Molecular-level characterization of changes in the mechanical properties of wood in response to thermal treatment

Dong Wang · Feng Fu · Lanying Lin

Received: 6 September 2021 / Accepted: 6 February 2022 / Published online: 8 March 2022
© The Author(s), under exclusive licence to Springer Nature B.V. 2022

Abstract Thermal treatment can improve the dimensional stability of wood, but it also decreases wood’s toughness, or increases its brittleness. In this paper, combining FTIR spectroscopy and mechanical analysis were used to monitor wood molecular straining and deepen the micromechanical understanding of thermally-treated wood. The degradation of hemicellulose increased as the thermal treatment temperature increase, and the 220 °C treatment also led to cellulose microfibrils reorientation. The results of static tension FTIR spectra of thermally-treated wood indicated that the absorption peak of cellulose glycosidic bond underwent a substantial bandshift to lower wave numbers as the tensile strain increase, but the characteristic peak position of the lignin was no obvious change during stretching. For the 160–200 °C treated samples, the bandshift ratios of cellulose C–O–C glycosidic bond increased upon increasing the temperature; Furthermore, the intensities of the two split peaks of cellulose at 1169 cm⁻¹ and 1435 cm⁻¹ in 0° polarization dynamic FTIR spectra decreased upon increasing the treatment temperature, indicating the elastic-like response of cellulose for thermally-treated wood decrease. For the 220 °C treated sample, the bandshift ratio of cellulose glycosidic bond decreased compared with other thermal treatment samples, but the intensities of the two split peaks of cellulose increased again. Those results indicated that the shear slipping between cellulose microfibrils decrease and microfibrils reorientation due to hemicellulose degradation after thermal treatment may cause the toughness of the thermally-treated wood decrease, or the brittleness increase.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10570-022-04471-3.

D. Wang
Northwestern Polytechnical University of Culture and Heritage, Xi’an, Shaanxi, China
e-mail: wangrookie@163.com

F. Fu · L. Lin (✉)
Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing, China
e-mail: linly@caf.ac.cn

F. Fu
e-mail: feng@caf.ac.cn
Introduction

Due to increased focus on energy conservation and pollution reduction, wooden materials are widely used in various fields because wood is a renewable resource with an exceptional strength-to-weight ratio; however, the utilization of wood during outdoor service is restricted by their lack of dimensional stability, low resistance to decay, and poor durability (Guo et al. 2015; Mastouri et al. 2021). Many wood modification technologies have rapidly advanced, including thermal, chemical, and other treatment processes (Hill 2006).

Thermal modification between 160 °C and 240 °C has been used to improve the dimensional stability and microbial resistance of wood (Sandberg et al. 2013; Hill et al. 2021), but several undesirable changes also occur which, depending upon the severity of thermal treatment, can cause losses in both strength and stiffness (Bekhta and Niemz 2003; Windiesen et al. 2009; Rautkari and Hill 2014; Kačíková et al. 2013; Candelier et al. 2016). For example, exposure of spruce wood to 200 °C for 4 h has been found to result in a 44–50% loss in bending strength and 4–9% loss in bending stiffness (Bekhta and Niemz 2003). Changes in the chemical structure of thermally-treated wood are aggravated, which also can increase its brittleness, or decrease its toughness (Hughes et al. 2015), rendering the materials unsuitable for structural applications (Arnold 2010; Widmann et al. 2012). Understanding at the molecular level the influence of thermal treatment on the mechanical behaviour is of fundamental interest from fundamental research and applications points of view.

Previous studies have clearly shown that thermal treatment causes massive chemical structure changes in wood polymers. The hemicellulose and amorphous regions of cellulose are more susceptible to thermal degradation, which increases wood’s crystallinity and dimensional stability (Hill et al. 2021; Alén et al. 2002; Lin et al. 2018; Yin et al. 2017). In addition, cellulose crystallite dimensions significantly increased after thermal treatment due to the rearrangement of adjacent cellulose chains (Inagaki et al. 2010; Guo et al. 2016). The result of 13C CPMAS NMR spectroscopy indicated the methoxyl group content decreased, leading to a more condensed lignin structure (Wikberg and Maunu 2004). The increased wood polymer interaction due to the thermal treatment was most likely caused by cross-linkages being formed between the different components of the cellulose, lignin, and xylan moieties (Salmén et al. 2008); however, so far these studies rarely proved direct evidence for determining how these chemical structural changes affect the mechanical properties of thermally-treated wood from molecular-level.

Combining FTIR spectroscopy and mechanical analysis is important method for obtaining...
information on the internal structure of wood polymers, such as polymer orientation (Salmén and Bergström 2009), interaction between wood polymers (Åkerholm and Salmén 2001; Hofstetter et al. 2006). Furthermore, the technology also provides an in situ method to study molecular-level responses to stresses and analyze mechanical interactions among chemical compositions in wood-based materials (Hinterstoisser et al. 2003; Salmén et al. 2016; Peng et al. 2019; Stevanic and Salmén 2020). In this paper, we used static tension and dynamic FTIR spectra to characterize response changes in the molecules of thermally-treated wood resulting from external mechanical stretching. These response changes mainly reflect in band positions and intensities of wood polymers in the FTIR spectra, which are evaluated the influence on thermal treatment on the changes of chemical structure and mechanical properties of wood. Furthermore, experiments on different thermal treatment intensities will help to deepen the micromechanical understanding of thermally-treated wood and associated macromolecules.

