Effects of a Partial Hydrolysis on the Stiffness and Mass Loss of Three Southern Hardwoods

T. Eric McConnell
Sheldon Q. Shi

Abstract

Red oak, sweetgum, and yellow-poplar lumber was machined into 3 by 15 by 150-mm (tangential by radial by longitudinal) miniature beams. Moisture content was determined from a subset for calculating the ovendry weight of test samples prior to treatment. Samples were weighed, water saturated, and subjected to a partial hydrolysis at 150°C for 30 minutes in 1 percent sulfuric acid, water, or 1 percent sodium hydroxide solutions. Untreated controls were also used. The beams were ovendried to a constant weight, and then the modulus of elasticity, density, and mass loss (ML) were determined. Modulus of elasticity values were corrected to eliminate density variation by calculating the specific modulus of elasticity (SM) for property comparisons. The species and treatments interacted to significantly affect SM. Sweetgum produced a lower SM in all treatments, and the water treatment consistently reduced SM. The species and treatment factors acted independently of one another with respect to ML. Sweetgum lost significantly more mass than the other species, likely because of corresponding reductions in holocellulose. An acid treatment produced the greatest ML.

The southeastern US wood composite market is primarily limited to southern yellow pine (*Pinus* spp.), which is intensively managed throughout the region. Strand-based composite mills are largely supplied by plantation first thinnings. However, the South also has an abundance of hardwood species, such as red oak (*Quercus* spp.), sweetgum (*Liquidambar styraciflua* L.), and yellow-poplar (*Liriodendron tulipifera* L.), readily available in small-diameter classes (Sheffield and Bechtold 1990). These species are currently used sparingly in the Southeast as a result of various wood properties that can adversely affect the composite's product quality. For example, thicker, high-density cell walls in red oak can prevent adequate adhesive penetration, while the heartwood of sweetgum is generally impermeable because of abundant phenolic glycosides (Halligan 1970, Rowe and Connor 1979). Acidic extractives can gel phenol-formaldehyde resin, while alkaline extractives can deactivate urea-formaldehyde resin (Beech 1975). These factors lead to inefficient compaction ratios for composites of mixed species, which weaken the wood–adhesive bond due to springback (Carll 1997). Hse (1975) evaluated nine hardwoods that commonly grow on southern pine sites and found only three produced adequate panels: sweetbay (*Magnolia virginiana* L.), red maple (*Acer rubrum* L.), and sweetgum. Sweetgum required the highest compaction ratio tested to meet minimum requirements. Biblis (1985) constructed two blends of three-layer oriented strandboard (OSB) from a mixture of southern hardwoods. Results varied as flexural properties were lower when compared with published values of southern pine plywood and aspen flakeboard, but shear properties were improved.

Challenges have long been presented to both foresters and wood scientists to efficiently manage and use our wood resources. One branch of research is focused on the hydrolyzing and use of easily extracted wood components, such as pentosan hemicelluloses from hardwoods (Richter 1932). The use of wood sugar molasses as a livestock feed supplement, for instance, dates to World War I (Colovos et al. 1949). In recent years, energy independence has led investigators to examine various pretreatments of hardwood species for conversion of wood sugars to ethanol (Sun and Cheng 2002). These studies use small-diameter trees that otherwise would have little or no market value. Many result in the complete hydrolysis of the polysaccharides, leaving

The authors are, respectively, Graduate Research Assistant and Assistant Professor, Dept. of Forest Products, Mississippi State Univ., Mississippi State (temcconnell@cfr.msstate.edu, sshi@cfr.msstate.edu). The first author is presently Assistant Extension Professor, School of Environment and Natural Resources, Ohio State Univ., Columbus. This manuscript was approved by the Forest and Wildlife Research Center, Mississippi State University, as FWRC Publication no. FP557. This paper was received for publication in February 2010. Article no. 10738.

