

# Changes of wood properties treated with aqueous amine solution, bending tests and X-ray analysis of wood after amine treatment

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**Abstract** Bending tests were conducted on oven-dried wood samples (*Picea jezoensis* Carr.) following treatment with various concentrations of aqueous ethylenediamine (EDA) to investigate the influence of amine treatment on the mechanical properties of wood. Under oven-drying conditions following EDA treatment and a methanol rinse, the densities of wood samples increased at concentrations above 50%, and the Young's modulus decreased at concentrations above 60%. The specific Young's modulus of wood samples decreased at concentrations above 60%, and stress- and strain-at-yield changed slightly at EDA concentrations in the range of 60–70%. X-ray analysis showed that the structures of cellulose changed at concentrations above 60% EDA and confirmed the transformation into cellulose III<sub>I</sub> at 70% EDA. These results indicate the possibility that changes in the structure of the cell wall, accompanied by changes in the structures of cellulose microfibrils, contributed to changes in the specific Young's modulus of the treated wood samples. In the same concentration range, changes in the Young's modulus of wood samples increased with increasing relative humidity (RH). This also suggests that changes in the cell wall structure during the treatment contributed to changes in the Young's modulus of wood at different RHs.

## Introduction

Wood is a renewable resource that is widely used for building materials, as well as in many other fields, following chemical treatment. Swelling agents alter the mechanical properties of wood; some cause decreased elastic modulus and increased strain-at-yield in the swollen state, and they have been studied in methods to plasticize wood [1–3] and manufacture bent wood.

Alkali treatment decreases the elastic modulus and increases strain in the longitudinal direction under water-saturated conditions after treatment with aqueous NaOH above a certain concentration [3]. Changes in mechanical properties are also evident in wood under oven-drying conditions following these treatments at the same NaOH concentration range [4, 5]. Alkali treatment changes the crystalline forms from cellulose I to II and decreases the crystallinity index in the cellulose of ramie and cotton linters in the same concentration range [6, 7]. Changes in cell wall structures caused by increasing the amorphous component of cellulose are thought to influence the mechanical properties of oven-dried wood after alkali treatment [4, 5].

Wood swells when impregnated with an aqueous amine solution [1, 8]. Average rigidity, calculated from shear stress–strain curves in torsional tests, decreases and deformation increases in amine-saturated wood [1]. Amines that can penetrate the cellulose crystals and change the structures of cotton, ramie, and valonia cellulose during amine treatments have been studied. Cellulose I, native cellulose, changes into a cellulose I–ethylenediamine (EDA) complex through saturation with EDA [9–13]. In addition, cellulose crystallite saturated with EDA changes into cellulose III<sub>I</sub> via methanol washing [10, 11, 14–18] and into cellulose I<sub>β</sub> through heating or water washing [11].

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However, a decrease in average rigidity in amine-saturated wood occurs even in wood without such swelling, and this loss of rigidity is thought to be independent of the swelling of cellulose crystallite [1].

Wood cell walls are composed of cellulose microfibrils, hemicelluloses, and lignin. Structural changes of wood cell walls after saturation with an aqueous amine solution followed by washing are expected to influence the mechanical properties of wood. However, no detailed report has described changes in the mechanical properties and cell wall structures following amine treatment.

In this study, changes in the mechanical properties of wood samples after impregnation with aqueous EDA followed by a methanol rinse were investigated using bending tests. In addition, the cellulose structure of the wood samples was investigated using X-ray diffraction analysis to study the relationship between the cellulose structures of the wood and the changes in the mechanical properties resulting from the amine treatment.

