no longer deform by any other mechanism and cracks form within the material to relieve the applied stress. Fracture toughness describes the critical condition at which cracks form. For the indention schematically shown in Figure 2b, the substrate has sufficient deformability to accommodate the indenter shape (i.e., no fracture), and the total displacement has both elastic and plastic contributions. Once the applied load is removed (Fig. 2c), the elastic deformation is recovered, whereas the permenanent deformation remains. If the material was viscoelastic, then the final indent displace-

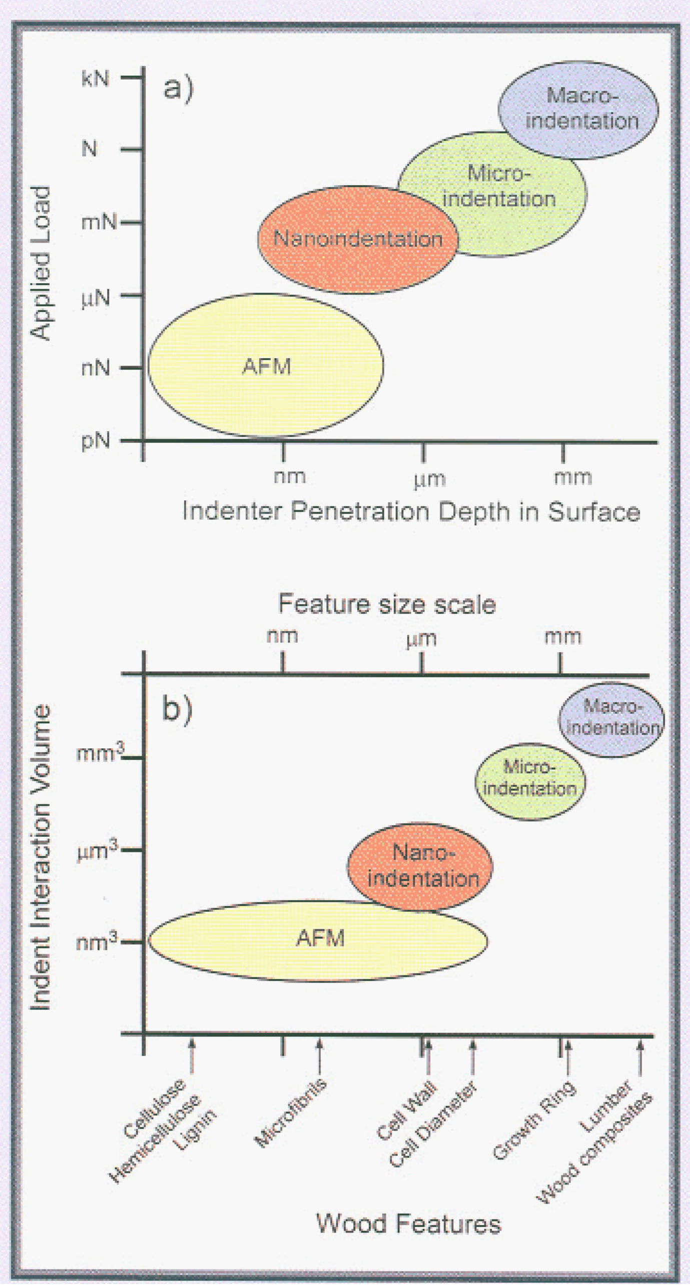


Figure 3. — Schematic representation of the approximate ranges of a) applied load versus indenter displacement; and b) interaction volume versus measurable feature sizes (and wood feature size) for macroindentations, microindentation, nanoindentation, and atomic force microscopy (AFM).

ment, h_f would continue to decrease for a period of time after the load was removed. If the material was susceptible to creep, then h_f would be dependent on the applied load-time profile, such as loading rate and hold segments.

The evolution of indentation techniques has been in decreasing the interaction volume size, which has allowed measurement of the mechanical properties of smaller sized features. However, as the indentation load decreases, the corresponding decreases in indenter penetration depth and interaction volume mean that the measured mechanical properties become increasingly dominated by the material directly at the surface. Figure 3. schematically shows the approximate range of the applied load, indenter displacement, interation volume, and feature size that can be measured for macroindentation (Brinell and Rockwell techniques), microindentation (vickers and Knoop techniques), nanoindentation, and AFM. Usually, AFM is not an indentation technique; however, the AFM can be used as a nanoindenter to probe the mechanical properties of material in the first few nanometers from the surface. But because AFMs are difficult to accurately calibrate in terms of load, displacement, adn indenter shape, the application of these instruments to perform careful nanoindentation-like measurements remains a highly specialized technique. More often, AFM is used in parallel with nanoindentation, providing surface topographical and chemical information, and is included in Figure 3 for reference.

