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Literature Review: Measuring Growth-strain by IR-spectroscopy

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EXECUTIVE SUMMARY

Growth-stresses cause problems in wood processing. Current measurement methods of growth-stresses are labour-intensive and destructive. Researches have shown that changes in stress levels, moisture content and temperature induce molecular deformations in wood, especially cellulose. It has also been shown that strain in cellulose can be measured by IR spectroscopy. Near infrared (NIR) contains information of overtones and combinations, while Raman and mid-range spectroscopy measures fundamental vibrations. Changes of hydrogen bonds are observable in the far-infrared region. It needs to be proven that molecular strain can be measured accurately enough in solid wood. Candidate IR technologies are Raman and NIR spectroscopy as they allow sampling of solids wood with portable devices.

INTRODUCTION

To meet the increasing international demand of wood, some fast-growing species like pines, eucalyptus and poplar are favoured for tree plantations. Fast-growing planted trees have wider growth rings and a higher juvenile wood content compared to wood from natural forests. Juvenile wood is the main cause for inferior wood properties from short-rotation tree crops (Bao et al., 2001). However, eucalyptus has relatively high density, which can be 0.46-0.57 g/cm^3 for *Eucalyptus globulus* and 0.43 -0.56 g/cm^3 for *Eucalyptus nitens* (Raymond & Muneri, 2001). Higher density is often associated with better mechanical and other wood properties.

Eucalyptus plantations have been estimated to cover more than 20 million ha in 2009, mainly distributed in Australia, India, Brazil, China and Africa (Iglesias & Wilstermann, 2009). Plantation eucalyptus is mainly used for low-value applications like pulp and firewood. There is an increasing interest in using this resource as higher-value solid wood products to narrow the gap between demand and supply. This applies to the current NZ eucalyptus resource, e.g. *E. nitens*. Recently, the New Zealand Dryland Forest Initiative (NZDFI) has established a project to breed *Eucalyptus bosistoana* as high value timber resource. Instead of merely focusing on high growth rate and improved form, favourable wood properties are key objectives in breeding programs to produce high-value timber and increase grower's profitability.

A major problem preventing eucalyptus from solid wood uses is its high growth-stress. The release of growth-stress will cause problems like heart checking, end-splitting, internal checking and board distortion during wood processing. Growth stress is variable between individuals and good logs exist. Currently, growth-stress is mainly evaluated by measuring strain released by drilling or cutting, which is both destructive and cumbersome. Stress causes changes in the wood structure on the molecular level, which can be studied by spectroscopy, including near infrared (NIR), Raman and far infrared (Far-IR). It is conceivable that a rapid and non-destructive method based on spectroscopy can be developed to predict the growth-stress levels in standing trees or logs. This would allow segregating from the existing eucalyptus resource those logs which are suitable for high value solid wood products.

Growth-stress

Growth-stress refers to the mechanical stresses developed in trees as they grow. It is believed that growth-stress results from two kinds of stress: support stress and maturation stress. Support stress is a response to the weight of the tree, while maturation stress occurs spontaneous during wood formation (Clair et al., 2006).

Two theories have been proposed to explain the mechanism for the generation of growth-stress (Archer, 1987; Okuyama et al., 1994). The "lignin swelling" theory claims that newly formed cells tend to increase their cell wall thickness during lignification of the cell wall. When cellulose fibrils are aligned in longitudinal direction, matrix substance swelling cause the cell wall to expand in transverse direction and the rigid fibrils forcing it to contract in longitudinal direction. When cellulose fibrils are in transverse direction, the opposite situation applies, which means the occurrence of a longitudinal compression stress. However, the theory fails to explain the large tensile strain in tension wood which has low lignin contents, especially that with gelatinous layer.

An alternative theory is the "cellulose contraction" theory. It is hypothesized that cellulose microfibrils tend to contract, and this induces longitudinal tensile stress. But, it is inappropriate to explain the longitudinal compressive stress in compression wood with low cellulose contents (Toba et al., 2013; Yang & Waugh, 2001). Microfibril angle (MFA) is the most important factor affecting the magnitude and direction of growth-stresses. It has been proposed that lignin swelling is effective when the MFA is larger than 30º, while cellulose contraction can explain cases with MFA smaller than 25º (Toba et al., 2013; Yamamoto, 1998).

Okuyama et al. (1994) combined those two theories and suggested that tensile stress from microfibril contraction and compressive stress from deposition of lignin exist at the same time. This "unified hypothesis" has been demonstrated by the detection and calculation of mechanical stresses both in the cellulose microfibrils and the matrix (Toba et al., 2013). However, the calculation needs further confirmation due to the use of estimated values for Young's modulus of cellulose crystals and Poison's ratios.

Distribution of growth-stress and its influence on wood utilization

Growth-stress accumulated during tree growth will be released when the trees are felled and sawn into boards. To demonstrate the effect of growth-stress, a procedure called "plank-stripping" was developed (Jacobs, 1945). Central planks were removed from trees and then sawn into strips. The changes in length as well as curvature of the strips were recorded. Results indicated that outer strips tend to contract and strips near the pitch tend to expand. Stress states can be inferred from the released strains.

Growth-stress can be resolved into three directions: longitudinal, tangential and radial. Although transverse stresses are causing shakes and checks, most research focused on the longitudinal growth-stress. Following the plank-stripping study, many models have been built with regard to the distribution of stress and strain in trees. Cutting will cause stress redistribution and stress concentration effects. Detailed mathematical methods and modelling for these have been discussed by Archer (1987).

