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Effects of thermo-hygro-mechanical (THM) treatment on the viscoelasticity of *in-situ* lignin

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Abstract: For producing wood products without fractures based on thermo-hygro-mechanical (THM) treatments, it is essential to understand how steaming and compression change the wood softening and cell wall components. In this paper, the effects of compression combined with steam treatment (CS) on the viscoelasticity of the *in-situ* lignin of Chinese fir has been investigated through dynamic mechanical analysis (DMA) under fully saturated conditions. Several variations were studied, such as the softening temperature (T_g) and apparent activation energy (ΔH_a) of the softening process in response to CS treatment conditions (such as steam temperature and compression ratio) under separate consideration of earlywood (EW) and latewood (LW). No difference between EW and LW with respect to the viscoelasticity was noted. T_g and ΔH_a of the lignin softening were nearly unaffected by the compression ratio, but were highly influenced by the steam temperature. The T_g decreased significantly with CS treatments at or above 160°C, but showed no appreciable change, compared to the native wood, at the lower steaming temperature of 140°C. ΔH_a increased at higher steam temperatures, while ΔH_a showed a decreasing tendency with decreasing T_g. This indicates that lignin undergoes a simultaneous depolymerization as well as a condensation during CS treatment.

Keywords: compression ratio, dynamic mechanical analysis, earlywood, latewood, lignin, softening, steam temperature, wood

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Introduction

The renewable wood has been an important construction material for thousands of years due to its availability, low cost and very good strength-to-weight ratio. On the other hand, its poor dimensional stability, low resistance to microbial degradation and moderate mechanical strength seriously restrict the development of high-performance construction materials based on wood. In the last decades, thermo-hygro-mechanical (THM) treatments were frequently the focus of research and industrial application for improving its properties. THM is an eco-friendly method, which relies on the combination of temperature (T), moisture content (MC) and mechanical action (Hill 2006). The THM treatment improves the dimensional stability, resistance to degradation and mechanical behavior (Yin et al. 2011; Sandberg et al. 2013; Navi and Pizzi 2015).

For the further development of THM treatment it is necessary to better understand the mechanisms of the treatment (Inoue et al. 1993; Navi and Sandberg 2011; Guo et al. 2016). The wood cell wall consisting of cellulose embedded in a matrix composed of lignin and hemicelluloses is complex (Fengel and Wegener 1984; Salmén 2015). The quantitative composition, the supramolecular architecture (the arrangement of the constituents) affect wood properties, especially under changing T, MC and mechanical actions. During THM treatment, densification under compressive conditions and the degradation and rearrangement of hemicelluloses, lignin and cellulose are the main parameters for the improvement of wood properties (Ito et al. 1998; Heger 2004; Diouf et al. 2011; Guo et al. 2015; Yin et al. 2016).

Wood softening is an important factor in this context. Compression below its glass transition temperature (T_g) leads to micro-fractures in the cell wall and causes serious mechanical damage. On the other hand, an unsuitably high treatment T could lead to severe chemical degradation, inferior performance and energy waste. Thus the change of wood viscoelasticity in the THM treatment is a key factor for process optimization. The viscoelastic properties of wood under THM treatment would reflect the structural arrangement of the cell wall components as well as the changes in their molecular and supramolecular structure. During steaming and heat treatment processes,

cleavage of β-aryl ether linkages, demethylation, demethoxylation as well as formation of phenolic hydroxyl groups have been reported (Sudo et al. 1985; Robert et al. 1988; Li et al. 2007; Martin-Sampedro et al. 2011; Pelaez-Samaniego et al. 2015). The high temperatures will also lead to an increased tendency for cross-linking reactions to occur (Funaoka et al. 1990).

