STRUCTURAL AND BENDING PROPERTIES OF JUVENILE AND MATURE SOFTWOOD

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Bending and structural properties of Todo fir (*Abies sachalinensis*) xylems were investigated to study the structural and mechanical properties of juvenile and mature wood. Samples obtained near the pith tended to have a small Young's modulus in the longitudinal direction. Investigation of the properties of samples revealed that juvenile wood near the pith tended to have larger microfibril angles, shorter fiber length, smaller α-cellulose content and a lower relative crystallinity index than mature wood. In addition, after chemical treatment to remove lignin and hemicelluloses, the samples of juvenile wood near the pith tended to have a slightly lower relative crystallinity index than those of mature wood. FTIR analysis of the samples after the treatment indicated that some hemicelluloses still remained within the samples, but it is also possible that the juvenile and mature wood under study contained cellulose I_β.

Keywords: cellulose microfibrils, fiber length, microfibril angle, α-cellulose content, relative crystallinity index

INTRODUCTION

Cellulose microfibrils, which comprise bundled linear chains of $\beta(1\rightarrow4)$ D-linked glucose units, have crystalline and non-crystalline regions and are reported to have high elastic modulus and strength in the longitudinal direction.[1,2] Cellulose microfibrils are a framework of cell walls of higher plants. Predominantly, trees are the major cellulose resource and one of the renewable resources on the earth.

Tree xylems are porous in nature with a cell wall, where matrix substances, such as lignin and hemicelluloses, fill among cellulose microfibrils. Cell wall structure, including the chemical component contents and properties, as well as the shape of the cells themselves, influences xylem properties.

Trees form xylems that have different mechanical and physical properties in the growth process. It is known that bending and tensile Young's modulus and strength in the longitudinal direction tend to be low in the xylems near the pith formed by cambium in the juvenile stage, whereas Young's modulus and strength are higher in the xylems outside formed by cambium in mature stages in softwood.[3-7] This results in the difference of the properties of wood, that is, the materials obtained from the xylems of trees, and leads to variation in the usage of wood.

It has been reported that these differences in longitudinal mechanical properties between juvenile and mature wood result from the differences in xylem density and structure, such as α-cellulose content and microfibril angles in S_2 layers that occupy approximately 80% of cell walls.[3-7] However, the properties of cellulose microfibrils that play an important role in the mechanical properties of xylems remain unclear.

Cellulose microfibrils are a crystalline polymer, and the crystalline structure of native cellulose is referred to as cellulose I. The elastic modulus along the molecular chain in the crystalline region of cellulose I is reported to be 138 GPa.[8] In addition, Young's modulus in amorphous regions is estimated to be lower than that in the crystalline region.[9] Moreover, cellulose I transforms into different polymorphs and the elastic moduli along the molecular chains in the crystalline region of these

polymorphs are estimated to be different.[8,9] These indicate that the structures or the ratio of crystalline regions in cellulose microfibrils would affect the mechanical properties of these microfibrils.

Recently, many studies have investigated the use of cellulose microfibrils, which have excellent properties as nanocellulose materials.[10-12] It has been reported that composites that contain cellulose fibers or nanofibers obtained from cellulose microfibrils as fillers also change their properties depending on the fiber/nanofiber structure, such as relative crystallinity, degree of polymerization (DP), and crystalline structures of cellulose, in addition to their content.[13,14] Therefore, it is important to obtain structural information on cellulose microfibrils in wood. However, there still remains a dearth of information concerning the properties of cellulose in the cell wall of juvenile and mature wood because the xylem properties of trees tend to be investigated in relation to the density of xylems or microfibril angles in S_2 layers. With regard to the usage of wood for obtaining nanocellulose materials, in addition to their usage as wood materials, it would also be important to investigate the structures of xylems or cellulose obtained from trees.

In this study, cell wall structures of juvenile and mature wood that have different mechanical properties were investigated in detail to obtain information on cellulose microfibrils, which are crystalline polymers and play important roles in the mechanical properties of wood in its different growth stages.

EXPERIMENTAL

Sample trees

Todo fir (*Abies sachalinensis*) grown in Biei, Hokkaido, Japan, was felled at 40 years of age in July 2013. Xylems obtained above the breast height were used for the following tests.

