Stress relaxation of wood partially non-crystallized
using aqueous NaOH solutions

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High lights

＞We examine the effect of the crystallinity on the mechanical properties of wood. ＞The relaxation modulus and relaxation rate decreased with decreasing crystallinity. ＞The crystallinity dependence on the relaxation rate increased with increasing time. ＞Non-crystallized regions formed along the microfibril longitudinal axis.

36   **Abstract**

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38   Wood samples (*Picea jezoensis* Carr.) were treated with aqueous NaOH solutions (0–0.20

39   concentration fraction, 12 conditions), and bending tests were performed to measure stress relaxation.

40   The relationship between mechanical properties and NaOH concentration is discussed.   The

41   relaxation modulus and relaxation rate were divided into three concentration ranges.   Both

42   decreased slightly for NaOH concentrations less than 0.10, decreased drastically for concentrations

43   between 0.11 and 0.14, and decreased slightly for concentrations greater than 0.15.   The change in

44   relaxation behavior upon NaOH treatment was due to an increase in molecular chain mobility in

45   non-crystallized regions along the microfibril longitudinal axis in wood as well as lignin swelling.

46   Furthermore, the molecular chain response in this region required time; thus, the dependence of

47   crystallinity on the relaxation rate was apparent in the long time region.

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Introduction

Wood treated with aqueous NaOH shows an anisotropic dimensional change, especially along the longitudinal axis, and the contraction depends on the alkali concentration. The researcher who discussed this phenomenon in detail for the first time was Stöchmann (1971a, 1971b), who pointed out the need for microfibril contraction based on thermodynamic considerations. Contraction is induced by NaOH and other alkaline solutions (Nakano, 1988a, 1988b, 1989), and the degree of contraction depends on the type and concentration of the alkaline solution and increases as NaOH < KOH < LiOH at the same concentration. Nakano et al. (2000) reported an experimental temperature dependence of longitudinal contraction and showed that contraction depends on a change in the ultrastructure of the cell wall, especially the non-crystallization of microfibrils. That is, contraction is due to a non-crystallized region along the microfibril longitudinal axis and the entropy elastic force caused by the non-crystallization of cellulose microfibril helical winding in cell walls. Moreover, Nakano (2010) formulated a relationship between anisotropic dimensional changes and the crystallinity change due to alkali treatment.

The treatment of native cellulose with NaOH aqueous solution has been well-known as mercerization and industrially used so long time. Cellulose exhibits various polymorphism with NaOH treatment (Okano et al., 1984; Fink et al., 1985) and changes its crystallinity during their processes (Fengel et al., 1995; Zhou et al., 2003; Ouajai et al., 2004). Cellulose in wood also examined the effect of NaOH treatment with NaOH solution on the structure. Revol et al. (1981) and Shiraishi et al. (1984) reported that the cellulose structure in wood hardly changed due to matrix consisted of lignin and hemicellulose. Most of these studies were examined at higher concentration of NaOH.

The mechanical behavior of alkali-treated wood also depends on the concentration of the alkaline solution. Stress–strain behavior depends on the alkali concentration and shows marked changes for NaOH concentrations between 0.10 and 013 (Nakano, 1989, 2000). Relaxation behavior during alkali treatment has also been reported (Nakano, 1988); however, the samples were oven-dried, and the effects of collapse were not considered. Also, the change in relative crystallinity was not discussed.

In the present study, mechanical relaxation behavior and crystallinity index were measured, and the effect of wood non-crystallization by NaOH treatment on mechanical relaxation behavior is discussed.