## Materials and methods

### Sample treatment with aqueous EDA

Rectangular wood samples  $1(T) \times 12(R) \times 90(L)$  mm were prepared from Yezo spruce (*Picea jezoensis* Carr.), where *T*, *R*, and *L* are the measurements in the tangential, radial, and longitudinal directions, respectively. The samples were dried at 30 °C under vacuum over  $P_2O_5$  for 7 days. Weight, dimensions, and Young's modulus of the oven-dried samples were determined. The samples were measured using a screw micrometer with a precision of 0.001 mm for the *T* and *R* directions and using a vernier micrometer with a precision of 0.01 mm for *L*. The oven-dried samples were treated as follows. First, they were impregnated with fixed concentrations of aqueous EDA ranging from 0 to 99% and left to stand at 20 °C for about 1 week. Then, they were soaked in 97% methanol for 1 week. After washing, samples were air-dried for more than 1 week and then dried at 30 °C under vacuum over  $P_2O_5$  for 7 days. The weight and dimensions of the oven-dried samples were measured. The ratios of the values of the measured weights and dimensions of the oven-dried samples after treatment to those before treatment were then calculated.

The oven-dried samples were subjected to bending tests to measure Young's modulus, stress-at-yield, and strain-at-yield and were also subjected to X-ray diffraction analysis.

### Young's modulus under different relative humidity (RH) conditions

Following treatment, oven-dried wood samples were conditioned at 25 °C in desiccators containing saturated

solutions at a fixed RH, 62% RH ( $NH_4NO_3$ ), 80% RH ( $(NH_4)_2SO_4$ ), and 97% RH ( $K_2SO_4$ ), successively for more than 1 month. After conditioning at each RH, the weights, dimensions, and Young's moduli of the wood samples were measured. Finally, the wood samples were soaked in distilled water. The dimensions and Young's modulus of the wood samples under water-saturated conditions were also measured.

### Bending tests

The samples were subjected to a three-point bending test using a Shimadzu AGS-500B universal material-testing machine at room temperature. The span length was about 60 mm, with a crosshead speed of 5 mm/min to measure Young's modulus and of 10 mm/min for the stress- and strain-at-yield measurements. Load was applied on the longitudinal-radial plane of the wood samples. The same samples were tested twice below the proportional limit for Young's modulus before and after treatment.

The ratios of the values after treatment to those before treatment were calculated for the Young's modulus and the specific Young's modulus; the data were expressed as the ratio of the value at 0% EDA. Five samples were used for bending tests, and the mean values were calculated from the data for three samples, excluding the maximum and minimum.

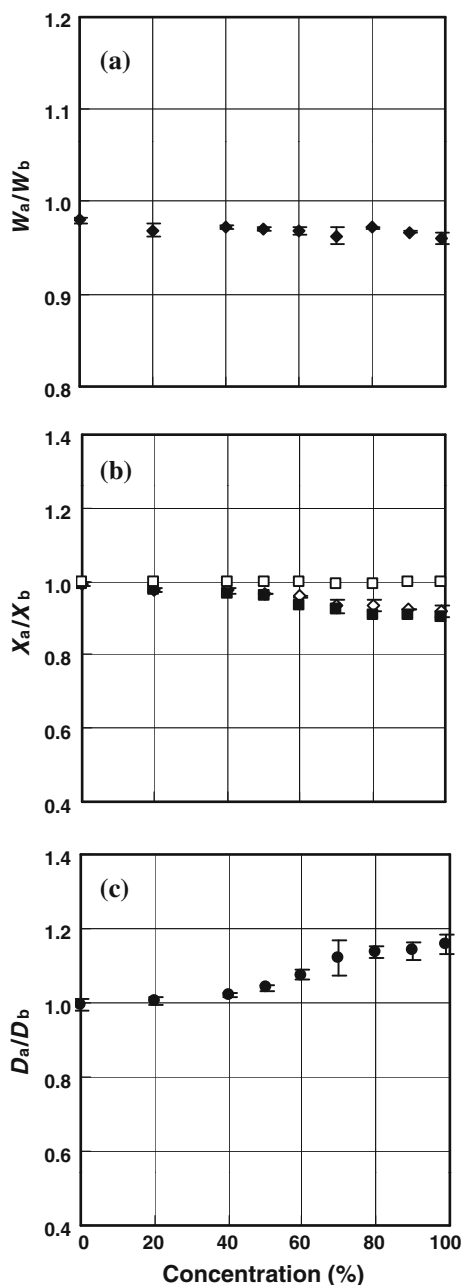
### X-ray diffraction

Diffraction patterns were obtained at room temperature from radiation generated by a MAC Science M03XHF (copper target) set to 40 kV and 20 mA, with the detector placed on a goniometer scanning a range of 5–40° at a rate of 1°/min. The crystallinity index was calculated from an X-ray diffraction profile in the range of 10–32° [19]. After subtracting air-scattering, the diffraction profile was resolved into crystalline and noncrystalline contributions by curve-fitting. The crystallinity index was defined as the percentage of the area of crystalline reflection relative to the whole area of the scattering profile. Three samples were used for X-ray diffraction analysis and the mean values were calculated from the data for three samples.