Properties of tree xylems

Mechanical properties

Samples were continuously obtained from the pith to the bark from three strips of the same tree. Samples [of 1/12/95 mm (tangential/radial/longitudinal, respectively)] were vacuum dried at 70 °C overnight over P_2O_5 and then dried at 105 °C for 1 h. Bending tests were performed after samples were weighed and measured. The span length was 60 mm, and the crosshead speed was 5 mm/min. Densities were calculated from weight and dimensions of oven-dried samples. The mean values were calculated from the data for three samples.

Fiber length and microfibril angles

Fiber length ($n > 100$ fibers) and microfibril angles ($n > 40$ fibers) were measured[15] from the xylem samples obtained every few rings from the pith to the bark. Microfibril angles of early wood in radial sections sliced by a sliding microtome were measured by iodine methods.[15-17]

α-Cellulose contents

Samples were obtained from juvenile wood near the pith and mature wood. In this study, mature wood was considered to be that in which xylem fiber length and microfibril angles were almost constant. Samples were sliced by a sliding microtome and extracted in a Soxhlet apparatus with a 2:1(v/v) mixture of benzene/ethanol for 8 h. Holocellulose was obtained from de-waxed samples by the methods of Wise,[18] and *α*-cellulose contents were obtained on the basis of the part that remained insoluble in a 17.5% NaOH aqueous solution of holocellulose. Measurements were repeated three times, and the mean values were calculated from the data for three samples.

X-ray diffraction analysis

Prior to the above treatment, the samples obtained from juvenile wood near the pith and mature wood were used for X-ray diffraction analysis after oven-drying at 105 °C. Diffraction patterns were obtained at room temperature by a Rigaku ULTIMA IV (copper target) set to 30 kV and 20 mA, with a scanning range of 5°-40° at a rate of 1°/min. The degree of relative crystallinity was calculated from the X-ray diffraction profile.[19] Three samples were used for X-ray diffraction analysis, and the mean values were calculated from the data for three samples.

Properties of samples after chemical treatment

Purified samples were obtained according to methods similar to those reported previously.[20-23] Holocellulose samples obtained from de-waxed samples by the methods of Wise were immersed in 6% KOH aqueous solution

and then allowed to stand undisturbed at room temperature overnight. The samples were then filtered and washed with distilled water. After the treatment, the samples were used for the following measurement.

X-ray diffraction analysis

The samples filtered after the treatment were oven-dried at 105 °C and used for X-ray diffraction analysis. Diffraction patterns were obtained at room temperature by a Rigaku ULTIMA IV (copper target) set to 30 kV and 20 mA, with a scanning range of 5°-40° at a rate of 1°/min. The degree of cellulose crystallinity was calculated from the X-ray diffraction profile.[19] Three samples were used for X-ray diffraction analysis, and the mean values were calculated from the data for three samples.

Degree of polymerization

The DP of cellulose was measured by the viscosity method with a copper ethylene diamine (CED) solution.[22,24,25] After the treatments, the samples were freeze-dried, and a defined amount of sample was dissolved in a CED solution, following which the solutions were stirred for 30 min at room temperature. The relative viscosities (t/t_0) of the sample solutions were measured with Canon Fenske viscometers in a water bath with a thermostat. The parameters t and t_0 are defined as the dropping times of the CED solution with and without the samples, respectively. The DP of the samples was estimated by the equation t/t_0.[24,25] Measurements were repeated three times, and the mean values were calculated from the data for three samples.

Fourier-transform infrared spectroscopy (FTIR) analysis

After the treatment, a fiber suspension was cast in the weighing tube, followed by drying over night at 50 °C and then at 70 °C for 2 h before analysis. Samples were prepared using the KBr pellet method. FTIR spectra were recorded using a Jusco FT/IR-4200 type A with IRT-5000, in the absorbance mode with 64 scans and a resolution of 4 cm^{-1} in the range from 4000 to 600 cm^{-1}.

