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Linear viscoelasticity of hot-pressed hybrid poplar relates to densification and to the in situ molecular parameters of cellulose

Isabela Reiniati · Noridah B. Osman · Armando G. Mc Donald · Marie-Pierre Laborie

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Abstract

• **Key message** Hot pressing leads to changes in wood water sorption properties, linear viscoelastic behavior, and chemistry. In hot-pressed hybrid poplar, storage modulus linearly correlates with cellulose apparent crystallinity index and degree of polymerization, revealing the impact of cellulose hydrolysis on wood viscoelasticity during hot pressing.

• **Context** Heat treatment and densification during hot pressing are known to alter wood chemical, physical, and viscoelastic properties. Interrelationships between these properties and their changes during hot pressing are, however, unknown. They are expected to play a significant role on mat consolidation during the manufacture of wood-based composites.

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Contribution of the co-authors I. Reiniati performed all experimental work concerning physical and viscoelastic properties and their interpretation and cowrote the manuscript. N. Osman performed all experiments on chemical analyses of cellulose and analyzed these data. A. Mc Donald supervised the work on chemical analysis and participated in data analysis and interpretation and cowrote the section on chemical analyses. M-P Laborie supervised the work on physico-viscoelastic analyses and participated in data interpretation and paper writing as well as coordinating the project. Armando McDonald and M.-P. Laborie conceived the project and designed the experiments to test the hypotheses.

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• **Aims** This study aims (1) to characterize the impact of hot pressing on the physical, viscoelastic, and chemical properties of hybrid-poplar wood and (2) to assess possible relationships between these properties.

• **Methods** Dry and moist wood samples were hot-pressed under various conditions of temperature. Specific gravity, water sorption isotherms, and dynamic viscoelastic properties of hot-pressed wood were measured together with cellulose apparent crystallinity and molecular weight. Possible relationships between these properties were assessed with statistical analyses.

• **Results** Wood specific gravity, sorption isotherm, dynamic moduli, and cellulose crystallinity were all affected by the hot-pressing conditions. The viscoelastic response of hot-pressed wood was found to relate not only to the extent of densification but also to in situ molecular properties of cellulose. Cellulose apparent crystallinity index and degree of polymerization in hot-pressed wood linearly correlated with storage modulus, revealing the importance of cellulose hydrolysis during hot pressing on wood viscoelastic response.

• **Conclusion** During hot pressing, wood cellulose hydrolysis appears to govern the viscoelastic response, in addition to wood densification.

Keywords Wood viscoelasticity · Specific properties · Wood polymer morphology · Hot pressing · Cellulose crystallinity · Cellulose depolymerization

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1 Introduction

In the wood industry, heat treatment has long been used to enhance various wood properties such as dimensional stability, density, and fungal resistance. Subjecting wood to high temperatures alters its chemistry as first evidenced by its weight loss (Kotilainen et al. 1999; Reinprecht et al. 1999; Hakkou et al. 2005a; Yildiz et al. 2005; Repellin and Guyonnet 2005; Boonstra et al. 2006). Kotilainen et al. (1999) investigated the changes in the chemical composition of Norway spruce and reported that mass loss was highly dependent on treatment temperature, with significant degradation occurring above 220 °C. Hemicelluloses, in particular galactoglucomannans and arabinoglucuronoxylans, were found to degrade first and to contribute most to wood mass loss (Tjeerdsma et al. 1998; Kotilainen et al. 1999, 2001). Navi and Heger (2004) reported the start of hemicellulose degradation with arabinose, galactose, mannose, and xylose at 180 and 200 °C in steamed, hot-pressed wood. Acetic acid, furfural, and formaldehyde form upon decomposition (Tjeerdsma et al. 1998). Thermal treatment affects lignin and cellulose as well. Osman et al. (2012, 2013) observed an increase in the dichloromethane extractive content (9 %) in hot-pressed poplar around 250 °C, which mainly comprised solubilized lignin. Reduction of lignin molecular weight was induced by lignin depolymerization. Tjeerdsma et al. (1998) hypothesized that heat treatment of wood enhances the demethoxylation of guaiacyl and syringyl units in lignin, thereby increasing the amount of reactive hydroxyl lignin sites. They also proposed that cross-linking of these free phenolic units with furfural compounds and acetic acid creates a more rigid structure around cellulose microfibrils, thereby hindering water penetration in the cell wall. This mechanism may be responsible for the improvement in the dimensional stability of heat-treated wood. Ito et al. (1998) postulated that semicrystalline cellulose is disturbed and damaged during compressive deformation, allowing the release of cellulose microfibrils' inner stress. Steam facilitates the rearrangement of the cellulose chains, which can form additional crystalline regions (Ito et al. 1998; Bhuyian et al. 2000). In addition, conformational changes in polysaccharides due to water desorption (Hakkou et al. 2005b) and crystallization of amorphous regions were proposed to increase the cellulose crystallinity (Akgül et al. 2007). Hydrolysis of amorphous cellulose has also been reported and results in higher crystallinity index of cellulose in hydrothermally treated wood (Silva et al. 2013; Xiao et al. 2014). As a result, heat-treated wood exhibits improved dimensional stability and decreased hygroscopicity; for example, heat-treated wood conditioned at 96 %

relative humidity experiences a moisture content decrease from 30 % to roughly 10 % but only a minor reduction of strength. However, depending on conditions, heat treatment of wood can increase or decrease mechanical properties. In general, heat treatment increases stiffness but reduces strength. Korkut et al. (2008) demonstrated that compression strength, bending strength, and modulus of elasticity are reduced by heat treatment above a certain temperature. Treating wood at 120 °C for 2 h does not significantly affect these properties.