Macroindentation uses relatively large-diameter indenters (10-mm-diameter sphere for Brinell testing), high applied loads, and deep indentations, thus the mechanical properties are measured from a larger interaction volume, typically across a wide range of cellular structures (earlywood and latewood bands, for example), where the hardness values will be approximately proportional to the density of the wood. This type of mechanical properties measurement can be directly applicable to the response of wood flooring to an impact (such as a falling object or a high-heel shoe) or to a scratch (such as a sliding chair or an overly rambunctious dog extending its claws in hopes of getting some traction ont he smooth wood floor). Similarly, macroindentation utilizes smaller diameter indenters and lower applied loads, and the corresponding interaction volumke is smaller. This technique can measure earlywood or latewood bands, where interaction volume is large enough to encompass many cell walls and empty lumen areas, this the measured properties will result from the response of both structures. This type of mechanical properties measurement can be directly applicable to sharp abrasive particles (such as sand, dirt, glass) impacting or scratching a wood surface.

For nanoindentation, the much smaller applied loads result in a much smaller interaction volume and the mechanical properties of much finer features can be measured; however, unlike macro- and microindentation, the results are more difficult to relate to the bulk physical properties of wood. The interaction volume is now sufficiently small that measured mechanical properties are not influenced by the larger scale hierarchical wood structures (cell wall structure, cell lattice, growth rings, etc); however, they are still influenced by the ultrastructure (fibril-matrix structure) and interaction of the three polymer components of wood (cellulose, hemicellulose, lignin). Nanoindentation can measure the mechanical properties within cell walls, in particular the S2 and middle lamella (ML), allowing the interaction between the wood polymer components to be more directly investigated with reduced influence of the wood hierarchical structure (Fig. 4).

Nanoindentation, also refferred to as depth-sensing indentation, uses high-resolution sensors and actuators to continuously control nd monitor the applied load and displacement as the indenter is driven into and withdrawn from

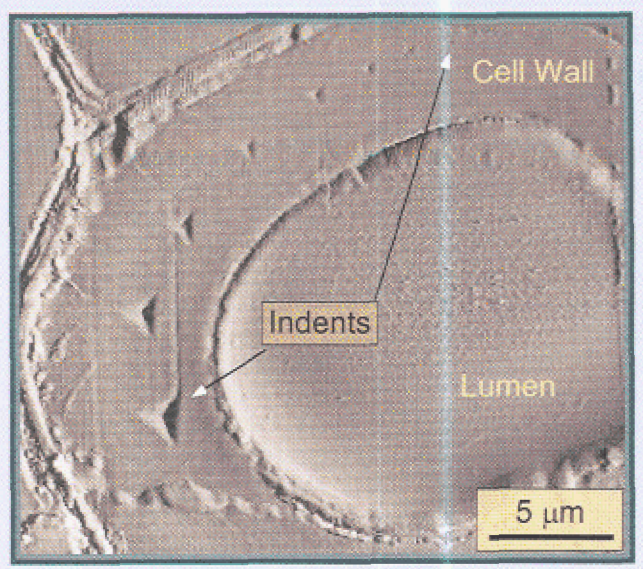


Figure 4. — Atomic force microscope image showing a series fo eight indents within the S2 layer of a cell wall. The arrows point to the first and last indents in the series, where the decreasing indent size resulted from the lower maximum applied load for each indent.

a material. Diamond is the most frequently used indenter material because of its high hardness and elastic modulus, which minimize the contribution of the indenter itself to the measured displacement. The shape of the indenter can vary, but typically a three-sided pyramidal indenter (such as the Berovich indenter) with and efective tip radius of 10 to 100 nm is used. During the indentation process, the applied load (P) adn indenter dispalcement (h) are simultaneously recorded (Fig. 5), and from this load-displacement data, the elastic modulus, relaxation modulus, hardness, and creep response are measured. Nanoindentation has been extensively used for measuring the properties of hard materials, such as metals and ceramics, and for thin wear-resistant ceramic coatings on ductile metals. Nanoindentation has also been used on wood and polymers; however, special consideration must be given to viscoelastic and creep properties, which are not necessarily accounted for in the standard methhods used to interprot load-displacement data. Additionally, special care must be taken to minimize surface damage that could be induced during sample preparation because this damage will modify the surface response to the indentation procedure.

