DE GRUYTER

Review

Parviz Navi* and Antonio Pizzi

Property changes in thermo-hydro-mechanical processing

COST Action FP0904 2010–2014: Thermo-hydro-mechanical wood behavior and processing

Abstract: Thermo-hydro-mechanical (THM) treatment is a combined action of temperature, moisture, and mechanical force, which leads to modified wood (THMW). Various types of eco-friendly THM processes have been developed to enhance wood properties and generate new materials, such as welding, densification, molding, bending, profiling, artificial aging, panel manufacture, and surface densification. The various transformation processes in the course of THM bring about positive effects in terms of the mechanical and physical properties as well as the biological durability. To the negative effects belong the loss in strength and fracture toughness, and one of the challenges is to minimize these negative aspects. The present paper reviews the chemical transformations processes during THM treatment in a closed processing system and presents the relationship between processing parameters and THMW properties. The discussion includes the problems associated with eliminating the set recovery of densified wood by THM posttreatments and the chemical origin of the relaxation of internal stresses induced by densification.

Keywords: chemical-mechanical, chemistry, densification, fixation of compression set, moisture content (MC), temperature, wood

DOI 10.1515/hf-2014-0198 Received July 3, 2014; accepted March 31, 2015; previously published online May 13, 2015

Introduction

Thermo-hydro-mechanical (THM) treatment of wood is one of the emerging eco-friendly methods in wood technology, which is based on the combined treatment of wood by elevated temperature, moisture, and application of mechanical forces. These processes can be subdivided into thermo-hydro (TH) and thermo-hydro-mechanical (THM) treatments. TH treatments (THT) change the intrinsic wood properties and dissipate internal stresses, while wood is dried and softened. THT also improves the properties of wood composites. THM treatments (THMT), on the other hand, are employed in molding, shaping, bending, profiling, welding (by friction), and densification of wood. The goals of THT and THMT are different, and for this reason, this paper aims to review and summarize details related solely to THMT and will focus on the chemical changes during the process and their relationship to the properties of THM wood (THMW). The unavoidable side effects of THMT will also be discussed.

Many THM techniques have a historical background. For example, the bending of wood in the longitudinal direction was known in Egypt around 1000 B.C. (Rivers and Umney 2005). In 1850, Michael Thonet (1796–1871) applied steam to soften beech wood and protected the side of the wood submitted to tensile forces during bending by steel strapping. Chair manufacture by this technique is still very successful. Hanemann (1917, 1928) developed a technique to compress plasticized wood along the fiber direction (crushing), which makes wood pliable, and the method found industrial application in the 1990s (Morsing 2000). Compressing softened wood in the transverse direction at high temperature leads to densified wood, which was patented by Stöckhart in 1886 (Vorreiter 1942).

Sandberg et al. (2013) reported the state of the art on THMW up to 1960. It was recognized that densified wood suffers from the "shape memory" or "compression set recovery". To eliminate this effect, Stamm and Seborg

^{*}Corresponding author: Parviz Navi, Institute for Materials and Wood Technology, Bern University of Applied Science, Biel, Switzerland; and Institute of Material Science and Engineering, Ecole Polytechnique Fédéral de Lausanne, Switzerland, e-mail: Parviz.navi@bfh.ch

Antonio Pizzi: LERMAB, University of Lorraine, Epinal, France; and Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

(1941) developed a multi-layered wood composite (called Impreg) consisting of thin veneers impregnated with phenol formaldehyde resin, which was densified under heat and pressure, while the resin eliminated the compression set recovery. Stamm et al. (1946) and Seborg et al. (1945) observed that a thin plate of densified wood, when treated at 180°C for 30 min, shows reduced compression set recovery following re-wetting and re-heating and called their successful THMW "Staypak" (Kollmann et al. 1975).

Since the 1990s, a renewed interest has arisen in developing THM products. In Japan, Norimoto et al. (1993), Ito et al. (1998a,b), and Tanahashi et al. (2001) adopted the THMT for Staypak production. Reportedly, the THM posttreatment of thin densified wood at 200°C and under conditions of saturated moisture for 4 min eliminated totally the shape memory. Ito et al. (1998a) developed a system to transform small round section wood trunks into trunks with squared cross sections. Another densification process was designed to obtain structural timber of high quality from low-density wood ("compressed lumber processing system", CLPS). In the first mentioned technique, the stages of moldings and posttreatment follow each other in a continuous process, whereas in CLPS production, the two stages are separated. However, the scaling up of the research results turned out to be difficult. Kyomori et al. (2000) pointed out that more fundamental knowledge is needed for the successful application of THMT in industrial scale.