During hot pressing, similar chemical changes might be expected and complicated by the combined action of pressure and densification. Indeed, compression can either fracture cell walls or allow viscoelastic and plastic deformation, depending on wood polymers' viscoelastic behavior under the compression conditions (Navi and Girardet 2000; Penneru et al. 2006). In particular, at high hot-pressing temperatures and wood moisture contents, densification of wood can intensify due to the higher deformability of wood polymers and higher level of cell wall fracture (Tabarsa and Chui 1997). Only one study reports on the chemical changes caused by hot pressing in conditions relevant to the manufacture of wood-based composites (Gardner et al. 1993). This study suggests that the increased mobility of wood amorphous polymers and the expansion of free volume above lignin glass transition temperature (T_g) allow the reorientation of the hydrophobic functionalities of amorphous polymers toward the surface. Enhanced crystallization of cellulose at temperatures near lignin T_g was also proposed (Gardner et al. 1993).

Overall, during hot pressing, heat-induced chemical, physical, and viscoelastic changes of wood all likely contribute to its response to hot pressing. However, little is known of the possible interdependences between chemical, physical, and viscoelastic changes during hot pressing. In particular, the impact of hot pressing on wood viscoelastic properties and the interrelationships between wood chemical changes and wood viscoelasticity, which are critical to mat consolidation, are not known. We hypothesize that changes in wood viscoelasticity might relate to changes in wood molecular structure. Hybrid poplars represent an alternative resource for wood-based composites and are well suited to shed light on such behavior, as they might be improved for composite manufacture.

2 Objectives

The overall goal of this work is to investigate the effect of hot-pressing conditions on the chemical, physical, and viscoelastic

properties of hybrid poplar wood. The specific objectives of this study are (1) to understand the impact and possible interactions of wood initial moisture content and hot-pressing temperature on wood morphology, specific gravity, and bending dynamic mechanical properties and (2) to unravel some of the molecular origins for changes in physical and viscoelastic properties.

3 Materials and methods

3.1 Sample preparation and hot-pressing treatments

A green hybrid poplar log (clone OP-367) supplied by Potlatch Corp. was sliced into flat sawn veneers. The bottom part of the log was divided into three sections (top, middle, and bottom), from which four sets of eight veneers, in nominal dimension of $100 \times 100 \times 2.3 \text{ mm}^3$, were randomly sampled. After drying under high vacuum at room temperature, wood samples were either stored in a desiccator with CaSO_4 or placed in 65 % relative humidity. An experimental plan was designed to test the impact of wood initial moisture content (0 and 9 %), hot-pressing temperature (150, 200, and 250 °C), and their interaction (Table 1). The veneers were hot-pressed in a $46 \times 46\text{-cm}^2$ Wabash hot press of 3.4 MPa for 5 min. Upon hot pressing, sample thickness was reduced to approximately 1.0 mm. Control specimens were also prepared.

3.2 Cellulose analysis

In situ cellulose relative crystallinity was monitored with Fourier transform infrared (FTIR) spectroscopy. In addition, cellulose was extracted from the wood samples and characterized for molecular weight by gel permeation chromatography (GPC). FTIR was performed in triplicate on wood samples using an Avatar 370 spectrometer (Thermo Nicolet) in the

Table 1 Hot-pressing conditions and resulting densification including average specific gravity for control and hot-pressed hybrid poplar samples

	Wood moisture content (%)	Pressing temperature (°C)	Oven-dry specific gravity ($SG_{0,OD}$)	% densification $= (SG_{\text{after}} - SG_{\text{before}}) / SG_{\text{before}} * 100$
Control	–	–	0.35 ± 0.03 C	–
9 %, 150 °C	9	150	0.90 ± 0.06 A	154
9 %, 200 °C	9	200	0.90 ± 0.06 A	153
9 %, 250 °C	9	250	0.80 ± 0.10 A,B	132
0 %, 150 °C	0	150	0.64 ± 0.16 B	81
0 %, 200 °C	0	200	0.85 ± 0.12 A	141
0 %, 250 °C	0	250	0.80 ± 0.05 A,B	124

Letters represent Tukey-Kramer grouping

attenuated total reflectance (ATR) mode (single-bounce ZnSe, Smart Performer). The spectra were averaged, corrected (ATR and baseline) using the Omnic v7 software (Thermo Scientific), and analyzed with curve (peak) fitted to separate overlapping bands in specific spectral regions using the IGOR Pro 6.03 (WaveMetrics, Inc.) software. Cellulose crystallinity was determined using both the relative band heights of $1,429/897 \text{ cm}^{-1}$ (Akerholm et al. 2004) and relative band areas of $1,375/2,900 \text{ cm}^{-1}$ (Nelson and O'Connor 1964a, b). For molecular weight analysis of cellulose, extractive-free wood (Osman et al. 2012) was first delignified using NaClO_2 to form holocellulose (Wise et al. 1946). The holocellulose samples (20 mg) were derivatized to their tricarbaniolate form on reaction with phenylisocyanate in pyridine at 80 °C for 48 h and isolated after precipitation with 30 % aqueous methanol (Suckling et al. 2001). Separation was performed on Jordi Gel DVB Mixed Bed and 500-Å columns at 40 °C on elution with THF (0.5 ml min^{-1}) with refractive index (Waters 2478) and right- and low-angle laser light scattering and differential viscometer detection (Viscotek model 270). Data were collected and analyzed using the OmniSEC v4.1 software (Viscotek). The weight-average degree of polymerization (DP_w) was calculated by dividing the weight-average molecular weight (M_w) to the tricarbaniolate glucosyl repeat unit (519 g mol^{-1}).

3.3 Specific gravity measurement

Specific gravity ($SG_{0,OD}$) and extent of densification were determined on oven-dry samples according to ASTM D 2395-07:

$$SG_{0,OD} = \frac{\text{weight}_{\text{ovendry}}}{\text{volume}_{\text{ovendry}}} \quad (1)$$

Nominal dimensions were 50 mm along the grain and 12 mm wide with a thickness of 2.3 mm. The degree of densification (%) was calculated from the difference in $SG_{0,OD}$ for control (before) and hot-pressed (after) hybrid poplar samples according to (2):

$$\text{Densification}(\%) = \frac{SG_{0,OD,\text{after}} - SG_{0,OD,\text{before}}}{SG_{0,OD,\text{before}}} * 100\% \quad (2)$$

3.4 Characterization of wood viscoelastic properties by dynamic mechanical analysis

Samples, $50 \text{ mm} \times 12 \text{ mm} \times 2.3 \text{ mm}^3$ (for control samples) or ca. 2 mm in thickness (for hot-pressed samples), were tested along the grain in 3-point bending mode on a Tritec 2000 DMA Instrument. Before testing, the samples were freeze dried to less than 0.7 % moisture content under vacuum and kept in a vacuum desiccator with P_2O_5 until use. DMA was

performed in the linear viscoelastic range, as determined by strain scans at room temperature and at 120 °C. After cooling to 25±2 °C with liquid nitrogen at ca. 5 °C min⁻¹, a temperature scan was performed from 30 to 120 °C at 1 Hz and at a heating rate of 2 °C min⁻¹.