Materials and methods

Materials

Spruce wood (Picea asperata, about 31 growth rings) was obtained from Shanghai province, China. Wood specimens with dimensions of 35 cm × 2 cm × 20 cm in the longitudinal (L), radial (R), and tangential (T) directions were prepared. All specimens were oven-dried at 65 °C for 48 h and then at 103 °C for 24 h, and were then divided into six groups. Their average basic density was 0.41 g/cm³.

Methods

Thermal treatment processing

Thermal treatments were conducted in a vacuum vessel equipped with two metal heating plates. First, the specimens were clamped between two metal heating plates, then residual gas was removed from the vessel by pulling a vacuum of −0.9 MPa for 1 h. The two metal heating plates were heated to a predetermined temperature (160 °C, 180 °C, 200 °C, and 220 °C) and heating rate was 30°C/min, then held for about 15 min in order to the center temperature of treated sample reach the predetermined temperature. Treatment time was set to 1 h. Finally, the vacuum was unloaded, and the specimens were taken out.

Chemical composition analysis

Chemical composition analysis was performed according to a previous research method (Wang et al. 2014). The untreated and treated samples were mashed to a length of 0.18–0.25 cm. Holocellulose analysis was performed according to Wises’s sodium chlorite method, the cellulose was determined by Pulps-Determination of alkali resistance method, and the lignin content was determined by acid-insoluble Klason lignin. The hemicellulose content was determined by subtracting the cellulose content from the holocellulose content. All percentages of chemical constituents were averages of six replicates.

X-ray diffraction measurements

The untreated and treated samples were ground using an ordinary mill (Speed was 32,000 revolutions per minute) and sieved using a steel sieves (60 mesh). The samples of 0.5 mm in thickness and 7 mm in diameter were formed from 0.05 g of the sieved powder by pressing in a mold under 10 kN. Three samples were formed for each treatment condition. The XRD patterns of the samples were measured using an X-ray diffractometer reflection mode (D8 Advance, BRUKER, Germany), with Ni-filtered CuKα radiation (λ = 0.154 nm) at 40 kV and 40 mA. The reflection intensity was recorded through the scanning angle (2θ) range of 5–45° at a scanning speed of 1°/min, as shown in (Supplementary materials Fig. S1). Peaks in diffraction intensity curve were resolved using PeakFitR (Sea-Solve Software, Inc., Richmond, CA). The crystallinity index (CI) was calculated by the Segal method (Segal et al. 1959) and the following equation:

\[
CI = \frac{I_{200} - I_{am}}{I_{200}} \times 100\%
\]

where \(I_{200}\) is the maximum intensity of the cellulose I (200) peak, and \(I_{am}\) is the minimum intensity at 20~18.5°.
The crystal width is defined as the average thickness of cellulose crystallites perpendicular to the cellulose (200) plane \((D_{200})\). Based on the Scherrer equation (Alexander 1969), \(D_{200}\) was calculated by the following equation:

\[
D_{200} = \frac{K\lambda}{\beta_{1/2} \cos \theta_{200}}
\]

(2)

where \(K\) is the Scherrer constant \((K=0.9)\), \(\lambda\) is the wavelength of the X-rays \((0.1542\ \text{nm})\), and \(\beta_{1/2}\) is the half bandwidth (full width at half maximum, FWHM) of the (200) peak in radians, and \(\theta_{200}\) is the Bragg angle for the (200) plane.

The microfibril angles (MFA) of thermally-treated wood samples were measured using an X-ray diffractometer transmission mode (D8 Advance, BRUKER, Germany). The samples with dimensions of 20 mm \(\times\) 10 mm \(\times\) 1 mm in the \(L, T,\) and \(R\) directions were fixed with double-side tape in a platform holder, with the direction of the zero scale of the platform holder parallel to the sample fiber axis. The platform rotated 360° at a rate of 0.5°/step. In the test, the incident light was perpendicular to the sample chord plane, exhibiting an angle 20 with the receiving light. Of particular note, the relationship between (200) reflections and the azimuth angle could be measured when the setting diffraction angle 20 was 22.1°. Subsequently, diffraction curves were fitted by GaussAmp bimodal functions (Hu et al. 2017) and the T-method average MFA values was calculated by utilizing the well-established 0.6 T method (Cave 1966), as shown in (Supplementary materials Fig. S2).

**Static-loading FTIR and Dynamic FTIR spectrosopies**

Static tension and dynamic Fourier-transform infrared (FTIR) spectra were recorded on a VERTEX 70 spectrometer combined with a polymer stretcher kit (A555/Z, Bruker, Ettlingen, Germany). The samples used in the static tension and dynamic FTIR experiments were cut into dimensions of 25 mm \((L)\times15\ \text{mm}\ \times20\ \mu\text{m}\ \(R)\), with the direction of the fiber axis parallel to the load direction. Before testing, samples were equilibrated in the sample chamber for 2 h \((25^\circ\text{C}, \ \text{RH 65\%})\).

