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Recovery of Thermally Compressed Scots Pine (*Pinus sylvestris* L.) Wood

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Heartwood and sapwood samples of Scots pine were subjected to densification and thermal compression (180 °C to 220 °C) using a hot press, and their recovery behaviors and the involved mechanisms were investigated. Compressed wood (CW) showed poor recovery after water uptake. This deformation effectively was fixed by the subsequent high temperature treatment. To explain the phenomenon, the sorption properties of wood before and after modification by the adsorption isotherms were evaluated. The model of Hailwood and Horrobin gave the changes of the monolayer and multilayer sorption of each group samples and the relationship with wood deformation. By analyzing hygroscopic hysteresis, it was found that the removed elastic components from wood under elevated temperature had an inescapable impact on hysteresis ratio and recovery, even if it was not the only cause. In other words, the modified wood's plasticity was responsible for its recovery.

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INTRODUCTION

Light lumber has some undesirable qualities, such as poor mechanical properties and weak decay resistance, despite the natural environmental characteristics. However, the physico-mechanical properties of wood depend closely on density, and many techniques of modification have been proposed to increase the density. Wood densification is commonly obtained using a hot-press device. After densification, wood exhibits enhanced mechanical properties and high density owing to a decrease in volume (Blomberg and Persson 2007; Kutnar *et al.* 2008; Belt *et al.* 2013).

Because of the environmentally friendly nature of the compression process, compressed wood (CW) is used extensively in the furniture and construction industries. However, CW exhibits poor recovery properties after absorbing water (Fang *et al.* 2012; Li *et al.* 2012; Laine *et al.* 2013; Popescu *et al.* 2014a). To prevent the deformation of CW after water uptake, researchers have suggested heating it at high temperatures in varying atmospheres (Welzbacher *et al.* 2008; Avila *et al.* 2012; Hill *et al.* 2012; Cai *et al.* 2013; Rautkari *et al.* 2013). This heat-treatment method hinders the deformation of CW. However, the underlying mechanism responsible for the recovery of the densified wood after heat treatment remains unknown.

It has been suggested that the wood microfibers are rearranged by the heat treatment (Tieman 1920). In addition, it is believed that the hemicelluloses in the wood are hydrolyzed at high temperatures to furfural, which may undergo chemical reactions, resulting in decreased hygroscopicity of the wood (Stamm 1964; Kuriyama 1967;

Funaoka *et al.* 1990). Because of the chemical reactions that occur during the heat treatment, amorphous components are produced in the wood (Stamm and Hansen 1937; Obataya *et al.* 2000). The flow of lignin at the high temperature may then result in the relaxation of the CW (Stamm 1964). Finally, the high-temperature treatment enables the formation of cross-links in the wood, as well as the crystallization of cellulose (Inoue and Norimoto 1991; Dwianto *et al.* 1997). Yet, the full details of the mechanism remain unknown.

In this study, the deformation of thermally compressed wood (TCW) was investigated using its water sorption behavior. Several theories have been proposed to explain water sorption in polymers (Skaar 1988). The Langmuir theory is a classic theory that explains monolayer sorption at low relative humidity (RH) levels. It can be used to explain the water vapor sorption behavior of polymers such as cotton, wood, and cellulose (Babbitt 1942). However, it does not explain sorption properties at high RH levels. Brunauer *et al.* (1938) proposed a theory, called the BET theory, to explain sorption in polymolecular layers, stating that the sorption process consists of primary sorption and secondary sorption.

Although the BET model is regarded as a more complete model, it is not applicable to polymers, because the BET equation is only applied at RH levels below 40%. Subsequently, Dent (1977) extended the original BET model and obtained a parabolic function in keeping with the Hailwood and Horrobin (H-H) model. However, the model from Hailwood and Horrobin (1946) assumes that the absorbing polymer is an ideal solution consisting of hydrated water, dissolved water, and the polymer itself. This model is used extensively to describe the sorption characteristics of wood and textiles. Likewise, a theory based on the formation of water clusters has also been proposed to explain water sorption in polymers (Hartley *et al.* 1992), which is similar to water condensation in capillaries under high RH conditions.

The sorption behavior of wood depends on the parts of the trunk (*i.e.*, heartwood, sapwood, earlywood, and latewood), as well as on the species. Such sorption is important because timber is a porous material and always exhibits anisotropic properties. It has been reported that there is a marked difference between the sorption properties of mature and juvenile wood (Majka and Olek 2008). Wangaard and Granados (1967) confirmed that the extractives deposited on the inner surfaces of the wood cell walls largely determine the dissolved water content using the H-H model. Therefore, the moisture content related to monolayer sorption remains constant, regardless of whether the wood sample in question has been subjected to extraction or not.

The chemical modification of wood also increases its dimensional stability, because of the corresponding decrease in the number of accessible OH groups (Chauhan *et al.* 2001; Papadopoulos and Hill 2003; Xie *et al.* 2011; Popescu *et al.* 2014b). A similar phenomenon has been observed in thermally modified wood (Hill *et al.* 2012; Murata *et al.* 2013). However, there have been few studies on the effects of thermal compression on the fixed deformation of wood.