## Results and discussion

Weights, dimensions, densities, and mechanical properties of oven-dried wood samples after treatment

Figure 1 shows the effects of EDA treatment on weight loss (a), dimensions (b), and density (c) of wood samples



**Fig. 1** Relationships between weight (a), dimensions (b), and densities (c) of wood samples and EDA concentration.  $W_a$  weight under oven-drying conditions after treatment,  $W_b$  weight under oven-drying conditions before treatment,  $X_a$  dimensions under oven-drying conditions after treatment,  $X_b$  dimensions under oven-drying conditions before treatment,  $D_a$  density under oven-drying conditions after treatment,  $D_b$  density under oven-drying conditions before treatment, filled diamond,  $W_a/W_b$ , open diamond,  $X_a/X_b$  in tangential direction, filled square,  $X_a/X_b$  in radial direction, open square,  $X_a/X_b$  in longitudinal direction, filled circle,  $D_a/D_b$

under oven-drying conditions. The weight loss was about 2% at a concentration of 0% EDA, 3% at 20% EDA, and 4% at 99% EDA. Weight decreased very slightly with increasing concentrations of aqueous EDA.

The density was almost constant in the concentration range of 0–50% and increased by 10% for concentrations of 50–70%. Changes in concentration greater than 50% EDA were due to dimensional changes because the weight remained nearly constant for EDA concentrations greater than 50%. At the concentration range in which density increased, the dimensions in the tangential and radial directions decreased. In contrast, the longitudinal dimension decreased slightly for the concentration range of 50–99%. The increase in density for concentrations less than 50% was slight because the dimensional change was small, but for concentrations greater than 50%, density increased due to contraction in the tangential and radial directions.

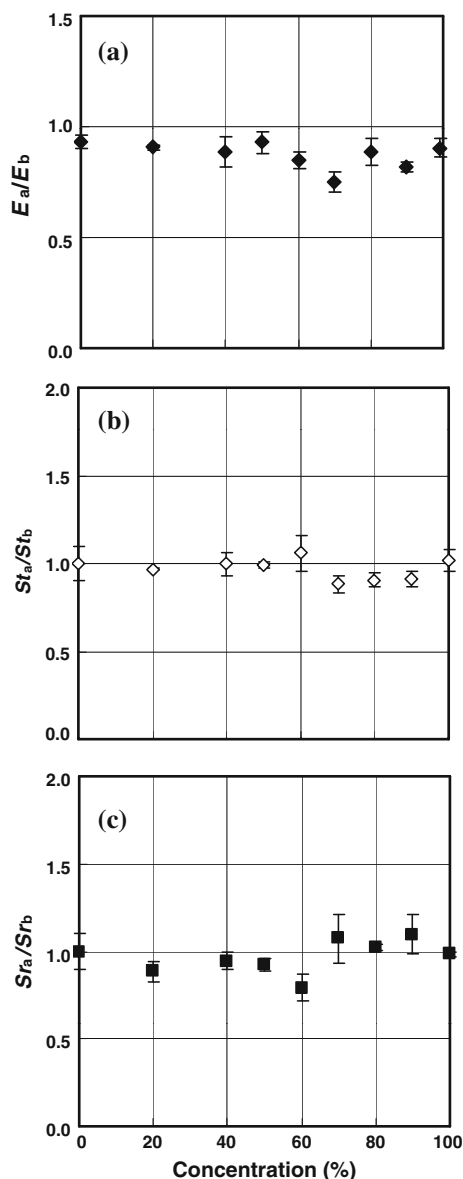
Figure 2 shows the Young’s modulus (a), stress-at-yield (b), and strain-at-yield (c) of oven-dried wood samples after treatment. Young’s modulus was almost constant in the concentration range of 0–50% and decreased in the range of 50–70%. The stress-at-yield remained almost unchanged at EDA concentrations of less than 60% and was virtually constant at 70–90%. The strain-at-yield changed slightly for concentrations of 60–70%.