RESULTS AND DISCUSSION

Properties of juvenile and mature wood

Mechanical properties of xylems

Figure 2 shows bending Young's modulus and density in the oven dried samples obtained from xylems continuously obtained from the pith to the bark. Although Young's modulus in the longitudinal direction tended to increase with an increase in wood density, there were some samples whose Young's modulus was low and density was high. Samples with high density and low Young's modulus tended to correspond to the samples obtained from the xylems near the pith. This tendency corresponds to the results reported on many other softwoods, in addition to Todo fir, where Young's modulus of core wood tended to be smaller than that of outer wood.[4-7]

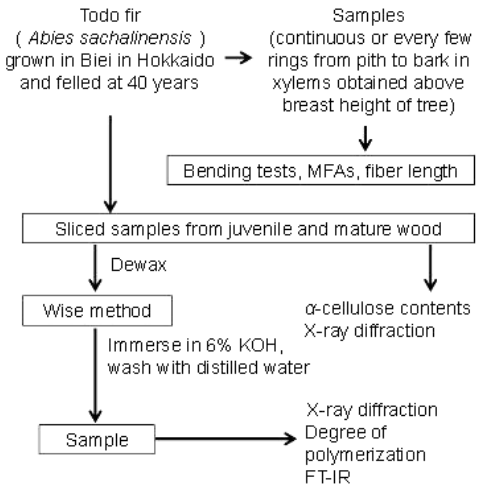

Figure 1: Scheme of experiment

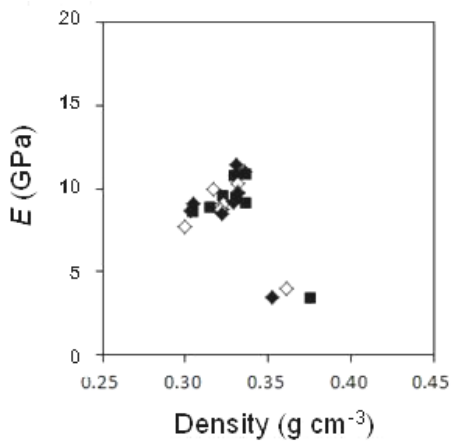

Figure 2: Relationship between Young's modulus and density of wood (E: Young's modulus of oven-dried samples, closed diamonds: strip 1, open diamonds: strip 2, closed squares: strip 3)

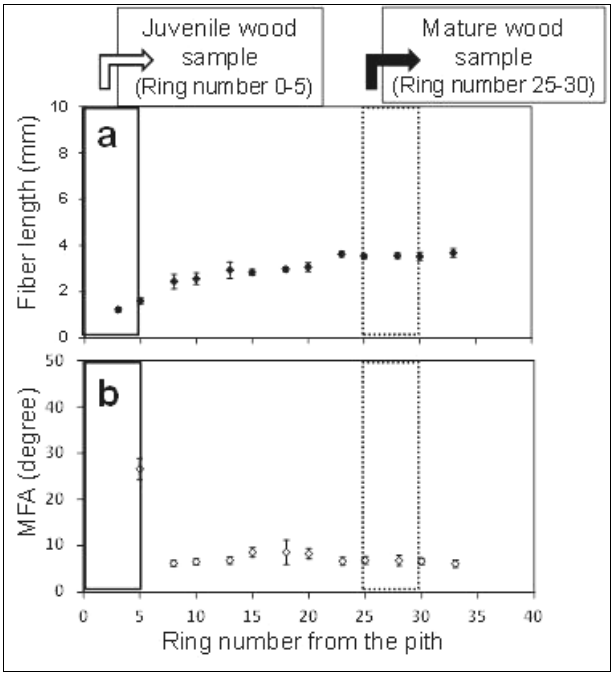

Figure 3: Relationship between ring number from the pith and fiber length (a) or microfibril angles (b) (MFA: microfibril angles)

Structural properties of xylems (fiber length, microfibril angles, α-cellulose contents, X-ray analysis)

Figure 3 shows the results of fiber length and microfibril angles of Todo fir from the pith to the bark. Radial variation of fiber length and microfibril angles showed a similar tendency to the results reported previously.[3-7] In other words, fiber length tended to be short and microfibril angles tended to be large in the samples obtained from the xylems near the pith. A trend where fiber length increased and microfibril angles decreased with increasing ring numbers from the pith was observed. Variations tended to be small in the xylems over a certain ring number. The xylems obtained from ring numbers 0-5 were considered juvenile wood near the pith and those obtained from ring numbers 25-30 were considered mature wood.