Biological-Based Research

Wood has a sophisticated hierarchical architecture, and nanoindentation provides a method to probe the mechanical properties at eh cell wall and sub-cell wall level. Wood cell walls are made up of several layers and the ML, each having differences in the cellulose:hemicellulose:lignin volume fraciton ration and cellulose fibril angle. Because of these changes in comopsition and internal structure, the mechanical properties of each layer will also be different, and nanoindentation provides a way to directly measure these mechanical property differences. Using nanoindentation to explore the mechanical properties of wood began in the late 1990s, but the amount of published work on the topic is limited. Initial nanoindentation studies on wood have investigated the influence of several biological features on the hardness and elastic modulus, in particular, the cell wall layers, orientation withing the cell wall, different woody tissues, and the degree of lignification. Thus far, mechanical properties have been measured only from the transverse section of wood cell walls.

Investigations on individual cell wall layer properties have focused on the S2 layer (thickest layer) and the ML. The S2 layer is rich in cellulose and has an ultrastructure that mirrors a unidicrectional fiber-reinforced matrix composite material, in which the cellulose fibrils are the reinforcement phase (orientated perpendicular to the transverse section), with a matrix of hemicellulose and lignin. In contrast, the ML is rich in lignin and has minimal cellulose. Wimmer and coworkers (Wimmer and Lucas 1997, Whimmer et awl. 1997) conducted nanoindentation on red spruce (Picea rubens Sarg.) latewood and found the average S2 elastic modulus was nearly twice that of the ML, while the average hardness for S2 was about 10 percent larger than that of the ML. These results demonstrated that nanoindentation is sensitive enough to measure differences between mechanical properties of different cell wall layers. This work highlighted that variations in composition and ultrastructure within the cell wall can influence mechanical properties. Experimental data can then be used as input parameters for mechanical properties modeling of the cell wall and whole wood cells.

Nanoindentation has also been used to investigate the influence of different locations within the cell wall on the mechanical properties. Sources for cell wall anisotropy may result from variations in cellulose fibril angle, aspect ratio of the cell wall thickness, and pits or other structures in the cell wall. These results may provide an indication as to the contribution of cell wall property anisotropy on the measured bulk wood anisotropy. For spruce, Wimmer and coworkers investigated the influence of tangentially and radially oriented cell walls (transverse section) on the S2 layer mechanical properties. They found that the hardness and elastic modulus were similar in these two locations, suggesting minimal contribution to bulk wood anisotropy.

Nanoindentation has also been used to investigate the S2 layer properties of different woody tissues. Growth rings are one of the more dramatic wood features seen macrosopically in wood. The differences in properties of earlywood and latewood have been investigated extensively in the bulk or macroscopic scale, where the increase in mechanical properties of the latewood has been explained in terms of higher density, for higher cell wall mass per unit volume. Using nanoindentation on spruce, Wimmer and coworkers found that hte average latewood elastic modulus was about 55 percent larger than that of earlywood, while the average hardness for latewood was about 30 percent larger than that of earlywood. The measured differences in mechanical properties suggest a difference in either composition, ultrastructure, or interaction among cellulose-hemicellulose-lignin within the earlywood and latewood. Regardless of the specific mechanism, this result suggests that changes in properties at the nanoscale domains within the cell wall tissue in earlywood and latewood may contribute to change in bulk mechanical properties.

Wood cell development occurs initially with the creation of a porous cellulose-hemicellulose structure followed by an intergrowth of lignin (lignification) within this structure. If one considered mature cells to have complete lignification while immature cells have incomplete lignification, then by comparing these two cases, the influence of lignin volume fraction on mechanical properties can be evaluated. Gindl et al. (2002) complete nanoindentation on the S2 layer of transverse sections of Norway spruce (Picea abies (L.) Karst.) wood cells in which the lignin content in the mature wood cell was twice that in the immature cell. The study found that for the mature wood cell, the elastic modulus was 22 percent higher and the hardness was 26 percent higher than those of the immature wood cell. This study demonstrated that degree of lignification will alter mechanical properties of cell walls. Additionally, this study showed that nanoindentation can help in assessing the biological development of woody tissue.

