J Wood Sci (2007) 53:175–177
DOI 10.1007/s10086-006-0870-8


RAPID COMMUNICATION

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# Contraction of the microfibrils of wood treated with aqueous NaOH: evidence from changes in the anisotropy of the longitudinal and transverse swelling rates of wood

Received: June 12, 2006 / Accepted: November 27, 2006 / Published online: January 13, 2007

**Key words** Microfibrils · Alkali treatment · Contraction · Swelling anisotropy

## Introduction

Previously, we reported that wood samples contract longitudinally, although the detailed mechanism for this contraction was undetermined.[1–6] Stöckmann[7,8] reported that wood cells contract longitudinally and twist into S-helixes while lignin and hemicelluloses are removed in pulping, and according to Nakano et al.,[9] the longitudinal contraction of Yezo spruce (*Picea jezoensis*) increases with both the concentration of the NaOH solution and temperature. Based on experimental results, Nakano et al.[9] proposed that the longitudinal contraction of samples resulted from the contraction of microfibrils via an entropy–elastic force. For Yezo spruce, Fujimoto and Nakano[10] reported that the fibril angle increased from 13° to 17° as the concentration of aqueous NaOH solution increased from 10% to 15%, while tracheid length decreased by about 10%.

Other than these reports showing indirect evidence that the longitudinal contraction of the microfibrils themselves influences the longitudinal contraction of wood samples, no definitive evidence has been presented. This study sought to clarify the contribution of microfibril contraction to the longitudinal contraction of wood samples by examining the basis of the anisotropic changes in the longitudinal and transverse swelling rates of wood samples.

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Part of this article was presented at the 56th Annual Meeting of the Japan Wood Research Society, Akita, August 2006

## Materials and methods

Samples of Yezo spruce, Sakhalin fir (*Abies sachalinensis*), Japanese larch (*Larix kaempferi*), and Erman's birch (*Betula ermanii*) measuring $20 \times 20 \times 5$ (mm) [tangential (T) $\times$ radial (R) $\times$ longitudinal (L)] were prepared. The samples were measured with a screw micrometer with a precision of 0.001 mm in the tangential (T), radial (R), and longitudinal (L) directions after drying at room temperature under vacuum over $P_2O_5$ for 4 days. The longitudinal dimensions were measured at the central cross section of the samples, while the tangential and radial dimensions were measured at the point dividing the sides in the tangential and radial directions of the samples into quarters, respectively. The oven-dried samples were impregnated with fixed concentrations of aqueous NaOH ranging from 0% to 20% (w/w) and then left standing at room temperature for 2 days. Then, they were soaked in distilled water for 1 week. Hereafter, this treatment is referred to as the alkali treatment. The samples were measured in the tangential (T), radial (R), and longitudinal (L) directions after the alkali treatment. The dimensional changes $\Delta L/L$ and $\Delta(T + R)/(T + R)$ with the alkali treatment were calculated from the measurements of the wet specimens after the alkali treatment versus the measurements of the oven-dried specimens before the alkali treatment.

## Results and discussion

Figure 1 plots the relationships between $\Delta L/L$ and $\Delta(T + R)/(T + R)$ for some of the wood samples subjected to alkali treatment. The plots parallel the *y*-axis with the value of $\Delta(T + R)/(T + R)$ nearly constant at NaOH concentration above 3%. In contrast, for all of the wood species, $\Delta L/L$ decreased markedly at NaOH concentrations above a threshold concentration. The major changes in $\Delta L/L$ occurred at NaOH concentrations between 7% and 15%, while the changes in $\Delta(T + R)/(T + R)$ were negligible in that range.