In order to elucidate the mechanism responsible for the reduced deformation of TCW, this study investigated the relationship between the deformation behavior of wood and its water content through recovery tests and water sorption measurements. A dynamic vapor sorption (DVS) apparatus was used for the tests. The device could accurately obtain data in real time in short intervals by automatically controlling the RH level. The measured sorption isotherms are discussed based on the H-H theory.

EXPERIMENTAL

Sample Preparation

Wood samples with dimensions of 30 mm (radial) × 150 mm (tangential) × 450 mm (longitudinal) were cut from the heartwood and sapwood of Scots pine (*Pinus sylvestris* L.) from Russia. The dried densities of the heartwood and sapwood were 0.4188 ± 0.0077 g/cm^3 and 0.4669 ± 0.0091 g/cm^3, respectively. In order to ensure the same moisture content (30%), the samples were placed in a conditioning chamber for a month. The conditioned wood samples were then subjected to densification and thermal compression. Some of the samples were used as controls.

Compression and Thermal Compression Processes

As shown in Fig. 1, the samples were compressed in the radial direction to a thickness of 18 mm using a hot press, in accordance with the methods of Li *et al.* (2016). The holding time was 1 h, and the temperature was 160 °C. The final thickness of the samples depended on a position-control process and not the commonly used pressure-based procedure. The pressure was then released, and the samples were cooled. In this manner, CW specimens with mean densities of 0.7783 g/cm^3 and 0.7602 g/cm^3 were obtained from the heartwood and sapwood, respectively.
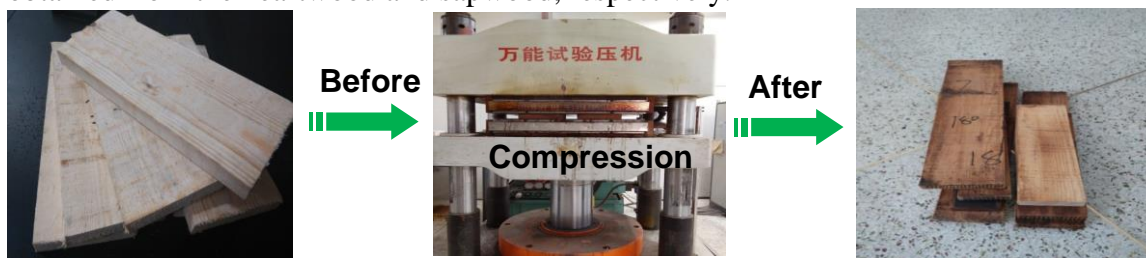

Fig. 1. Hot-pressing diagram of heartwood and sapwood samples

Compressed heartwood and sapwood samples were heat-treated at 180 °C, 200 °C, or 220 °C for 3 h using the hot press. The density in the compressed heartwood varied from 0.7509 g/cm^3 to 0.7268 g/cm^3 with increasing temperature. The density of the sapwood decreased from 0.7267 g/cm^3 to 0.6465 g/cm^3. This process yielded the TCW samples (see Fig. 1). The experimental conditions for the sapwood and heartwood are given in Table 1.

Table 1. Hot-Pressing Conditions of Heartwood and Sapwood Samples

Specimen Groups		Duration (h)	Temperature (°C)
Heartwood	1 (Control)		
	2 (CW)	1	160
	3	3	180
	4	3	200
	5	3	220
Sapwood	6 (Control)		
	7 (CW)	1	160
	8	3	180
	9	3	200
	10	3	220

Compression Recovery of Heartwood and Sapwood in the Radial Direction

Five wood blocks with dimensions of 18 mm (radial) × 20 mm (tangential) × 20 mm (longitudinal) were cut from each treated and untreated wood specimen. Thus, the number of wood blocks in each group was 15. The initial samples were dried, and their masses and thicknesses were measured using an electronic balance and a Vernier caliper. Subsequently, the blocks were immersed in distilled water for 48 h at room temperature, and their masses and thicknesses were recorded every 24 h. The samples were then dried for 24 h at 100 °C, and the masses and thicknesses were recorded again. Thus, the immersion and drying of the wood blocks were performed over 3 days. Five immersion-drying cycles were carried out over 15 days. The recovery of each specimen was calculated using the following equation,

$$R = \frac{L_1 - L_0}{L_0} \times 100\% \tag{1}$$

where R is the swelling rate along the thickness direction (%), L_0 is the thickness of the dried wood sample (mm), and L_1 is the thickness of the wood sample after water immersion for 1 day (mm).

The weight gain rate of each specimen was calculated using the following equation,

$$W = \frac{W_1 - W_0}{W_0} \times 100\% \tag{2}$$

where W is the weight gain rate (%), W_1 is the weight of the dried wood sample (g), and W_0 is the weight of the wood sample after water immersion for 1 day (g).