Static tension FTIR spectra were recorded at different tensile strains to study the molecular responses to the loading of thermally-treated wood (Salmén and Bergström, 2009). A sample was mounted in the stretcher kit, with the longitudinal direction of specimens parallel to the tensile direction. The spectra were recorded at a 1 cm\(^{-1}\) resolution, using an average of 16 scans at each strain. Five samples were tested in each kind of treatment intensity. The spectra were baseline corrected at 1800 cm\(^{-1}\) and 2300 cm\(^{-1}\), and the 1st derivative of each spectrum was used to determine the peak position for each specific absorption peak of wood polymers (Wang et al. 2020).

Dynamic FTIR spectroscopy can be used to observe the molecular responses of wood constituents in strained wood (Salmén et al. 2016; Wang et al. 2020). The samples were pre-stretched in the longitudinal direction by using the stretcher to apply a load of 4 N (approximately 50% of the breaking stress). A small sinusoidal strain (<0.3% by a 4 N pre-stretched load) with a frequency of 16 Hz was applied to the sample, and the transition dipole responses were monitored as a phase lag with respect to the external perturbation. An interferometer was run in a step-scan mode with a scanning speed of 1.0 Hz. An in-phase spectrum was obtained to indicate immediate changes or elastic responses (0° phase loss angle) and an out-of-phase spectrum was used to represent the time-delayed changes or viscous response (90° phase loss angle). IR radiation was polarized by a wire grid polarizer at 0° relative to the stretching direction. An optical filter was added after the polarizer to reduce the spectral range 3000–700 cm\(^{-1}\). Three samples in each kind of thermal treatment intensity were tested. The spectra were baseline corrected. All spectra were baseline corrected at 2300 cm\(^{-1}\), 1800 cm\(^{-1}\), and 700 cm\(^{-1}\), and were normalized to 1 at 1435 cm\(^{-1}\) (Salmén et al. 2008).

**Statistics**

Statistical analyses of chemical compositions, crystallinity, crystallite size, MFAs were performed employing one-way ANOVA to assess the significance \((P<0.05)\) of the thermal treatment affected differences. All the statistical analyses were performed using the beta version of SAS software (version 8, SAS Institute Inc, USA).
Results and discussion

Chemical compositions

The chemical compositions relative percentages of the thermally-treated wood were shown in Table 1. The least thermally-stable hemicellulose began to degrade at 160 °C, consistent with a previous study (Alén et al. 2002). One-factor ANOVA was used to investigate the statistical significance of the relative contents of chemical compositions as a function of temperature (Table 1). The result indicated that the degradation of hemicellulose increased with temperature, but the 180 °C had not a significant influence on the degradation of hemicellulose at a significance level of 5% compared with the 160 and 200 °C. Furthermore, as shown in Table 1, the cellulose almost no degradation occurred. The main reasons were that cellulose has better thermal stability than hemicellulose (Kim et al. 2001; Inagaki et al. 2010; Guo et al. 2016); it also could have to do with shorter thermal treatment time in our study (Bekhta and Niemz 2003). Finally, the loss of hemicellulose during heating also increased the relative content of lignin.

Cellulose crystalline structure

Table 2 displays the crystallinity CI and crystal width of thermally-treated wood as functions of temperature. The crystallinity and crystal width of thermally-treated wood samples increased with respect to the untreated samples. For the untreated wood samples, the CI was 48.32%, in agreement with a previous study (Andersson et al. 2005). The CI of the wood samples thermally-treated from 160 to 200 °C increased to 53.96%, which is similar to variations in the CI after heating in air or nitrogen (Kubojima et al. 1998); however, there was a slight decrease in the crystallinity at 220 °C, and had no significant difference at a significance level of 5% compared with the 200 °C thermally-treated sample. Furthermore, the average crystallite thickness ($D_{200}$) of the untreated wood was 2.77 nm, and the values of the thermally-treated wood from 160 to 220 °C increased to 2.97 nm, indicating a 7.2% increase compared with the untreated sample.

Table 1 Chemical compositions of different thermally-treated samples

| Temperatures | Holocellulose (%) | Lignin (%) | α-Cellulose (%) | Hemicelluloses (%) |
|--------------|------------------|------------|----------------|------------------|
| Untreated    | 68.39 ± 0.16$^A$| 21.65 ± 0.31$^D$| 43.65 ± 0.29$^A$| 24.74 ± 0.45$^A$|
| 160°C        | 65.55 ± 0.24$^B$| 22.71 ± 0.12$^C$| 43.89 ± 0.59$^A$| 21.66 ± 0.34$^B$|
| 180°C        | 64.86 ± 0.87$^{BC}$| 22.77 ± 0.88$^C$| 43.68 ± 0.11$^A$| 21.18 ± 0.23$^{BC}$|
| 200°C        | 64.16 ± 0.38$^C$| 23.57 ± 0.07$^B$| 43.47 ± 0.19$^A$| 20.69 ± 0.30$^C$|
| 220°C        | 61.39 ± 0.18$^D$| 24.90 ± 0.13$^A$| 42.98 ± 0.78$^A$| 18.41 ± 0.64$^B$|

Superscripts A, B, C, D, denote analysis of variance, where the same letter indicates no statistically significant difference at a significance level of 5%