Experimental

Materials and NaOH treatment

85 Wood samples were prepared from Yezo spuruce (*Picea jezoensis* Carr.) with rectangular dimensions

86 of 70 (L) × 7.5 (R) × 2 (T) (mm), where L, R, and T are the longitudinal, radial, and tangential

87 directions, respectively. Samples were oven-dried at 60°C under vacuum for 1 day. The weight and

88 dimensions of the oven-dried samples were measured; they were then soaked in aqueous NaOH

89 solutions (0–0.20 concentration fraction) and stored at room temperature for 2 days, after which they

90 were washed in distilled water for 2 weeks. The weight and dimensions of the treated samples were

91 measured again. Three samples were treated using each NaOH concentration, and two unwarped

92 samples were selected: one was subjected to stress relaxation measurements and the other was

93 analyzed using X-ray diffraction (XRD). The sample selected for stress relaxation measurements

94 remained in distilled water until the measurements were taken.

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96 *Stress relaxation measurements*

97 Stress relaxation measurements were conducted in water at 25°C using a three-point center

98 concentrated-load bending test with a span of 50 mm. The displacement of 0.27 mm was less than

99 one-third of the proportional displacement limit for the samples, which was applied to the LR-plane.

100 The measurement period was about 24 hours, and the relaxation modulus was calculated as a

101 function of time based on the measurement load.

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103 *X-ray analysis*

104 Alkali-treated samples were freeze-dried under vacuum overnight after being frozen with liquid

105 nitrogen. Freeze-dried samples were oven-dried at 60°C under vacuum over P_2O_5 for 1 day. The

106 diffraction patterns were obtained for the LR-plane at room temperature by a Rigaku Ultima IV, set to

107 40 kV and 40 mA in the scanning range of 5–35°. The relative crystallinity of the samples was

108 calculated from the diffraction profile in the range of 10–28°. That is, X-ray diffraction profile was

109 isolated to a crystalline part and a non-crystalline part using commercial software the PeakFit

110 (SeaSolve Software, Inc.) for peak isolation and then each area and the whole area were calculated.

111 The relative crystallinity was calculated as the proportion of the area of crystalline part to the whole

112 area of the scattering area (Iwamoto et al. 2007).

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115 **Results and Discussion**

116 Studies on the characteristic changes in mechanical behavior and dimension after alkali treatment

117 have reported that structural changes in wood microfibrils are a key factor (Nakano, 1988, 1989, 2000,

118 2010). Moreover, the relative crystallinity of wood microfibrils reportedly decreases due to alkali

119 treatment. Additionally, wood microfibrils do not undergo a lattice transformation from cellulose I to

120 cellulose II; the cellulose alone changes. Thus, we start by discussing the lattice transformation of

121 the samples.

122   Lattice transformation during alkali treatment is discussed based on XRD analysis. Figure

123 1 shows typical X-ray diffractograms, and Figure 2 illustrates the relationship between the NaOH

124 concentration and the relative crystallinity. A lattice transformation from cellulose I to cellulose II

125 during alkali treatment is well-known to not occur in wood (Revol et al. (1981), Shiraishi et al. (1984)), and

126 Figure 1 confirms that the lattice transformation did not take place. However, the relative

127 crystallinity was nearly constant for concentrations less than 0.10 but decreased with increasing

128 concentration above 0.11. This dependence on alkali concentration is consistent with previous

129 reports (Ishikura, 2010; Nakano, 2010).

130   The proportion of microfibrils and the fibril angle influence the mechanical properties of

131 wood. Fujimoto et al. (2000) reported that the fibril angle increased slightly for NaOH concentrations

132 between 0.10 and 015 in alkali-treated Yezo spruce samples, and Nakano (2010) stated that the fibril

133 angle changed little during alkali treatment. In the present study, the change in the fibril angle

134 appears to be slight. Based on the study of Reiterer et al. (1999) on the relationship between Young's

135 modulus and fibril angle, our result was probably due to a decrease in crystalline cellulose, which has

136 a high Young's modulus. Thus, the change in fibril angle is neglected in the following discussion.

137   Figure 3 shows relaxation curves for each NaOH concentration. Plots of $E(t)$ vs. $\ln(t)$ did

138 not show a clear difference in relaxation behavior, but the relaxation modulus displayed characteristic

139 concentration dependence.