Hygroscopicity Measurements

A micro mill was used to grind the untreated and treated heartwood and sapwood samples into 100-mesh powders. The dried wood flour samples were tested using a DVS (dynamic vapor sorption) device (3H-2000PW, Beijing, China). The device consisted of a vacuum chamber, an electric microbalance, a multi-sample conversion system, and a temperature sensor. It could simultaneously measure four specimens, with a precision of 0.1 µg and a weight range of 10 mg to 1000 mg. In this study, 50-mg samples of the wood powders were tested. A mixture of nitrogen gas and water vapor was made to flow through the vacuum chamber, in order to maintain the RH level. Based on a preset sequence, the RH was increased from 0% to 90% in intervals of 10%, and then decreased to 10% in intervals of 10%. The water vapor sorption and desorption processes were performed at a steady temperature of 25 ± 0.5 °C. The instrument was kept at a constant RH until the change in the sample mass was less than 0.1 mg for a 60-min period.

Hailwood and Horrobin Model

In general, the sorption model proposed by Hailwood and Horrobin (1946) describes the sigmoid type II sorption isotherms of textile materials. In this study, we chose the single hydrate model to explain the sorption principle of wood samples. This model can be expressed as follows,

$$M = M_{\mathrm{h}} + M_{\mathrm{s}} = \frac{1800}{W}\left(\frac{K_1 K_2 \mathrm{RH}}{100 + K_1 K_2 \mathrm{RH}}\right) + \frac{1800}{W}\left(\frac{K_2 \mathrm{RH}}{100 - K_2 \mathrm{RH}}\right) \tag{3}$$

where M_h is the amount of hydrated water corresponding to monomolecular sorption (%); M_s is the amount of dissolved water corresponding to multimolecular sorption (%); M is the sum of the amount of water present because of primary sorption, M_h, and the amount of water present because of secondary sorption, M_s (%); K_1 is the equilibrium constant for the dissolved water and hydrated water in the dry cell wall; K_2 is the equilibrium constant for the atmospheric vapor pressure and the dissolved water; W is defined as the mass of dried wood per mole of sorption sites (g/mole); RH is the percent relative humidity (%).

Equation 3 can also be written as follows,

$$\frac{\text{RH}}{M} = \frac{W}{18}\left[\frac{1}{K_2(K_1+1)}\right] + \frac{W(K_1-1)\text{RH}}{1800(K_1+1)} - \frac{W}{180,000}\left(\frac{K_1K_2\text{RH}^2}{K_1+1}\right) \tag{4}$$

or,

$$\frac{\text{RH}}{M} = A + B\text{RH} - C\text{RH}^2 \tag{5}$$

$$A = \frac{W}{18}\left[\frac{1}{K_2(K_1+1)}\right]; \quad B = \frac{W(K_1-1)}{1800(K_1+1)}; \quad C = \frac{W}{180,000}\left(\frac{K_1K_2}{K_1+1}\right) \tag{6}$$

RESULTS AND DISCUSSION

Analysis of Deformation Recovery of Treated Heartwood and Sapwood

As shown in Fig. 2(a), the recovery percentage of the sapwood samples after five cycles ranged from 9.46% to 55.41%, while that of the heartwood samples ranged from 9.45% to 31.1%. The swelling extent of compressed sapwood increased from 33.6% to 55.4% after water uptake, while the value of the compressed heartwood varied from 17.2% to 29.6%.
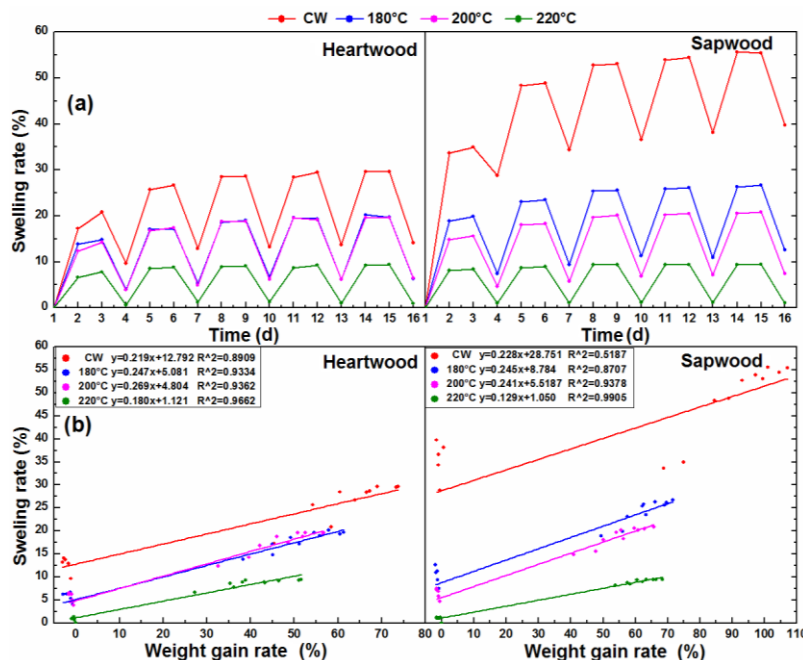
Fig. 2. Recovery of heartwood and sapwood under various conditions: (a) swelling extents, (b) relationships between swelling rates and weight gain rates.