The α-cellulose content in juvenile wood near the pith tended to be slightly smaller than that in mature wood (Table 1). Figure 4 shows the X-ray diffraction pattern of wood samples obtained from juvenile wood near the pith and mature wood. X-ray diffraction indicated a cellulose I pattern in juvenile and mature wood. The relative crystallinity index tended to be slightly smaller in juvenile

wood than in mature wood (Table 2). These results indicate that the ratios of cellulose and cellulose crystals in xylems tend to be slightly lower in juvenile wood near the pith, that is, the xylem with larger microfibril angles and shorter fiber length, than in mature wood.

In general, bending or tensile Young's modulus in the longitudinal direction of softwood is reported to be affected by wood structure, such as wood density and microfibril angles in S_2 layers of cell walls. It is reported that Young's modulus is smaller and strain at yield is larger in wood with larger microfibril angles, such as compression wood.[26-29] Young's moduli in the longitudinal direction of juvenile wood in softwood are also reported to be low and present large microfibril angles, in addition to sample density.[4-7]

On the other hand, Fujimoto *et al*.[30] investigated the feasibility of near-infrared spectroscopy for estimating wood mechanical properties and reported that *α*-cellulose contents and cellulose crystallinity of wood samples moderately correlated with bending Young's modulus in hybrid larch.

As shown in Figures 2-4 and Tables 1 and 2, the samples obtained from juvenile wood near the pith, *i.e.* the xylems with larger microfibril angles, lower *α*-cellulose contents, and lower relative crystallinity, had lower bending Young's modulus than the samples obtained from mature wood, where the xylems have smaller microfibril angles, higher *α*-cellulose contents, and higher relative crystallinity.

Table 1
α-cellulose content of juvenile and mature wood samples

Sample	*α*-cellulose (%)	
	Average	S.D.
Juvenile wood	43.5	1.7
Mature wood	47.7	0.6

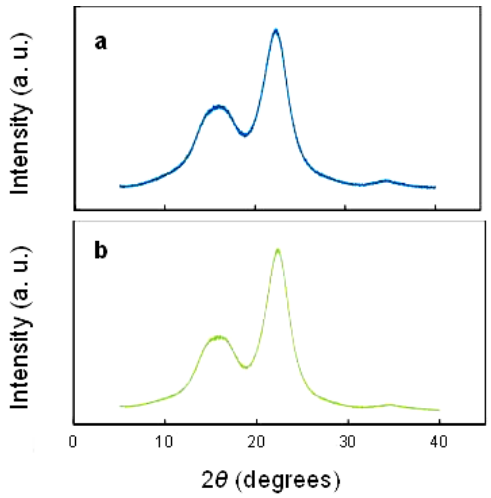

Figure 4: X-ray diffraction of juvenile (a) and mature (b) wood samples

Table 2
Relative crystallinity index of juvenile and mature wood samples

Sample	CrI (%)	
	Average	S.D.
Juvenile wood	68.4	1.5
Mature wood	74.2	0.9

Note: CrI, relative crystallinity index

It has been reported that ramie fibers with less lignin and hemicelluloses change their mechanical properties after transformation into different crystal structures upon treatment.[9] Through the conversion from cellulose I into II, III_I and IV_I, the integral crystallinity index and the crystallite size decreased and the internal surface area increased, while Young's modulus of the fibers decreased and the ultimate strain increased.[9] Young's moduli along the chain direction of the crystalline regions of cellulose II, III_I, and IV_I are estimated to be different from those of cellulose I.[8,9] In addition, Young's moduli along the chain direction of the crystalline region are estimated to be higher than those of the amorphous region.[9]

The longitudinal Young's modulus of wood also decreases[31,32] and strain at yield increases[32] after the alkali treatment. The changes in the mechanical properties of wood upon alkali treatment can be attributed to an increase in the amorphous region within cellulose microfibrils and an increase in microfibril angles in wood cell walls, because a reduction in the relative crystallinity index was observed and the relative crystallinity index correlated with the specific Young's modulus of wood samples.[32] Additional observations revealed that the concentration range for the alkali treatment, where the mechanical properties changed,[31,32] corresponded to the range in which an increase in microfibril angles was reported to be observed.[15]

Thus, fibers or wood with different mechanical properties may sometimes tend to have different structures of cellulose microfibrils, in addition to cell shapes or cell wall structures, such as orientation of cellulose microfibrils.