Table 2 XRD and static tensile FTIR analysis results of different thermally-treated samples

| Treatment Temp | CI (%) | $D_{200}$ (nm) | MFA (°) | Bandshift of cellulose C–O–C (cm$^{-1}$/de) |
|---------------|--------|---------------|--------|-----------------------------------------|
| Untreated     | 48.32 ± 0.32$^D$ | 2.77 ± 0.02$^D$ | 19.81 ± 0.41$^A$ | $y = -2.92 \times e^{-0.50} R^2 = 0.87$ |
| 160 °C        | 49.48 ± 0.06$^C$ | 2.83 ± 0.01$^C$ | 19.71 ± 0.31$^A$ | $y = -3.15 \times e^{-0.06} R^2 = 0.74$ |
| 180 °C        | 52.54 ± 0.19$^B$ | 2.90 ± 0.02$^B$ | 19.48 ± 0.62$^A$ | $y = -3.31 \times e^{-0.06} R^2 = 0.87$ |
| 200 °C        | 55.96 ± 0.63$^A$ | 2.95 ± 0.04$^A$ | 19.41 ± 0.38$^A$ | $y = -3.36 \times e^{0.01} R^2 = 0.87$ |
| 220 °C        | 53.27 ± 0.83$^{AB}$ | 2.97 ± 0.02$^A$ | 18.56 ± 0.24$^B$ | $y = -2.70 \times e^{-0.10} R^2 = 0.81$ |

Superscripts A, B, C, D, denoted analysis of variance, same letter indicated no statistically significant difference at a significance level of 5%
One-factor ANOVA was used to investigate the statistical significance of the crystallinity and crystal width as a function of temperature (Table 2). Analysis showed that temperature (160–200 °C) had a significant influence on the crystallinity at a significance level of 5%. The main reason for the increase in the degree of crystallinity was hemicellulose degradation, which also was related to the rearrangement of amorphous cellulose molecules (Hori and Wada 2005; Xing et al. 2016; Yin et al. 2017); however, the crystallinity of the sample treated at 220 °C was not significantly different than that of the sample treated at 200 °C. Furthermore, ANOVA analysis showed that temperature (160–220 °C) had a significant influence on the cellulose crystallite dimensions at a significance level of 5%.

Arrangement of cellulose microfibril

As shown in Table 2, the average MFA of the untreated sample wood was 19.81°. The mean MFAs decreased from 19.71 to 18.56° upon increasing the temperature from 160 to 220 °C, and the standard deviations were in the range 0.31–0.62°. The one-factor ANOVA results indicated no variation in the MFA with temperature from 160 to 200 °C, but for the sample treated at 220 °C, the MFA significantly decreased to 18.56° compared with the untreated and other thermally-treated samples (Table 2). Early study results, by transmission electron microscopy micrographs to a fast Fourier transformation algorithm, also indicated that the thermal treatment from 200 to 225 °C led to cellulose microfibrils reorientation processes (Zollfrank and Fromm 2009; Björn 2010). One possible reason was that the additional free space created by polysaccharose degradation might be filled with the remaining cellulose fraction yielding a limited reorientation of the cellulose microfibrils (Zollfrank and Fromm 2009).

Results of static tension FTIR

Figure 1 shows the spectral changes as a function of longitudinal tensile strain applied to the thermally-treated (the 180 °C treated sample as a general example of thermal treated samples, Fig. 1A) and untreated samples (Fig. 1B). The absorption peak at 1160 cm\(^{-1}\) (glycosidic C–O–C vibration of cellulose) underwent a substantial shift to lower wave numbers as the tensile strain increases, which signified an increase in the

---

**Fig. 1** Static FTIR spectra of thermally-treated treatment (A: 180 °C) or untreated (B) wood samples subjected to different strains

**Fig. 2** Shifts in the absorption peaks at 1160 cm\(^{-1}\) (cellulose) and 1150 cm\(^{-1}\) (lignin), as a function of the longitudinal strain for samples subjected to different thermal treatments
length of the covalent bonds involved in the vibration absorption, i.e., a decrease in the force constant of the bond (Wool 1981). This response was attributed to the deformation of the glycosidic bond of cellulose, which has also been observed in previous studies (Eichhorn et al. 2001; Salmén and Bergström 2009; Wang et al. 2020).

As shown in Fig. 1, the longitudinal tensile strain of 180 °C treated sample was less than that of the untreated sample, but the bandshifts of the cellulose glycosidic bond before the sample break were more. To examine the effect of the treatment temperature on the deformation of cellulose, the bandshift in the absorption peak at 1160 cm⁻¹ was plotted against the applied strain. The peak shifted approximately linearly with the tensile strain towards a lower wavenumber ($R^2 > 0.7$, Fig. 2). As shown in Table 2, the bandshift ratio of the untreated sample was $-2.92$ cm⁻¹/dε, and the bandshift ratios of the samples treated from 160 to 200 °C increased upon increasing the temperature; however, the bandshift ratio of the sample treated at 220 °C was $-2.72$ cm⁻¹/dε, which was smaller than that of the other samples. The ANOVA results indicated that temperatures from 160 to 180 °C significantly influenced the shift of the absorption peak at a significance level of 5%, but there was no significant difference between the samples treated at 180 °C and 200 °C. Finally, the bandshift ratio of the sample treated at 220 °C was significantly reduced compared with the untreated and other treated samples.