Forest Prod. J. 60(7/8):654–658.

behind the lignin that is primarily burned for energy (Garrote and Parajo 2002). Conversely, it may be possible to conduct only a partial hydrolysis pretreatment on the woody material, forming some hydrolyzed sugars to ferment but also leaving behind a partially modified wood substrate. Linking pulp and paper manufacturing to biofuel production has been reviewed, but few studies have been conducted on wood properties following treatment in a heated solution (Hill 2006, Ragauskas et al. 2006). Modified wood material from previously unusable hardwood resources may possess improved properties for producing strand-based wood composites.

A partial hydrolysis pretreatment would use relatively low temperatures and/or chemical concentrations; therefore, the wood remains structurally whole rather than being pulped to individual fibers. This may lead to a reduction in stiffness, which in turn could lead to improved compaction during pressing. The hemicelluloses are most susceptible to hydrolysis and subsequent extraction followed by some lignin while cellulose's degree of polymerization (DP) is lowered (Connor 1984). An overall decrease in mechanical properties usually occurs with increased treatment time and changes in chemical composition (Thompson 1969, Winandy and Lebow 2001). Wangaard (1966) investigated the chemical degradation of several softwoods and hardwoods and found strength retention was higher when wood was exposed to an acid versus an alkaline treatment. Producing OSB from red maple using strands hydrolyzed in water with different severity factors has been investigated (Paredes et al. 2008, Howell et al. 2009, Mills et al. 2009, Paredes et al. 2009). These studies found that most hemicelluloses can be removed, and at the same time, the wettability of the wood was improved. Mechanical, physical, and durability properties were maintained or improved.

Partially hydrolyzing hardwood furnish not only would allow for the use of hemicelluloses for ethanol conversion, but also could create a value-added composite product from small-diameter underused hardwood resources. The goals of this study were to understand the effects of three partial hydrolysis treatments on red oak, sweetgum, and yellow-poplar miniature beams in pressurized, heated conditions. The influence of the species and treatments on modulus of elasticity (MOE), density, and mass loss (ML) were investigated.

Materials and Methods

Red oak, sweetgum, and yellow-poplar specimens were treated in a 2-liter reactor at 150°C for 30 minutes, dried, and then weighed and tested by static bending. Three solutions, 1.0 percent sulfuric acid (H_2SO_4), water, and 1.0 percent sodium hydroxide (NaOH), along with untreated controls were used. The MOE (GPa), ovendry density (grams per cubic centimeter), and ML (%) were then determined. Six replications were performed for the 12 treatment combinations. Static bending followed American Wood Protection Association (AWPA) Standard E23 (2009), while ML was determined by the methods described in AWPA Standard E1 (2009).

Rough-cut red oak, sweetgum, and yellow-poplar lumber was obtained from a local sawmill. The red oak and sweetgum lumber had been freshly sawn within the past 24 hours, while the yellow-poplar had been air drying for approximately 3 weeks. The rough lumber size was 50 mm thick by 292 mm wide by 2.44 m long. Care was taken to select wood free of sawing and drying defects. The selection of boards was randomized. Five boards from each species were selected. The lumber was stored at 2°C.

One board was randomly selected from each species for further processing to minimize sample variation. The board was ripped into six pieces sized 50 by 76 by 813 mm. The pieces were then sawn into strips measuring 3 by 15 by 150 mm (tangential by radial by longitudinal). The samples were sealed in plastic bags and stored at 2°C.

The initial moisture content (MC) was calculated from a subset and averaged for each species. Eighteen samples from each species were selected to determine the initial MC. Samples ($n = 54$) were oven dried at 103°C ± 3°C for 24 hours. Using the initial MC of the lumber, the ovendry weight of the test samples could then be estimated.