Transversal compression combined with steam (CS) treatment is a promising THM technique. Under this water-soaked condition, the amorphous carbohydrate components of wood (mainly hemicelluloses) are already softened at room temperature (rT) (Cousins 1978; Olsson and Salmén 1992). In addition, noncovalent interactions (mainly hydrogen bonding interactions) among the wood components are much weaker than that between water and the wood cell wall. Under soaked condition, the T_g is between 50°C and 100°C, depending on the native lignin structure and the frequency of the measurement (Sadoh 1981; Hagen and Salmén 1994; Song et al. 2014; Zhan et al. 2016). A clear relation between lignin structure and wood softening has not yet been established. The content of methoxy (OMe) and free phenolic hydroxyl (OH_{phen}) groups, number and type of cross-links, and molecular weight are only a few parameters influencing the wood softening. The T_g generally increases with decreasing OMe and OH_{phen} contents and with increasing molecular weight and degree of cross-linking (Yoshisa et al. 1987; Olsson and Salmén 1992, 1997).

In this paper, Chinese fir [*Cunninghamia lanceolata* (Lamb.) Hook], an important commercial conifer species planted in China, was submitted to CS treatment at 140°C, 160°C and 180°C under the compression ratios of 25% and 50%. The viscoelastic behavior of the samples was studied by dynamic mechanical analysis (DMA), (Placet et al. 2007; Jiang et al. 2008; Chowdhury and Frazier 2013; Salmén and Olsson 2016). Ethylene glycol (EG) was applied as a softening agent, which facilitates a better determination of the T_g even above 100°C (Wennerblom et al. 1996). EG has a similar softening effect on lignin as that of water (Wennerblom et al. 1996). The behavior of earlywood (EW) and latewood (LW) should be observed in separate DMA experiments because the lignin content of EW is somewhat higher than that of LW mainly due to the higher proportion of middle lamella material in the former (Fergus et al. 1969).

Material and methods

Materials: Chinese fir *C. lanceolata* was harvested from a 28 years old stand located in Jiangxi Province of China. Wood specimens ($20\times20\times25$ mm^3, T×R×L) including the 25th growth ring were cut from the mature wood. Ethylene glycol (EG) was purchased from Merck KGaA Company in Germany.

Compression combined with steam (CS) treatment: CS treatment was conducted in a laboratory-scale autoclave at Kyoto University as reported by Guo et al. (2016). Small specimens were treated with a 25% or 50% radial compression (C_R) ratio (the percentage of the decrease in thickness as compared to the initial thickness of the specimen) at 110°C for 6 min was followed by a steaming process at 140°C, 160°C, or 180°C for 30 min, respectively. Wood specimens treated with a 25% C_R ratio combined with the steam temperatures indicated above are labeled as $S_{140,25}$, $S_{160,25}$ and $S_{180,25}$, respectively, and those treated with a 50% C_R ratio are designated as $S_{140,50}$, $S_{160,50}$ and $S_{180,50}$, respectively. The control wood specimen without treatment is labeled S_{untr}.

Sample preparation for DMA: The wood samples were saturated with EG for several days at rT by submersion. T sections with the thickness of around 150 μm were cut both from EW and LW from the 25th growth ring of each wood specimen by a sliding microtome (Leica SM 2010R, Leica Company, Germany). From these T sections, DMA measurement samples (150 μm×5 mm×20 mm in the R, T and L directions) were cut.

DMA measurement: A Perkin Elmer DMA 7e instrument (Perkin Elmer Corp., Norwalk, CT, USA) was available. Throughout the measurement, the specimens were immersed in EG within a poly(tretrafluorethylene) cup specifically manufactured to fit the DMA furnace. Samples were tested in tension with the fibers (the L direction) aligned in the loading direction with a clamping span of around 13 mm. Dynamic mechanical properties were measured between 30°C and 130°C at a heating rate of 2°C min^{-1} with a dynamic strain not greater than 0.5% and with a static load of 120% of the dynamic load. Forced sinusoidal vibrations at the frequencies of 0.5 Hz, 1.0 Hz, 2.0 Hz and 5 Hz, respectively, were applied. Prior to testing, a temperature scan from 30 to 120°C at a heating rate of 40°C min^{-1} was conducted to erase the sample thermal history.

