Enhancing Composite Durability: Using Thermal Treatments

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Abstract

The use of thermal treatments to enhance the moisture resistance and aboveground durability of solid wood materials has been studied for years. Much work was done at the Forest Products Laboratory in the last 15 years on the fundamental process of both short- and long-term exposure to heat on wood materials and its interaction with various treatment chemicals. This work eventually resulted in predictive models to assess both the effect of thermal exposure on both mechanical properties and wood chemistry as a function of temperature, time of exposure, and chemical environment. More recently, significant progress, primarily in Europe, has focused on the goal of developing heat treatments for aboveground durability. Several new technologies have been commercialized. It is reasonable to assume that the manufacturing process for engineered wood composites, which utilizes several thermal treatments, could impart some similar measure of moisture resistance, or possibly even enhanced durability, should these critical fundamental principles of thermal treatment be better understood and properly controlled. This paper reviews the recent research on heat treatments for moisture and durability enhancement and then discusses what is known and what may yet need to be done to effectively understand and control thermal process conditions during the manufacturing process of engineered wood composites to produce more moisture-resistant and durable wood composites.

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Heat Treatments of Composites

Controlled exposure of woody materials to high temperatures can enhance resistance of the solid wood material to moisture absorption and enhance durability (Scheffer and Eslyn 1961, Stamm 1964). Over the last 10 to 15 years, several heat-treating processes have been commercialized in Europe. These processes expose wood to a specific thermal exposure (temperature and duration) using various fluid exposure medias varying from pressurized or non-pressurized hot dry air, to steam, to hot oil. Each is basically a non-toxic, chemical-free means of imparting both enhanced resistance to moisture and varying degrees of enhanced biological durability. Militz (2006) provides a review of the substantiating literature of heat treatments, while Rapp (2001) reviews the various commercial processes that have been developed.

The following discussion is limited to woodfiber and agricultural-fiber composites. Together they will be termed biocomposites. Wood composites represent a broad range of densities, particle morphologies, and process technologies (USDA 1999). A general overview of this continuum of composite types is shown in **Figure 1.**

One of the real commonalities among the various types of wood and biocomposites is that to consolidate and manufacture the composite product virtually all products require hot pressing to drive off residual moisture and establish hydrolytic bonding for resin-free systems and/or react the adhesive resin(s). These hot-pressing processes then become a truly viable candidate process for controlled heat treatment to enhance composite durability. While not systematically studied or understood, several studies have investigated heat treatment of

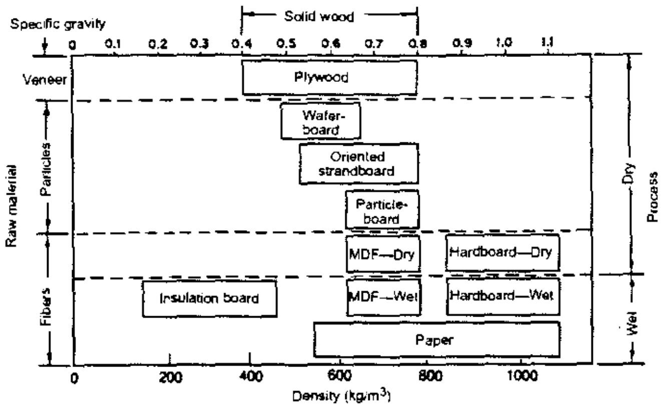

Figure 1. – *Classification of wood composite boards by panicle size, density, and process type (Suchsland and Woodson 1986).*

composites. Most have evaluated mechanical properties effects or modifications to wood chemistry: some have directly evaluated durability enhancement.

Tests on hardboards without a resin binder, made by alkaline process, showed that heat treatment decreased water sorption and swelling and increased bending strength (Voss 1952). Increasing the pressing temperature (up to 175°C) improved the strength properties of the board and reduced thickness swelling (TS) (Liiri 1969). Pressing time also affected board properties at outer and middle layer moisture contents (MC) of 18 percent, 9 percent, and 11 percent, respectively, using phenol-formaldehyde (PF) resin contents of 7 to 10 percent. Post-pressing heat treatment (immediately after pressing) was also found to he beneficial (Liiri 1969). It is possible to improve the hygroscopic properties of boards by modifying the physico-chemical properties of the particles by thermal treatment (Antoine et al. 1971). Dry-felted boards were given various thermal treatments (150° to 180°C for 1.5 to 5.0 hours), but while the treatments had little effect on board strength they improved moisture resistance (Szymankiewicz 1971). As with solid wood, for composites water absorption and TS decreased progressively with increasing temperature (Andre and Oost 1964). For medium density fiberboard (MDF), the time–temperature effect is related to moisture environment just as previously noted for solid wood (Houts 2001a, b).