In Denmark, a machine was developed for the precompression of wood in the longitudinal direction based on the idea of Morsing (2000). This type of wood element can be bent without the application of steam or jigs. In Switzerland, Navi et al. (1997, 2000), Heger (2004), Navi and Heger (2005), and Popescu et al. (2013) investigated the set recovery of densified wood fabricated in a closed system. In Germany, a system for posttreatment of THM densified wood was developed by means of heating oil (rapeseed oil at 200°C, OHT). Haller and Wehsener (2004) and Welzbacher et al. (2008) investigated the suitability of OHT for large-scale industrial densification by focusing on the elimination of compression set recovery and found that the compression set recovery of large densified spruce panels was completely eliminated. The product has improved resistance to biodegradation, but the mechanical strength is considerably reduced. In Canada, Fang et al. (2011) have also investigated the effects of OHT on densified wood veneer. In the USA, Kamke (2004) and Kutnar et al. (2008) densified fast-grown, low-density wood to composite panels. A semi-open THM reactor was developed for densifying thin layers of hybrid poplar specimens by Kamke and Sizemore (2005).

Militz and Lande (2009) summarized that only a few TH techniques could be industrialized, and the same conclusions were drawn by Kamke (2013) and Sandberg et al. (2013) in terms of THMT. As pointed out previously, more basic knowledge is needed to change this situation. In view of the complexity of the chemical and physical changes of wood in the course of THMT, it can be stated that THM processing is a highly researchoriented technology. Large wood elements behave differently to the small-sized wood elements tested in the laboratory. This is especially true for the detrimental compression set recovery of densified wood. Moreover, the shape memory effects of products manufactured in open systems cannot be compared with the results of materials manufactured in a closed system. Only the closed system provides the possibility of controlling all processing parameters, namely, temperature, MC, and force. Moreover, in a closed system, the moisture content (MC) can be varied from zero to saturated conditions in the course of the whole THM processing including the posttreatment. This is the reason why in this paper, only the chemical changes and subsequent mechanical and physical properties of THMW prepared in a closed system will be reviewed and discussed.

The main aim of this paper is to contribute to a better understanding of the chemical changes that the polymeric constituents of wood undergo during THMT. In other words, the focus is on the chemical origin of the elimination of compression set recovery and the relationship between THMT parameters, and the physical and mechanical performance of the products obtained in a closed system should be illuminated.

Methods for THM processing

Densification can be carried out in open, semi-open, or closed systems. In an open system, the process runs at atmospheric pressure, 130°C, and the MC is limited to 13% (Welzbacher et al. 2008). Under this condition, the shape memory effect is pronounced. In a closed system, there is a pressurized gas environment, and thus, the MC can attain saturation conditions, and the temperature can be increased close to pyrolysis conditions. In a semi-open system, called viscoelastic thermal compression (VTC), some stages are controlled by pressurized gas and the others by atmospheric pressure (Kamke and Sizemore 2005). Navi and Sandberg (2012) described examples of the THM processing systems and pointed out the advantages of closed systems that allows for

exact controlling the parameters also in terms of shape memory.

The closed system equipment for densification or molding of wood consists of a reactor, a press, and a high-temperature steam generator (Figure 1). This multichamber device is suitable for densification of small wood elements with dimensions $15\times4\times4$ cm³ (r, t, l), followed by a posttreatment in saturated or nonsaturated steam at temperatures up to 200°C.

Treatments often comprise four stages: plasticization, densification, posttreatment, and cooling. A schematic overview of THM processing, including posttreatment is given in Figure 2.

Figure 1: Multichamber THM closed reactor. Steam injection into the containment cylinder (3 and 4) and the mantel (yellow circuit 1 and 2) are shown (designed by RINO Sàrl, Switzerland).

Compression set recovery as a function of temperature and time

Densified wood is submitted to soaking-drying cycles, and the compression set, short-recovery R observed provides information about the dimensional stability as a function of the parameters (Norimoto et al. 1993; Takahashi et al. 1998; Ito et al. 1998a). Heger (2004) observed the influence of temperature and time separately in two experimental series. In the first one, small wood specimens were densified and posttreated between 110°C and 200°C under saturated steam conditions. The postprocessing time was 9 min, and compression set was at ca. 60%. The recovery test consisted of five cycles, which involved immersing the compressed samples in water at 60°C for 5 days and then drying at 30°C for 5 days. Finally, the samples were totally dried over a period of another 5 days. The recovery R was determined based on the following relationship:

$$
R = \frac{X_c' \cdot X_c}{X_o \cdot X_c} \times 100
$$
 (1)

where, X_{\circ} is the initial length of specimen before densification, X_c is the length after densification, and X_c' is the length of the specimen after recovery test. The variation of R (Figure 3) indicates that each treatment modifies the wood with new moisture-related properties that are different from native wood and to each other. It is important to note that the value of the (X'_{\cdot}, X_{\cdot}) represents the sum of two deformations accounted for moisture-related swelling and compression set recovery. To separate these two deformations, curves have been constructed for each temperature (shown as the dashed-line) by connecting the origin of Figure 3 to the points at the end of each cycle after

Figure 2: Diagram of THM processing of small elements: THM densification and posttreatment under saturated steam.

Figure 3: Set recovery R measured during soaking-drying cycles of densified and posttreated wood at saturated vapor under different temperatures for similar processing time and compression rate of 10 mm min-1. Curves with dashed line show the variation of compression set recovery for the indicated temperature.