3.5 Sorption tests

At least 12 specimens were machined from each veneer groups to 50×12 mm² and subsequently freeze-dried to ~0.7 % moisture content. These samples were placed in a humidity chamber (G-64 Elite, Russells Technical Products) at 20±1 °C and 30±1 % relative humidity (RH). The moisture uptake was gravimetrically measured daily with a 0.0001-g accuracy balance until weight stabilized to the equilibrium moisture content (EMC). The chamber RH was then increased to 45 % and moisture uptake measured again. The procedure was repeated for RH of 60±1, 80±1, and 90±1 %. Generally, the equilibrium condition was achieved after approximately 5 to 10 days of conditioning. Wood EMC (%) was calculated based on final mass (m_{wet}) and freeze-dried mass (m_{dry}) as (3):

$$EMC(\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (3)$$

Adsorption isotherms were then constructed by plotting the EMC corresponding to each RH at 20 °C.

3.6 Statistical analyses

As there is a well-established correlation between wood mechanical properties and density of wood, all measured properties were first tested for dependency on specific gravity via simple linear regression. When such a dependency was observed, an analysis of covariance (ANCOVA) using specific gravity as a covariate was performed at an α level of 0.05 using SAS 9.1 statistical software to reveal significant differences independently of density effects. Properties of interest were also normalized to specific gravity, leading to specific properties. For example, the storage modulus of a wood sample divided by its specific gravity defines the specific storage modulus of that sample. All specific properties were analyzed with ANOVA followed by a Tukey-Kramer post hoc analysis when significant differences had been detected. Specific gravity, storage and loss moduli at 3 and 120 °C, relative modulus drop between these temperatures, and peak temperature observed on the loss modulus thermogram were considered for these analyses.