Generally, the Young’s modulus correlated closely with density and increased with increasing density. However, the results for concentrations above 50% in Figs. 1 and 2 appear to contradict this tendency.

In NaOH-treated wood, the density increased at concentrations above 12%, but Young’s modulus decreased [4, 5]. In addition, the strain-at-yield of NaOH-treated wood increased, and the stress-at-yield remained almost constant in the same concentration range [5]. Increases in the density of NaOH-treated wood have been reported to be due to longitudinal contraction and to decreases in the cross-sectional dimensions caused by longitudinal contraction of microfibrils [4, 5, 20]. For EDA-treated samples, no significant decrease in the longitudinal dimension was observed. Increased density was primarily due to decreased cross-sectional dimensions. Changes in the strain-at-yield of EDA-treated wood in Fig. 2 were very small compared with those of NaOH-treated wood. These results were different from those with NaOH treatment.

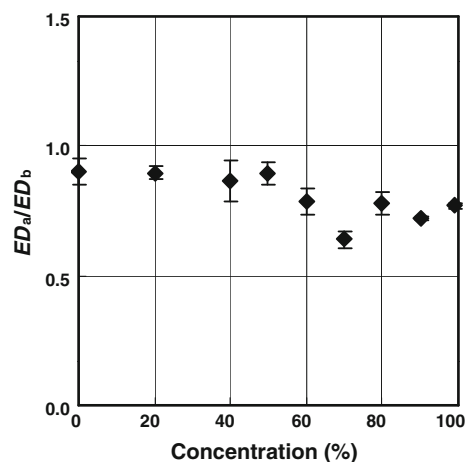
Figure 3 shows the effect of EDA treatment on the specific Young’s modulus. The specific Young’s modulus was almost constant for EDA concentrations of less than 50% and decreased linearly for EDA concentrations in the range of 50–70%. The mechanical properties of the EDA-treated wood samples tended to change in the concentration range of 60–70%. These results indicate the possibility that the cell wall structures changed during EDA treatment.

Sadoh and Yamaguchi [1] investigated the swelling of wood in EDA and the torsional properties of the swollen wood. They reported that X-ray diffraction analysis of hinoki wood after aqueous EDA saturation showed that



**Fig. 2** Relationships between Young's modulus (a), stress-at-yield (b), and strain-at-yield (c) of wood samples and EDA concentration.  $E_a$  Young's modulus under oven-drying conditions after treatment,  $E_b$  Young's modulus under oven-drying conditions before treatment,  $St_a$  stress-at-yield under oven-drying conditions after treatment,  $St_b$  stress-at-yield under oven-drying conditions before treatment,  $Sr_a$  strain-at-yield under oven-drying conditions after treatment,  $Sr_b$  strain-at-yield under oven-drying conditions before treatment

transformation into the cellulose I–EDA complex occurred at concentrations above 65%. A decrease in average rigidity was observed even in wood without such swelling, and they concluded that the loss of rigidity was independent of the swelling of cellulose crystallite [1]. The concentration range in which the changes occurred in Figs. 2 and 3 is consistent with the range in which crystalline transformation took place in the study by Sadoh and Yamaguchi [1].