Products-Based Research

Many nanotechnology programs are focused on basic research that may be several levels removed from product development. However, there are definite opportunities for nanotechnology to have a significant influence on improving product performance or altering the path of product development. Two cases are considered here: wood hardening and adhesive bonding.

Flooring applications require wear- and impact-resistant surfaces. generally, the wear resistance of a given surface increases as hardness and elastic modulus increase. The following approaches can increase wear resistance by modifying wood to improve mechanical properties: wood densification, wood chemical modification, and wood impregnation by resisn. For the case of wood impregnation, hardening of the wood may result by filling of microscopic cell cavities, by diffusion into the cell walls, or a combination of the two. For the latter case, analytical techniques are avaliable to measure the diffusion of polymer components into the cell walls; however, only nanoindentation can provide a clear method to assess if these polymer components modifies the cell wall properties. By understanding how changes in mechanical properties occurred, further development of the modification treatment can be tailored for a specific hardening mechanism.

An example of this is described here for melamine-based compounds used for wood modification to increase mechanical properties ans to improve surface adhesion. Milroy et at. (1995) found that melamine-modified European beech had a Brinell hardness that was two to three times larger than that of untreated wood. However, because of the large interaction volume in the Brinell indentation technique, it is impossible to know if changes in properties were a result of filled wood cell cavities or changes in cell wall mechanical properties. Analysis techniques such as electron loss spectroscopy, UV-microscopy, and infrared spectroscopy have confirmed that melamine can diffuse into all layers of the cell wall; however, there was no experimental verificaiton that this modifice the cell wall properties. Gindl and Gupta (2002) used nanoindentation and showed that melamine-modified cell walls had a 33 percent increase in elastic modulus and a 115 percent increase in hardness. This study clearly demonstrated that melamine treatment of wood improves the mechanical properties of cell walls; from this insight, further development of this treatment will likely focus on improving cell wall properties.

Adhesives are used extensively in the wood industry to bond a variety of surfaces together in such products as laminated lumber, veneer, plywood, engineered composites, oriented strandboard, and particleboard. An adhesive in service must be able to dissipate and transfer stress across the bondline, and the mechanism by which this occurs varies with the viscoelasticity of the adhesive and adhesive penetration into the wood surface. By understanding the particular mechanism of bond formation and the mechanism of stress dissipation and transfer along the bondline, further product development can be tailored for the given mechanism that may be responsible for producing more durable bonds.

An example of this type of research is the work by Gindl et al. (2004), where nanoindentation was used to study mechanical properties across the bondline region. UV-microscopy showed that phenol-formaldehyde (PF) resin diffused into cell walls, whereas polymeric methylene diphenyl-di-isocyanate (pMDI) resin did not. Correspondingly, nanoindentation revealed that the PF-impregnated cell walls had higher hardness and elastic modulus than those of the PF-free cell walls, whereas the cell walls in the pMDI case were not noticeably changed. For the PF bondline, cell wall hardness and elastic modulus were found to decrease as functions of distance from the bondline, up to about 100 µm, at which point the cell wall properties were similar to those of the unmodified cell wall. Because the pMDI did not penetrate or modify cell wall properties, the mechanical properties will remain constant as a function of distance from the bondline. For these types of adhesives, a typical bondline thickness is <100µm and the region influenced by the PF resin diffusion is comparatively large and will have a significant influence on the stress response of the bondline. Thus, the mechanical response of pMDI and PF bondlines would be expected to be considerable different; however, its contribution to the resulting bondline fracture properties is still uncertain. This study showed that nanoindentation can be used to evaluate properties in the bondline region, and