For hemicellulose and lignin, the characteristic peaks at 1735 cm⁻¹, 1510 cm⁻¹, and 810 cm⁻¹, belonged to C=O stretching vibrations in the O=C–OH group of the glucuronic acid unit in xylan (Åkerholm and Salmén 2001), to the aromatic skeletal vibrations and C=O stretching of lignin (Faix 1991), and to vibrations caused by equatorial hydrogens on the C₂ atom in the mannose residues of glucomannan (Åkerholm and Salmén 2001; Guo et al. 2015). As shown in Fig. 2, for the untreated or treated wood samples, no substantial shift in the specific absorption peaks of hemicellulose and lignin occurred, which has also been widely confirmed by earlier researches (Eichhorn et al. 2001; Salmén and Bergström 2009; Wang et al. 2020). For all the samples, taking the characteristic peak at 1510 cm⁻¹ of lignin as an example, the characteristic peak position of the matrix in the static FTIR spectra was no obvious change during stretching (Fig. 2).

A schematic showing the cell wall deformation of wood is shown in Fig. 3. The $S_2$ layer of the wood cell wall, generally the thickest with the smallest distribution of MFA, is the layer directly responsible for the axial mechanics of cells (Jarvis 2009). When the tracheid was stretched to a strain ($\varepsilon_0$) along the cell axial direction, the strain along the cellulose microfibril longitudinal direction was $\varepsilon_0 \cos \theta$, which was the sum of shear slipping strain between microfibrils ($\varepsilon_2$) and the stretching strain of microfibril itself ($\varepsilon_1$) (Adler and Buehler 2013), as shown in Eq. (3):

$$\varepsilon_0 \cos \theta = \varepsilon_1 + \varepsilon_2$$

It was assumed that the MFA ($\theta$) did not change during stretching, and then the first derivative with respect to the deformation ($\varepsilon_0$) was calculated using Eq. (4):

$$\frac{1}{\cos \theta} = \frac{d\varepsilon_1}{d\varepsilon_0} + \frac{d\varepsilon_2}{d\varepsilon_0}$$

The former deformation was a relationship of the deformation of cellulose, which was related to the shift in the absorption peak at 1160 cm⁻¹. The later deformation had contributions from shear slipping between microfibrils, which was related to bridges between microfibrils, such as hemicellulose and intermolecular hydrogen bonds (Kretschmann 2003). For the samples treated at 160–200 °C, the absolute values of the bandshift ratios of the cellulose
characteristic peak increased upon increasing the temperature, which indicated the stretching deformation of cellulose increased with the thermal treatment temperature. According to Eq. (4) \((1 / \cos \theta = \text{constant})\), the stretching deformation increase of cellulose microfibrils led to the shear slipping between cellulose microfibrils decreasing. According to the chemical compositions of thermally-treated wood at 160–200 °C (Table 1), the degradation of hemicellulose mainly led to shear slipping between cellulose microfibrils decreasing. Hemicellulose, as the interface between cellulose and lignin, caused the cellulose microfibrils to undergo shear slip and provided ‘Velcro mechanics’ in wood, which increased the plastic deformation and toughness of cell walls (Kretschmann 2003; Adler and Buehler 2013). However, for the samples treated at 220 °C, the bandshift ratio of the C–O–C bonds of cellulose decreased compared with other thermally-treated samples. One of the main reasons was the MFA of the 220 °C treated samples decrease. The decrease of shear slipping and reorientation along cell axis of cellulose microfibrils might lead to the toughness of the thermally-treated wood decreasing, or the brittleness increasing (Hughes et al. 2015).

Results of dynamic FTIR

Figure 4 shows the mean dynamic FTIR spectra of untreated wood samples with an IR beam polarized 0° and 90° relative to the strain direction. Molecular changes due to deformation are reflected in a split absorption band in the dynamic spectra, consisting of adjacent positive and negative responses. The in-phase spectrum is a measure of the elastic-like response, and the out-of-phase spectrum is associated with the viscous-like behavior (Hofstetter et al. 2006; Åkerholm and Salmén 2003). In the 0° and 90° polarization modes, the signal intensities of the in-phase spectra in both polarization directions were several times higher than those of the out-of-phase spectra, which mean that there were no molecular groups with a time-delayed response (Åkerholm and Salmén 2003).

Two clear split bands at 1169 cm\(^{-1}\) and 1435 cm\(^{-1}\) can be seen in the in-phase spectrum at 0° polarization. The C–O–H bending vibrations of the \(\text{CH}_2\text{–OH}\) group appeared at 1435 cm\(^{-1}\), and the cellulose skeleton vibrations, including the C–O–C bridge stretching, appeared at 1169 cm\(^{-1}\) (Tashiro and Kobayashi 1991; Hinterstoisser et al. 2001). The two split peaks at 0° polarization reflected changes in the energy of these bonds of cellulose due to stretching deformation by the applied load, and indicated that the cellulose was the primary load-bearing material during the longitudinal stretching of wood (Åkerholm and Salmén 2003). At 90° polarization, the two split peaks of cellulose disappeared in the in-phase spectrum in Fig. 4, but two single peaks of lignin at 90° polarization can be seen. At 1035 cm\(^{-1}\), a peak appeared due to C–O deformation and aromatic C–H deformation in lignin, and the peak at 1510 cm\(^{-1}\) was assigned to the aromatic structure of lignin (Faix 1991). In addition, a weaker peak at 1730 cm\(^{-1}\) can also be seen in Fig. 4, and was attributed to the aromatic structure of the xylan (Collier et al. 1992). In softwood, xylan
and lignin are closely associated, and gulcomannan crosslinks on the surface of microfibrils (Åkerholm and Salmén 2001). Those single peaks of lignin and hemicellulose in the dynamic FTIR spectra indicated the matrix in the wood participated in the stress transfer (Bergander and Salmén 2002).