Figure 4: Set recovery R during soaking-drying cycles; R curves of densified samples treated at saturated vapor at 180°C under different processing times.

10, 20, 30, 40, and 50 days. These dashed line curves indicate the variation of R $(\%)$ of the densified wood, which are smaller if the compressed wood is treated at higher temperatures. Figure 3 also shows that the moisturerelated behavior becomes entirely fixed only when the specimen is densified at 200°C. When the R is about 2%, the recovery is considered to be completely eliminated.

Another experimental series of Heger (2004) under constant temperature at different postprocessing times between 5 and 35 min are presented in Figure 4 showing R after five cycles. Accordingly, longer posttreatment times entail smaller R. The recovery is entirely eliminated at 180°C with 10 min posttreatment time.

Chemical degradation as a function of processing parameters

Chemical changes in heat-treated wood were reported, among others, by Windeisen et al. (2009). No doubt, chemical analysis contributes a lot to estimate the optimal THT (Hill 2006; Militz and Lande 2009). Wood degrades faster when heated by steam or water (Millet and Gerhards 1972; Hillis 1975). Heat treatments are mainly conducted in a dry environment in an inert gas or in a moist environment with steam at temperatures up to 240°C. Under these conditions, the hemicelluloses are hydrolyzed, and

Table 1: Percentage of neutral monosaccharide in treated and native wood from the GPC spectra (Heger 2004).

a Eliminated.

the crystallinity index of cellulose increases, but lignin is only slightly affected (Pelaez-Samaniego et al. 2013). The pyrolysis of hemicelluloses begins at about 270°C followed closely by cellulose (Rowell et al. 2009). The THM processing diagram (Figure 2) illustrates that the period of plasticization and densification for small elements is short even at lower temperatures. However, the posttreatment temperature must be higher, and the treatment time depends on the MC. It was demonstrated that at higher temperature and MC with long processing time, the wood constituents can be seriously degraded, and as a result, the mechanical and fracture strength of THM wood is lowered.

Chemical degradation of hemicelluloses

The pH of softwood varies between 4 and 6 (Sandermann and Rothkam 1959). For example, the pH of spruce (*Picea abies* Linn) is 5.3 at ambient temperature. At elevated temperatures, the dissociation constant of water is higher (Sweeton et al. 1974; Verma 2003). Thus, during THM and particularly during posttreatment, the pH of the water inside the wood at 200°C is around 5.8, based on data from the International Critical Tables. The degradation reactions liberate acetic acid, the concentration of which is almost constant during processing. According to Hsu et al. (1988), the pH of pine decreases rapidly in the beginning of the heat treatment and stabilizes at about 3.5. The major reason for pH decrement is deacetylation of hemicelluloses, which is the best established reaction in wood chemistry.

Under these acidic conditions, the hemicelluloses are easily hydrolyzed, their DP is lowering, and mainly xylan fragments down to monomeric sugars can be solubilized by water (Fengel and Wegener 1984). Typical yield of neutral monosaccharides (glucose, galactose, mannose, xylose, and arabinose) of native spruce such as densified spruce, and densified posttreated spruce are presented in Table 1 (Heger 2004). Accordingly, the mass loss (ML) is 6.9% after densification and washing of the specimens. The ML increases significantly when the specimen undergoes posttreatment, i.e., ML is 15.1% and 14.6% after posttreatment at 180°C for 30 min and at 200°C for 5 min, respectively. The 175-ppm NMR signal characteristic of acetyl -COOH groups of hemicelluloses decreases markedly upon THMT, which is a proof that the increasing acidity is due to hemicellulose degradation. This effect is also seen by the decrease of the 20- to 22-ppm signal characteristic of the -CH $_{3}$ group of acetic acid and by the corresponding FTIR bands.

Chemical degradation of lignin

The degree of cross-linking and glass transition temperature $(T_{\rm g})$ of lignin might be affected by THMT. According to Heger (2004), the Tg of lignin between 140°C and 210°C decreases with increasing treatment time (Figure 5). This might be interpreted as a partial depolymerization of lignin in the initial phase and degradation during posttreatment. Microcracking occurs between cells in the lignin-rich intercellular region during posttreatment at 200°C and above. During wood welding, similar observations were made.