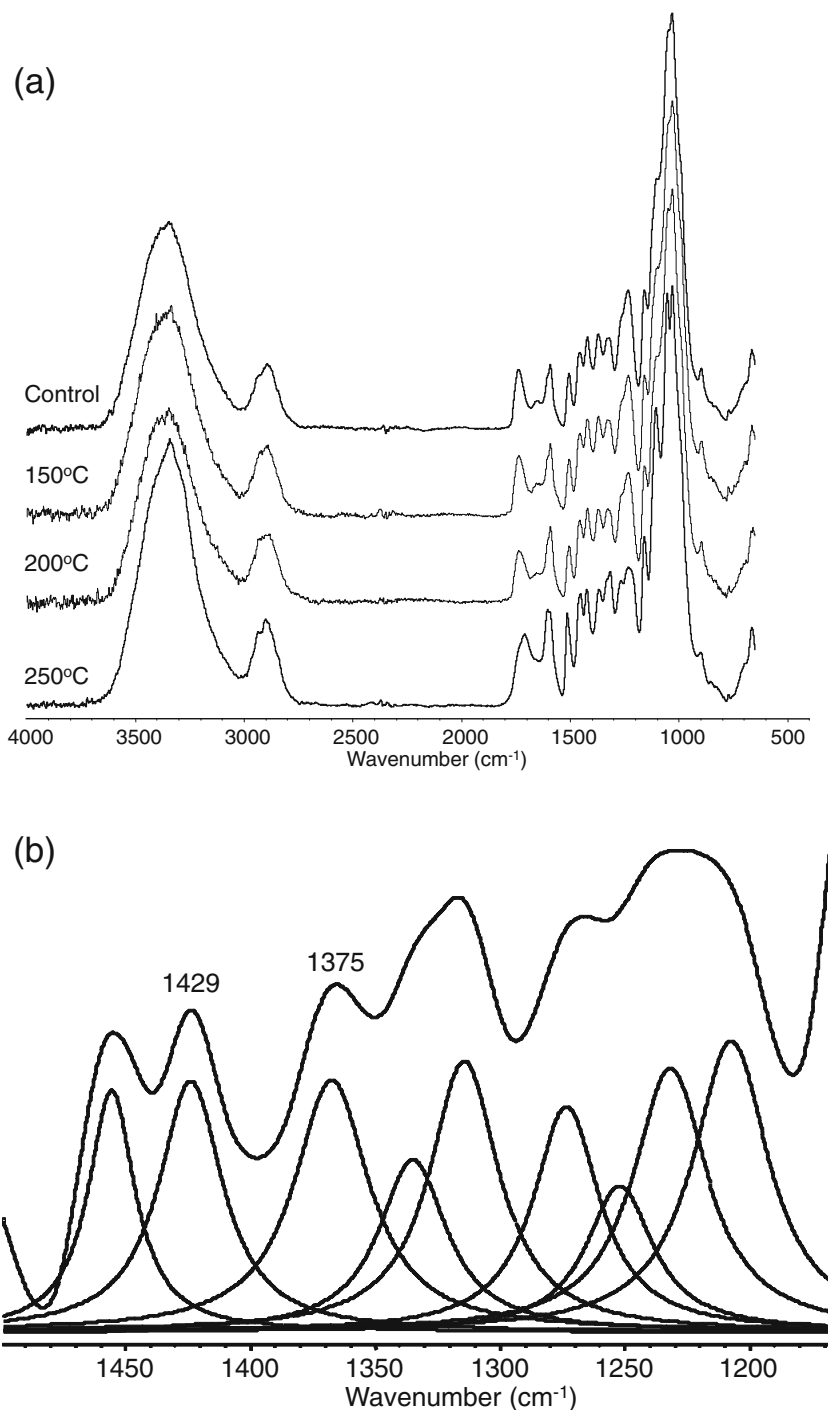
4 Results

4.1 Effect of hot pressing on cellulose in situ chemistry

FTIR spectra of control and 9 % moisture content (MC) hot-pressed poplar are shown in Fig. 1a. The cellulose-assigned bands at 897 cm⁻¹ (asymmetric out-of-phase ring stretch in the C₁-O-C₄ glycosidic linkage), 1,375 cm⁻¹ (C-H bending), 1,429 cm⁻¹ (C-H wagging), and 2,900 cm⁻¹ (C-H stretching) were shown to change upon hot pressing, indicating changes in cellulose (Nelson and O'Connor 1964a, b). To correctly resolve, assign, and quantify overlapping bands, curve fitting was applied (Fig. 1b). In situ cellulose crystallinity was assessed by FTIR spectroscopy using two methods: (i) lateral order index (LOI) from ratios of band heights $H_{1,429}/H_{897}$ (Akerholm et al. 2004) and (ii) total crystalline index (TCI) from ratios of band areas $A_{1,375}/A_{2900}$ (Nelson and O'Connor 1964a, b). For the LOI method, band height values were used based on findings by Akerholm et al. (2004), Carrillo et al. (2004), and Yildiz and Gumuskaya (2007). The results are given in Table 2. The band height ratios of $H_{1,429}/H_{897}$ of the hot-pressed group at 0 and 9 % at 200 °C, as well as at 0 % and 150 °C, were the same as those of the control group, indicating no change in crystallinity. This ratio significantly increased when wood was hot-pressed at the highest temperature of 250 °C, especially for wood with 9 % MC. The band increase suggested that at 250 °C, cellulose underwent further crystallization, especially when moisture was present (Table 2). While this crystallinity increase remained small, the increase was consistent with treatment severity. The increase in crystallinity was attributed to the reduction in the amorphous region by crystallization of amorphous cellulose induced by hot pressing, in particular, under the plasticizing action of water (Bhuyian et al. 2000; Xiao et al. 2014). For the TCI method, band area was used after peak fitting, and this resulted in a better fit than using band height. TCI was also significantly affected by hot pressing ($p < 0.0001$) (Table 2) above 200 °C.

Additionally, the effect of hot pressing on cellulose DP_w was assessed from GPC of the extracted and tricarbanilated holocellulose. The low DP_w value of 1,033 of the control poplar sample compared to red maple (Schroeder and Haigh 1979) and aspen (Laka and Chernyavskaya 2007) suggested significant degradation of cellulose during delignification, as observed with chlorite treatment by others (Cael et al. 1980). Still, this analysis allowed evidencing the trend of decreasing cellulose molecular weight with hot-pressing severity (Table 2) in agreement with previous studies on birch and aspen (Laka and Chernyavskaya 2007). For molecular weight, temperature appeared to be the most significant factor, while initial MC had no impact.

Fig. 1 **a** FTIR spectra for control and hot-pressed poplar (9 % MC) samples and **b** expanded spectral region of hot-pressed poplar at 250 °C and 9 % MC showing curve fitting of bands



4.2 Effect of hot pressing on wood physical properties: specific gravity and water adsorption behavior

Untreated poplar samples had an average specific gravity (SG) of 0.35 ± 0.03 ; it increased twofold to threefold upon hot pressing, reaching values of 0.64 ± 0.16 to 0.90 ± 0.06 SG range (p value=0.0001). Based on Tukey-Kramer analysis, distinct increases in SG were evidenced for the different hot-pressing conditions. All hot-pressed samples pertained to the

same A grouping, except for that hot-pressed at 0 % at 150 °C, which experienced a smaller increase in SG (group B) (Table 3 and Fig. 2). On average, moist samples experienced a higher densification level than dry samples, as expected from water plasticizing effect on wood polymers. During hot pressing, the steam generated from wood moisture further mobilizes the cell wall polymers thus enhancing densification (Wolcott et al. 1990). High-pressure steam pretreatment is also known to cause partial hydrolysis of hemicelluloses resulting

Table 2 Cellulose crystallinity (TCI and LOI) and DP_w of hot-pressed poplar

Treatment	TCI method $A_{1,375}/A_{2,900}$	LOI method $H_{1,429}/H_{898}$	DP_w
Control	0.4013 (0.0247)	1.598 (0.035)	1,033 (0.2)
9 % MC, 150 °C	0.1075 (0.0084)	1.471 (0.095)	842 (0.5)
9 % MC, 200 °C	0.3521 (0.0262)	1.638 (0.062)	769 (1.1)
9 % MC, 250 °C	0.4333 (0.1019)	2.314 (0.207)	614 (0.1)
0 % MC, 150 °C	0.3482 (0.0241)	1.627 (0.051)	893 (3.8)
0 % MC, 200 °C	0.3398 (0.0177)	1.590 (0.136)	703 (3.9)
0 % MC, 250 °C	0.3537 (0.0340)	1.736 (0.253)	607 (0.1)

Standard deviation given in parenthesis

in increased wood compressibility (Hsu et al. 1988; Xiao et al. 2014). In the absence of moisture, the cell wall is more rigid and brittle and is easily crushed during hot pressing.