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Since the heartwood of pine species contains a large amount of extractives in the resin canals and the cell walls, these extractives occupy most of the empty space within the cell walls and prevent water from being absorbed, in contrast to sapwood. After heat treatment, both sapwood and heartwood exhibited decreased recovery rates, ranging from 9% to 26%. Additionally, their recovery percentages were similar for all the treatment temperatures, with the exception of 180 °C. The compressed wood samples heated to 220 °C for 3 h showed the lowest recovery percentages. Therefore, it can be concluded that the heat treatment was an effective technique in limiting the deformation of the CW samples. The more severe the thermal treatment was, the lower the recovery of the heat-compressed samples was. Previous studies have suggested that this result could be due to some residual stress remaining in the wood after compression, with the heat treatment facilitating stress relaxation within the compressed wood (Cheng *et al.* 2008).

Figure 2(b) shows the positive linear relationship between the swelling rate and the weight gain rate caused by injecting water for each type of specimen. This result indicated that the increased swelling of the wood samples in the compression direction was more or less caused by the increasing water. Combined with the phenomenon in Fig. 2(a), this result indicates that the radial recovery of compressed wood may be caused by the interaction of the residual stress and the moisture swelling.

It has been observed that compressed wood deforms in the direction of compression, with residual stress maintaining the change in structure after the pressure is removed, as described in the literature (Li 2001; He 2002). It should also be noted that elastic deformation is recoverable, while plastic deformation is irreversible. The permanent deformation of wood is mainly caused by deformation of the plastic component (Cheng 1985). Based on this fact, it was extrapolated that the unstable residual stress may primarily remain in the elastic zone of CW, and give rise to recovery. Under the condition of a dried atmosphere, this kind of residual stress temporarily restricts the deformation of the elastic component. Inversely, water molecules, as a "swelling agent," can enable the wooden cell walls to swell and disrupt the temporary deformation balance inside the CW during intruding water. This phenomenon further contributes to the release of unstable residual stress stored in the CW. Thus, water molecules seem to function as the "activator," and are an imperative factor in the recovery of compressed wood.

However, radial compression led to the closure of the tracheid lumen in pine. That closure shortened the distances between cellulose-microfibril molecular chains, and some weak intermolecular hydrogen bonds were formed. When the wood absorbed a sufficient amount of water, the water molecules broke the unstable intermolecular hydrogen bonds, and formed new hydrogen bonds among water molecules and the molecules of the cellulose-microfibrils (Skaar 1972). Because of water intrusion, the bonding energy from cellulose-microfibril molecular chains would be released, which seems to be consistent with residual stress. This concept, when played out on the macro scale, further accounts for the corresponding radial swelling of compressed wood.

The recovery of CW, with and without the subsequent heat treatment, is mainly in connection with the following points. On the macro scale, wood elasticity decreased as temperature increased. Its recovery is mainly derived from the residual stress left in the elastic zone. Thus, as the elastic substances of thermally compressed wood decrease, the smaller the remaining residual stress and recovery become. On the micro scale, with increasing temperature, the elastic cellulose and hemicellulose of wooden cell walls increasingly degrade (Li *et al.* 2016). This degradation leads to the decrement of

hydrophilic groups and hydrogen bonds among cellulose-microfibril molecular chains, accompanied by the fall of responding residual stress. Consequently, the recovery of heat-treated wood samples remarkably decreased compared to compressed wood.