Solid phase CP MAS¹³C NMR spectra reveal the cleavage of linkages at $C\alpha$ and 4-O, and demethylation and demethoxylation reactions are also typical. NMR analysis confirms that initially, hydrolysis occurs only on the positions C3 and C5 but not on the C1 and C4 of the ring (Delmotte et al. 2008). The appearance of phenolic hydroxyl groups, as a result of lignin splitting, was also shown during welding, which is as a special type of THMT and which also leads to polycondensation of the aromatic nuclei accompanied by formation of Ar-Ar and Ar-CH₂-Ar bridges (Delmotte et al. 2008). The Tg of lignin may be affected in two ways, while during welding cross-linking reactions are typical. Under HTM conditions in the heating phase, however, the

Figure 5: Tg of the lignin of densified and posttreated specimens in saturated steam, function of the temperature, and posttreatment time.

situation is more complex. The lignin rearrangement leads to (1) a decrease in the Tg of lignin due to its partial depolymerization, and (2) to a change in Tg due to the internal rearrangements without cross-linking that would occur during dry heating. A notable increase in the NMR signals between 190 and 220 ppm indicates the formation of aldehydes. The predominance of the NMR bands at 191–192 ppm and particularly at 196 ppm are for formaldehyde, furfural, or methyl furfural. The considerable rise of the 148-ppm and 152-ppm NMR signals during wood welding confirms the formation of considerable proportions of furfural (Delmotte et al. 2008). The formation of aldehyde groups implies extensive depolymerization of both lignin and carbohydrates and can also be interpreted as sign of lignin rearrangement, which is obvious by Tg change.

DP of cellulose

The degree of polymerization of the cellulose decreases during THM posttreatment as measured by capillary viscosimetry (Table 2). The average *DP̅v* value can be determined from its intrinsic viscosity measured in cupriethylene-diamine (CED) based on French norm AFNOR, Heger (2004).

Fixation of compression set

Salmén and Burgert (2009) and Stevanic and Salmén (2009) reviewed the supramolecular architecture of the cell wall with the special arrangement of cellulose, hemicelluloses, **Table 2:** Cellulose overall viscosimetric degree of polymerization *DP̅v* of three spruce samples.

and lignin. In this model, the amorphous hemicelluloses adjacent to the microfibrils (MF) are connected by hydrogen bonds and joined to the lignin mainly by covalent bonding. The cellulose domain consists of crystalline and semi-crystalline regions. With the exception of the crystalline cellulose, nearly all regions of the cell wall are plasticized during the densification process under the combined action of steam and high temperature (over 100°C) (Back and Salmén 1982). When wood is transversally compressed in these conditions, elastic and elastic-viscoplastic deformations occur. The elastic energy stored in the helical semi-crystalline microfibrils and the lignin is rather high; the applied compression stress on the sample at the end of the densification reaches about 17.5 MPa. This stored elastic energy is the main cause of the compression set recovery, R.

Two mechanisms account for the fixation of R: After the hot densified wood is cooled down below the Tg of lignin, the lignin passes from the rubbery to the glassy state, and the deformed cellulose is confined in this rigid matrix. During drying, the formation of hydrogen bonds between the cell wall polymers also contributes to the fixation of the deformed state. The fixation is not permanent (Navi and Heger 2005). After re-humidification/heating, the hydrogen bonds disrupt, and lignin may become rubbery again. The release of the elastic energy leads to total or partial R of the densified wood.

Norimoto et al. (1993) and Morsing (2000) proposed three methods for avoiding R: 1. To prevent wood from being re-softened by changing the hygroscopicity of the cell wall; 2. Promoting formation of covalent crosslinks between wood components in the deformed state; 3. To relax the stresses stored in the microfibrils and matrix polymers during densification. The latter can be considered as the most promising approach in practice.

Fixation of compression set by THM treatment

To obtain stable densified wood without R or with low R, a THM posttreatment is necessary. Fixation by means of saturated steam was investigated by Van Niekerk and Pizzi

Table 3: Posttreatment processing time for complete fixation of the compression-set (R∼2) at different temperatures (T) and relative humidities (RH).

| T (°C) | | 40% | Fixation time (min) at RH | | | |
|--------|----------------------|---------|----------------------------------|------|------|--|
| | 0% | | 60% | 80% | 100% | |
| 140 | No fix. ^a | 6000 | No fix. | 2020 | 210 | |
| 160 | 24250 | No fix. | No fix. | 135 | 70 | |
| 180 | 5680 | 341 | 167 | 50 | 20 | |
| 200 | No fix. | No fix. | 43 | 16 | 4 | |

a No fixation.

(1994), Inoue et al. (1993), Dwianto et al. (1997), Ito et al. (1998a,b), Heger (2004), Navi and Girardet (2000), and Navi and Heger (2005). Heger (2004) and Groux (2004) observed the parameters influencing R in a closed thermohydro-mechanical multichamber reactor (Figure 1).

Table 3 gives the posttreatment time necessary for complete fixation of compression-set at different temperatures under saturated and unsaturated conditions. Obviously, a complete fixation of R (R∼2%) at any temperature and RH could not be achieved. When the specimens with low MC were kept for more than 50 min at 200°C in the reactor, the specimens started to burn at 0 and 40% RH. Probably, complete fixation was unsuccessful under these conditions because the lignin remained glassy (Salmén 1982).