All samples were saturated in deionized water under vacuum pressure at 85 kPa to achieve full saturation. The 12 treatment combinations were selected in random order each day for 6 days for blocking (3 species × 4 treatments × 6 replicates, $n = 72$). Chemical treatment with 1 percent H_2SO_4, water and 1 percent NaOH was conducted using a Parr 4843 2-liter pressure reactor. The vessel was filled with 1,700 mL of solution, and a miniature beam was immersed. Glass fiber was placed over the wood sample to ensure full immersion in the liquid. The vessel was locked in place and electrically heated. Time measurement began when the reactor reached 150°C. After 30 minutes had elapsed, the vessel was cooled and the pressure was then released. The specimen was washed with deionized water and placed in a bath of distilled water for 24 hours. The reactor was thoroughly cleaned after each run. A blank run of only the next solution was conducted between treatments to prevent contamination by the previous species/solution combination.

The samples were stored for 1 week in a conditioning chamber. The MC of the miniature beams was then gradually ramped downward to minimize sample distortion. They were first put in a dehumidification chamber at a temperature of 20°C ± 3°C and a relative humidity of 65 ± 5 percent until a constant weight was achieved. They were then placed in a convection oven at 60°C until attaining constant weight and then measured, weighed, and tested by static bending per AWPA E23 (AWPA 2009). Static bending used a 45 N load cell on a bending machine designed to be used for small three-point bending tests of preservative-treated samples. The specimens were tested to a maximum deflection of 1.0 mm. The loading speed was 10 to 20 mm/min, the loading span was 120 mm, and span-to-depth ratio was 40. The stress/strain data obtained was used to calculate the MOE for each sample. The ovendry density was determined. The ML was calculated as the percentage (%) of change in dry mass at the end of the test. Results were analyzed using analysis of variance with a 0.05 level of significance. Multiple comparisons were made using Fisher's protected least significant difference in SAS 9.1.3 (2003).

Results and Discussion

Summary statistics are presented in Table 1 for MOE and ovendry density. Initial MCs were 55.6, 44.8, and 20.1 percent for the red oak, sweetgum, and yellow-poplar samples, respectively. Treatment pH averaged 3.5 for the acid, 6.5 for the water, and 10.0 for the base.

Table 1.—Average MOE and ovendry density.[a]

Species	Treatment	MOE (GPa)	Density (g/cm^3)
Oak	Acid	13.44 (1.52)	0.72 (0.06)
	Water	19.05 (1.54)	0.76 (0.01)
	Base	20.49 (3.08)	0.87 (0.09)
	Control	17.50 (0.67)	0.69 (0.01)
Sweetgum	Acid	8.73 (3.26)	0.58 (0.04)
	Water	10.94 (3.81)	0.68 (0.03)
	Base	12.23 (3.34)	0.71 (0.04)
	Control	11.47 (2.57)	0.67 (0.03)
Yellow-poplar	Acid	9.54 (1.51)	0.35 (0.03)
	Water	9.78 (0.76)	0.40 (0.01)
	Base	9.53 (1.45)	0.48 (0.02)
	Control	10.31 (1.15)	0.41 (0.02)

[a] Values are means (standard deviations). MOE = modulus of elasticity.

Modulus

Wood properties are well known to vary widely among species (e.g., Panshin and de Zeeuw 1980). Mechanical properties are usually dependent upon the density; for instance, the higher the density, the greater the MOE (Haygreen and Bowyer 1996). Moreover, density can vary among and within a species and also within a single tree (Sjöström 1993).

There were many inherent differences among the species and the solvents chosen for this experiment. Accounting for the density variation both among and within the species in addition to any wood–treatment interactions allowed for higher accuracy when comparing mechanical properties (Sun and Hawke 1997). Thus, SM was used for property comparisons to eliminate the density effect (Shi and Gardner 1999). It is expressed as

$$SM = \frac{S}{SG} \quad (1)$$

where SM is the specific modulus, S is the modulus of elasticity, and SG is the specific gravity of the wood specimen at the designated MC, which in this case is equal to the sample density since both weight and volume are ovendry basis.