In this study, the temperature at which tanδ reached its maximum was defined as the softening temperature (T_g) of the *in-situ* lignin, because it is independent of the specimen's dimension (Hagen and Salmén 1994). The apparent activation energy (ΔH_a) for the softening process was determined by Equation (1).

$$\Delta H_a(\text{Arrhenius}) = 2.303\times R(\Delta \log f)/\Delta(1/T_g) \quad (1)$$

where R is the gas constant (8.3143 J mol^{-1}K^{-1}), T_g is the softening temperature, and f is the frequency. For better statistics, three different specimens for each of the EW and LW samples were measured and evaluated.

Statistical analysis: The analysis of variance (ANOVA) was applied (SAS program, SAS Institute 9.0, USA). Least-significant difference tests were performed. If the P-value is less than 0.05, it indicates that values are significantly different at a significance level of 5%.

Results and discussion

The viscoelastic data are displayed in Figure 1 concerning the CS treated wood (50% C_R at 180°C steam treatment)

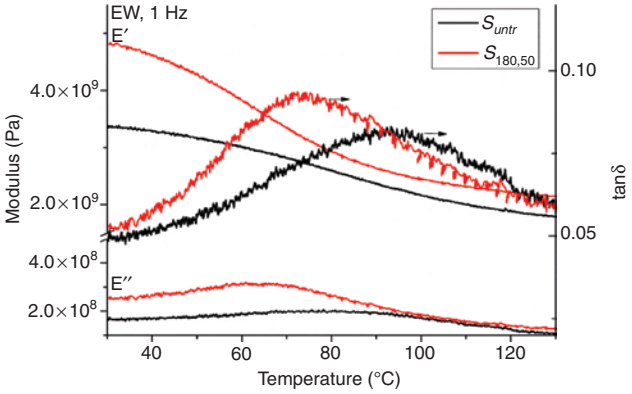

Figure 1: Typical examples of temperature ramp measurements for EW of untreated wood (black line) and CS treated wood ($S_{180,50}$, red line) at a frequency of 1 Hz.
The year old stands left axis is the modulus where data display both the storage, E′ and the loss, E″ moduli, and the right axis shows the damping as tanδ.

and an untreated wood (S_{untr}). The storage modulus E′ shows the typical behavior of a viscoelastic material with the secondary transition in the temperature range of 30°C–130°C (Hillis and Rozsa 1978; Salmén 1984). The T_g region is visible on the single maximum for both the mechanical loss coefficient (tanδ) and the loss modulus (E″). Due to possible variations in the specimens size, the E″ data represent approximate values but this is not relevant because only relative trends are compared. In Figure 2, the effects of frequency are presented for the storage modulus, E′ and tanδ; both data are positively correlated with the frequency, in agreement with previous studies of different wood samples (Wennerblom et al. 1996; Song et al. 2014).

The viscoelasticity of the *in-situ* lignin is significantly influenced by the CS treatment, as indicated in Figure 1. The T_g of the *in-situ* lignin in the EW_{untr}, S_{untr} under EG-saturated condition was around 91°C at a frequency of 1 Hz, similar to the reported T_g for spruce (Olsson and Salmén 1997). For the CS treated EW, $S_{180,50}$, the T_g decreased to 76°C, which is ca 17% lower than that for S_{untr}. At the same time, the modulus of the wood increased in accordance with the indentation modulus increment after CS treatment (Guo et al. 2015). The modulus increase is probably a result of the densification occurring under the compressive