Lenth and Kamke (2001) stated that one specific area where additional knowledge can be of great benefit is the joint influence of heat and moisture on the softening behavior of wood. They also found that modeling by time–temperature superposition was directly applicable to the wood and water system. The effects of steam-injection treatments (0.6 to 1.0 MPa) caused significant degradation of hemicelluloses, lignin, and cellulose and conventional hot pressing of dry material caused a lower degree of degradation of the chemical components (Widyorini et al. 2005). This partial degradation of chemical components during wet-heat treatments increased the bonding performance and dimensional stability of the binderless boards more than hot, dry pressing treatments.

The addition of kraft lignin in combination with a di- or trivalent metal salt has also been considered as an economic alternative to heat treatment of fiberboards (Westin et al. 2001).

Dimensional Stabilization

More work has studied the ability of heat treatment to impart dimensional stability and strength than has investigated durability. TS of particleboard decreased with an increase in the time and temperatures of post-heat treatment (Zhang et al. 1997). Dimensionally stable wood-based composites also have a better inherent ability to withstand severe exposure conditions than do regular boards (CARC 1987, Hsu et al. 1989). Prolonged heating at 175° and 218°C for 0.5 to 2 hours improved the performance of the board. Improvement increased with the increasing severity of treatment, but with a slight reduction in strength (Suchsland and Enlow 1968). Heat treatment of hardboard increases its stiffness, bending strength, modulus of elasticity, and elastic bending strength (Ogland and Emilsson 1951). Static bending properties and moisture absorption of particleboards were improved more by hot oil treatments than by dry heat treatments (Gupta et al. 1980). Nishikawa (et al. 1979) found that the strength properties of 12-mm-thick fiberboards of 0.70 g/cm^3 density were related to manufacturing conditions. Optimum conditions were:

- the use of phenolic resin;
- hot pressing with 30 kg/cm^2 at 190°C for 15 minutes with distance bars; and
- heat-treatment at 150°C for 2 hours.

Pulp freeness and heat treatment had significant effects on modulus of rupture and internal bond addition of phenolic resin and MC of the wet mat were important for screw holding. Heat treatment caused a significant decrease in TS and water absorption and a small reduction in bending and tensile strength (Roffael and Rauch 1973). As particleboard density was reduced, a smaller benefit in terms of increased bond strength and reduced swelling was noted (Roffael et al. 1973). Results suggested that two processes or zero-order reactions proceeded independently:

a. physical strengthening of the bonds between wood fibers, beginning at ca. 150°C; and
b. chemical depolymerization of cellulose chains in the fibers, accelerating above 170°C (Pulikowski 1975).

A model was presented for predicting the strength of tempered hardboard. Burmester and Deppe (1973) found that a 3-hour heat-treatment reduced TS of boards made with isocyanate or phenol resin after immersion in water.

Heat treatment reduced IB strength and bending strength depending on duration of heat treatment and the binder used. This reduction was less for isocyanate than for phenol resin. Later, Burmeister (1981) reviewed the results of 12 of his German-language studies on heat and/or formaldehyde treatments that showed that the extent of enhanced dimensional stability was more related to heat than to formaldehyde addition.

Effects on Mechanical Properties

Youh et al. (2000) found they could improve the physico-mechanical properties of board products by applying high frequency heating. They found the optimum conditions of high frequency heating compared with the technique of hot-platen heating. They also studied isocyanate resins for composite board production as a way to address the problem of free formaldehyde emission from urea resin which is generally used in the wood composites industry. For this study, 30-mm-thick MDF bonded with isocyanate resin were manufactured by the techniques of hot platen heating, high frequency heating, and a combination of the techniques. Goroyias and Hale (2002a) found that heat treatments of wood strands to greater than –235°Cprior to pressing imparted a noticeable increase in their resistance to moisture, but also imparted a sizable loss (approx. 20%) in the strength and stiffness of wood strands.

