

ANNUAL REPORT

July 1, 2007 – June 30, 2008

Sustainable Engineered Materials Institute (SEMI)

College of Natural Resources
Virginia Tech
Blacksburg, Virginia

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Sustainable Engineered Materials Institute
Annual Center Report
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I. Mission of Center

The Sustainable Engineered Materials Institute (SEMI) at Virginia Tech was established in July 2002 to coordinate research efforts funded by the Sustainable Engineered Materials from Renewable Resources (SEMRR) projects. SEMI's mission is to be the leading, national research program that creates the next generation of high-performance wood composites linked to sustained and innovative forest management.

SEMI encourages and supports continued advances in the science and technology of composite materials derived from ligno-cellulosics, particularly woody plants, and promoting the transfer of these new developments to industries and government organizations in Virginia, the nation, and the world.

II. Classification of Center and Organizational Structure

SEMI is a College Center, under the administrative and fiscal control of the Dean of the College of Natural Resources. SEMI's steering committee is comprised of faculty from participating departments (Forestry and Wood Science and Forest Products). An organizational chart is shown in Figure 1.

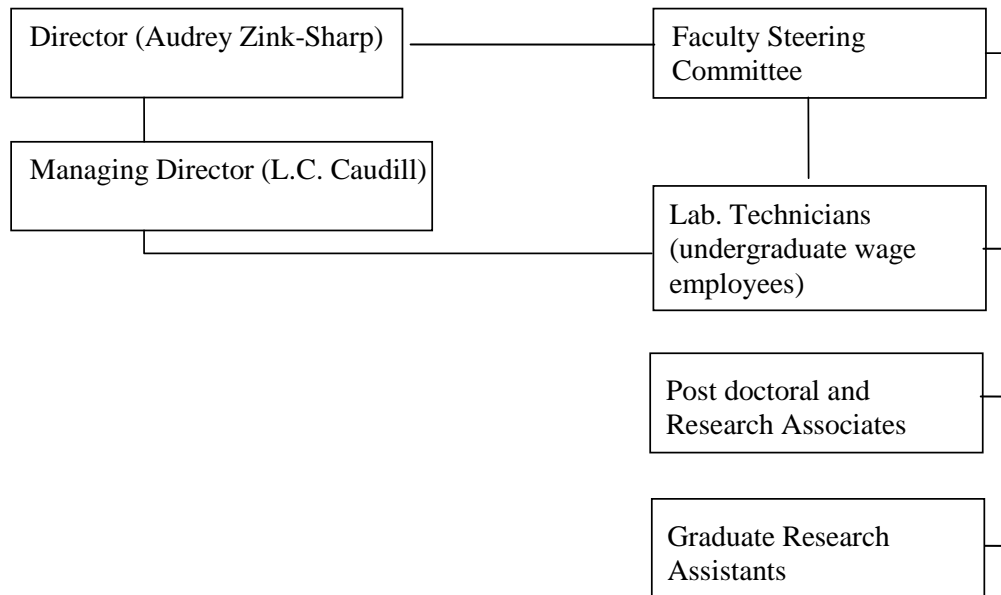


Figure 1. Organizational structure of SEMI.

Faculty Affiliated with the Center

C.A. Copenheaver (FOR) K.J. Edgar (WOOD)
T.R. Fox (FOR) C.E. Frazier (WOOD)
S.H. Renneckar (WOOD) M. Roman (WOOD)
S.M. Zedaker (FOR)
A. Zink-Sharp (WOOD), SEMI Director & contact person, <http://www.semi.vt.edu/>

Post-doctoral Associates

O. Kwon (WOOD) P.D. Jones (FOR)
T. Fujino (FOR)

Research Associates

L.C. Caudill (WOOD)

Graduate Students

S. Chowdhury (WOOD) Z. Lin (WOOD)
K.E. Kovach (FOR) J.K. Hong (WOOD)
T. Mettanaruk (WOOD) R.K. Johnson (WOOD)
Z. Yu (WOOD) T.M. Jeffries (WOOD)

Classified Staff and Administrative Positions

n/a

III. Amendments to Center Charter

none

IV. Stakeholder Committee

J. M. Kelly, Dean, College of Natural Resources
H.E. Burkhart, Department Head, Forestry
P.M. Winistorfer, Department Head, Wood Science and Forest Products
A. Zink-Sharp, SEMI Director

V. Major Contracts Received in 2007-2008

USDA/CSREES Hatch Project 135820; \$425,222; September 1, 2007 – August 31, 2008

VI. Major Proposals Pending

USDA/CSREES Special Grant 2008-34489-19377; \$481,515; September 1, 2008 – August 31, 2009

VII. Significant Accomplishments in 2007-08

Graduate Degrees Completed

Thomas M. Jeffries. 2008. M.S. Relationships of Growth Rate and Mechanical Properties in Sweetgum, *Liquidambar styraciflua*. Major Professor: Audrey Zink-Sharp.