Figure 3 presents the sorption isotherms conducted at 20 °C for control and hot-pressed samples. The maximum EMC at 20 °C and 90 % RH reaches 18 %, which is the range of that reported for hardwoods (Kolin and Janezic 1996; Navi and Girardet 2000). Hot pressing clearly decreases wood hygroscopicity, and the effect is more pronounced with the most severe hot-pressing conditions. These results corroborate previous observations for heat-treated wood (Kolin and Janezic 1996; Tabarsa and Chui 1997; Navi and Girardet 2000; Repellin and Guyonnet 2005). While at the lowest thermal treatment temperatures, the reduction of hygroscopicity is practically small, especially for oven-dry wood, it is again very marked when wood is hot-pressed at 250 °C. For example, dry samples hot pressed at 250 °C equilibrate at ca. 10 % EMC at an RH of 90 %, compared to 18 % for control samples and 15–18 % for samples hot-pressed at 150–200 °C. This

suggests a turning point in wood-water relationships when hot-pressing temperatures reach such high levels. Additionally, moist wood samples appear to be more affected by hot pressing than oven-dry samples (Fig. 3). This observation is in line with the findings of Navi and Girardet (2000), showing that steamed, hot-pressed wood exhibits a lower FSP and hygroscopicity than wood hot-pressed in the absence of steam. Such behavior has been explained on the basis of amorphous cellulose content and the propensity for cellulose to further crystallize when thermally activated in the presence of water (Kolin and Janezic 1996). Also, this reduction of wood hygroscopicity could be due to the disappearance or reduced accessibility of high-water-affinity functional groups, such as hydroxyl groups in wood polysaccharides. Almeida et al. (2009) indeed reported that hot pressing above 190 °C removed some hemicelluloses from the wood matrix and therefore reduced the amount of hydroxyl groups available for water binding. Homification is also known to occur during heat treatment of wood; it involves the rearrangements of cellulose hydroxyl groups through irreversible microfibrils' bonding and stiffening of wood amorphous matrix after collapse of the pores in the cell wall. A recently proposed mechanism of the impact of hydroxyl group accessibility on wood MC might also be at play (Ratkauri et al. 2013). Namely, EMC decrease in heat-treated wood has been related to wood cell wall modulus (Hill et al. 2012; Rautkari et al. 2013; Borrega and Kärenlampi 2010).

4.3 Effect of hot pressing on wood viscoelastic properties

Temperature scans performed from room temperature to 120 °C showed a typical E' decrease with temperature for both control and hot-pressed samples, while a peak in E'' was observed around 50 °C (Fig. 4). No particular shift of this

Table 3 The oven-dry specific gravity and storage modulus (E') and evaluation of statistical analysis at an $\alpha=0.05$ (with at least three replicates)

Treatment	Oven-dry specific gravity ($SG_{0,OD}$)	Storage modulus (E' (GPa))		Specific storage modulus ($(E'/SG_{0,OD})$ (GPa))		$E'_{decrease} = \frac{(E'_{30^\circ C} - E'_{120^\circ C})}{E'_{30^\circ C}}$ (°C)
	Specific gravity (SG)	30 °C	120 °C	30 °C	120 °C	
Control	0.35±0.03 C	5.7±1.6	5.2±1.5	16.4±6.1 B	14.9±5.4 C	9±3
9 %, 150 °C	0.90±0.06 A	28.2±5.8	25.5±5.4	31.7±7.1 A	28.6±7.1 A	10±2
9 %, 200 °C	0.90±0.06 A	21.1±3.2	19.6±3.1	23.6±2.9 A,B	22.0±2.8 A,B,C	7±2
9 %, 250 °C	0.80±0.10 A,B	21.9±4.5	20.3±4.1	27.6±5.1 A	25.5±3.9 A,B	7±2
0 %, 150 °C	0.64±0.16 B	10.9±3.2	10.3±3.0	16.9±2.3 B	16.0±2.4 C	6±2
0 %, 200 °C	0.85±0.12 A	19.3±5.0	17.1±5.3	22.5±3.5 A,B	19.8±4.0 B,C	12±8
0 %, 250 °C	0.80±0.05 A,B	22.0±4.2	20.7±3.9	27.8±4.9 A	26.1±4.5 A,B	6±1
ANOVA p value	0.0001	–	–	0.0001	0.0001	0.1417
ANCOVA	p value (treatment)	0.0038	0.0054	–	–	–
	p value (SG)	0.0015	0.0007	–	–	–

ANCOVA analysis of covariance

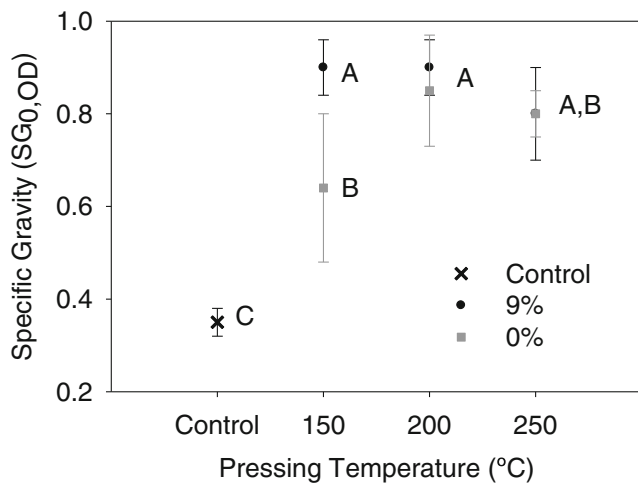


Fig. 2 Average specific gravity for control and hot-pressed hybrid poplar wood samples and its Tukey-Kramer grouping

relaxation temperature with hot-pressing treatment was observed ($p=0.99$, Tables 3 and 4). Sugiyama et al. (1998) first reported a $\tan \delta$ peak ($\tan \delta = E''/E'$) around 75 °C on oven-dried wood, which he ascribed to drying history. Using dielectric analysis, Jafarpous et al. (2008) similarly reported a relaxation peak around 39 °C on dried poplar and cellulose powder and assigned it to the desorption of entrapped water. For absolutely dried specimens as in our study, Sun et al. (2007) also reported the onset of $\tan \delta$ peak between 75 and 150 °C, which they tentatively ascribed to the onset of hemi-cellulose glass transition temperature and determined to be extremely moisture sensitive, even between 0 and 0.7 % MC. Here, the observed relaxation at 50 °C most likely reflects molecular motions from adsorbed water molecules.