A longitudinal stress model was developed by Kubler (1987). Wood near the pitch is under compression while wood close to the cambium is under tension. According to this model, longitudinal strain can be expressed as a function of peripheral strain and distance across the radius as follows:

$$E_l = \varepsilon_{lp} [1 + 2 \ln(r/R)]$$

Where ε_l is the longitudinal strain, ε_{lp} is the peripheral strain, r is the distance to the pith and R is the radius.

Growth-stress can cause detrimental effects on wood utilization. When timber is cut, the growth-stress will redistribute to reach a new equilibrium state. End-splits can occur following the cross-cut because the longitudinal stress is released and transformed into transverse stresses. For a full-diameter board, the centre near the pith tends to expand while the outer part tends to contract longitudinally. Considering the inferior strength of the pitch, the board will split at the centre and bend outward. Growth-stresses are related to internal checking during drying, board distortion during sawing and brittle-heart and other wood defects (Archer, 1987; McKinley et al., 2002).

Some methods have been developed to reduce undesirable effects of growth-stresses on timber production. For instance, hammering S-shaped hooks into the cut surfaces can reduce end-splitting. Frame saws and double edging saws equally redistribute growth-stresses on both sides of cants (Dinwoodie, 1966). Long-term water-spray storage can reduce the residual growth-stress (Yang & Waugh, 2001). However, these methods are not aiming at the root causes. The generation of growth-stress is a biological process and thus are genetically controlled and affected by silviculture (Archer, 1987; Yang & Waugh, 2001). Therefore, breeding programs based on the accurate and rapid evaluation of growth-stress are likely to solve this problem.

Measurement of Growth-stress

It is impossible to measure growth-stresses directly. Growth-stresses are usually calculated by the measured strain and modulus of elasticity of wood. The approaches to measure strains are destructive and involve cutting or drilling to release the growth-stress.

Those methods have been reviewed by Yang and Waugh (2001). In the Nicholson method, two studs are attached to the surface of a debarked tree stem parallel to wood grain. Then a wood segment containing those studs is removed from the tree. The change in distances between the two studs after removal is the measured strain. The French (CIRAD) method involves two pins punched into the wood. Then the distance between those two points is measured before and after drilling a hole in the middle. The strain gauge method originated from Japan. A strain gauge is glued to the wood and growth-stresses are released by kerfing or boring around the strain gauge. It is to note that strain data measured by different approaches cannot be directly compared (Yang & Waugh, 2001). Researchers from the University of Canterbury developed a splitting test method, which involves sawing a log into two halves. The opening gaps measured at both ends is highly correlated to the axial growth-stress. This method is suitable to measure growth-stress quickly in small diameter trees (Chauhan & Entwistle, 2010).

Growth-stress is variable within a tress. Single local growth-strain measurements are not necessarily representative of the processing characteristics of a log. Therefore several local measurements need to be averaged.

All those approaches are destructive and more or less time-consuming. Rapid and non-destructive evaluation methods for growth-stress are desirable. There have been some attempts using stress waves to predict growth-strain based on the relationship between MOE and growth-stresses. But the relationship is inconsistent (Yang & Waugh, 2001). SiliviScan measurements were made to establish relationships between growth-stresses and various wood properties (Yang et al., 2006). With a better understanding of the molecular response of wood to stress, spectroscopic methods including NIR and Raman could provide an accurate approach.

LITERATURE REVIEW

The woody cell wall

Nature optimized plant cell walls to fulfil various functions. Plant cell walls have a delicate hierarchical architecture, such as cell shape, cell wall layers, orientation of microfibrils and chemical composition in different layers (Burgert, 2006).

Wood is a natural composite of oriented cellulose microfibrils embedded in a matrix of lignin and hemicellulose. Cellulose has a partly crystalline structure and provides tensile strength and stiffness to the cell wall (Altaner, Thomas, et al., 2014). Cellulose is believed to be the main component to bear tensile stress while no response from lignin and hemicellulose was detected for wood samples under tensile stress (Salmén & Bergström, 2009). The role of the matrix under tensile stress and its interaction with microfibrils remains elusive.

Wood cell walls have layered structures, consisting of a middle lamella, primary walls and secondary walls. The middle lamella consists principally of lignin and pectin, but only 25% of the total lignin exists in this layer because of its thin thickness compared to the secondary wall. The primary cell wall needs to be rigid to withstand stresses and stretchable to accommodate growth. The transverse orientation of microfibrils restrains dimensional changes in circumferential direction and facilitates longitudinal extension (Burgert, 2006).

Secondary walls have three layers: S1, S2 and S3, among which S2 is the thickest layer and dominates wood properties. Cellulose microfibrils in the S2 are oriented in a certain angle with respect to the long axis of the cell. This angle is referred to as microfibril angle (MFA) and its variation has significant effect on the mechanical and physical properties of wood (Donaldson, 2008; Downes et al., 2002). MFA varies between plant fibre sources. Table 1 summarized the microfibril angle of some plant fibres.

Plants can control and adjust their mechanical performances by changing the MFA such as in reaction wood. Another example is the higher MFA in juvenile wood compared to mature wood. A higher microfibril angle means less cell wall stiffness and but higher strain to failure. Young trees protect themselves from potential bending forces by increasing its MFA (Burgert, 2006).