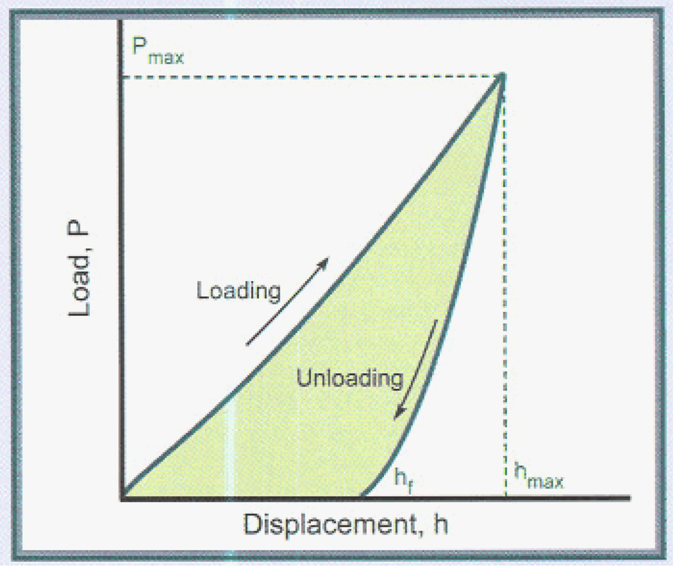
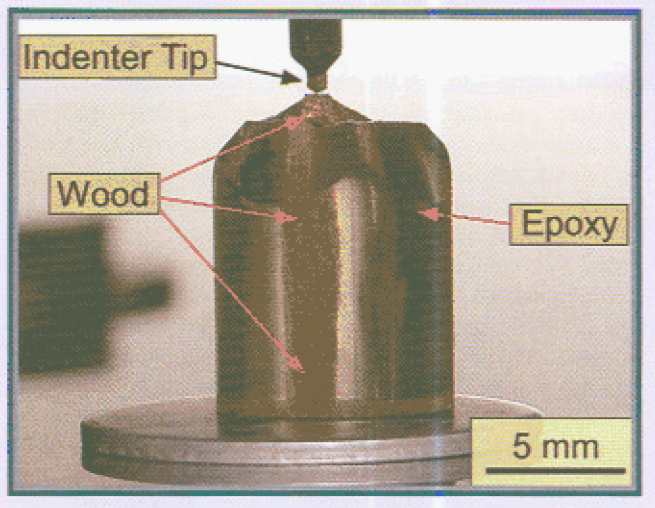


Figure 5. – Schematic showing the recorded load-displacement curve of nanoindentation.



Nanoindenter tip makes contact with a matchstick-sized wood sample encased in epoxy resin. The exposed wood at the epoxy mount top survace has been microtomed, providing a smooth surface for nanoindentation.

future product development could focus on mechanisms to tailor the mechanical properties next to the bondline to maximize bond durability.

Future Work

Nanoindentation of wood is effectively in its infancy. Only a few papers have been published, but these studies already provide a clear indication regarding the potential uses of nanoindentation in forest products R&D. Nanoindentation can explore the interactions among cellulose-hemicellulose-lignin, providing a new perspective in evaluating the response of a given biological feature to a given environment, and may provide insight regarding how to address property degradation. In addition, nanoindentation may be useful in measuring mechanical properties changes during incipient decay (fungal mechanisms of lignocellulosic degradation), which may provide a better understanding of wood mechanics and lead to the development of better preservative systems. The interactions of ultraviolet radiation and short wavelength of visible light cause photodegradation of lignocellulosic materials, and understanding the resulting mechanical degradation at the nanoscale could provide insight or a new approach in developing photo-resistant surfaces. Also, understanding how chemical reactions during wood modification alter mechanical interactions with cellulose, hemicellulose, and lignin may provide insight toward a new approach in developing new chemical treatments.

Nanoindentation of wood will require immprovements in nanoindentation techniques, data analysis, and specimen preparation. Enhanced indenter design and loading techniques combined with improved interpretation of the load-displacement curve (Fig. 5) will provide increased accuracy regarding 1) time-dependent deformation (viscoelasticity, creep); 2) fracture property measurements; and 3) influences of the anisotropic ultrastructure within the interaction volume on measured properties, as highlighted by Gindl Schöberl (2004). Equally important will be the necessary improvements in preparing the ultra-smooth surfaces needed for nanoindentation. Surface preparation techniques can impart a variety of damage mechanisms into the surface: mechancal, thermal, chemical or a combination of these. The response of this damaged surface to nanoindentation will then be different from the undamaged case.

Our ability to understand a given phenomenon is tightly linded to our evaluation techniques. Nanoindentation provides the ability to measure mechanical properties at the submicron level, information that is not attainable with other analytical techniques. Because of this, using nanoindentation on forest products has enormous potential. Nanoindentation, when used in parallel with other analytical techniques, will provide a more complete understanding of a given phenomenon and thus provide insight for new R&D avenues for macimizing a desired property.

This example of ongoing nanoindentation research is just a small part of the total nanotechnology R&D picture. Exciting research is taking place in many areas. The partnership among industry, universities, and government will be moving thihs research forward, and important applications are on the horizon.

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