To further evaluate the effect of hot pressing on wood viscoelastic properties, storage moduli at 30 °C ($E'_{(30\text{ }^\circ\text{C})}$)

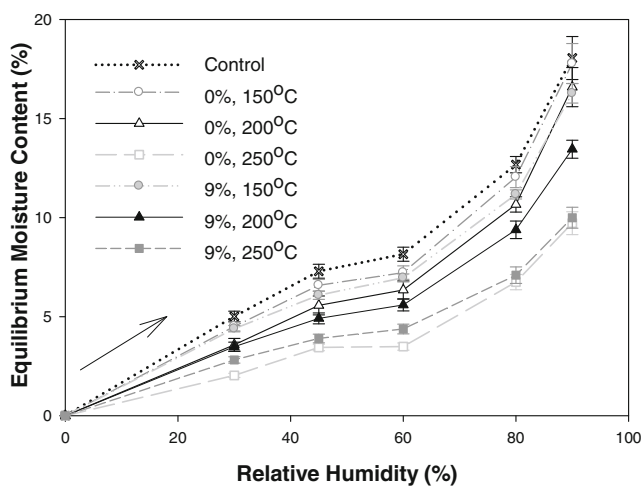


Fig. 3 Adsorption isotherms of control and hot-pressed hybrid poplar wood at 20 °C (12 replicates each)

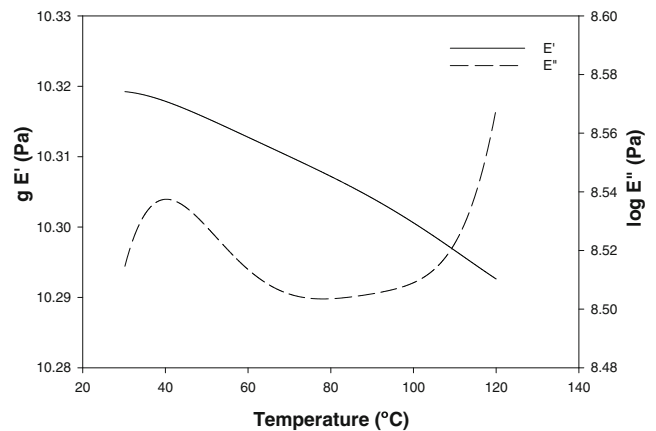
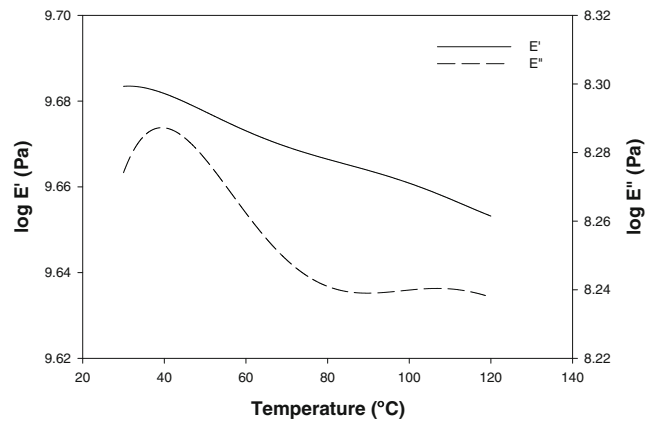


Fig. 4 Typical DMA temperature scan of hybrid poplar wood at 1 Hz utilizing 2 °C min⁻¹ heating rate for control (*top*) and hot-pressed (9 % MC, 250 °C) hybrid poplar sample (*bottom*) tested in 3-point bending mode along the grain

and at 120 °C ($E'_{(120\text{ }^\circ\text{C})}$) were compared, along with the relative modulus drop over that temperature range,

$$E'_{\text{decrease}}(\%) = \frac{E'_{(30\text{ }^\circ\text{C})} - E'_{(120\text{ }^\circ\text{C})}}{E'_{(30\text{ }^\circ\text{C})}} * 100 \tag{4}$$

Hot pressing appeared to increase the absolute value of both moduli (Fig. 5) in agreement with established relationships between wood mechanical properties and density (Bowyer et al. 2003). Figure 6 further reveals strong linear dependencies of storage modulus ($R^2=0.84$) and loss modulus ($R^2_{E'_{(30\text{ }^\circ\text{C})}}=0.77$ and $R^2_{E'_{(120\text{ }^\circ\text{C})}}=0.91$) on specific gravity at both 30 and 120 °C; that is, the large increase in dynamic moduli upon hot pressing can be largely explained by increases in specific gravity. In contrast, $E'_{\text{decrease}}(\%)$ over the temperature range did not depend on specific gravity ($R^2=0.0125$) or on the hot-pressing treatment (p value=0.1417).

To assess whether densification alone could explain the variations in E' and E'' , ANCOVA was performed using specific gravity as a covariate. It evidenced no significant difference in loss moduli ($E''_{(30\text{ }^\circ\text{C})}$ p value=0.54 and

Table 4 Oven-dry specific gravity of hot-pressed poplar, loss modulus (E'') data, and evaluation of statistical analysis at an $\alpha=0.05$ (at least three replicates)

Treatment	Oven-dry specific gravity ($SG_{0,OD}$)		Loss modulus (E'' (GPa))		Specific loss modulus (E'' (GPa))		E'' peak ($^{\circ}C$)
			30 $^{\circ}C$	120 $^{\circ}C$	30 $^{\circ}C$	120 $^{\circ}C$	
Control	0.35±0.03	C	0.6±0.2	0.5±0.2	0.6±0.2	0.5±0.2	48±10
9 %, 150 $^{\circ}C$	0.90±0.06	A	0.6±0.1	0.7±0.1	0.6±0.1	0.7±0.1	47±4
9 %, 200 $^{\circ}C$	0.90±0.06	A	0.5±0.1	0.6±0.1	0.5±0.1	0.6±0.1	50±6
9 %, 250 $^{\circ}C$	0.80±0.10	A,B	0.5±0.3	0.6±0.2	0.5±0.3	0.6±0.2	50±10
0 %, 150 $^{\circ}C$	0.64±0.16	B	0.4±0.1	0.5±0.1	0.4±0.1	0.5±0.1	48±3
0 %, 200 $^{\circ}C$	0.85±0.12	A	0.6±0.3	0.6±0.2	0.6±0.3	0.6±0.2	50±13
0 %, 250 $^{\circ}C$	0.80±0.05	A,B	0.5±0.1	0.5±0.1	0.5±0.1	0.5±0.1	–
ANOVA p value	0.0001		–	–	0.5220	0.7196	0.99
ANCOVA	p value (treatment)		0.5440	0.7794	–	–	–
	p value (SG)		0.0125	0.0058	–	–	–