Analysis of Hygroscopicity of Untreated and Treated Heartwood and Sapwood

As shown in Fig. 3(a), the moisture contents of the sapwood and heartwood samples decreased more sharply with increasing temperature than those of the control and CW samples. Overall, the sorption capacity of every sapwood group was greater than that of the corresponding heartwood group. However, the sapwood and heartwood had approximately the same moisture contents of 25% and 12% in the control and TCW samples, respectively, when treated at 220 °C.
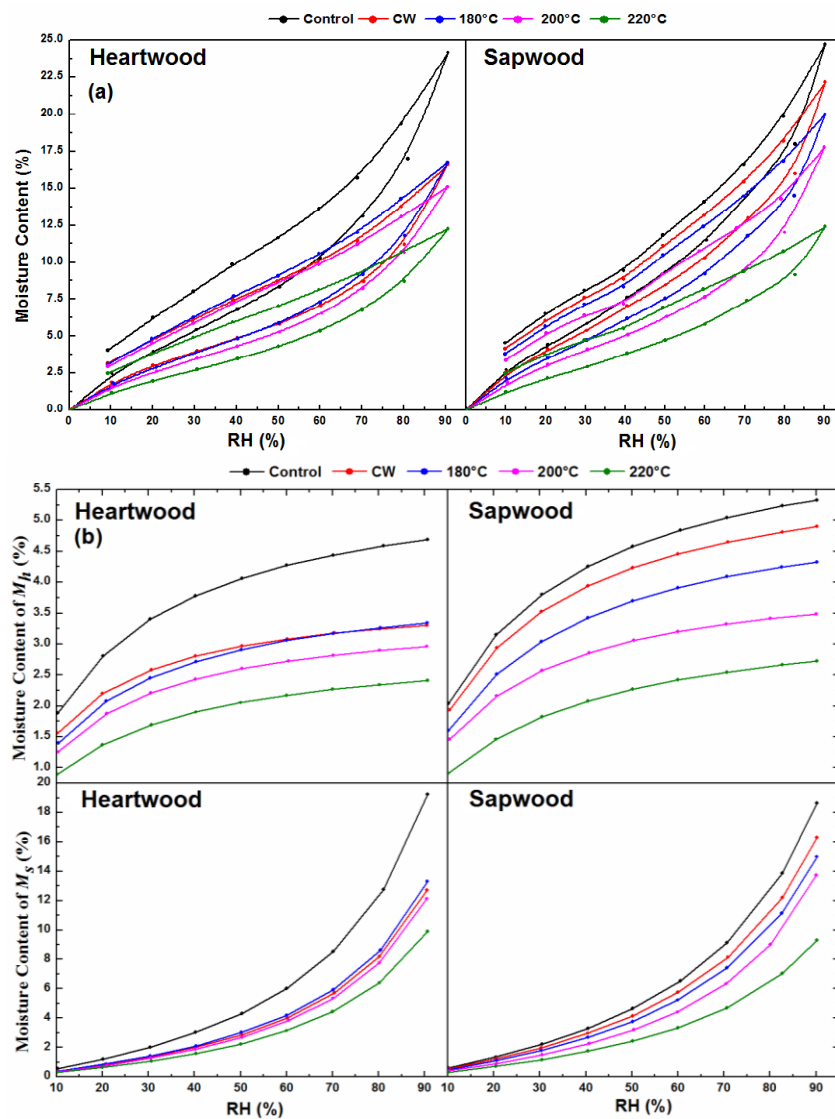
Fig. 3. Sorption properties of heartwood and sapwood under various conditions: (a) the measured moisture contents, (b) the M_h and M_s values

These results are in agreement with the conclusion that the thermal modification of CW reduces its hydrophilicity and improves its dimensional stability (Fang *et al.* 2011; Cai *et al.* 2013; Candan *et al.* 2013; Xing *et al.* 2016).

To understand the above-described phenomenon, a theory of the H-H model was employed to fit the measured data. Origin 8.0 software (OriginLab, Hampton, America) was used to obtain the regression function for the ratio of the relative humidity to the moisture content (*RH*/*M*) and the relative humidity (*RH*), as shown in Eq. 5. The R^2 values, which indicate the strength of fit, for sapwood and heartwood were approximately 0.94 and 0.99, respectively (Table 2), confirming that the model was a suitable one. The values of parameters *A*, *B*, and *C* were obtained separately using fitting functions. The values of constants K_1, K_2, *W* were calculated using Eq. 6 (Table 2). Finally, the amounts of hydrated water, M_h, dissolved water, M_d, and total water, *M*, were also calculated. The differences between the predicted *M* values and the measured *M* values at RH 90% were almost negligible (Table 2).

Table 2. Parameters of Heartwood and Sapwood under Various Conditions as Obtained using the H-H Model

Groups		*A*	*B*	*C* (×10⁻³)	K_1	K_2	R_2	M_1 (%)	$M_{predicted}$ (%)	$M_{measured}$ (%)
Heart-wood	1	3.133	0.119	1.237	5.492	0.848	0.995	5.80	23.93	24.18
	2	3.457	0.201	1.952	7.857	0.848	0.986	3.85	16.02	16.56
	3	4.239	0.173	1.763	5.829	0.845	0.996	4.09	16.66	16.74
	4	4.597	0.200	2.041	6.101	0.853	0.997	3.59	15.09	15.09
	5	6.711	0.212	2.262	4.751	0.842	0.997	3.08	12.32	12.26
Sap-wood	6	2.912	0.102	1.023	5.280	0.816	0.941	6.70	23.97	24.71
	7	3.098	0.113	1.116	5.544	0.806	0.941	6.12	21.19	22.14
	8	3.730	0.121	1.225	4.997	0.811	0.941	5.51	19.32	19.98
	9	4.015	0.166	1.698	5.889	0.847	0.985	4.27	17.22	17.78
	10	6.734	0.167	1.757	4.115	0.796	0.947	3.65	12.01	12.39