Properties of samples obtained from juvenile and mature wood after chemical treatment

FTIR analysis and DP analysis

In the spectra of the samples obtained from juvenile wood near the pith and mature wood after the treatment for removing lignin and hemicelluloses, a peak at 710 cm^{-1} was observed (Fig. 5). Cellulose I is reported to be composed of cellulose I_α and I_β, and the ratio of each is different with varying sample origins. It is reported that cellulose I_β is abundant in the cell walls of higher plants, such as trees, and the spectral signature at 710 cm^{-1} is reported to correspond to the typical spectra of cellulose I_β.[33] Figure 5 indicates the possibility that cellulose I_β is richly present in the juvenile and mature wood samples after the treatment.

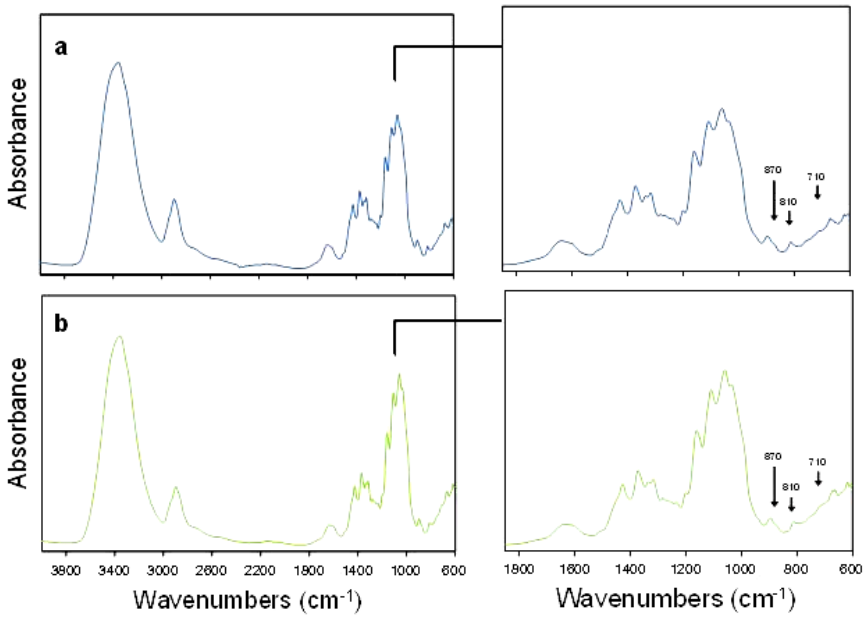

Figure 5: FTIR spectra of samples from juvenile (a) and mature (b) wood after chemical treatment

Table 3
Degree of polymerization of juvenile and mature wood samples after chemical treatment

Sample	DP
Juvenile wood	1529
Mature wood	1610

Note: DP, degree of polymerization measured by the viscosity method with copper ethylene diamine

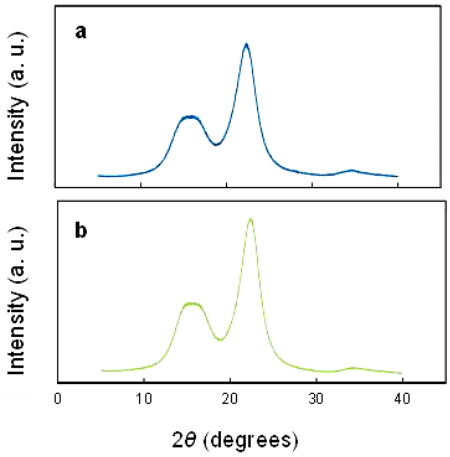

Figure 6: X-ray diffraction of juvenile (a) and mature (b) wood samples after chemical treatment

Table 4
Relative crystallinity index of juvenile and mature wood samples after chemical treatment