Thammarat Mettanurak. 2008. M.S. Effect of Suppression and Release on Compression Parallel to Grain Property for Small-sized Yellow-poplar (*Liriodendron tulipifera* L.) Specimens. Major Professor: Audrey Zink-Sharp.

Progress toward Research Objectives

Our main research project “Sustainable Engineered Materials from Renewable Resources” (SEMRR) is a long-term program that deals with the broad issue of sustainability of natural resources from an ecological, social, and economic standpoint. Our research plan reflects the necessity to attack this issue with a systematic approach and is composed of several subtasks conducted by a multi-disciplinary research team. We are addressing the research by linking design and study of wood-and cellulose-based composites with improvement of forest management practices.

We are investigating innovative modifications to traditional forest management practices that will result in a more sustainable supply of consumer products and eventually an improvement in wood quality in standing forests. In one particular subtask, our research focuses on examining genetic variability within and between yellow-poplar trees in the mountains and coastal plain of the southeastern United States. *Liriodendron tulipifera* is prolific throughout the Southeastern United States and has increasingly important roles in forestry and wood products in this region. Little is known concerning the genetic makeup of this species and genetic polymorphisms throughout its native range. Our study utilizes a molecular marker technique, amplified fragment length polymorphism (AFLP), to determine the degree of genetic polymorphism of *L. tulipifera* throughout its range. In addition to identifying genetic polymorphisms, this study addresses genetic correlations with variations in wood density. It has been found that the greatest differences in wood density are between mountain sites of high latitude and coastal plain sites of low latitude. The study sites include unmanaged stands in Mississippi, North Carolina, Ohio, South Carolina, Tennessee, and Virginia. Sites have been characterized by physiographic region, and latitude/longitude. The range of average wood density for *L. tulipifera* has been found to be greater in the mountains, 389.1 kg/m³ to 475.3 kg/m³, than in the coastal plain, 404.33 kg/m³ to 466.34 kg/m³. Significant differences in wood density between sites range from 86kg/m³ to 31kg/m³. The highest levels of genetic differences are expected within populations, with the Virginia Coastal Plain site having a Dice coefficient of 0.9087. The highest levels of inter site genetic differences are expected between the mountain sites of highest latitude and coastal plain sites of lowest latitude.

Emergence of nanoscience utilizing cellulose from woody biomass is offering many opportunities for creation of new products from renewable and sustainable natural materials. We are vigorously exploring several avenues of nanoscale products and processes. Our nanoscience subtasks include nanocomposite-based wood fibers for reinforcement in thermoplastic composites and nanoscale coatings on wood and fiber-based composites. Our research goals are to create nanoscale modifications and coatings on wood and agricultural fibers that promote

durability, increased mechanical performance, and uniqueness. To date we have concentrated on establishing the modification of wood fibers with a highly controlled assembly of layers of nanoclay and polymer. Aqueous dispersions of clay nanoplatelets were created and characterized with dynamic light scattering, electrophoresis measurements, and atomic force microscopy, in which individual clay nanoplatelets were confirmed that had a negative charge.

We have used these clay platelets with a negative charge to modify the surface of fiber by first adsorbing a positively charged polymer, poly(diallyldimethylammonium chloride) (PDDA), to the fiber surface and then sequentially adsorbing the negatively charge clay to the treated fiber surface. We were able to characterize the surface of the fiber after each adsorption step by measuring the zeta potential thereby demonstrating that we are adding a new layer of material after each deposition cycle, as reflected by the sign of the zeta potential measurement. Scanning electron microscopy images revealed the Layer-by-Layer (LbL) film masked the cellulose microfibril structure. The thermal properties of the fiber were studied using a thermogravimetric analyzer, where LbL modified steam-exploded wood had increased thermal stability relative to the unmodified material tested. Significant char for the LbL clay coated steam-exploded wood suggests the clay multilayer film serves as a surface barrier creating an insulating layer to prevent further decomposition of the material. A barrier on the fiber surface is needed to protect the wood fiber surface from decay without having to use a known poison like arsenic.