Table 1 Chemical composition and MFA of various plant fibers

Fiber type	Cellulose (%)	Hemicellu -lose (%)	Lignin (%)	MFA (º)	References
Flax	64.1–71.9	16.7–20.6	2.0–2.2	5–10	(De Rosa *et al.*, 2010)
Hemp	70.2–74.4	17.9–22.4	3.7–5.7	2–6.2	(De Rosa *et al*., 2010)
Jute	61–71.5	12.0–20.4	11.8–13	8	(De Rosa *et al*., 2010)
Ramie	68.6–76.2	13.1–16.7	0.6–0.7	7.5	(De Rosa *et al*., 2010)
Bamboo	26-43	15-26	21-31	9	(Yu *et al.*, 2007)
Sisal	43-78	10-13	4-12	10-22	(Mwaikambo, 2006)
New Zealand flax	45.1–72.0	30.1	11.2	4-40	(Richter *et al.*, 2011)
Banana	63-64	10–19	5	11	(De Rosa *et al*., 2010)
Cotton	82-96	2-6	0.5-1	20-30	(Mwaikambo, 2006)
Coir	32-43	0.15-0.25	40-45	30–49	(De Rosa *et al*., 2010)

MFA of New Zealand flax (*Phormium tenax*) is measured in sclerenchymatic tissue.

The MFA of wood varies significantly between and within trees. The MFA of softwood is generally higher than that of hardwood, and it decreases from pitch to bark for both. In spruce latewood, MFA is 20º as measured by small angle X-Ray scattering (Lichtenegger et al., 1999). MFA of *Pinus radiata* (more than 25 years old) has mean values between 18º and 22° (Downes et al., 2002). In comparison, the MFA of balsa wood can be as low as 1.4° (Borrega et al., 2015). Tree height affects MFA as well. MFA is reported larger at the base of the tree for a given growth ring. MFA can also be strongly influenced by environmental factors. For instance, MFA for compression wood is higher than in normal wood, while that for tension wood is smaller (Donaldson, 2008).

Cellulose microfibrils and crystalline structure

Cellulose is the most abundant organic polymer resource on earth. The most common sources of cellulose are higher plants including trees, cotton, hemp, flax, jute, cereal straw etc.. It can also be found in some bacteria, fungi, algae and even some animals like tunicate (Eichhorn et al., 2010; Pérez & Samain, 2010). The high stiffness, low cost and biodegradability of cellulose make it an attractive candidate for the design of novel materials. Recently, cellulose fibres have been used as reinforcement for nanocomposites. New applications like optically transparent paper, DNA/cellulose hybrid materials, foams and aerogels have aroused widespread research interest (Eichhorn et al., 2010).

Native cellulose is a long chain polymer with glucose units connected by β-1,4-glycosidic linkages. The degree of polymerization of cellulose can range from 500 to 15,000 (Brett, 2000). Several cellulose chains constitute a microfibril of a few nanometres in thickness, and cellulose microfibrils combine into aggregates of 10-20 nm for conifer wood (Fernandes et al., 2011). Microfibril diameters depend on the source, and it can be 1.5-3 nm in primary cell walls, 2.2-3.6 nm for wood and as large as 15-25 nm for algae (Fernandes et al., 2011; Pérez & Samain, 2010).

Cellulose has crystalline/orderd regions and non-crystalline/disordered (amorphous) regions. Crystalline cellulose are those with cellulose chains closely and regularly connected by hydrogen bonds, while cellulose chains in the disordered domain are accessible to water and chemical reactions. The degree of crystallinity refers to the degree of structural order in cellulose, which can be measured by X-ray diffraction and other techniques. The degree of crystallinity in cellulose varies between plant species. The crystallinity index varies significantly depends on the measuring techniques (Park et al., 2009). Crystallinity index of wood measured by X-ray scattering is reported 52% for both pine and spruce wood (Andersson et al., 2004).

It is reported that cellulose synthase complexes in the plasma membrane are responsible for the polymerization of glucan chains (Wertz et al., 2010). It is believed that the microtubules control the movement of the terminal complexes, and therefore the orientation of microfibrils (Brett, 2000). Terminal complexes have two types of spatial arrangement, which is supposed to affect the shape and size of microfibrils (Wertz et al., 2010). In bacteria and some algae, subunits of terminal complexes are arranged linearly in single or multiple rows, while terminal complexes in shape of hexagonal rosettes were observed in ferns and vascular plants. The synthetic subunits of the complex can synthesize cellulose chains and nascent chains close to each other assemble to a microfibril.

Since the terminal complexes in higher plant have six units, it is hypothesized the numbers of chains in cellulose microfibrils should be divisible by six. A 36-chain microfibril model has been frequently discussed (Wertz et al., 2010). However, a 24-chain microfibril model is favored in spruce wood according to experimental data (Fernandes et al., 2011; Thomas et al., 2013). Newman et al. (2013) suggested that an 18-chain model showed good consistency with both X-ray scattering and solid NMR results.

Cellulose can form different crystal polymorphs, including cellulose I, II, III and IV, which differ in crystalline cell parameters. All native celluloses are cellulose I. Based on NMR techniques, researchers found native cellulose (cellulose I) is a composite of two distinct allomorphs: Iα and Iβ (Atalla & Vanderhart, 1984; VanderHart & Atalla, 1984). The proportion of the two crystalline forms

depends on the cellulose origin. Cellulose Iα dominates in bacteria and algae, while cellulose Iβ exists more in higher plants like wood, cotton, flax etc. Almost pure cellulose Iβ can be found in the outer membrane of the marine animals tunicate (*Halocynthia roretzi*) (Nishiyama et al., 2002; Pérez & Samain, 2010).