Letters represent Tukey-Kramer grouping

ANCOVA analysis of covariance

E'' ($_{120\text{ }^{\circ}C}$) p value=0.78), besides density effect. Comparing the specific loss moduli (sE'') with ANOVA (sE'' ($_{30\text{ }^{\circ}C}$) p value=0.52 and sE'' ($_{120\text{ }^{\circ}C}$) p value=0.72) confirmed this conclusion (Table 3). On the other hand, over the temperature range tested, the hot-pressing treatment had an effect on E' (E' ($_{30\text{ }^{\circ}C}$) p value=0.0038 and E' ($_{120\text{ }^{\circ}C}$) p value=0.0054), besides that of density (see Table 4). Expectedly then, the specific storage modulus for some hot-pressed samples differed significantly from that of control samples (ANOVA p value=0.0001). Specifically, the Tukey-Kramer grouping indicated that at both MCs, samples hot-pressed at 250 $^{\circ}C$ had higher specific storage moduli than control samples. All other hot-pressing conditions (at 150 and 200 $^{\circ}C$) resulted in

no change in specific storage moduli, except for the 9 % MC sample hot-pressed at 150 $^{\circ}C$, which appeared in many subsequent analyses to behave as an outlier. This finding coincides with results from a study investigating the effect of compressive strain and press temperature. Tabarsa and Chui (1997) found that differences in mechanical properties in hot-pressed white spruce were small for pressing temperatures of 150 and 200 $^{\circ}C$ and wood MC of 15 %. The unique viscoelastic behavior of wood samples hot-pressed at 250 $^{\circ}C$ suggests again that a turning point in wood properties occurs over this hot-pressing temperature.

5 Discussion on the molecular mechanism underlying changes in wood physical and viscoelastic properties during hot pressing

The viscoelastic and hygroscopic changes observed in hybrid poplar during hot pressing are consistent with prior literature already evidencing increases in dynamic moduli, decreases in hygroscopicity and cellulose hydrolysis, and apparent crystallinity increase. Additionally, this study clearly establishes a turning point in wood behavior when hot-pressing temperature reaches 250 $^{\circ}C$. At this temperature, a change in the morphology of wood polymers may be expected. For example, an increase in stiffness might reflect cellulose crystallinity increases.

The statistical analyses of this study further demonstrate that the viscoelastic changes observed upon hot pressing relate, in part, not only to the degree of densification but also to other factors. Indeed, specific modulus was also found to be dependent on hot-pressing treatment. This effect was especially marked when reaching hot-pressing temperatures of

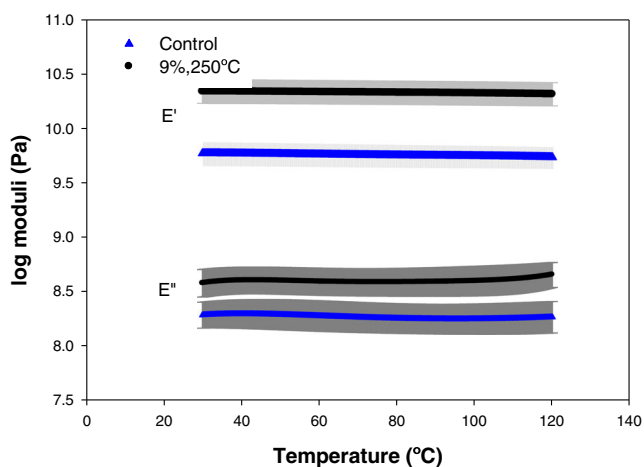


Fig. 5 Average storage (E') and loss moduli (E'') curves during a temperature scan for control and hot-pressed samples (9 % MC, 250 $^{\circ}C$) at 1 Hz with a 2 $^{\circ}C\text{ min}^{-1}$ heating rate. Samples tested in 3-point bending mode along the grain with at least three replicates (with standard deviation)