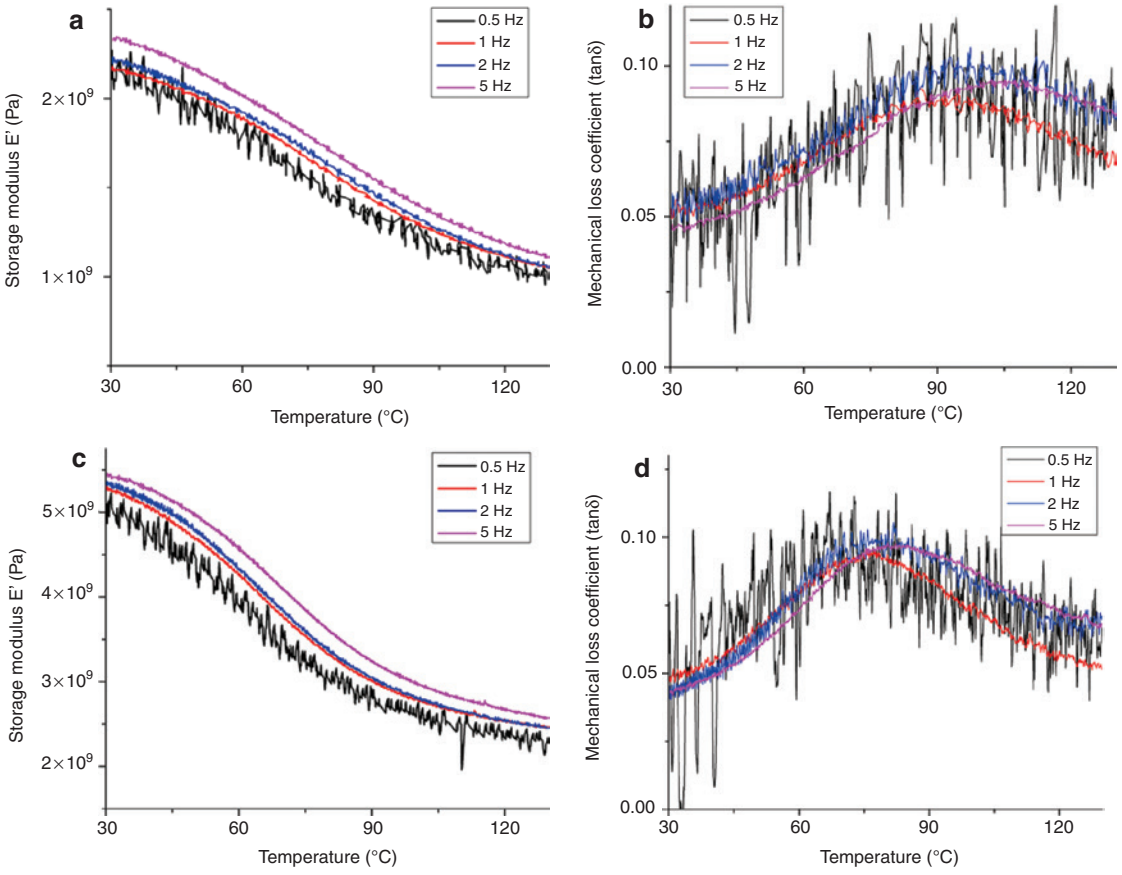

Figure 2: Storage modulus E′ (a and c) and mechanical loss coefficient tanδ (b and d) as a function of temperature for wood samples tested along the fiber direction at ethylene glycol-saturated condition; LW S_{untr}: a and b; EW $S_{180,50}$: c and d.
Frequencies: 0.5 Hz (black line), 1 Hz (red line), 2 Hz (blue line) and 5 Hz (purple line).

condition as well as a higher cellulose crystallinity and more perfectly arranged cellulose crystals after CS treatment (Navi and Sandberg 2011; Guo et al. 2016).

The effects of the CS treatments on the T_g for all the studied samples are summarized in Figure 3. The ANOVA analysis data are compiled in Table 1. There is no significant difference between the T_g of EW and LW ($P = 0.9123$) as indicated by the same symbol letter. This is consistent with the data of Wennerblom et al. (1996). The T_g is clearly dependent upon the CS treatment conditions for T_g at a significant level of 5% ($P < 0.0001$). This is in line with the studies of Heger (2004) showing that T_g of THM-treated wood decreases by increasing T and time. As shown in Figure 3, the average T_g of *in-situ* lignin of untreated wood, S_{untr} were 88°C and 92°C for EW and LW, respectively. With CS treatment, T_g decreased for both EW and LW, except for samples treated at 140°C. In comparison with S_{untr}, the average T_g for EW and LW under severe conditions ($S_{180,50}$) showed a 12% and 15% decrease, respectively, which was similar to the effects of high-T drying (Jiang et al. 2008) and for steam-exploded bamboo (Shao et al. 2009). Concerning the statistical relevance, lignin T_g was essentially more dependent upon the steam T rather than the C_R ratio. The decrease in T_g means that the lignin displays a higher molecular mobility which could be an effect of depolymerization.