Cellulose Iα and Iβ differ in the crystal structure and the hydrogen bonding system. Phase Iα has a one-chain triclinic unit with a P1 space group whereas phase Iβ features a two-chain monoclinic unit with a P21 space group (Wertz et al., 2010, Dumitriu, 2004).

Both Iα and Iβ allomorphs arrange in the "parallel up" configuration with the reducing ends on one side and all the hydroxymethyl groups in tg conformation. The main difference between the Iα and Iβ structures is the relative displacement of adjacent cellulose sheets in the chain axis direction (Nishiyama et al., 2003).

Hydrogen bonds in cellulose

Cellulose has a substantial amount of intramolecular and intermolecular hydrogen bonds. In plant cells, parallel cellulose chains are laterally bonded into sheets by intermolecular hydrogen bonds. Intramolecular hydrogen bonds in the chain axis direction provide linear stability. Those sheets stacked on the top of each and are held together by weak CH…O bonds and van der Waals forces (French et al., 2014). The large number of hydrogen bonds and van der Waals interactions makes cellulose a stable structure (Jarvis, 2003; Stokke et al., 2013).

Nishiyama et al. (2002) studied the hydrogen bonding system of cellulose Iβ using X-ray and neutron fibre diffraction. The results showed that the O3H…O5 intramolecular hydrogen bond has well defined positions, while other hydrogen bonds involving O6 and O2 are relatively disordered. This result suggests an inherent disorganization of the intermolecular hydrogen bonding system.

Based on the locations of hydrogen atoms from neutron crystallography, researchers proposed two hydrogen bonding networks for centre chains of cellulose Iβ. Most chains (70-80%) are arranged in the hydrogen bonding scheme A and surface regions with defects showed features of scheme B (Nishiyama et al., 2008).

According to Hofstetter et al. (2006), different hydrogen bonds have different accessibilities. They studied the interaction of hydrogen bonds from wood pulps with water using Fourier Transform infrared spectroscopy (FT-IR) combined with deuteration. Results showed that few O3-H...O5 bonds were exchanged by deuterium, while O2-H...O6 bonds were much more accessible to deuteration. But the assignments of hydrogen bonds in this study are different from recent assignments (Lee et al., 2015).

Hydrogen bonds contribute greatly to the mechanical performance of cellulose. By studying the changes in molecular structure of cellulose under tension, researchers found that hydrogen and covalent bonds cooperate to form molecular leverage, thus provide stiffness to cellulose chains (Altaner, Thomas, et al., 2014).

The assignment of hydrogen bonds in IR spectra is challenging for a couple of reasons. First, the O-H stretching region is quite broad (3000-3800 cm^{-1} in mid-range) because of the overlap of several hydrogen bonds and stretching modes. According to (Lee et al., 2015), previous attempts to assign O-H vibration peaks are inaccurate due to use of outdated cellulose models with incorrect bond lengths and angles. In addition, vibrational coupling of the OH groups leads to the inaccurate assignment based on the simple correlation of peak position to the O-H…O distance. They compared calculation results from density functional theory (DFT) and molecular dynamics (MD) simulations with experimental data of IR and sum frequency generation (SFG), and obtained a full assignment of OH stretching peaks (Table 2) for cellulose (Lee et al., 2015).

Table 2 Assignment of OH groups in native cellulose (Lee et al., 2015)

IR (cm^{-1})	main OH groups	hydrogen bond	6CH2OH conformation
3240	2O-H	Iα (intrachain), 2O−H···6O	tg
3270	2O-H	Iβ (intrachain), 2O−H···6O	tg
3300-3310	2,3,6O-H	(coupled) 2O−H···6O−H···3O−H···5O	tg
~3340	2,3,6O-H	(coupled) 2O−H···6O−H···3O−H···5O	tg
~3350	2,3,6O-H	(coupled) 2O−H···6O−H···3O−H···5O	tg
3370-3380	3O-H	(intrachain) 3O−H···5O	-
3400-3410	6O-H	(interchain) 6O−H···3O	tg
~3450	2,3,6O-H	weakly hydrogen-bonded OH groups in the less-crystalline or surface regions	tg>gt>gg

Molecular deformation of wood and cellulose in response to stress

Cellulose crystals have extraordinary mechanical properties and their high stiffness provides a framework for wood. There is still no consensus on the modulus of crystalline cellulose (Eichhorn et al., 2010). Recent determinations with a few exceptions are in the range of 100-160 GPa. Considering the low density, crystalline cellulose has a stronger specific modulus than steel and glass. However, this value is not found in native plant fibres because the existence of disordered cellulose. Much research has been done to isolate cellulose nanofibers for use in strong materials as reinforcement (Eichhorn et al., 2010).

Applied mechanical stress

Tensile mechanical stress is the most straightforward and widely applied method to study the deformation of wood and cellulose fibres. It cannot only provide information on the mechanical properties of biomaterials but also shed light on the interaction between wood components.

The changes of cellulose lattice parameters during deformation can be monitored by X-ray diffraction (XRD). According to a study on Norway spruce (Peura et al., 2007) cellulose chains elongated along the axis (c-direction) and distances between cellulose sheets (a-direction) decreased under axial stress. The relative elongation of the unit cell is lower than the macroscopic strain of the sample, which indicates that the deformation of non-crystalline components contribute to the overall elongation (Peura et al., 2007). A contraction in the b dimension and increase in the monoclinic angle were also reported under axial tension (Altaner, Thomas, et al., 2014).