A novel rheological technique has been developed to investigate the structure/property relationship of wood polymers using the smallest possible specimen size. This small specimen size should be very useful for certain size-constrained sample types, such as from the stem of genetically modified saplings, or from a tree increment bore, or even from within an adhesive bondline. Parallel plate torsion analysis, in oscillation (dynamic) mode, was used with 8 mm diameter discs of yellow-poplar with a thickness of 3 and 6 mm for three different grain orientations (tangential, radial and longitudinal). In dry wood, the glass transition (T_g) of lignin and hemicellulose occurs over 180°C. This high temperature causes thermal decomposition of wood and makes the study of unaltered wood polymers impossible. To solve this problem, specimens were tested while submerged in plasticizing solvents, reducing the T_g of lignin and hemicellulose to non-damaging or less damaging temperatures. Rheology of plasticized wood was investigated by a systematic mapping of time/frequency and temperature dependence on lignin transition. Effects of three different plasticizing solvents, namely glycerol, ethylene glycol, and N,N-dimethylformamide (DMF), on wood polymer properties were investigated using dynamic thermal scans and time temperature superposition (TTS). As expected, dynamic thermal scans for wood in different plasticizing solvents showed different lignin T_g 's. This demonstrated that different solvents have different plasticizing ability.

It was also observed that the lignin T_g is dependent on the grain orientation. TTS in oscillation mode produced good storage modulus (E') master curves for all solvent systems and for each grain orientation. However, the loss modulus master curves shift effectively in ethylene glycol and glycerol plasticized wood but not for wood in DMF. In other words, oscillation mode TTS is valid only in ethylene glycol and glycerol. Since all solvent systems produced good storage modulus master curves, we elected to investigate creep mode TTS experiments. Creep mode TTS of southern yellow pine and yellow-poplar wood discs in ethylene glycol produced very uniform creep-compliance master curves. Consequently, we have established conditions for the

effective TTS analysis of the lignin-glass transition using both dynamic and static methods. These methods are now being used to determine how various chemical treatments influence the lignin Tg.

Publications

Johnson, R.K., A. Zink-Sharp, S.H. Rennekar, W.G. Glasser. 2008. Mechanical properties of wetlaid lyocell and hybrid fiber-reinforced composites with polypropylene. *Composites Part A: Applied Science and Manufacturing* 39(2008) 470-477.

Johnson, R.K., A. Zink-Sharp, S.H. Rennekar, W.G. Glasser. in press. A new bio-based nanocomposite: fibrillated TEMPO-oxidized celluloses in hydroxypropyl-cellulose Matrix. accepted by *Cellulose*.

Jones, P.D., and T.R. Fox. 2007. Wood density in *Pinus taeda* x *Pinus rigida* and response 10 years after thinning in Virginia. *Forest Products Journal*. 57(12):70-73.

Lin, Z., S. Rennekar, and D. P. Hindman . 2008. Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers. *Cellulose* 15(2):333-346.

Kwon, O. and A. Zink-Sharp. in review. Changes in autofluorescence from heat-treated loblolly pine. submitted to *Holzforschung*.

Presentations

Edgar, K.J. 2008. Ethanol from biomass and cellulose; challenges & solutions. NAASF Conference, Blacksburg, VA, June 3, 2008.

A. Zink-Sharp and T. M. Jeffries. 2008. Relationships between growth rate and mechanical properties in sweetgum plantation trees. 62nd International Conference of the Forest Products Society, June 22-25, 2008, St. Louis, MO.

Johnson, R.K., A. Zink-Sharp, and W.G. Glasser. 2008. Effects of fiber size and size distribution on performance of cellulose-reinforced composites. 235th American Chemical Society National Meeting and Exposition, April 6 - 10, 2008, New Orleans, LA.

Hong, J. K., C. E. Frazier, and M. Roman. 2008. Cellulose nanocrystals as additives for wood adhesives. 235th American Chemical Society National Meeting, New Orleans, LA, April 6-10, 2008. CELL-126.

VIII. Industrial Affiliates Program

none

IX. Major Issues of the Center

none