The role of hemicelluloses hydrolysis on the fixation

The effect of the THM parameters on R (Table 3) is illustrated in Figure 6. As indicated, the posttreatment time (log scale) is a function of temperature and RH. For a given RH, the logarithm of time varies linearly with respect to the inverse of the absolute value of temperature. This regularity suggests a mathematical relationship between the time, temperature, and RH for eliminating shape memory, or relaxation of the strain energy accumulated during densification. The plot in Figure 6 allows the calculation of the activation energy (E_A) of the process responsible for eliminating the shape memory effect for each RH:

$$
t(T,h) = \alpha \, \mathrm{e}^{E_A/\,RT} \tag{2}
$$

where, α is a parameter that depends on RH and pH of the water during the posttreatment.

 E_A is measured from the slope of the lines at different RH and are given in Table 4. The value is roughly constant at around 98.5–118.4 kJ mol¹ and independent of RH. These E_A data are very close to the value E_A =118 kJ mol¹

Figure 6: Value of posttreatment time of complete fixation of the compression set vs. 1/(RT) and relative humidity (RH) for spruce wood.

Table 4: Values of the activation energy E_A (kJ mol⁻¹) at various relative humidities derived from Figure 6.

| | Relative humidity (%) | | | | | | |
|------------------------------|------------------------------|-------|-------|-------|-------|--|--|
| | 100 | 80 | 60 | 40 | o | | |
| $E_A(k)$ mol ⁻¹) | 98.5 | 116.6 | 118.8 | 111.5 | 118.4 | | |

found by Springer (1966) for the hydrolysis of xylan. The low value measured under 100% RH might be due to the easy initiation of hydrolysis in the presence of saturated steam. There are several literature data available with this regard. Experiments were conducted by Mittal et al. (2009), Nabarlatz et al. (2004), Garrote et al. (1999), and Grénman et al. (2011) concerning the extraction of hemicelluloses from various wood species (Table 5). Accordingly, the E_A varies with the experimental parameters and the wood species. The result obtained by Grénman et al. (2011) on spruce can be compared with the one calculated from the results given in Figure 6 for spruce. The difference between the two results might be attributed to the different extraction methods. Grénman et al. (2011) used a cascade type reactor with solid-liquid aqueous extraction, whereas Heger (2004) used a single reactor and saturated steam.

Obviously, the hydrolysis of hemicelluloses as manifested by ML, the subsequent lowering of hydrophylicity and reactions of furfural leading to cross-linking reactions, increasing of porosity, and mainly microcracks and new surfaces in the hemicellulose matrix, play an essential role for low R values. Table 1 shows about 2/3 ML of hemicelluloses. This finding was also presented by Van Niekerk and Pizzi (1994), who checked more than 29 000 full-scale industrial panels made of eucalyptus wood and

| | | | | Wood species | |
|---------------------------------|--------------------------|-----------------------|--------------------------------|---------------------|--|
| Parameter | Sugar maple ^a | Corn cob ^b | Eucalyptus ^c | Spruced | |
| Chip thickness (mm) | < 0.6 | | $<$ 8 | $1.25 - 2$ | |
| Temperature $(^{\circ}C)$ | $145 - 185$ | $150 - 190$ | $145 - 190$ | $150 - 170$ | |
| Liquid/solid ratio | 20 | 8 | $6 - 10$ | 160 | |
| E_{A} (kJ mol ⁻¹) | $114 - 117$ | $127 - 251$ | $82 - 156$ | $150 - 170$ | |

Table 5: Activation energies E_A (kJ mol⁻¹) and the experimental parameters (Grénman et al. 2011).

Mittal et al. (2009); ʰNabarlatz et al. (2004); ʿCarrote et al. (1999); ªGrénman et al. (2011).

Figure 7: Short-term strength (Rm) and longitudinal Young's modulus (E) of natural spruce, densified, densified, and posttreated at 140°C during 3 h, 160°C during 1 h, 180°C during 16 min, and 200°C during 4 min under saturated steam.

found evidence that hemicelluloses hydrolysis is the main cause of R fixation. This effect was greater in the case of high MC of the wood furnish. The compression strength of the eucalyptus wood cells is relatively high, and the cell walls are only deformed under standard particleboard producing conditions, which is a source of considerable residual strain in the particles. However, if much higher specific pressure is applied at higher MC of the furnish, hemicelluloses are more degraded, then more micropores arise, and the residual strain is lowered.

Effect of processing parameters on the wood mechanical properties

The effects of processing parameters on longitudinal strength and Young's modulus of THMW are exemplified in Figure 7 for spruce wood according to Heger (2004). Here, the density of the wood and consequently its longitudinal tensile strength (without posttreatment) were increased by a factor of 3. As indicated, the tensile strength was 364 MPa, which is by a factor of 3 is less than that of natural spruce. Posttreatment at 140°C leads to a loss of about 7% of the wood strength, but the reductions are greater at 160°C, 180°C, and 200°C, where the corresponding losses are 23%, 28%, and 73%, respectively.

The high stress losses at higher temperatures are partly due to microcracking in the samples, which are prominent around 200°C. In fact, the pressure of saturated steam increases exponentially with temperature. The pressure of the saturated steam at 200°C is about 16 kg cm², whereas it is only 4 kg cm² at 140 \degree C. The middle lamella becomes also fragile above 190° due to lignin softening (Navi and Sandberg 2012), which leads to fractures and heavy distortions relative to the other cells. Microfissures during processing and drying contribute a lot to strength losses.