The term 1800/*W* has been denoted as the moisture water, M_1, which represents the ratio of the weight of water per mole of water in the wood, 1800, to the weight of dried wood per mole of adsorption sites (Skaar 1972). The M_1 values of heartwood and sapwood decreased markedly during the sorption of water vapor moving from the control samples to the CW samples, and then to the TCW samples (Table 2). Additionally, the number of sorption sites for each heartwood group was smaller than that for the corresponding sapwood group. This difference can be explained by the higher extractive content in the heartwood. Compared with untreated heartwood, the number of sorption sites of CW samples decreased by 33.6%, and the number of sorption sites of TCW samples treated at 180 °C, 200 °C, and 220 °C decreased by 29.5%, 38.1%, and 46.9%, respectively. Similarly, compared with the untreated sapwood, the number of sorption sites of CW sapwood samples decreased by 8.7%, and the number of sorption sites of TCW samples treated at 180 °C, 200 °C, and 220 °C decreased by 17.7%, 36.3%, and 45.6%, respectively (Fig. 4). The reduction in the number of sorption sites in the CW sample relates to an increase in the overlap of cell walls caused by compression. However, the intermolecular forces of water vapor are well below those of the aforementioned cellulose-microfibril molecular chains, so water vapor would diffuse to the exposed sorption sites rather than the covered sorption sites. Therefore, the measured sorption sites are lower than the true values in CW by the H-H model. Hot-pressing

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temperature also leads to a slight reduction in the number of sorption sites of CW because of the slight decomposition in hemicelluloses, and the rupturing of some of the hydrogen bonds under pressure. The M_1 value of the heartwood CW samples was lower than that of the corresponding sapwood samples. This result may be attributed to differences in hemicellulose content, as the hemicellulose content in heartwood CW was significantly less than that in sapwood CW. Engelund *et al.* (2013) reported that, for all the components of wood, the hemicelluloses contain the most sorption sites, followed by cellulose and lignin. The high percentage of hemicellulose enables the cell wall of sapwood CW to possess higher elasticity. This high elasticity can help delay the compressive deformation and prevent the cleavage of the chemisorption bonds. Conversely, heartwood, which is more mature, is much stiffer. As a result, hydrogen bonds readily rupture in heartwood during compression. These results also indicated that the heartwood and sapwood TCW samples that were exposed to higher temperatures contained fewer accessible sorption sites (Fig. 4). Their densities (listed in the Experimental section) present a significant reduction compared with the CW specimens. This finding is consistent with previous studies, as the heat treatment of wood primarily results in the degradation of the hemicelluloses and celluloses, and the formation of cross-links in the lignin phase (Brito *et al.* 2008; Esteves *et al.* 2008; Li *et al.* 2015, 2016). As depicted in Fig. 4, the decomposition of the hemicelluloses promotes the removal of sorption sites, which results in a decrease in the moisture content, M_1. Thus, the temperature of a heat treatment has a significant effect on the water adsorption and elasticity of the wood.
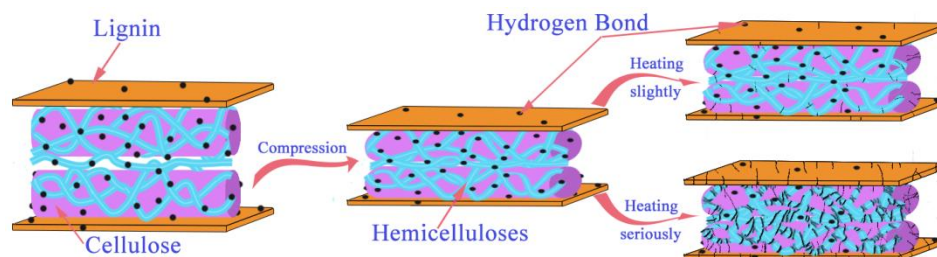
Fig. 4. Schematic of the changes in the chemical composition of wood after compression and thermal treatment

Based on the H-H model, the amounts of the hydrated water, M_h, and dissolved water, M_s, were plotted separately as functions of RH in Fig. 3(b). Skaar (1988) reported that the curve for M_h could be considered a type I curve, as per the IUPAC classification system, and is indicative of primary monolayer sorption, while the curve of M_s is a type III curve and represents secondary multilayer sorption. Generally, monolayer sorption is characterized by a rapid increase in the sorption degree at low RH levels, while rapid sorption caused by multimolecular adsorption occurs at high RH levels. In this study, monolayer sorption was observed at RH levels of 10% to 30%, while multilayer sorption was observed at RH levels of 70% to 90% (Fig. 3(b)).

The measured hydrated water content, M_h, of the Scots pine samples under various conditions reached a plateau of 2.4% to 5.32% at RH 90%, while the dissolved water content, M_s, was 9.2% to 19.2%. This result indicated that multilayer sorption was the primary determinant of the moisture content of the wood samples. Likewise, as the heat treatment progressed, the curves for the M_h and M_s values of the heartwood and sapwood samples exhibited similar variations, as shown in the curve for M in Fig. 3(a).