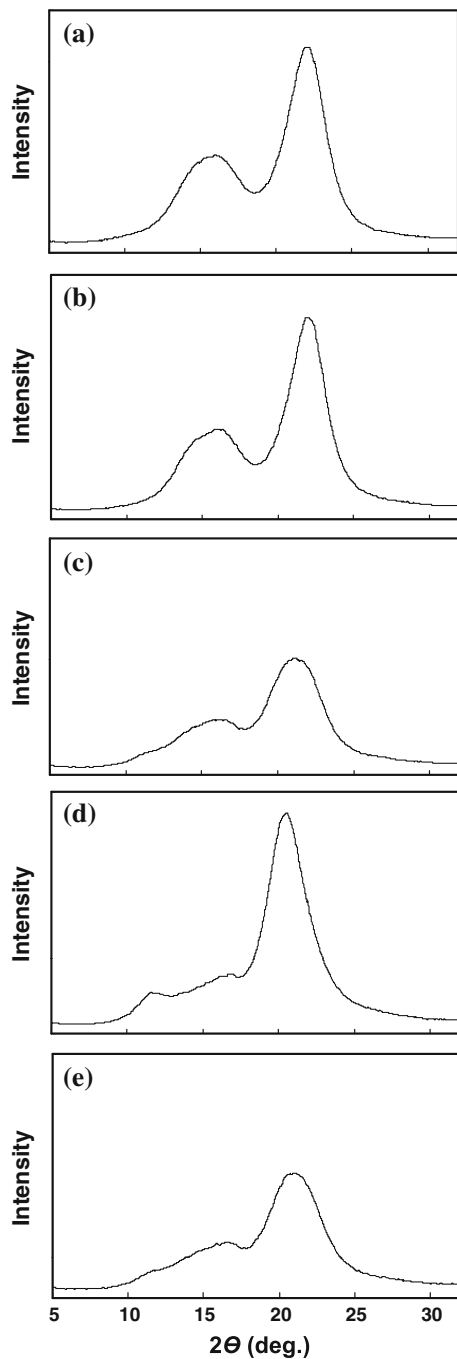
**Fig. 3** Relationship between specific Young's modulus of wood samples and EDA concentration.  $ED_a$  specific Young's modulus under oven-drying conditions after treatment,  $ED_b$  specific Young's modulus under oven-drying conditions before treatment

#### X-ray analysis of treated wood samples

Figure 4 shows the results of X-ray analysis of dried wood after EDA treatment. Only cellulose I was seen at concentrations less than 50%. Crystalline transformation of cellulose was observed at 70%. That is, peaks at 11.7 and 20.7 of  $2\theta$ , corresponding to cellulose III<sub>I</sub>, were observed at 70% EDA. The peak intensity of  $2\theta = 11.7$  increased at 70% EDA, whereas the peak intensities of  $2\theta = 14.9$  and 16.6 for cellulose I decreased above 60% EDA. Above 80% EDA, the peak intensity at  $2\theta = 11.7$  decreased compared with that at 70% EDA. These results indicate that changes in the structures of cellulose were observed above 60% EDA and that transformation into cellulose III<sub>I</sub> increased at 70% EDA.

The structure of cellulose I, native cellulose, transformed into different crystalline forms during the treatments. These changes have been reported to be different in simple cellulose fibers from those in wood that contains matrix substances such as hemicelluloses and lignin. For example, cellulose I changes into cellulose II in cellulose fibers through alkali treatment [6, 7]. One assumes that the parallel chains in cellulose I transform into antiparallel chains in cellulose II during the treatment [21]. This transformation has been explained by an intermingling of cellulose chains from neighboring microfibrils of opposite polarity [21, 22]. In wood, however, transformation of cellulose I into cellulose II is difficult [23–26]. This is thought to be due to matrix substances, such as lignin and hemicellulose in the cell walls that prevent cellulose from swelling during alkali treatment.

Transformation of cellulose I into cellulose III<sub>I</sub> is shown in Fig. 4. Cellulose III<sub>I</sub> has a parallel-chain orientation, as



**Fig. 4** X-ray diffraction patterns of EDA-treated wood. EDA concentration: **a** 0%, **b** 50%, **c** 60%, **d** 70%, **e** 99%

does cellulose I [22, 27, 28]. The results in Fig. 4 can be explained by these reports, and transformation into cellulose III<sub>I</sub> via EDA treatment occurs even in wood.

The relative crystallinity index was almost constant at concentrations below 50% EDA where the crystalline form was cellulose I. The results in Fig. 4 indicated that cellulose microfibrils in wood cell walls changed into different structures above 60%.