Theoretically, the Young's modulus (MOE) of the three times densified spruce should be triplicated, but MOE increased only by a factor of 1.9. Table 1 shows that about 2/3 of hemicelluloses was washed out by water in the densification stage that generated pores. MOE is sensitive to variations in the material porosity. The MOE was increased by 3% at 140°C and 13% at 160°C. Above 160°C, the MOE begins to decrease for the effects indicated above. It can be safely concluded that the increased number of pores in the wood are responsible for MOE losses, though the cell wall crystallinity index, C_{r} I, and the diameter of cellulose crystallite are increased (Heger 2004).

Conclusions

Various types of THM processing technique can be utilized to enhance wood properties and produce eco-friendly new materials. The modification of mechanical properties, dimensional stability, resistance to microorganisms, change in the color, and odor are functions of the broad array of processing parameters and consequences of wood chemical degradation. The changes show positive as well as negative aspects. Examples of these unwanted features are diminution of strength, increased brittleness, and recovery of compression set.

Altering the processing parameters, in which wood is treated, alters the product performance. THM posttreatment is an effective method of permanently fixing the compression set. The temperature should not, however, exceed 160°C or 170°C as the mechanical properties of products may then greatly deteriorate.

Hydrolysis of hemicelluloses during THM treatment plays an active role in the dissipation of the stresses stored in the microfibrils and lignin. About 2/3 of the mass of hemicellulose hydrolysis leaves the wood during THM treatment and produces new surfaces, and pores helping dissipate the strain energy. To achieve a total elimination of shape memory, the lignin must be in its rubbery state during the THM treatment.

One of the important challenges for expanding the commercialization of THM technology is scaling up the laboratory processes to industrial levels. The time required for densification and posttreatment of a specimen is approximately proportional to the second power of the principal length of the densification. For large elements, the consequence of this time on the chemical degradation of wood would be dramatic, i.e., would be prohibitive for the industrial production. In order to reduce the processing time, investigations with interdisciplinary approach are required under participation of researchers from academia and industry.

Acknowledgments: The authors gratefully acknowledge the support for promotion of Thermo Hydro Mechanical wood behavior and processing through COST Action FP0904 by COST (European Cooperation for Science and Technology).

References

- Back, E.L., Salmén, N.L. (1982) Glass transition of wood components hold implications for molding and pulping processes. Tappi 65:107–110.
- Delmotte, L., Ganne-Chedeville, C., Leban, J.M., Pizzi, A., Pichelin, F. (2008) CP-MAS C-13 NMR and FT-IR investigation of the degradation reactions of polymer constituents in wood welding. Polym. Degrad. Stabil. 93:406–412.
- Dwianto, W., Inoue, M., Norimoto, M. (1997) Fixation of compressive deformation of wood by heat treatment (In Japanese). Mokuzai Gakkaishi. 34:303–309.
- Fang, C.H., Cloutier, A., Blanchet, P., Koubaa, A. (2011) Densification of wood veneer with heat and steam combined with oil-heat,

In: COST Action FP0904 Workshop, "Book of Abstract", Eds. Navi, P., Roth, A. Biel (Bienne), Switzerland. pp. 93–94, ISBN 978-3-9523787-0-0.