Molecular responses to stress can be detected by various spectroscopic techniques, including mid-range infrared, Raman and NIR spectroscopy. As shown by a dynamic FTIR study on the deformation behaviour of cellulose, stress was mainly distributed in the glucose ring, the C-O-C glycosidic linkage and intramolecular the O3-H…O5 bond, while the O2-H…O6 played a minor role (Hinterstoisser et al., 2003). Another FTIR research on wood sections showed that, the shift of the 1160 cm^{-1} peak corresponding to C-O-C vibrations was linearly correlated to the applied stress (Salmén & Bergström, 2009).

Raman spectroscopy was applied to study the deformation mechanisms of different cellulose fibres, wood and paper (Eichhorn et al., 2010). Results showed that the 1095 cm^{-1} band assigned to cellulose ring stretching shifted to lower wavenumbers during tensile stretching. Moreover, stress-induced Raman band shifts of various cellulosic materials are different with strain, and invariant with stress, which indicates that the shift is controlled by stress. This band shift has been confirmed by other researchers (Peetla et al., 2006). Gierlinger et al. (2006) also proposed that the change in the height ratio of the 1127 and 1097 cm^{-1} bands can be interpreted as the change of

the torsion angle of the glycosidic C-O-C bond. The changes in the OH stretching region around 3375 cm^{-1} are a sign of weakened hydrogen bonding but need further investigation.

Based on some multivariate statistical methods like Partial Least Squares (PLS) models, NIR has been used as a non-destructive tool to predict the changes in molecular structures, chemical composition and other wood properties (Tsuchikawa, 2007). Wood responses to tensile stress on the molecular level were monitored by NIR spectroscopy and a model was built on the base of NIR spectra to predict the stress level (Sandak et al., 2013). NIR spectroscopy combined with a PLS model was also applied to predict the load applied to small wood beams in four-point bending (André et al., 2006). Knowledge about the functional groups and band assignment is not necessary for building multivariate models. A deeper understanding of the underlying chemistry is required to promote further applications of this method.

Growth-stress

Dimensional changes of cellulose microfibrils in tension wood can be detected by X-ray diffraction. It was found that, cellulose lattice spacing (c-axis direction) decreased after the release of maturation stress (Clair et al., 2006). In the gelatinous layer of tension wood, this value is larger than that in normal wood (Clair et al., 2011).

Another research group measured the lattice spacings of crystalline cellulose in wood samples before and after boiling using wide-angle X-ray diffraction (Toba et al., 2013). Results showed an increase in the 200 and a decrease in the 004 lattice spacing after boiling, which indicates that growth-stresses remained in wood even after removal from the tree stem.

A recent study tried to predict longitudinal growth-strain using a partial least squares regression model based on NIR spectra collected on the surface of Sugi (*Cryptomeria japonica* D. Don) green logs (Watanabe et al., 2013). The results indicated NIR is a possible approach but needs further refinement with more samples. This research did not analyse band shifts and band assignments. A detailed study on the relationship between band shifts and stress levels will help to justify this method.

Molecular deformation due to moisture and temperature

Apart from mechanical stress, temperature can affect the cellulose structure at the molecular level. A study by Altaner, Horikawa, et al. (2014) investigated the changes of IR-spectra of cellulose Iβ at low temperatures. The results are consistent with weak C–H…O hydrogen bonds between cellulose sheets. Furthermore, it was suggested that the blue-shifts of O-H stretching with increasing temperature were not caused by the thermal expansion of crystal structure.

The thermal expansion behaviour of cellulose Iβ at temperatures from 20 to 300 °C was studied using X-ray diffraction (Wada et al., 2010). The anisotropic thermal expansion behaviour of cellulose Iβ was interpreted as a result of the intermolecular hydrogen-bonding system (Wada, 2002; Wada et al., 2010).

It is widely accepted that moisture affects the amorphous matrix substance in the cell wall, but has little effect on cellulose crystals. However, X-ray measurements of wood samples revealed that cellulose crystals shrink longitudinally and expand transversely during drying (Abe & Yamamoto, 2006).

The deformations of cellulose crystals as results of tensile and dehydration stress were measured through X-ray diffraction (Zabler et al., 2010). Those two kinds of deformation were different in nature and magnitude. Dehydration shortened cellulose crystals in the longitudinal direction (by 0.2%), but expanded it in the transverse direction (by 0.6%). However, upon tensile straining a longitudinal elongation was observed without transverse contraction.

Researchers hold different views on the mechanisms for cellulose deformations caused by moisture content change. Abe and Yamamoto (2006) thought that cellulose crystals in green wood were compressed by the swollen matrix. During drying, the decline of compression stress resulted in the transverse expansion of the cellulose crystals. However, considering the strong lateral stiffness of cellulose crystals, Zabler et al. (2010) proposed that, it is unlikely for the matrix to generate enough compressive stress. It was assumed that, the capillary condensation of water in nanoporous structures lead to strong compressive stresses, which are sufficient to shorten the lateral a-axis by 0.6%.