Chemistry and Resin Reaction Effects

Heat treatment of hardboards at temperatures above 160°C gives higher bending strength, lower water absorption, and lower swelling tendency in damp air and water (Ogland 1949). The effect of the heat treatment seems to be due mainly to a change in the properties of the hemicellulose. Pre-treatment of chips by steaming at 230° to 3009: reduced TS of hardwood particleboards by 45 to 50 percent (Tomek 1965, 1966). Also, the reduction in TS was less effective in coniferous particleboards than hardwoods. Hemicelluloses is hydrolyzed during heat treatment (200°C for 20 min.) and these changes cause reduced hygroscopity of heat-treated fiberboard (Solecnik and Siskina 1964). Results showed the heat treatment to be more effective when the boards contained less urea-formaldehyde binder and that wax had little influence (El'bert 1962). Strength loss after high pressing temperatures was less when pressing occurred in a nitrogen-atmosphere than when pressed in a steamed atmosphere, which was in turn less than when pressed in an air environment (Brauns and Strand 1958). Fiberboards made of lignin-free material display the same increase due to heat treatment as those made of a non-delignified material. It was is concluded that lignin does not play any significant role in the strength increase (Klauditz and Stegmen 1951). The heat-treated boards were found to be built from shorter fibers and to contain cellulose of a lower degree of polymerization than the untreated ones. Thus, it seems that the higher strength values of heat-treated boards can only be due to the banding effect of the polyuronide portions of the hemicellulose.

Previous work has clearly established the viability and usefulness of such a cumulative thermal-pH damage modeling approach. For example, the thermal effect of a secondary thermal treatment is different depending on whether lumber is first kiln-dried at 75°C or at 150°C (Winandy and Barnes 1991). Winandy (2002) found that the most important issue to consider when discussing the effects of any heat-treatment on properties is that in any thermal mitigated, hydrolytic degradation scenario, the total environment including temperature, time at temperature, and the pH of the environment all need to be considered. Lebow and Winandy (1999) found that cumulative thermal effect was not only related to exposure duration but also to the pH of the environment in which the biomaterials were exposed processing and in service. Thus, borate-treated wood with its higher pH was less prone to strength loss than is acid-treated wood when exposed to the same time–temperature scenario. Accordingly, consideration of environmental pH becomes exceedingly critical when considering the effects of hot-pressing temperature and duration for biocomposites because the resins used as binders significantly influence the environmental pH experienced by the hot-pressed composite. Thus, any discussion of heat treatments of wood and biocomposites must also include consideration of the pH-effect from urea-formaldehyde (UF), phenol formaldehyde (PF), polymeric diphenylmethane diisocyanate (pMDI), or binderless systems. Poblete and Poffael (1985) found that thermal treatment alone in particleboard hot pressing lead to decreased wood pH. They also found that the magnitude of pH-mediated hydrolyze for UF-bound particleboard was more severe in the hotter face layers than the cooler core layer.

In most reports discussing the influence of thermal treatments, the authors discuss temperature but usually do not systematically consider the complex interdependent relationships of heat, duration of exposure, changing resin and wood chemistry. interactive moisture relationships, and wood strength/stiffness. Most authors who have considered heat-treatment effects on solid-wood have very accurately defined the absolute magnitude of the thermal environment, but not other critical issues such as duration and chemical environment. To understand heat effects, it is critical to embrace the concept that the eventual effect of any thermal or thermo-chemical process is relative to multiple issues (temperature, time of exposure to those temperatures, pH of environment, etc.) not just temperature itself. For example, Matsuoka's (2002) work from 90° to 150°C and Tjeerdsma's (2000, 2002) work might have produced varying thermal thresholds for bioefficacy had they increased or decreased by two to four times the durations of their thermal treatments. The same might be said when interpreting the results of Popper et al. (2005). The work of Seborg et al. (1953) at the FPL would have produced much less strength loss had he halved or quartered his thermal exposure durations.

Durability Enhancement

Particleboards made with an isocyanate binder were exposed to decay and boards made from heat-treated chips showed improved decay resistance by remaining below the 16 percent MC necessary for fungal growth (Burmester 1974). Goroyias and Hale (2002b) found that several heat treatment scenarios for composites could substantially enhance dimensional stability, but decay resistance was enhanced to a far lesser extent. They also concluded that high degrees of decay resistance for situations such as direct outdoor exposure or ground contact would require chemical treatments of strands prior to composite manufacture (Goroyias and Hale 2004). Recent work is now beginning to systematically model the influence of both hot-pressing temperature and extended pressing duration and may soon show how it can be controlled to measurably enhance mositure resistance and resulting TS with MDF **(Fig. 2).**

Summary

The work of dozens of scientists has been reviewed and discussed. It clearly shows that to understand or predict the effects of temperature on strength or durability or on chemical composition, we will systematically need to sonsider the temperature, the cumulative duration(s) of life-long thermal exposures, the material morphology, and the overall chemical environment.