- Fengel, D., Wegener, G. Wood-Chemistry, Ultrastructure, Reactions. De Gruyter, Berlin, (1984).
- Garrote, G., Dominguez, H., Parajo, J.C. (1999) Mild autohydrolysis: an environmentally friendly technology for xylooligosacccharide production from wood. J. Chem. Technol. Biotechnol. 74:1101–1109.
- Grénman, H., Eränen, K., Krogell, J., Willför, S., Salmi, T., Murzin, D.Y. (2011) Kinetics of aqueous extraction of hemicelluloses from spruce in an intensified reactor system. Ind. Eng. Chem. Res. 50:3818–3828.
- Groux, M. (2004) Effet de la pression de vapeur lors des traitements thermo-hydro-mécaniques sur la stabilité de l'épicea densifié: influence de l'hydrolyse sur l'élimination de la forme. (Effect of steam during thermo-hydro-mechanic treatment on the stability of densified spruce: influence of hydrolysis on the elimination of the form.) Master of Science Thesis, EPFL, Lausanne, Switzerland.
- Haller, P., Wehsener, J. (2004) Festigkeitsuntersuchungen an Fichtenpressholz (FPH). Holz Roh Werkst. 62:452–454.
- Hanemann, M. (1917) Holzaufbereitungsverfahren. (Wood treatment process.) Deutsches Reichs Reichpatentamt, Patentschrift, No. 318197.
- Hanemann, M. (1928) Verfahren und Vorrichtung zur Herstellung von weichbiegsamem Holz. (Method and apparatus for producing soft and flexible wood.) Deutsches Reichs Reichpatentamt, Patentschrift, No. 458923.
- Heger, F. (2004) Etude du phénomène de l'élimination de la mémoire de forme du bois densifié par post-traitement thermohydro-mécanique. (Study of the mechanisms of elimination of the memory form of densified wood by post-processing thermo-hydro-mechanics.) PhD. Thesis No. 3004, EPFL, Lausanne, Switzerland.
- Hill, C.A.S. Wood Modification Chemical, Thermal and other Processes. John Wiley & Sons, Chichester, 2006.
- Hillis, W.E. (1975). The role of wood characteristics in high temperature drying. J. Institute Wood Sci. 7:60–67.
- Hsu, W.E., Schwald, W., Schwald, J., Shields, J.A. (1988) Chemical and physical changes required for producing dimensionally stable wood-based composites. Part I: Steam treatment. Wood Sci. Technol. 22:224–289.
- Inoue, M., Norimoto, M., Tanahashi, M., Rowell, R.M. (1993) Steam or heat fixation of compressed wood. Wood Fiber Sci. 25:224–235.
- Ito, Y., Tanahashi, M., Shigematsu, M., Shinoda, Y., Otha, C. (1998a) Compressive-molding of wood by high-pressure steamtreatment: Part 1. Development of compressively molded squares from thinnings. Holzforschung 52:211–216.
- Ito, Y., Tanahashi, M., Shigematsu, M., Shinoda, Y. (1998b) Compressive-molding of wood by high-pressure steam-treatment: Part 2. Mechanism of permanent fixation. Holzforschung 52:217–221.
- Kamke, F.A. (2013) THM a technology platform or novelty product. In: Proceedings of the COST FP0904 & FP1006 International Workshop, Characterization of modified wood in relation to wood bonding and coating performance. Eds. Medved, M., Kutnar, A. University of Ljubljana, Biotechnical Faculty, Rogla, Slovenia. pp. 8–15.

Kamke, F.A. (2004) A novel structural composite from low density wood. In: Proceedings of the 7th Pacific Rim Bio-Based Composites Symposium. Eds. Zhou, X., Mei, C., Jin, J., Xu, X. Oct. 31–Nov. 2, Nanjing, China, pp. 176–185.

- Kamke, F.A., Sizemore, H. (2005) Viscoelastic thermal compression of wood. US Patent Application No. US2005/006004AI, 13 Jan. 2005.
- Kollmann, F.P., Kuenzi, E.W., Stamm, A.J. (1975) Principles of wood science and technology. Vol. II. Wood Based Materials. Springer-Verlag, New York, Heidelberg, Berlin. pp. 139–149.
- Kutnar, A., Kamke, F.A., Sernek, M. (2008). The mechanical properties of densified VTC wood relevant for structural composites. Holz als Roh-und Wekstoff. 66:439–446.

Kyomori, K., Shigematsu, M., Onwona-Agyeman, S., Tanahashi, M. (2000) Virtual models of the molding process of wood compressed by the high-pressure steam technique-towards the development of an aid-system for designing and manufacturing. In: Proceedings of the 6th International Symposium on Virtual System and MultiMedia (VSMM 2000), Gifu, pp. 403–408. IOS Press. ISBN 1-58603-108-2.