The effect of the treating solution on SM was species specific (Table 2) because the interaction between the two factors was significant ($P = 0.0027$). Red oak SM was consistently reduced by the treatments, with the acid treatment being the least. While all treatments were statistically similar for sweetgum, the acid and water treatments were lower than the control. Treating yellow-poplar in a caustic solution significantly decreased SM over the other treatments. Though similar to the controls for all species, water was the only treatment that consistently lowered SM. Prior work on the initial effect of chemically treating wood found a larger reduction in MOE for sweetgum versus the other species (McConnell et al. 2009). A similar effect was observed in our study, in which the SM for sweetgum was lower than for the other species in all treatments and was significantly lower in water.

Varying results can be produced within the same treatment; therefore, treatment effects depend in large part upon the species (Rowell et al. 1986). Wood structure, chemical composition, and mechanics all contribute. This was confirmed by our experiment because the SM results were inconsistent within both the acid and base solutions.

Table 2.—Least significant difference results for the SM treatment means.

Treatment	SM (GPa)[a]	t grouping[b]	No. of observations
Yellow-poplar/acid	27.15 (2.76)	A	6
Red oak/control	25.27 (0.70)	A	6
Yellow-poplar/control	25.12 (2.30)	A	6
Red oak/water	25.05 (1.81)	A	6
Yellow-poplar/water	24.61 (2.04)	A	6
Red oak/base	23.58 (2.86)	AB	6
Yellow-poplar/base	20.02 (3.55)	BC	6
Red oak/acid	18.69 (1.35)	CD	6
Sweetgum/base	17.30 (4.46)	CD	6
Sweetgum/control	17.18 (4.81)	CD	6
Sweetgum/water	16.34 (6.24)	CD	6
Sweetgum/acid	14.77 (4.68)	D	6

[a] Values are means (standard deviations). SM = specific modulus.
[b] Means with the same letter are not significantly different at $\alpha = 0.05$. Least significant difference = 4.04.

The SM decreased in both treatments for red oak versus the controls, whereas the alkaline treatment increased SM for sweetgum and the acid treatment increased SM for yellow-poplar. The alkaline treatment increased the density for each species, while the acid treatment consistently lowered the density. The water treatment did not affect the density with the exception of red oak.

Heating wood in alkaline solutions is known to lower cellulose DP through peeling reactions and random scission (Sjöström 1993). Treating wood in acid quickens the decrease in cellulose DP (Winandy and Lebow 2001). NaOH originally bulks the cell wall before collapsing upon drying, reducing void content, and increasing bulk density, while acid makes the wood brash and friable (Wangaard 1966). Heating wood in water at 150°C lowers the pH by cleaving acetyl groups, which decreases the cellulose chain's DP as a result of some autohydrolysis (Connor 1984). These differing effects were eliminated through use of SM, though inconsistencies across both the species and the treatments were still present.

Mass loss

Both factors, species and treatment, independently and significantly affected mean ML, with the treating solution being the more significant of the two (treatment, $P < 0.0001$; species, $P = 0.0004$). All treatments resulted in statistically significant ML, with the acid treatment producing the highest (Table 3). The controls exhibited very minor ML due to water saturation and subsequent oven drying. Sweetgum averaged a significantly higher overall ML than the other species (sweetgum, 17.0%; yellow-poplar, 14.6%; red oak, 12.7%; least significant difference = 2.02).

As wood is heated in water, nonstructural extractives are first removed, followed by a loss in DP of the polysaccharides through autohydrolysis, with some degraded polysaccharide-derived compounds becoming water soluble, via the production and subsequent reactions with acetic acid (Rowell 1984, Mitchell 1988). The presence of an acid or caustic can accelerate this deterioration, with acid being the more severe (Kass et al. 1970, Hill 2006). The caustic solution also likely affects the lignin, while the acid

Table 3.—Least significant difference results for the treatment mass loss means.