Furthermore, multimolecular sorption in the sapwood samples was markedly greater than that in the corresponding heartwood samples under the same conditions, where the higher extractives content in the heartwood covered more hydrophilic sites (Hill *et al.* 2012). However, compared with untreated specimens, the decrease in the M_h and M_s values of the compressed sapwood samples was pronouncedly less than that observed in the heartwood samples. As mentioned above, this may be because of the different elastic substances within the compressed sapwood samples and the compressed heartwood samples. With increasing temperature, the M_h value of the treated sample principally depended on the density or degraded elastic hemicelluloses and celluloses, as did the M_s value (Hill *et al.* 2012). The lower the density is, the less elastic the components are, and the fewer the sorption sites become, impairing the hydrophilicity of the samples. On the other hand, the decrease of sorption sites seems to refer to the decline of the effect of water swelling on wood. Combined with the discussion in the above section, this result will be a hindrance to the recovery of treated heartwood and sapwood.

Thus, it can be concluded that the sorption capacity and recovery behavior of the treated samples were primarily determined by the numbers of primary and secondary sorption sites, as well as the elastic components of the wood.

Analysis of Hysteresis Ratio of Wood

The hysteresis ratio is defined in Eq. 7,

$$(\text{EMC}_{\text{desorption}} - \text{EMC}_{\text{adsorption}}) \times 100 / \text{EMC}_{\text{adsorption}} \tag{7}$$

where EMC is the equilibrium moisture content at the same RH level (Jalaludin *et al.* 2010).

Several theories have been proposed to explain the phenomenon of sorption hysteresis in wood. It has been attributed to the presence of "ink bottle" pores, incomplete wetting, and accessible sorption sites (Time 1998). Brakas (1942) investigated the essential difference in sorption hysteresis between an elastic gel and anisotropic wood during adsorbing water, and confirmed that the plasticity of wood plays a significant role in the phenomenon. He stated that the elastic gel does not show hysteresis, whereas viscoelastic wood shows hysteresis, as a result of its plastic portion. On this basis, Skaar (1988) modeled wood as a hydrophilic spring. When wood adsorbs water, the water within the wood cell walls exerts pressure on the cell walls. This pressure results in swelling stress, and it causes the wood to swell on a macroscopic scale. If wood is assumed to be a perfect elastic spring, it will recover fully from the deformation without any heat loss once the pressure has been released, in a manner similar to that of a spring (Fig. 5(b)). In reality, however, some of the energy produced by the stress is lost as a result of the damping of the plastic polymer molecules, which results in the incomplete recovery of the material (Fig. 5(b)). By that analogy, during desorption, some fraction of the adsorbed water within the wood remains in the plastic zone, which causes the moisture content of the wood at the same RH level to increase after desorption (Fig. 5(b)). Conversely, the adsorbed water in the elastic region is easily removed from the wood. In contrast to previous views, this new perspective suggests that wood plasticity is largely responsible for its hysteresis (Fig. 5(a)).

The heartwood and sapwood both became increasingly stiff when subjected to thermal compression because of the degradation of the elastic hemicellulose and cellulose in the wood at high temperatures (Boonstra and Tjeerdsma 2006; Poletto *et al.* 2012;

Giudicianni *et al.* 2013). Their hysteresis ratios increased with increasing temperature, as compared to those of the untreated wood (Fig. 5(a)).
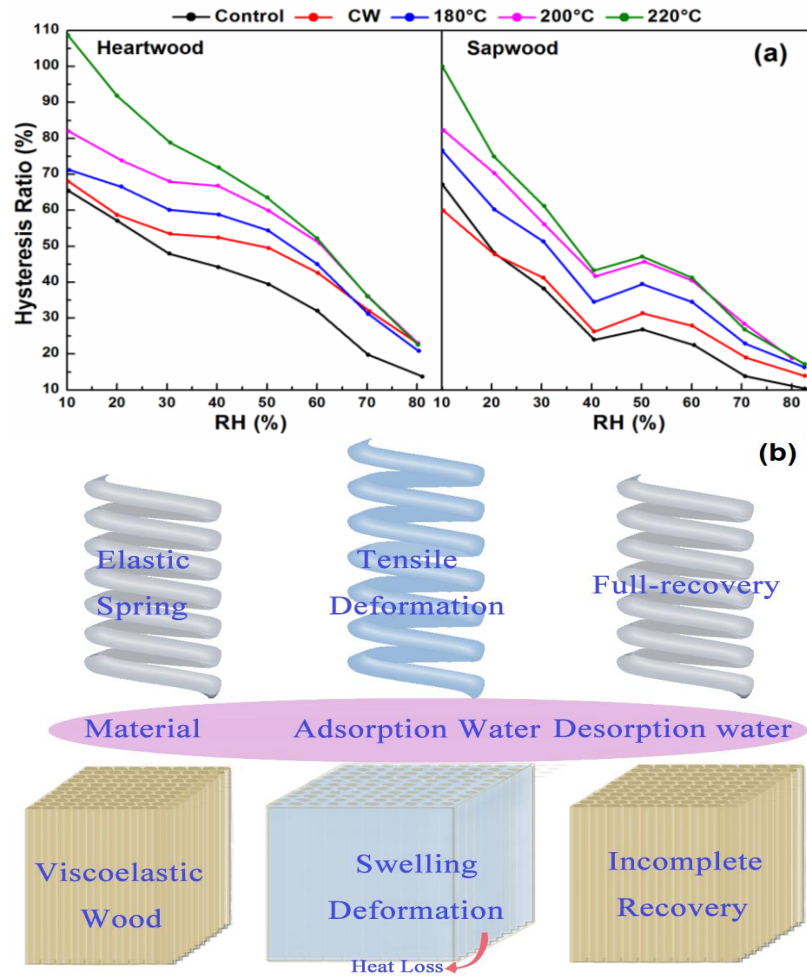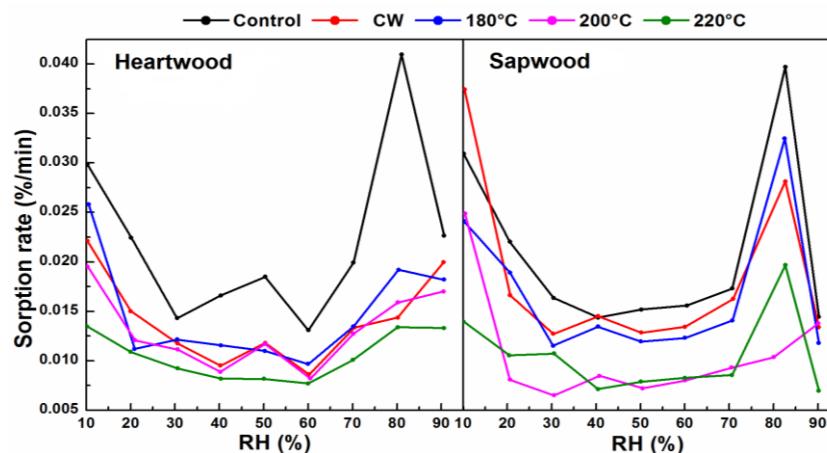