- Militz, H., Lande, S. (2009) Challenges in wood modification Technology on the way to practical applications. In: Proceedings of "The 4th European Conference on Wood Modification 2009". Stockholm, Sweden. 3–11.
- Millet, M.A., Gerhards, C.C. (1972). Accelerated ageing: residual weight and flexural properties of wood heated in air at 115°C to 175°C. Wood Sci. 4:193–201.
- Mittal, A., Chatterjee, S.J., Scott, G.M., Amidon, T.E. (2009) Modelling xylan solubilisation during autohydrolysis of sugar Maple wood meal: reaction kinetics, Holzforschung 63:307–314.
- Morsing, N. Densification of Wood: The Influence of Hygrothermal Treatment on Compression of Beech Perpendicular to the Grain, PhD thesis, Technical University of Denmark, 2000.
- Nabarlatz, D., Farriol, X., Montane, D. (2004), Kinetic modelling of the autohydrolysis of Lignocellulosic Biomass for the production of hemicellulose derived oligosaccharides. Ind. Eng. Chem. Res. 43:4124–4131.
- Navi, P., Huguenin, P., Girardet, F. (1997) Development of syntheticfree plasticized wood by thermohygromechanical treatment. In: Proceedings of the Use of Recycled Wood and Paper in Building Applications Conference. Forest Prod. Soc. No. 7286, Madison, Wisc. 168–171.
- Navi, P., Girardet. F. (2000) Effect of thermo-hydro-mechanical treatment on the structure and properties of wood. Holzforschung 54:287–293.
- Navi, P., Girardet, F. Heger, F. (2000) Thermo-hydro-mechanical post-treatment of densified wood. In: Proceedings of 5th Pacific Rim Bio-Based Composites Symposium Canberra, Australia. pp. 439–447.
- Navi, P., Heger, F. Comportement thermo-hydromécanique du bois. (Behavior of thermo-hydro-mechanical wood). Presses Polytechniques et Universitaires Romandes, Lausanne, 2005.
- Navi, P., Sandberg, D. Thermo-Hydro-Mechanical Processing of Wood. EPFL Press, Lausanne Switzerland, Distributed by CRC Press, 2012.
- Norimoto, M., Ota, C., Akitsu, H., Yamada, T. (1993) Permanent fixation of bending deformation in wood by heat treatment. Wood Research: Bulletin of the Wood Research Institute Kyoto University. 79:23–33.
- Pelaez-Samaniego, M.R., Yadama, V., Lowell, E., Espinoza-Herrera, R. (2013) A review of wood thermal pretreatments to improve wood composite properties. Wood Sci. Technol. 47:1285–1319.
- Popescu, MC, Froidevaux, J, Navi, P. (2013) Structural modifications of *Tilia cordata* wood during heat treatment investigated by FT-IR and 2D IR correlation spectroscopy. J. Mol. Struct. 1033:176–186.
- Rivers, S., Umney, N. (2005). Conservation of Furniture. Butterworth-Heinemman, Oxford, 2005.
- Rowell, R.M., Ibach, E., McSweeny, J., Nilsson, T. (2009). Understanding decay resistance, dimensional stability and strength changes in heat treated and acetylated wood. In: Proceedings of "The 4th European Conference on Wood Modification 2009". Stockholm, Sweden. 489–502.
- Salmén, N.L. Temperature and Water Induced Softening Behavior of Wood Fiber Based Materials. PhD thesis, Royal Institute of Technology, KTH, Stockholm, 1982.
- Salmén, N.L., Burgert, I. (2009) Cell wall features with regard to mechanical performance. A review. COST Action E35 2004–2008: wood machining – micromechanics and fracture. Holzforschung 63:121–129.
- Stevanic, J.S., Salmén, L. (2009) Orientation of the wood polymers in the cell wall of spruce wood fibres. Holzforschung 63:497–503.
- Sandberg, D., Haller, P., Navi, P. (2013) Thermo-hydro and thermohydro-mechanical wood processing: An opportunity for future environmentally friendly wood products. Wood Mat. Sci. Eng. 8:64–88.
- Sandermann, W., Rothkam, M. (1959) Über die Bestimmung der pH-Werte von Handelshölzern und deren Beteudung für die Praxis. Holz Roh Werkst. 17:433–440.
- Seborg, R.M., Millet, M.A., Stamm, A.J. (1945) Heat stablized compressed wood: Staypack. Mech. Eng. 67:25–31.
- Springer, E.L. (1966) Hydrolysis of Aspenwood xylan with aqueous solutions of hydrochloric acid. Tappi 49:102–106.
- Stamm, A.J., Seborg, R.M. (1941) Resin-treated, laminated, compressed wood. Trans. Am. Inst. Chem. Eng. 37:385–398.
- Stamm, A.J., Burr, H.K., Kline, A.A. (1946) Staywood. Heat stabilized wood. Ind. Eng. Chem. 38:630–634.
- Sweeton, F.H., Mesmer, R.E., Baes, C.F., (1974). Activity measurements at elevated temperatures. VII. Dissociation of water. J. Solution Chem. 3:191–214.
- Takahashi, K., Morooka, T., Norimoto, M. (1998). Thermal softening of wet wood in the temperature range of 200°C. Wood Research 85:78–80.
- Tanahashi, M., Kyomori, K., Shigematsu, M., Onwona-Agyeman S. (2001) Development of compressive molding process of wood by high-pressure steam and mechanism of permanent fixation for transformed shape. In: Processing of First International Conference of the European Society for Wood Mechanics, Ed. Navi, P., Lausanne, Switzerland, pp. 523–524.
- Van Niekerk, J., Pizzi, A. (1994). Characteristic industrial technology for exterior Eucalyptus particleboard. Holz Roh- Werkst. 52:109–112.
- Verma, M. P. (2003) A thermodynamic assessment of dissociation of water. In: Proceedings, of Twenty-Eighth Workshop on Geothermal Reservoir Engineering. Stanford University, Stanford, California, January 27–29. SGP – TR-173.
- Vorreiter, L. (1942). Gehärtete und mit Metall oder Öl getränkte Hölzer. Holz Roh-Werkst 5:59–69.
- Welzbacher, C.R., Wehsener, J., Rapp. A.O., Haller, P. (2008) Thermo-mechanical densification combined with thermal modification of Norway spruce (*Picea abies* Karst) in industrial scale – dimensional stability and durability aspects. Holz Roh-Werkst 66:39–49.
- Windeisen, E., Bächle, H., Zimmer, B., Wegener, G. (2009) Relations between chemical changes and mechanical properties of thermally treated wood 10th EWLP, Stockholm, Sweden, August 25–28, 2008. Holzforschung 63:773–778.