Figure 4 shows Arrhenius plots for T_g data of EW and LW with or without CS treatment. An apparent activation energy of the softening (ΔH_a) may be evaluated from the slopes of the regression lines according to Equation (1),

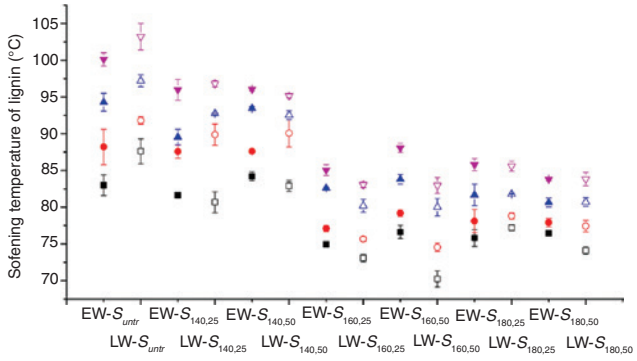

Figure 3: Softening temperature of *in-situ* lignin for EW and LW samples of both CS treated wood and untreated wood measured at different frequencies (0.5 Hz, ■; 1 Hz, ●; 2 Hz, ▲; 5 Hz, ▼ for EW; 0.5 Hz, □; 1Hz, ○; 2Hz, △; 5Hz, ▽ for LW).
With increasing treatment temperature T_g was lowered. No difference between LW and EW was seen.

Table 1: Two-factor ANOVA results for the effects of EW/LW and CS treatment conditions on the softening temperature (T_g) measured at the frequency of 1 Hz and of the apparent activation energy for the softening process (ΔH_a).

Parameter		S_{untr}	$S_{140,25}$	$S_{140,50}$	$S_{160,25}$	$S_{160,50}$	$S_{180,25}$	$S_{180,50}$
T_g (°C)	EW (a) LW (a)	89.9 ± 2.7 A	88.8 ± 1.8 AB	87.9 ± 1.5 B	76.8 ± 1.6 D	76.9 ± 2.6 CD	78.4 ± 1.3 C	77.7 ± 0.8 CD
ΔH_a (kJ mol^{-1})	EW (a) LW (a)	−149 ± 12 A	−163 ± 22 A	−188 ± 17 B	−209 ± 15 C	−188 ± 19 B	−254 ± 31 D	−276 ± 41 E

Different letters indicate that there is a significant difference between the samples at $P < 0.05$ (least-significant difference test); letter (a) for the wood type (EW and LW) and A–E for CS treatment conditions.

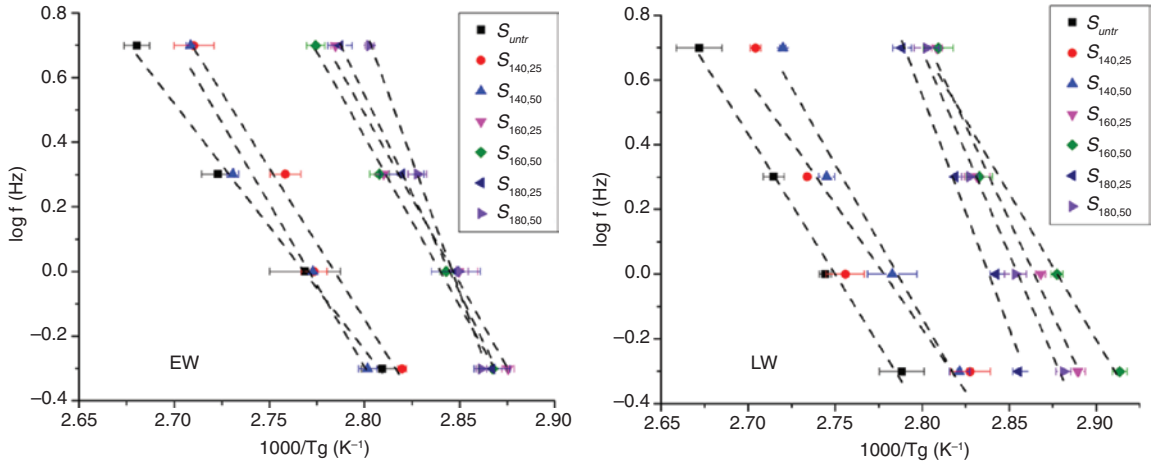

Figure 4: Arrhenius plots of log frequency against the reciprocal absolute temperature for the *in-situ* lignin softening in EW left and LW right for untreated wood and wood samples after CS treatment.
Measurements were made under ethylene glycol saturated condition.