Fig. 5. Hysteresis of heartwood and sapwood under various conditions: (a) the hysteresis ratio, (b) a diagram of the hysteresis phenomenon

Thus, the stiffer a wood sample was, the greater its hysteresis ratio was. Because of the higher elasticity, the hysteresis of the sapwood samples was always lower than that of the corresponding heartwood samples. In addition, the hysteresis ratios of specimens within the same group increased as RH level decreased. This result may have occurred because the plasticity of the wood samples resulted in an additional increase after desorption, compared to the original property during adsorption. More heat was lost during desorption as RH decreased. Therefore, for the same wood specimen, the hysteresis ratio is indicative of increased wood plasticity as it transitions from adsorption to desorption.

In the same manner, the enhanced plasticity of thermally compressed wood further limits its recovery, and develops its dimensional stability. In conclusion, compared with natural wood, the reduced elasticity of treated wood has an inescapable impact on hysteresis ratio and recovery, even if not the only cause.

Sorption Rates of Wood Samples

The average sorption rate is termed as the change in EMC in response to the RH change, divided by the time spent in obtaining the new EMC. The average sorption rate of each sapwood group was generally greater than that of the corresponding heartwood group (Fig. 6). The sorption rates of the samples could be divided into three zones, based on the RH level. For RH levels lower than 30%, the sorption rates of the heartwood and sapwood samples decreased rapidly. This phenomenon can be attributed to a decrease in the remaining accessible sites for monolayer sorption with the increase in RH level. With increasing temperature, the values of the TCW samples showed a downward trend, resulting from a decrease in the number of accessible sorption sites in the degradable components. The sorption rates of the heartwood samples decreased for RH levels between 30% and 60%, and then increased sharply for RH levels higher than 60%. The sorption rates of the sapwood samples underwent negligible changes for RH levels of 30% to 70%, and then increased with higher RH levels. This result may have occurred because multimolecular sorption was dominant at these RH levels. A greater number of secondary sites and empty spaces were exposed because of the swelling of the wood cell walls. The adsorbed water molecules formed larger clusters in one secondary site, resulting in capillary condensation (Hartley *et al.* 1992). Hence, this region contained more free spaces, as well as large water clusters.

Fig. 6. Average sorption rates of heartwood and sapwood under various conditions

In short, the changes in the sorption rates of the heartwood and sapwood samples were probably related to the primary and secondary sorption sites within the wood cell walls.

CONCLUSIONS

1. After heat treatment, wood swelling extent decreased noticeably, because of the degraded elastic cellulose and hemicellulose of wooden cell walls. This promoted the release of residual stress in elastic zone.

2. Water sorption characteristics indicated that the higher plasticity and decreased number of sorption sites of TCW limited its swelling, and confirmed that the

plasticity of wood was a primary factor in recovery behavior. Thus, the heartwood groups exhibited lower recovery and sorption properties than the sapwood groups because of the lower inherent hygroscopic sites and elasticity in heartwood. The sorption rates of the heartwood and sapwood samples depended on the primary sites and the secondary sorption sites.

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