#### Changes in the specific Young's modulus and the cellulose structure of wood samples

Wood consists of cellulose, hemicellulose, and lignin, and the mechanical properties of wood depend on the structure of the cell walls [29–31]. In wood cell walls, cellulose microfibrils and bundles of cellulose are surrounded by hemicellulose and embedded in lignin. Changes in the structures of wood components and interactions of components affect the mechanical properties.

Microfibrils are oriented along the longitudinal direction in the S<sub>2</sub> layer, which contains most of the cellulose, and the microfibril angle is about 13° in yezo spruce [32]. Cellulose microfibrils have high longitudinal Young's moduli and strength and play an important role in the mechanical properties of wood [29, 30]. The structure of cellulose microfibrils is expected to affect the mechanical properties of wood longitudinally.

It has been reported that the elastic modulus of the cellulose crystalline regions parallel to the chain axis is different for each cellulose polymorph: Nishino et al. [33] described an elastic modulus of 138 GPa for cellulose I and 87 GPa for cellulose III<sub>I</sub>, as measured by X-ray diffraction. Ishikawa et al. [7, 18] investigated the changes in cellulose crystallites and tensile properties of ramie fibers. The integral crystallinity index and Young's modulus of ramie fibers decreased, and ultimate strain increased via EDA treatment for crystalline conversion from cellulose I into III<sub>I</sub> [7]. The estimated value of Young's modulus of the cellulose crystalline region was much higher than that of the amorphous region in both cellulose I and III<sub>I</sub> [7, 18].

Compared with the results in Figs. 3 and 4, at the concentration range in which the specific Young's modulus decreased, the transformation into cellulose III<sub>I</sub> increased. It is difficult to accurately discuss the changes in the crystallinity because a mixture of cellulose I and III<sub>I</sub> was observed above 60% EDA in Fig. 4. However, changes in the structures of cellulose microfibrils during the treatment may affect the decrease in the specific Young's modulus in Fig. 3.

Structures of lignin and hemicelluloses also changed during treatment. It is expected that the interaction of wood components changed after swelling with EDA and washing with methanol. Because the concentration range in which the specific Young's modulus decreased corresponded to the concentration range in which the structure of cellulose changed, it was concluded that changes in cell wall structure, accompanied by cellulose transformations, during EDA treatment influenced the specific Young's modulus of EDA-treated wood. At the concentration range in which EDA aqueous solutions swell cellulose crystallite, in addition to matrix substances, changes in the cell wall structures affected the mechanical properties of the wood.



In NaOH-treated wood, the concentration range in which the specific Young's modulus decreased, the strain-at-yield increased, and longitudinal contraction of treated wood occurred corresponded to the concentration range in which the crystallinity index decreased [5]. These three properties were highly correlated with the crystallinity index, indicating the possibility that a decrease in the crystallinity index may affect these properties in NaOH-treated wood [5]. The marked longitudinal contraction of wood samples and increase in strain-at-yield that occurred in NaOH-treated wood were not observed in EDA-treated wood samples. This indicates that the properties, structures, and location of the amorphous region in microfibrils, in addition to the changes in the crystalline regions and in the matrix substances, would be different from those in NaOH-treated wood. Differences in changes in cell wall structures between NaOH-treated and EDA-treated wood would affect the mechanical properties of the treated woods.

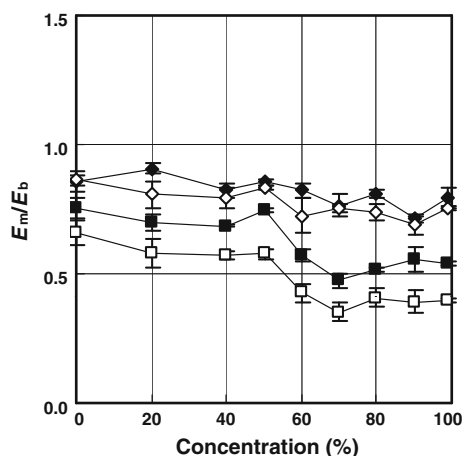
#### Changes in Young's modulus of treated wood under different RH conditions