Recently, by studying the dimension changes of cellulose microfibrils in wood during repeated wet-dry treatments using X-ray diffraction, researchers concluded that microfibrils expand laterally during drying because the matrix shrinks laterally (Toba et al., 2012). They found an interfacial separation between cellulose microfibrils and matrix will occur after repeated wetting and drying.

To predict drying stress levels of wood, a PLS model was built based on NIR spectra in relation to released strain (Watanabe et al., 2013). However, it is difficult to separate the effect of strain on NIR spectra from that of moisture content changes. Because the variation of moisture content and other wood properties, a relatively poor estimation ability (R^2=0.72) were obtained.

Infrared spectroscopy techniques

Molecules can absorb and emit electromagnetic radiation of certain frequency, which cause the transition of energy states of specific bonds. Infrared spectra contain rich information about the molecular structure as the absorbed energy differs between bonds.

The electromagnetic spectrum can be divided into three regions (Osborne et al., 1993). Normally, the near infrared (NIR) region ranges from 14300 cm^{-1} to 4000 cm^{-1} (700 - 2500 nm), the mid-infrared (MIR) region from 4000 cm^{-1} to 200 cm^{-1}, and the far-infrared (FIR) region from 200 cm^{-1} to 10 cm^{-1}.

Near infrared spectroscopy compared to mid-infrared

Fundamental vibrations, including stretching and deformation, are mainly in the mid-infrared region. NIR spectra contain the overtones and combinations of fundamental vibrations of bands. NIR spectra are dominated by bonds involving hydrogen due to the low reduced mass of H related bonds, like O-H and C-H bonds (Osborne et al., 1993). Therefore, NIR is sensitive to hydrogen bonding and interactions with water.

Since overtones are weaker than fundamental vibrations, less energy is absorbed in the NIR region. This allows analysing wood samples up to a several millimetres in transmission mode (Schwanninger et al., 2011). For MIR, only very thin samples (20-30 µm) can be used in transmission mode (Tsuchikawa & Siesler, 2003a). Powdered sample is an alternative, but factors like particle size, surface roughness and porosity affect the spectra. Sample size has been reported to affect mechanical performance (Buchelt & Pfriem, 2011). Thicker samples keep their cellular wood structure intact. Specimens with a thickness in the microscopic range showed increasing strength with thickness and lower values than ‘normal’ sized wood (Yu et al., 2009). This suggests that damage caused by cutting has a significant effect on the mechanical performance of microtomed wood samples. Interactions between thick wood samples and water or mechanical stress are observable only by NIR.

MIR and NIR spectroscopy can be performed in transmission and reflection mode. Instead of measuring light transmitted through a sample, the reflection mode measures absorption properties of a sample from the reflected light. Diffuse reflection mode is very useful for powders and solid samples with rough surfaces (Khoshhesab, 2012). Spectroscopy of wood in diffuse reflection mode does not need sample preparation. NIR spectra obtained by transmission mode have a longer path length compared to MIR, which means samples can be easily prepared. In contrast, MIR has a higher requirement for sample preparation like cutting thin tissue sections with a microtome or

pressing KBr pellet with powder. The simplicity of sample preparation is a significant advantage of NIR.

The transmission mode provides strong signal and consequently good spectra. Diffusely reflected radiation is scattered to all directions most of which cannot be collected by the detector. For mid-IR, since more energy is absorbed and less is scattered compared to NIR, the diffuse reflection is weak. Therefore, the diffuse reflection mode is less common for mid-IR (Khoshhesab, 2012). Due to the easy sample preparation and more efficient diffuse reflection, it is possible for NIR spectrometers to be manufactured as portable devices.

NIR analysis can be non-destructive, fast and simple to perform and allows deeper sampling rather than the surface. These advantages enable NIR to be used for online monitoring and production control (Meglen & Kelley, 2003) and have potential to measure growth-stress in standing trees. However, NIR spectra are less resolved and dominated by CH and OH bonds.

Interpretation of NIR spectra

NIR spectra contain rich information, but it is challenging to understand the underlying molecular causes. Many factors make it difficult to establish a good relationship between NIR spectra and the molecular structure. First, wood is a natural composite of cellulose, hemicellulose and lignin, and their signals overlap with each other due to their similar molecular structure. NIR spectra of wood contain more complicated information than pure cellulose.

As mentioned above, the NIR region corresponds to the overtones and combinations of fundamental vibration. Overtones are weaker compared to fundamental vibrations. Relative absorption intensity of the first overtone is approximately 1% of the fundamental vibrations (Schwanninger et al., 2011). The low absorption and broad shape result in highly overlapped NIR bands.

Although quantum theory and inharmonic oscillators can be applied to calculate the location of overtones, the chemical environment and coupling between neighbouring bonds make it difficult to predict signal frequencies. For instance, the fundamental stretching of C-H bonds occurs in the region of 2972-2843 cm^{-1} for alkanes, 3010-3095 cm^{-1} for alkenes and 3310-3320 cm^{-1} for alkynes (Osborne et al., 1993). As two or more bonds are connected to a common atom or the frequencies of two vibrations are similar, their frequencies will change due to the coupling effect. In addition to coupling, combination bands that represent the sum of two or more different vibrations make it a rather entangled situation.

NIR contains repetitive information. C-H bonds are present in all organic compounds and C-H vibrations occur throughout the entire NIR spectrum. According to Schwanninger et al. (2011), the first overtone of C-H stretching in methyl groups can have four bands. Deformation vibrations and different combinations make it even more difficult to assign.