Figure 5 presents the mean spectra of the thermally-treated wood samples at 0° polarization. There are two split peaks at 1169 cm⁻¹ and 1435 cm⁻¹ related to cellulose, but their intensities in the spectra of thermally-treated samples were different. This indicated that the cellulose still was load-bearing material of thermally-treated wood during the longitudinal stretching, but the stiffness of thermally-treated woods was different for various intensities treatment. For the samples treated from 160 to 200 °C, the intensities of the two split peaks decreased upon increasing the temperature, which indicated that the elastic-like response of cellulose or the stiffness of thermally-treated wood were decreased (Hofstetter et al. 2006; Åkerholm and Salmén 2003). The main reason for this was that the hemicellulose, as the microfibril-matrix interface, crosslinked on the surface of the microfibrils, which also increased the stiffness of the cell wall (Berglund et al. 2020). This was also demonstrated by the relationship between the hemicellulose content and elastic modulus of thermally-treated wood (Kačíková et al. 2013). Therefore, for the samples treated from 160 to 200 °C, the degradation of hemicellulose mainly caused the two split peaks intensities of cellulose or the stiffness of thermally-treated wood decreases. But for the sample treated at 220 °C, the intensities of the two split peaks of cellulose again increased, indicating the stiffness recovery of thermally-treated wood. It was related to reorientation along cell axis of cellulose microfibrils.

The mean dynamic spectra of thermally-treated samples at 90° polarization are shown in Fig. 6. The intensities of many peaks decreased upon increasing the treatment temperature. For example, the characteristic peak of xylan at 1730 cm⁻¹ disappeared in the spectra of thermally-treated samples. The main reason for this was that xylan, which led to the disappearance of the characteristic peak of xylan at 1730 cm⁻¹. In the in-phase spectra, the peaks at 1200–1300 cm⁻¹, which were related to the C–C and Caryl-O vibrations of lignin (Collier et al. 1992; Salmén et al. 2008), remained, but their peak intensities decreased upon increasing the treatment temperature. Furthermore, the peak at 1035 cm⁻¹, assigned to the aromatic C–H deformation of lignin, also decreased upon increasing the treatment temperature. The degradation of xylan, as the cellulose-lignin bridge material in softwood (Åkerholm and Salmén 2001), may have also resulted in a decrease in the mechanical responses of lignin in the cell transverse direction. Finally, the peak at 1510 cm⁻¹, assigned to the aromatic structure of lignin, still appeared in the dynamic spectra at 90° polarization, but the intensities of the peak were various for different thermally-treated intensities samples. The decrease in the intensities of several peaks in the lignin spectra might indicate that the cross-linking between cellulose and lignin did not occur. In earlier studies, the hemicellulose degradation products of thermal treatment wood may function as catalysts in an auto-crosslinking reaction forming covalent hemiacetal bonds between the different components of the cellulose, lignin and hemicellulose (Salmén et al. 2008). But there was no evidence in our study that whether or not a cross-linking reaction between wood polymers occurred.

**Conclusion**

It has been demonstrated here that static tension and dynamic FTIR measurements may be used to monitor molecular straining during the longitudinal tension loading, and help to deepen the micromechanical understanding of thermally-treated wood. For the native wood or thermally-treated wood, the cellulose
was load-bearing material, but the lignin mainly participated in the stress transfer. For the 160–200 °C treated wood, the degradation of hemicellulose led to shear slipping between cellulose microfibrils and elastic-like response of cellulose decrease. For the 220 °C treated wood, the cellulose microfibrils reorientation also may cause the toughness of the thermally-treated wood decrease, or the brittleness increase.

Acknowledgments The authors gratefully acknowledge the financial support of the Nature Science Foundation of China (No.32101458), the Fundamental Research Funds for the Central Universities (D5000210672) and the Nature Science Foundation of China (No. 31890772).

Authors’ contributions DW: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Visualization. LL: Conceptualization, Writing – review and editing. FF: Conceptualization, Writing – review and editing.

Funding The authors have not disclosed any funding.

Declarations

Conflict of interest The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

References

Adler DC, Buehler MJ (2013) Mesoscale mechanics of wood cell walls under axial strain. Soft Matter 9:7138–7144. https://doi.org/10.1039/c3sm50183c

Åkerholm M, Salmén L (2001) Interactions between wood polymers studied by dynamic FTIR spectroscopy. Polymer 42:963–969. https://doi.org/10.1016/S0032-3861(00)00434-1

Åkerholm M, Salmén L (2003) The oriented structure of lignin and its viscoelastic properties studied by static and dynamic FT-IR spectroscopy. Holzforschung 57:459–465. https://doi.org/10.1515/HF.2003.069

Alén R, Kotilainen R, Zaman A (2002) Thermochemical behavior of Norway spruce (Picea abies) at 180–225 °C. Wood Sci Technol 36:163–171. https://doi.org/10.1007/s00226-001-0133-1

Alexander LE (1969) X-ray diffraction methods in polymer science. Wiley, Amsterdam, pp 423–424