Treatment	Mass loss (%)	*t* grouping[a]	No. of observations
Acid	−35.53	A	18
Base	−18.47	B	18
Water	−3.85	C	18
Control	−1.24	D	18

[a] Means with the same letter are not significantly different at $\alpha = 0.05$. Least significant difference = 2.33.

treatment likely causes further degradation of the sugars to form furans, a portion of which can condense to form a pseudolignin (T. Schultz, Forest Products Laboratory, Mississippi State, personal communication, February 2010). Further, pentosan content and wood degradation are directly related (Kass et al. 1970). Hergert et al. (1977) reported that sweetgum possessed higher cellulose and hemicellulose contents than red oak or yellow-poplar, which may explain the results obtained in this study. Further, holocellulose retention, as a percentage of the control, has subsequently been found to be less in sweetgum than red oak and yellow-poplar following a partial hydrolysis in each of the solutions tested herein (McConnell 2010).

Conclusions

Specific modulus was calculated for bending comparisons to eliminate the density variations. The SM was both species- and treatment-dependent. Red oak SM was consistently reduced by the treatments. All treatments were statistically similar for sweetgum. Treating wood by a partial hydrolysis in solution resulted in statistically significant ML. Using an acid treatment produced the most significant treatment effect on ML.

Future research will investigate using sweetgum as the primary species in a mixed furnish of water-treated partially hydrolyzed hardwood flakes. Sweetgum is the most populous hardwood species growing on southern pine sites in the US South (Koch 1985). In this study, sweetgum's ML was significantly greater than for the other species, and water treatments lowered the SM for all species. Moreover, SM was lower for sweetgum versus the other species in each treatment and was significantly so in water.

Acknowledgments

This research was supported by the USDA and the Southern Wood to Energy Research Group (SoWER). The authors thank Rives and Reynolds Co., Inc. of Louisville, Mississippi, for donating the lumber for this project as well as Dr. Tor Schultz for his input. The constructive comments of the anonymous reviewers are greatly appreciated

Literature Cited

American Wood Protection Association (AWPA). 2009. AWPA Book of Standards. AWPA, Birmingham, Alabama.

Beech, J. 1975. The thickness swelling of particleboard. *Holzforschung* 29(1):11–18.

Biblis, E. 1985. Properties of three-layer strandboard from southern hardwoods. *Forest Prod. J*. 35(2):28–32.

Carll, C. 1997. Review of thickness swell in hardboard siding—Effect of processing variables. General Technical Report FPL-GTR-96. USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin. 10 pp. http://www.fpl.fs.fed.us/documnts/fplgtr/fplgtr96.pdf. Accessed February 14, 2011.

Colovos, N., H. Keener, J. Prescott, and A. Teeri. 1949. The nutritive value of wood molasses as compared with cane molasses. *J. Dairy Sci*. 32(11):907–913.

Connor, A. 1984. Kinetic modeling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. *Wood Fiber Sci*. 16(2): 268–277.

Garrote, G. and J. Parajo. 2002. Non-isothermal autohydrolysis of Eucalyptus wood. *Wood Sci. Technol*. 36:111–123.

Halligan, A. 1970. A review of thickness swelling in particleboard. *Wood Sci. Technol*. 4(4):301–312.

Haygreen, J. and J. Bowyer. 1996. Forest Products and Wood Science. An Introduction. 3rd ed. Iowa State University Press, Ames. 484 pp.

Hergert, H., T. Sloan, J. Gray, and K. Sandberg. 1977. The chemical composition of southeast hardwoods. *In:* Utilization of Hardwoods Growing on Southern Pine Sites. P. Koch. USDA Forest Service Agriculture Handbook. US Government Printing Office, Washington, D.C. p. 368.

Hill, C. 2006. Wood Modification. Chemical, Thermal and Other Processes. Wiley & Sons, Sussex, UK. 239 pp.

Howell, C., J. Paredes, and J. Jellison. 2009. Decay resistance properties of hot water extracted oriented strandboard. *Wood Fiber Sci*. 41(2): 201–208.

Hse, C. 1975. Properties of flakeboards from hardwoods growing on southern pine sites. *Forest Prod. J*. 25(3):48–53.

Kass, A., F. Wangaard, and H. Schroeder. 1970. Chemical degradation of wood: The relationship between strength retention and pentosan content. *Wood Fiber Sci*. 2(1):31–39.