Hydroxyl groups are often involved in hydrogen bonding, which affect the strength of the O-H bonds and results in a band shift compared to free O-H groups. Cellulose has abundant intermolecular and intramolecular hydrogen bonds. Temperature and mechanical stress can induce changes in bond length and bond strength (Altaner, Horikawa, et al., 2014; Altaner, Thomas, et al., 2014). These changes of O-H bonds are reflected in mid-IR and NIR spectra. The NIR spectra of hydrophilic materials like wood are affected by water. Changes of moisture content in wood are associated with the formation and breaking of hydrogen bonds. In summary, NIR spectra are informative, but it is challenging to understand the origin of spectral bands.

Far-infrared spectroscopy

Far-infrared spectroscopy, also termed as “terahertz spectroscopy”, fills the gap between the mid-infrared region and microwaves (Mantsch & Naumann, 2010). There is no consensus on the delimitation of the terahertz region, and definitions of 10-100 cm^{-1} (0.3-3 THz), or a wider region of

3.3-333.3 cm^{-1} (0.1-10 THz) are used. Time domain terahertz spectroscopy measures the transmitted and reflected terahertz pulse as a function of time, which then can be Fourier-transformed into a spectrum. Compared to traditional frequency domain spectroscopy, time domain terahertz spectroscopy can detect both the amplitude and the phase of terahertz radiation (Mantsch & Naumann, 2010).

Far-infrared spectroscopy has several advantages. Many non-conducting materials are transparent to terahertz waves, including paper, wood, clothing, plastics. This means materials can be detected through packaging and clothing. Water and metal are opaque to far-infrared. Terahertz radiation is non-ionizing and safe for biological tissues.

Apart from imaging, another important application of terahertz technology is spectroscopy, which can be informative regarding to the molecular structure. Many materials have a special fingerprint in far-infrared spectra. Therefore, it can be used as a spectroscopic imaging method to identify materials such as explosives in the security area or cellulosic fibres like ramie and bamboo (Mantsch & Naumann, 2010; Yan et al., 2013). For small molecules like water, rotational frequencies can be observed in this region. For organics and biopolymers, this region contains information about collective vibrational motions and intermolecular interactions, and is sensitive to hydrogen bonds (Lee, 2009).

Far-infrared spectra of powdered saccharides samples including glucose and cellobiose were measured in the region of 500 to 50 cm^{-1} several decades ago, but the observed peaks were not assigned (Hineno & Yoshinaga, 1972). A variety of modified cellulose samples pressed into tablets were studied in the region of 700-10 cm^{-1} and it was indicated that absorption bands can be assigned to the vibrations of polymeric chains in the crystalline area (Mukhamadeeva et al., 1990). By studying pentitols and pyranosides using infrared spectra, peaks in the range of 400 to 1000 cm^{-1} were related to hydrogen bonds (Rozenberg et al., 2000).

To date, the application of far-infrared in wood science area is limited. Terahertz imaging was examined as a non-destructive method for density mapping and absorption correlated well with wood density (Koch et al., 1998). Solid wood showed birefringence and attenuation properties in the far-infrared region and wood samples as thick as 1 cm can be penetrated by far-infrared radiation (Reid & Fedosejevs, 2006).

Very limited work has been done regarding the far-infrared spectrum of wood. Considering the sensitivity of far-infrared to water and hydrogen bonds, it might be a useful tool to study the molecular deformation of cellulose and the hydrogen bonding system.

Raman spectroscopy

When electromagnetic radiation is directed onto a sample, it will be scattered elastically and inelastically. Elastic scattering is referred as Rayleigh scattering; inelastic scattering from the interaction of laser light with matter is called Raman scattering. Raman scattering contains information of molecular vibration. Rayleigh scattering is much stronger compared to Raman scattering.

Raman spectroscopy and mid-IR are in the same wavelength region and both are based on the transitions between vibrational energy levels. Raman spectroscopy can use visible light or NIR as light source and only a small portion of the energy is absorbed by the sample causing changes in vibrational energy levels. A vibration is IR active if there is a change in the electric dipole moment of a bond. In order for a molecule to be Raman active, there must be a change in its polarizability. As a result, those two techniques are complimentary. Some vibrations that are weak or inactive in IR spectra can be strong or active in Raman spectra and vice versa. Water has a weak signal in Raman spectra. No disturbance from moisture changes can be a great advantage for Raman spectroscopy over IR spectroscopy in hydrophilic materials like wood and cellulose.

Raman spectroscopy has evolved greatly in the past 30 years. It is becoming increasingly popular because it's easy sampling and high resolution. Nowadays, portable Raman spectrometers with a resolution of 8-12 cm^{-1} are available. Portability opens up a wide range of applications including plastics identification, forensic science and medical diagnostics (Carron & Cox, 2010). Raman spectroscopy has potential to measure wood properties on standing trees or logs as a non-destructive method.

FT-Raman spectroscopy has been a feasible method to determine the chemical composition of *Eucalyptus* sp. (Ona et al., 1997). A recent study of various cellulose materials using Raman spectroscopy indicated that internal chains of never-dried wood cellulose are accessible to deuterium exchange. This work also suggested cellulose exists in both tg and gt conformations (Agarwal et al., 2016). Apart from spectroscopy, Raman imaging is another important application. Raman microscopy is becoming increasing popular due to its high resolution. It has been used to characterise the chemical distribution within wood cell walls (Gierlinger & Schwanninger, 2006; Richter et al., 2011).