Andersson S, Serimaa R, Vaeaenaenen T, Paakkari T, Jaemsae S, Viitaniemi P (2005) X-ray scattering studies of thermally modified scots pine (Pinus sylvestris L.). Holzforschung 35:155–427. https://doi.org/10.1515/HF.2005.069

Arnold M (2010) Effect of moisture on the bending properties of thermally modified beech and spruce. J Mater Sci 45:669–680. https://doi.org/10.1007/s10853-009-3984-8

Bekhta P, Nienz P (2003) Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. Holzforschung 57:539–546. https://doi.org/10.1515/HF.2003.080

Bergander A, Salmén L (2002) Cell wall properties and their effects on the mechanical properties of fibers. J Mater Sci 37:151–156. https://doi.org/10.1023/A:1013115925679

Berglund J, Mikkelsen D, Flanagan BM, Ditial S, Vilaplana F (2020) Wood hemicellulose exert distinct biomechanical contributions to cellulose fibrillar networks. Nat Commun 11:4692. https://doi.org/10.1038/s41467-020-18390-z

Björn B, Cordt Z, Oliver F, Jörg F, Mathias G, Karsten D (2010) Micromechanics and ultrastructure of pyrolysed softwood cell walls. Acta Biomater 6:4345–4351. https://doi.org/10.1016/j.actbio.2010.05.026

Candelier K, Thevenon MF, Pettrissans A, Dumarcay S, Gerardin P, Pettrissans M (2016) Control of wood thermal treatment and its effects on decay resistance: a review. Ann Forest Sci 73:571–583. https://doi.org/10.1007/s13595-016-0541-x

Cave ID (1966) Theory of X-ray measurement of microfibril angle in wood. For Prod J 16:37–43

Collier WE, Schultz TP, Kalasinsky VF (1992) Infrared study of lignin: reexamination of aryl-alkyl ether C-O stretching peak assignments. Holzforschung 46:523–528. https://doi.org/10.1515/hfsg.1992.46.6.523

Eichhorn SJ, Sirichaisit J, Young RJ (2001) Deformation mechanisms in cellulose fibres, paper and wood. J Mater Sci 36:3129–3135. https://doi.org/10.1007/A1017969916020

Faix O (1991) Classification of lignin from different botanical origins by FT-IR spectroscopy. Holzforschung 45:21–27. https://doi.org/10.1515/hfsg.1991.45.s1.21

Guo J, Yin YF, Song KL, Yin YF (2015) Changes of wood cell walls in response to hygro-mechanical steam treatment. Carbohydr Polym 115:207–214. https://doi.org/10.1016/j.carbpol.2014.08.040

Guo J, Rennhofer H, Yin Y, Lichtenegger HC (2016) The influence of thermo-hygro-mechanical treatment on the micro- and nanoscale architecture of wood cell walls using small- and wide-angle x-ray scattering. Cellulose 23:2325–2340. https://doi.org/10.1007/s10570-016-0982-2

Hill CAS (2006) Thermal modification of wood. Hill CAS(ed) Wood modification: chemical, thermal and other processes. Wiley, New York, pp 99–126

Hill C, Altgen M, Rautkari L (2021) Thermal modification of wood—a review: chemical changes and hygroscopicity. J Mater Sci 56:6581–6614. https://doi.org/10.1007/s10853-020-05722-z

Hinterstoissberger, Åkerholm M, Salmén L (2001) Effect of fiber orientation in dynamic FTIR study on native cellulose. Carbohydr Res 334:27–37. https://doi.org/10.1016/S0008-6215(01)00167-7

Hinterstoissberger, Åkerholm M, Salmén L (2003) Load distribution in native cellulose. Biomacromol 4:1232–1237. https://doi.org/10.1021/bm030017k

Hofstetter K, Hinterstoissberger B, Salmén L (2006) Moisture uptake in native cellulose - the roles of different
hydrogen bonds: a dynamic FT-IR study using deuterium exchange. Cellulose 13:131–145. https://doi.org/10.1007/s10570-006-9055-2

Hori R, Wada M (2005) The thermal expansion of wood cellulose crystals. Cellulose 12:479–484. https://doi.org/10.1007/s10570-005-5967-5

Hu K, Huang Y, Fei B, Yao C, Zhao C (2017) Investigation of the multilayered structure and microfibril angle of different types of bamboo cell walls at the micro/nano level using a LC-PolScope imaging system. Cellulose 24:4611–4625. https://doi.org/10.1007/s10570-017-1447-y

Hughes M, Hill C, Ptriem A (2015) The toughness of hygro-thermally modified wood. Holzforschung 69:851–862. https://doi.org/10.1515/hf-2014-0184

Inagaki T, Siesler HW, Mitsuji K, Tsuchikawa S (2014) Effect of initial moisture content on the anti-swelling efficiency of thermally modified scots pine sapwood treated in a high-pressure reactor under saturated steam. Holzforschung 68:323–326. https://doi.org/10.1515/hf-2013-0084

Kim DY, Nishiyama Y, Wada M, Kuga S, Okano T (2001) Thermal decomposition of cellulose crystallites in wood. Holzforschung 55:521–524. https://doi.org/10.1515/HF.2001.084

Kretschmann D (2003) Nature materials: velcro mechanics in wood. Nat Mater 2:775. https://doi.org/10.1038/nmat1025