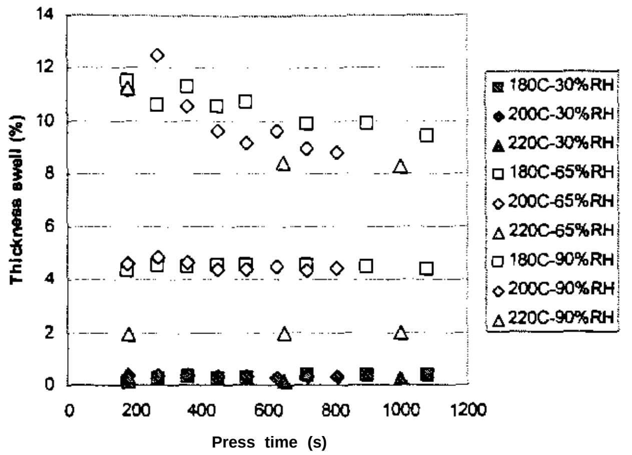

Figure 2. – *Relationship between thickness swell and hot-pressing temperature and duration during fiberboard production (from Winandy and Krzysik 2006).*

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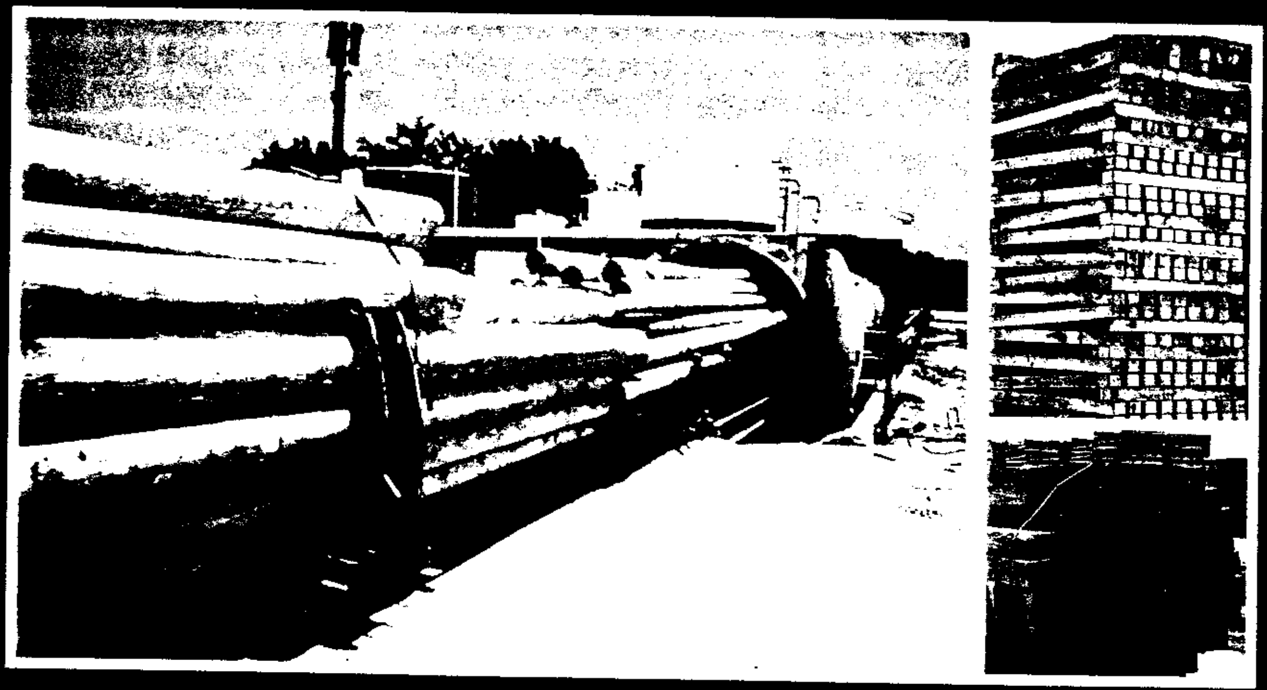

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