Raman spectroscopy has been proven to be a powerful tool to study the response of wood or cellulose to stress on a molecular level. The band shift of the stretching motion of the cellulose ring around 1095 cm^{-1} has been investigated by different research groups (Eichhorn et al., 2001; Gierlinger et al., 2006; Peetla et al., 2006). Considering the easy sampling, good resolution and portability of advanced Raman spectrometers, it could be a powerful tool to predict the stress level in standing trees.

Polarisation combined with spectroscopy

Polarisers are useful tools in spectroscopy for the measurement of samples with molecular orientation. It is an optical filter that orients light. Polarisers are usually made of a fine grid placed on a suitable transparent substrate. When the grid spacing is much smaller than the wavelength of the light, light can only pass in the direction parallel to the grid.

The main use of polarisers is to study the molecular orientation of samples. The absorption intensity increases when the polarised light coincides with the orientation of molecular groups of interest. Through the comparison of polarised spectra obtained from different directions (dichroic behaviour), it is possible to get an insight in band assignment and orientation of chemical bonds.

Cellulose chains are linear structures. Native cellulose microfibrils are not necessarily aligned along the cell wall axis. Peak intensities in polarized spectra depend on the angle between the polarisation direction and the fibre axis and are closely related to MFA (Schmidt et al., 2006).

Polarisation combined with infrared spectroscopy has been widely used to study the molecular structure of native cellulose. Researchers applied this technique to distinguish OH bonds in different orientation. Results suggested that there is no significant difference in the temperature-induced band shifts between parallel-polarised OH bonds and perpendicular-polarised OH groups (Altaner, Horikawa, et al., 2014). A study on the hydrated fractions of cellulosic fibres indicated that hydroxyls in hydrated cellulose have an almost randomised orientation (Driemeier et al., 2015). A recent research studied the dichroism of cellulose Iβ and calculated the angle between the OH stretching dipole moment and the chain axis. The calculated values were rather close to random and ranged from 38º to 57º. The authors pointed out that it is unsuitable to compare those values to individual OH groups in cellulose Iβ (Lee et al., 2015).

Hydrogen-deuterium exchange

Hydrogen-deuterium exchange happens in the hydroxyl groups, what can provide valuable information about the hydrogen bonding system and molecular structure. For native cellulose exposed to heavy water in the vapour or the liquid state, only the amorphous/disordered area and surface of the crystalline region are accessible for deuterium exchange. Therefore, deuteration

makes it possible to label accessible hydroxyls and has been widely used to evaluate the accessibility of cellulose combined with spectroscopic (Hofstetter et al., 2006) or gravimetrical methods. High temperature or a swelling agent like NaOD can lead all hydroxyl groups, including intracrystalline ones, to be deuterated (Nishiyama et al., 1999).

The advantage of deuteration is that it does not change the original structure of cellulose (Nishiyama et al., 2002). The hydrothermal deuteration conducted to *Halocynthia* and *Cladophora* cellulose materials showed that, absorption bands in the OH stretching region shifted to lower wavenumbers without any loss of resolution and retained all peak features (Nishiyama et al., 1999). However, vapour-phase deuteration only happens in accessible hydroxyls, and signals from disordered surface chains are different from crystalline cellulose. Therefore, for partial deuterated cellulose, OD band patterns differ from OH bands (Thomas et al., 2013).

According to vibration theory, the mass increase of deuterium compared to hydrogen will cause a theoretical shift factor of 1.34 (Hofstetter et al., 2006; Šturcová et al., 2004). The wavenumber of OD bands will be the corresponding wavenumber of OH bands divided by 1.34, although experiments showed a more complicated case (Driemeier et al., 2015).

Studying the deuteration process in combination with spectroscopic techniques can help us better understand the fine structure of cellulose in wood. By comparing the diffusion process of hardwood and softwood using different deuteration agents, researchers proposed that the spaces between aggregates of elementary fibrils vary with species (Tsuchikawa & Siesler, 2003a, 2003b).

Hydrogen-deuterium exchange is a powerful tool to study the structure change of native cellulose in relation to moisture. To study the role of hydrogen bonds in native cellulose, dynamic FT-IR (samples under sinusoidal strain) and deuterium exchange were combined and suggested that, there is limited exchange for load bearing bonds like O3-H…O5 and that deuterated regions do not carry load (Hofstetter et al., 2006). Deuterium exchange was also used to assist in the analysis of the OH bending region 700-1900 cm^{-1} (Driemeier et al., 2015).

Another application of vapour-phase deuteration is to reduce the interference of hydroxyls from the amorphous region, so that signals from ordered crystalline cellulose can be obtained (Lee et al., 2015; Šturcová et al., 2004). Oppositely, we can achieve a deuteration in only the crystalline region by partial internal deuteration (Altaner, Thomas, et al., 2014). First, samples were immersed in alkali solution in D_2O to exchange all OH groups including internal crystalline ones. Then, samples were washed with H_2O to reconvert only accessible OH groups. This method gave OD stretching bands from crystalline regions (Altaner, Thomas, et al., 2014).

CONCLUSION

Growth-strain results in molecular deformation of cellulose in wood. Molecular deformations of cellulose have been measured my mid-range IR spectroscopy under laboratory conditions. Raman and NIR spectroscopy are IR techniques which are able to sample solid wood with portable devices. It needs to be proven if Raman or NIR are able to measure molecular strain in green solid wood precisely enough to assess growth-strain.

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