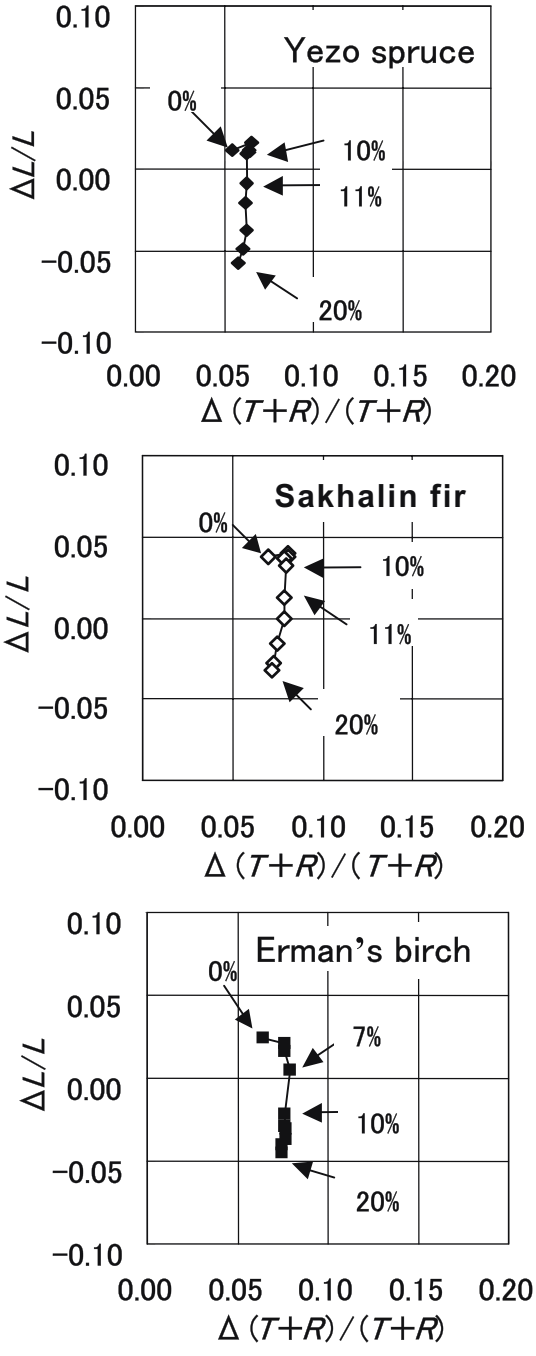


**Fig. 1.** Relationship between the rate of change in the longitudinal dimension ($\Delta L/L$) and the rate of change in the sum of the radial and tangential dimensions [$\Delta(T+R)/(T+R)$] for Yezo spruce, Sakhalin fir, and Erman's birch

Considering the helical winding of microfibrils and the small fibril angle of the middle layer of the secondary wall ($S_2$) in the wood cell wall, which constitutes the greatest fraction, the factors influencing the remarkable decrease in $\Delta L/L$ were the changes in the $S_2$ layer.

Fujimoto and Nakano[10] reported that the microfibril angle of Yezo spruce was nearly constant at NaOH concentrations of 0%–10% and increased from 13° to 17° at concentrations of 10%–15%. An increase in the fibril angle should lead to changes in both $\Delta(T+R)/(T+R)$ and $\Delta L/L$. However, $\Delta L/L$ decreased markedly, while $\Delta(T+R)/(T+R)$ remained nearly constant, as shown in Fig. 1, indicating that another mechanism causes the reductions in $\Delta L/L$ and $\Delta(T+R)/(T+R)$.

A decrease in the space between microfibrils should also lower both $\Delta(T+R)/(T+R)$ and $\Delta L/L$. However, this does not explain the results reported by Nakano et al.,[9] who measured the change in stress relaxation and twist angle with time and found that the alkali treatment caused contraction and twisting forces in the longitudinal and tangential directions of wood cells. Matrix contraction could not have been responsible because the matrix should have contracted isotropically. Therefore, the plots of $\Delta(T+R)/(T+R)$ and $\Delta L/L$ in Fig. 1 can be explained only in terms of microfibril contraction.

The concentration range at which the remarkable longitudinal contraction of wood samples takes place corresponds to the range at which crystalline transformation occurs in cellulose. Okano and Sarko[11,12] determined the types of alkali-cellulose structures of ramie fibers that occur as intermediates during the conversion of cellulose I to cellulose II. Five structures could be generated reproducibly, depending only on the alkali concentration used. In X-ray diffraction and Fourier transform-infrared spectroscopy studies on the lattice transformation of cellulose I to cellulose II, Fengel et al.[13] revealed that the degree of crystallinity of cotton cellulose decreased from about 0.6 to 0.5 as the concentration of NaOH increased from 11% to 13.5%. In wood, transformation of cellulose I to cellulose II does not occur as it does in cotton.[14–16] This is postulated to be due to the effect of lignin in wood.

These reports support the possibility that microfibrils contract longitudinally during the decrystallization of cellulose. To explain the contraction, Nakano et al.[9] proposed that the transformation might be related to a reduction in the end-to-end distance of the chain segments in the amorphous regions, if two-phase microfibrils occur during alkali treatment.

Based on our findings and previous reports, we conclude that the remarkable longitudinal contraction of the wood samples shown in Fig. 1 is evidence of the longitudinal contraction of the microfibrils themselves.

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