Kubojima Y, Okano T, Ohta M (1998) Vibrational properties of Sitka spruce heat-treated in nitrogen gas. J Wood Sci 44:73–77. https://doi.org/10.1007/BF00521878

Lin BJ, Colin B, Chen WH, PetriSSans A, Rousset P, Petris-sans M (2018) Thermal degradation and compositional changes of wood treated in a semi-industrial scale reactor in vacuum. J Ana App Pyrol 130:8–18. https://doi.org/10.1016/j.jaap.2018.02.005

Mastouri A, EfhamiSSi D, ShirMohammadli Y, Oladi R (2021) Physicochemical properties of thermally treated poplar wood in silicone and rapeseed oils: a comparative study. J Build Eng 43:102511. https://doi.org/10.1016/j.jobe.2021.102511

Peng H, Salmén L, Jiang J, Lu J (2019) Contribution of lignin to the stress transfer in compression wood viewed by tensile FTIR loading. Holzforschung 74:459–467. https://doi.org/10.1515/hf-2019-0206

Rautkari L, Hill C (2014) Effect of initial moisture content on the anti-swelling efficiency of thermally modified scots pine sapwood treated in a high-pressure reactor under saturated steam. Holzforschung 68:323–326. https://doi.org/10.1515/hf-2013-0078

Salmén L, Bergström E (2009) Cellulose structural arrangement in relation to spectral changes in tensile loading FTIR. Cellulose 16:975–982. https://doi.org/10.1007/s10570-009-9331-z

Salmén L, Possler H, Stevanic JS, Stanzl-Tschegg SE (2008) Analysis of thermally treated wood samples using dynamic FT-IR-spectroscopy. Holzforschung 62:676–678. https://doi.org/10.1515/HF.2008.113

Salmén L, Stevanic JS, Olsson AM (2016) Contribution of lignin to the strength properties in wood fibres studied by dynamic FTIR spectroscopy and dynamic mechanical analysis (DMA). Holzforschung 70:1155–1163. https://doi.org/10.1515/hf-2016-0050

Sandberg D, Haller P, Navi P (2013) Thermo-hydro and thermo-hydro-mechanical wood processing: an opportunity for future environmentally friendly wood products. Wood Mater Sci Eng 8:64–88. https://doi.org/10.1080/17480272.2012.751935

Segal L, Creely JJ, Martin AE, Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. Text Res J 29:786–794. https://doi.org/10.1177/00405755902901003

Stevanic JS, Salmén L (2020) Molecular origin of mechnano-sorptive creep in cellulosic fibres. Carbohydr Polym 230:11615. https://doi.org/10.1016/j.carbpol.2019.115615

Tashiro K, Kobayashi M (1991) Theoretical evaluation of three-dimensional elastic constants of native and regener-ated cellulososes: role of hydrogen bonds. Polymer 32:1516–1526. https://doi.org/10.1016/0032-3861(91)90435-L

Tumen I, Aydemir D, Gunduz G, Uner B, Cetin H (2010) Changes in the chemical structure of thermally treated wood. Bioresources 5:1936–1944

Wang X, Deng Y, Wang S, Min C, Meng Y, Pham T, Ying Y (2014) Evaluation of the effects of compression combined with heat treatment by nanoindentation (NI) of poplar cell walls. Holzforschung 68:167–173. https://doi.org/10.1515/hf-2013-0084

Wang D, Lin L, Fu F (2020) Deformation mechanisms of wood cell walls under tensile loading: a comparative study of compression wood (CW) and normal wood (NW). Cellulose 27:4161–4172. https://doi.org/10.1007/s10570-020-03095-9

Wang X, Chen X, Xie X, Wu Y, Zhao L, Li Y, Wang S (2018) Effects of thermal modification on the physical, chemical and micromechanical properties of Masson pine wood (Pinus massoniana Lamb.). Holzforschung 72:1063–1070. https://doi.org/10.1515/hf-2017-0205

Widmann R, Fernandez-Cabo JL, Steiger R (2012) Mechanical properties of thermally modified beech timber for structural purposes. Eur J Wood Prod 70:775–784. https://doi.org/10.1007/s00107-012-0615-x

Wikberg H, Maunu SL (2004) Characterisation of thermally modified hard- and softwoods by 13C CP/MAS NMR. Carbohyd Polym 58:461–466. https://doi.org/10.1016/j.carbpol.2004.08.008

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. https://doi.org/10.1515/HF.2009.084
Wool RP (1981) Measurements of infrared frequency shifts in stressed polymers. J Polym Sci Pol Chem 19:449–457. https://doi.org/10.1002/pol.1981.180190305

Xing D, Li J, Wang X, Wang S (2016) In situ measurement of heat-treated wood cell wall at elevated temperature by nanoindentation. Ind Crop Prod 87:142–149. https://doi.org/10.1016/j.indcrop.2016.04.017

Yin J, Yuan T, Lu Y, Song K, Li H, Zhao G, Yin Y (2017) Effect of compression combined with steam treatment on the porosity, chemical composition and cellulose crystalline structure of wood cell walls. Carbohydr Polym 155:163–172. https://doi.org/10.1016/j.carbpol.2016.08.013

Zollfrank C, Fromm J (2009) Ultrastructural development of the softwood cell wall during pyrolysis. Holzforschung 63:248–253. https://doi.org/10.1515/HF.2009.031

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.