Sample	CrI (%)	
	Average	S. D.
Juvenile wood	74.0	0.3
Mature wood	78.0	0.7

Note: CrI, relative crystallinity index

Table 3 shows the results of DP calculated from the viscosity measured by the CED methods. The DP values tended to be smaller in juvenile wood than in mature wood, but the differences between them were small. The DP and degree of crystallinity are reported to decrease during the grinding treatment to obtain nano-sized fibers from pulp fibers.[13] In other words, the degree of crystallinity decreased from approximately 60% to 40%, and the DP calculated from the viscosity measured by the CED methods decreased from approximately 750 to 450 as the number of passes through the grinder increased.[13] In addition, it is reported that the degrees of polymerization are affected by acid chlorite delignification.[34] In this study, samples of juvenile and mature wood were obtained from sliced wood treated by the same methods. Therefore, the degradation effects of grinding, such as fibrillation, and the differences in the effects of treatment between the two types of samples are small.

Absorption around 810 cm^{-1} and 870 cm^{-1} may be observed in Figure 5 and this may suggest that glucomannan still remained within the samples,[35] because the samples were treated mildly to avoid deterioration of cellulose. However, the α-cellulose content in the samples after the chemical treatment was almost the same (above 83%) in both juvenile and mature wood.

X-ray diffraction analysis

Figure 6 shows X-ray diffraction patterns of juvenile wood near the pith and mature wood after chemical treatment. X-ray diffraction indicates a cellulose I pattern in juvenile wood near the pith and mature wood. The relative crystallinity index was higher than those before the treatment (Fig. 4). The same tendency was observed in the study of materials such as wood, bamboo, rice straw and flax. The

increase in relative crystallinity after the treatment is reported to be due to the removal of lignin and hemicelluloses, which exist in amorphous regions.[23] In addition, the relative crystallinity index tended to be slightly smaller in juvenile wood near the pith than in mature wood (Table 4). This tendency is in agreement with the results of the relative crystallinity index (Fig. 4) and α-cellulose contents of the xylems of juvenile wood near the pith and mature wood (Table 1). Differences in the relative crystallinity index of the juvenile and mature wood samples before the treatment (Fig. 4) may result from changes in the α-cellulose content of the xylems and the relative crystallinity index of cellulose, because after the chemical treatment the α-cellulose content was almost the same in juvenile wood near the pith and mature wood.

The characteristics of cellulose microfibril aggregates of various plants isolated by one-time grinding treatment of purified samples after treatment to remove lignin and hemicelluloses were investigated earlier, and it was suggested that the inherent characteristics of cellulose microfibril aggregates in a dry state are very similar, regardless of plant sources (wood, rice straw, and potato tuber).[20] The characteristics of cellulose microfibril aggregates from fiber and parenchyma cells of mature Moso banboo (*Phyllostachys pubescens*) were also investigated, and it was suggested that all the cellulose microfibrils synthesized in the same individual exhibited the same characteristics in a dry state, regardless of cell function.[21]

In contrast, with regard to the xylem microfibrils of trees, it has been reported that severe compression wood had fewer microfibrils and abundant dislocations in microfibrils, compared with normal core wood with equally high S_2 microfibril angles, likely affecting the differences in mechanical properties of compression and normal wood.[36]

Figures 2-4 indicate that juvenile wood near the pith tended to have a slightly lower relative crystallinity index, in addition to different properties of xylems, such as shorter fiber length, larger microfibril angles, lower α-cellulose contents, and lower Young's modulus, than those of mature wood. Although these results do not directly quantify the properties of cellulose microfibrils in the cell walls of tree xylems, Figures 5 and 6 indicate the possibility of some slight differences in the properties of the samples from juvenile and mature wood obtained by the same method.

CONCLUSION

Both bending and structural properties of Todo fir xylems obtained from the pith to the bark were investigated to study structural and mechanical properties of juvenile and mature wood. Sample properties of juvenile wood near the pith and mature wood before and after chemical treatment to remove lignin and hemicelluloses were also assessed. The following conclusions could be drawn from the study:

- Samples obtained near the pith tended to have low Young's modulus in the longitudinal direction;
- Juvenile wood near the pith tended to have larger microfibril angles, shorter fiber length, slightly lower α-cellulose content and a lower relative crystallinity index than mature wood;
- After chemical treatment to remove lignin and hemicelluloses, juvenile wood samples had a slightly lower relative crystallinity index than mature wood ones. FTIR analysis of the samples after the treatment indicated that cellulose I_β is possibly present in juvenile and mature wood.

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