Koch, P. 1985. Utilization of Hardwoods Growing on Southern Pine Sites. Vol. I: The Raw Material. USDA Forest Service Agriculture Handbook. US Government Printing Office, Washington, D.C. 1,418 pp.

McConnell, T. 2010. Utilization of extracted hardwood flakes for manufacturing oriented strand lumber. PhD dissertation. Department of Forest Products, Mississippi State University, Mississippi State. 89 pp.

McConnell, T., S. Shi, and R. Shmulsky. 2009. A preliminary study on the bending stiffness of chemically treated wood material for structural composite lumber. *Wood Fiber Sci*. 41(3):322–324.

Mills, R., J. Jara, D. Gardner, and A. van Heiningen. 2009. Inverse gas chromatography for determining the surface free energy and acid-base chemical characteristics of a water extracted hardwood (*Acer rubrum*). *J. Wood Chem*. 29:11–23.

Mitchell, P. 1988. Irreversible property changes of small loblolly pine specimens heated in air, nitrogen, or oxygen. *Wood Fiber Sci*. 20(3): 320–355.

Panshin, A. and C. de Zeeuw. 1980. Textbook of Wood Technology: Structure, Identification, Properties, and Uses of the Commercial Woods of the United States and Canada. 4th ed. McGraw-Hill, Inc., New York. 722 pp.

Paredes, J., R. Mills, S. Shaler, D. Gardner, and A. van Heiningen. 2008. Influence of hot water extraction on the physical and mechanical behavior of OSB. *Forest Prod. J*. 58(12):56–62.

Paredes, J., R. Mills, S. Shaler, D. Gardner, and A. van Heiningen. 2009. Surface characterization of red maple strands after hot water extraction. *Wood Fiber Sci*. 41(1):38–50.

Ragauskas, A., M. Nagy, D. Kim, C. Eckert, J. Hallett, and C. Liotta. 2006. From wood to fuels: Integrating biofuels and pulp production. *Ind. Biotechnol*. 12(1):55–65.

Richter, G. 1932. Multistage process of pulping raw cellulosic material. US patent 1,880,048.

Rowe, J. W. and A. H. Connor. 1979. Extractives in eastern hardwoods—A review. General Technical Report FPL-GTR-18. USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin. 72 pp.

Rowell, R. 1984. The Chemistry of Solid Wood. American Chemical Society, Washington, D.C. 614 pp.

Rowell, R., A. Tillman, and R. Simonson. 1986. A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. *J. Wood Chem*. 6(3):427–448.

SAS Institute. 2003. Version 9.1.3. SAS Institute, Cary, North Carolina.

Sheffield, R. and W. Bechtold. 1990. Volume and availability of eastern hardwoods. *In:* Proceedings of the 18th Annual Hardwood

Symposium of the Hardwood Research Council, May 1990, Cashiers, North Carolina. pp. 55–65.
Shi, S. and D. Gardner. 1999. An evaluation of analysis methods to eliminate the effect of density variation in property comparisons of wood composites. *Wood Fiber Sci*. 31(2):164–172.
Sjöström, E. 1993. Wood Chemistry: Fundamentals and Applications. Academic Press, San Diego, California. 293 pp.
Sun, B. and R. Hawke. 1997. Properties of polyisocyanate resin consolidated composites made from secondary fibers of corrugated containers. *Forest Prod. J*. 47(2):80–88.
Sun, Y. and J. Cheng. 2002. Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresour. Technol*. 83(2002):1–11.
Thompson, W. 1969. Effect of steaming and kiln drying on the properties of southern pine poles. Part II: Chemical properties. *Forest Prod. J*. 19(2):37–43.
Wangaard, F. 1966. Resistance of wood to chemical degradation. *Forest Prod. J*. 16(2):53–64.
Winandy, J. and P. Lebow. 2001. Modeling strength loss in wood by chemical composition. Part I. An individual component model for southern pine. *Wood Fiber Sci*. 33(2):239–254.