Figure 5 shows the effect of RH on Young's modulus. At concentrations from 0 to 50% EDA, changes in Young's modulus were very slight at each RH. Above 60% EDA, larger decreases in Young's modulus were observed for RHs from 80.3 to 97%. The same tendency, that is, the decrease in the Young's modulus becoming larger above a certain concentration at higher RHs, was observed in NaOH-treated wood [4]. These changes in NaOH-treated wood were due to an increase in the amorphous region of cellulose that can absorb water, because the concentration

range in which these changes occurred was the same concentration range in which the relative crystallinity index decreased and moisture content increased [4]. The EDA concentration range in which changes of Young's modulus of wood samples became larger with increasing RHs (Fig. 5) corresponded to that in which crystalline transformation was observed (Fig. 4). These results indicate that changes in the structure of the cell wall caused by changes in the structures of cellulose microfibril, as well as changes in matrix substances, contributed to the changes in the Young's modulus of wood at different RHs.

Table 1 shows that changes in moisture content were very small at 62% RH and 80% RH with increasing aqueous EDA concentrations. Moisture content increased for ramie fibers treated with aqueous EDA solution compared with non-treated fibers [7]. The results in Table 1 contradict the results in NaOH-treated wood and in ramie fibers treated with aqueous EDA solution. As noted previously, wood consists of cellulose, hemicellulose, and lignin, and the hygroscopic properties of these components are different [34]. The results in Table 1 indicate the possibility that the amorphous region did not increase in EDA-treated wood, or that both an increase of the amorphous region in cellulose microfibrils and a decrease in the hygroscopic properties of amorphous components, such as hemicelluloses, lignin, and the amorphous region of cellulose, occurred during treatment. To clarify the factors that influence the hygroscopicity of wood after EDA treatment, further investigations are needed.

Figures 4 and 5 show that changes in the structure of the cell wall accompanied by changes in the structures of cellulose microfibrils, in addition to matrix substances, also affected the changes in the Young's modulus of wood at different RHs.



**Fig. 5** Young's modulus of EDA-treated wood samples after conditioning at different relative humidities.  $E_m$  Young's modulus of EDA-treated wood samples after conditioning at different relative humidities,  $E_b$  Young's modulus under oven-drying conditions before treatment, filled diamond 62% RH, open diamond 80% RH, filled square 97% RH, open square water-saturated condition

**Table 1** Moisture content of EDA-treated wood samples after conditioning at different relative humidities

Concentration (%)	Moisture content (%)					
	62% RH		80% RH		97% RH	
	Average	SD	Average	SD	Average	SD
0	9.38	0.23	13.34	0.27	23.42	0.37
20	9.53	0.19	13.63	0.13	25.16	0.19
40	9.63	0.17	13.84	0.04	25.95	0.22
50	9.89	0.08	13.75	0.26	25.31	1.38
60	9.47	0.24	13.60	0.15	24.05	0.99
70	9.51	0.15	13.53	0.07	25.98	0.03
80	9.68	0.19	13.74	0.30	25.96	0.26
90	9.55	0.25	13.85	0.16	26.02	0.34
99	9.47	0.28	13.72	0.34	25.99	0.41

## Conclusions

The bending properties and cellulose structure of wood samples following EDA treatment were investigated. The Young's modulus of oven-dried wood changed above 60% EDA. The specific Young's modulus of oven-dried wood samples decreased at 70% EDA and increased between 70 and 80%. Stress- and strain-at-yield changed at 60–70% EDA. X-ray analysis of dried wood confirmed the transformation of cellulose I into a cellulose III<sub>I</sub> at 70% EDA. The concentration range in which transformation into cellulose III<sub>I</sub> occurred corresponded to the concentration at which the specific Young's modulus decreased, indicating that changes in cell wall structures of wood, accompanied by changes in structures of cellulose microfibrils, contributed to the changes in the specific Young's modulus of wood. Changes in the Young's modulus of treated wood at different RHs also suggest that changes in the cell wall contributed to changes in the Young's modulus of wood with increasing RH.

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