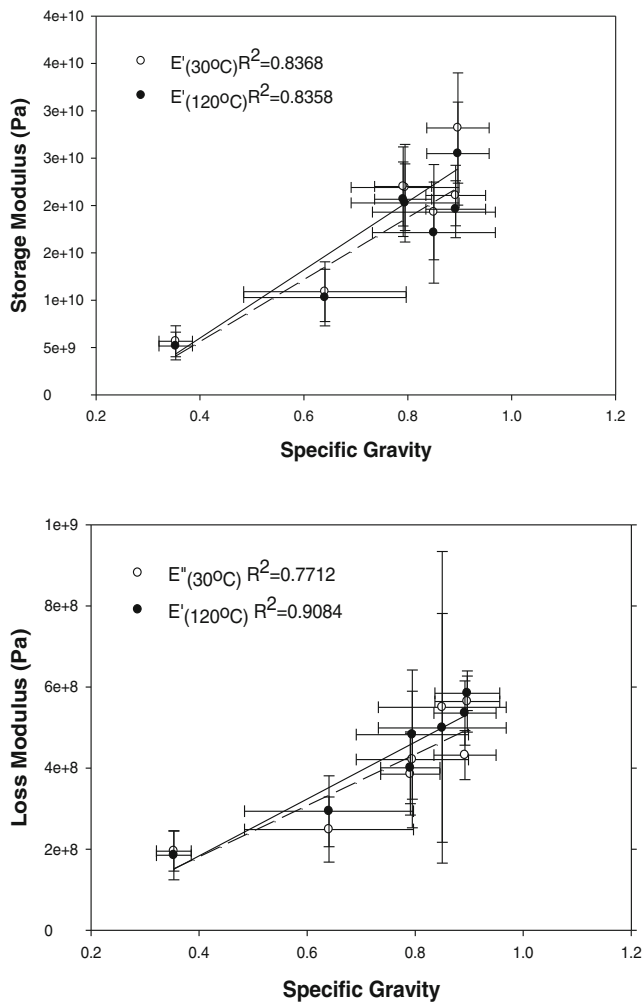


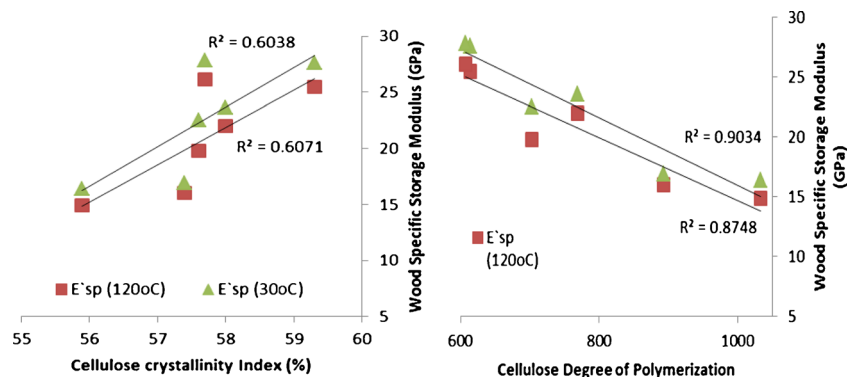
Fig. 6 Relationship between the storage modulus (E') (s) or the drop in storage modulus $[(E'_{30\text{ }^\circ\text{C}} - E'_{120\text{ }^\circ\text{C}}) / E'_{30\text{ }^\circ\text{C}} * 100]$ (middle and bottom) oven-dry specific gravity

250 °C. Molecular changes in wood constituents during hot pressing might well be determining factors or possible covariates of the viscoelastic changes observed as a result of hot pressing.

To further investigate whether the measured viscoelastic and hygroscopic properties could relate to wood molecular

or morphological changes, attempts were made to relate viscoelastic properties with cellulose molecular parameters viz. apparent crystallinity index and DP_w . Note that in these attempts, the dry sample hot-pressed at 150 °C was not considered as it emerged as an outlier for all properties measured (Reiniati 2009). Hot pressing presumably did not properly function for this sample. Overall, the crystallinity determination using FTIR band height ratios of $H_{1,429}/H_{897}$ showed a direct relationship to the specific storage modulus (Fig. 7). As apparent crystallinity of cellulose increases, so does wood specific storage modulus. The linear regression analysis further indicates that the changes in cellulose apparent crystallinity explain ca. 60 % of the variations in the specific storage modulus of hot-pressed wood (Fig. 7). An increase in the storage modulus could therefore be ascribed to an increase in cellulose crystallinity, especially at the most severe hot-pressing conditions and in the case of moist wood. Further exploration and insight into the molecular origin of wood specific moduli after hot pressing were sought by assessing relationships between specific storage moduli and cellulose DP_w . Indeed, the data also clearly established an inverse linear relationship between cellulose in situ crystallinity index and cellulose DP_w (not shown). This relationship confirms that the apparent increases in crystallinity of cellulose stem in large part from hydrolysis and thus removal of cellulose amorphous regions. Interestingly, an even stronger linear correlation is evidenced between specific storage modulus and cellulose DP_w . About 90 % of the variation in the specific storage modulus in hot-pressed wood can be explained by variations in cellulose DP_w . Such direct linear relationship has, to our knowledge, never been reported in hot-pressed wood; it clearly illustrates the high level of correlation between molecular changes in wood constituents and wood macroscopic properties. This behavior is consistent with previous reports on various wood species, which evidenced correlations between wood elastic strain under bending and cellulose crystal strain (Montero et al. 2012). Whether this strong correlation reflects a cause-effect relationship or is an incidental codependency cannot be

Fig. 7 Relationship between wood storage modulus (E') and in situ cellulose properties, viz. apparent crystallinity index and degree of polymerization



established on the sole basis of this analysis. However, clearly evidenced here are quantifiable parallel trends between a molecular parameter of wood polymeric constituent and a macroscopic property of bulk wood at various degrees of heat compression.

In addition to the changes occurring on wood carbohydrates, changes on lignin may play a role in alteration of wood hygroscopicity and viscoelasticity (Osman 2010; Xiao et al. 2014). Tjeerdsma et al. (1998) hypothesized that heat enhances the demethoxylation of guaiacyl and syringyl units in lignin, which increases the amount of reactive phenolic lignin sites available for reaction. Once the lignin demethoxylation and cross-linking of free phenolic units occur at approximately 220 °C, a more rigid structure forms around cellulose microfibrils and hinders water penetration in the cell wall (Tjeerdsma et al. 1998). Demethoxylation of lignin is likely to change its softening point and the resulting loss moduli properties. Lignin cross-linking and cellulose crystallinity increase both likely contribute to augment wood moduli, which is proposed to correlate with wood hygroscopicity (Hill et al. 2012). Further work on the viscoelastic properties of hot-pressed wood under plasticized conditions in relation to lignin molecular mobility is the topic of subsequent publication.

6 Conclusions

Hot pressing of hybrid poplar was found to significantly influence the specific gravity, dynamic mechanical properties, and hygroscopicity of the resulting hot-pressed wood. Specific storage modulus under bending was largely influenced by hot-pressing conditions, while loss modulus, drop in storage modulus with temperature, and wood polymer relaxation at ca. 50 °C were not affected. Cellulose in situ apparent crystallinity index was found to increase with hot-pressing severity, and this increase was accompanied with a DP_w decrease, evidencing hydrolysis and depolymerization of cellulose amorphous regions during hot pressing. While the changes in viscoelastic properties could be in large part ascribed to densification, covariate analysis along with the determination of specific viscoelastic properties allowed evidencing that factors other than density determined wood viscoelastic behavior. In particular, strong linear correlations between wood specific storage moduli on the one hand and apparent cellulose crystallinity (positive correlation with $R^2 > 0.6$) and cellulose DP_w (negative correlation, $R^2 > 0.9$) on the other hand were established. Direct correlations between the molecular parameters of wood constituents and resulting macroscopic behavior might not be of causal nature but do provide some molecular insight of wood property changes during hot pressing.

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