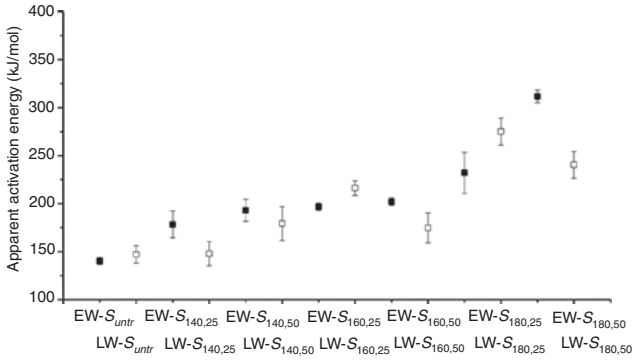

Figure 5: The apparent activation energy ΔH_a for the *in-situ* lignin softening for EW ■ and LW □ samples of both CS treated wood and untreated wood.
With increasing treatment temperature ΔH_a increased.

which shows that these are dependent upon the CS treatment conditions, i.e. ΔH_a is also dependent upon the processing parameters. Obviously, ΔH_a increased with CS treatment for both EW and LW, except for the treatment at 140°C (Figure 5). In comparison to the average ΔH_a of 140 kJ mol^{-1} and 150 kJ mol^{-1} for EW and LW of untreated wood, S_{untr}, the ΔH_a increased to ca 310 kJ mol^{-1} and 240 kJ mol^{-1}, i.e. by 125% and 65%, respectively, in case of $S_{180,50}$. The ΔH_a of S_{untr} is slightly lower than that reported for spruce treated under similar conditions (Wennerblom et al. 1996). The statistical analysis showed that the CS treatment ($P < 0.0001$) results in significant differences of ΔH_a (Table 1). On the other hand, the ΔH_a difference between EW and LW samples is not highly significant ($P = 0.1084$), which is consistent with the similar T_g values measured for EW and LW after CS treatment. Furthermore, the ΔH_a seemed to increase with increasing steam T. The increase in ΔH_a would be in line with an increased cross-linking of a polymer in general (Lewis 1963) and also observed for lignin (Olsson and Salmén 1992). Cross-linking due to steam treatment of wood has also been noted by dynamic fourier transform infrared spectroscopy (Salmén et al. 2008). The fact that the activation energy increases most drastically for the highest treatment temperatures is in line with the fact that cross-linking reactions was not observed for milder steam treatment processes (Martin-Sampedro et al. 2011). In general, the condensation reactions of lignin increase with increasing temperature (Funaoka et al. 1990).

For native lignin of different composition in S/G ratio the ΔH_a increases with increasing T_g (Olsson and Salmén 1992). The higher T_g was assumed to be related to the increased possibility of cross-linking with increasing S/G ratio (Olsson and Salmén 1997). The fact that CS treatment leads to a decrease in T_g accompanied by an increasing ΔH_a may be interpreted in terms of competitive depolymerization and re-condensation reactions. One should however be aware of that some parts of the lignin could have been rearranged and become inactive due to redeposition on cell walls at these high temperatures (Selig et al. 2007; Donohoe et al. 2008; Navi and Pizzi 2015), thus affecting the viscoelastic properties of the remaining lignin.

Conclusions

CS treatment at steam temperatures of 160°C or higher results in a lowering of the *in-situ* lignin softening temperature as well as an increased apparent activation energy of the softening process. This is probably related to simultaneous depolymerization and re-condensation reactions occurring of the lignin. The compression ratio had little effect on those changes. There is no difference in the THM behavior of EW and LW.

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