140   Previous studies have demonstrated that the concentration dependence of the relaxation

141 modulus was due to an internal structural change during alkali treatment. Figure 4 shows the

142 dependences of the relaxation modulus at $\ln(t) = 0$ and the dimensional change along the longitudinal

143 axis on NaOH concentration and the degree of crystallinity. Both show similar concentration and

144 crystallinity dependence, indicating that both changes were due to the same factor, i.e., the change in

145 relative crystallinity.

146   The concentration dependence of the relaxation modulus in Figure 4 was divided into three

147 ranges. The relaxation modulus decreased slightly for NaOH concentrations less than 0.10,

148 decreased considerably for concentrations between 0.11 and 0.14, and decreased slightly for

149 concentrations greater than 0.15. This result is consistent with a previous report (Nakano et al., 2000).

150 Nakano et al. (2000) showed that the longitudinal contraction in wood during alkali treatment was

151 due to a non-crystallized region along the microfibril longitudinal axis, and that contraction was due to

152 the entropy elastic force because of an increase in the heating temperature. Additionally, Nakano

153 (2010) reported that anisotropic swelling during alkali treatment can be explained by the

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154   aforementioned mechanism.   Similar relationships between the relaxation modulus and the

155   dimensional change along the longitudinal axis on the NaOH concentration and the degree of

156   crystallinity are consistent with the above discussion.

157   Considering the change in relative crystallinity, a decrease in the relaxation modulus for

158   NaOH concentrations less than 0.10 (Fig. 4) was not due to the change in relative crystallinity. It

159   probably occurred because of an increase in the geometrical moment of inertia during alkali treatment,

160   which increased linearly for NaOH concentrations less than 0.10 and was nearly constant for

161   concentrations greater than 0.11.

162   The concentration dependence of the relaxation modulus in Figure 3 suggests that

163   non-crystallization due to alkali treatment affected the relaxation modulus during measurements.

164   This makes comparison among the relaxation spectra difficult because the relaxation modulus

165   changed drastically during alkali treatment, and comparing the change in relaxation behavior using

166   an absolute value is difficult.   Thus, relaxation behavior was evaluated based on the relaxation rate,

167    $d \ln E(t) / d \ln t$.   This value represents the relaxation level at each time, making the change in

168   relaxation behavior clear.

169   Figure 5 shows $d \ln E(t) / d \ln t$ vs. ln(t).   The relaxation rate was divided into three

170   concentration ranges: non-alkali treated (0), 0.03–0.12, and greater than 0.13.   The concentration

171   ranges correspond to the three ranges in Figure 4.   That is, the relaxation behavior changed due to

172   non-crystallization during alkali treatment.   Figure 5 shows that the absolute relaxation rate

173   increased in the long time region for NaOH concentrations less than 0.12, and that the rate increased

174   in the short and long time regions for concentrations greater than 0.13.

175   The relationship between the relaxation rate and relative crystallinity is shown in Figure 6.

176   The relaxation rate changed markedly for relative crystallinities between 0.30 and 0.33.   Although

177   the relaxation modulus changed considerably, the relaxation rate changed slightly in the short time

178   region but significantly in the long time region.   The relaxation rate at ln(t) = 11 changed

179   considerably for relative crystallinities between 0.30 and 0.33.   Additionally, the long-term relaxation

180   rate recovered for relative crystallinities of less than 0.30.   For relative crystallinities greater than

181   0.33 or for NaOH concentrations less than 0.12, the relaxation rate changed little, regardless of time.

182   The mechanism of the change in relaxation behavior with decreasing relative crystallinity is

183   discussed.   Two mechanisms must be considered: one is a crystallinity dependence on the relaxation

184   modulus (Fig. 4), and the other is a crystallinity dependence on the relaxation rate (Fig. 6).   The

185   former is not time-dependent, but the latter is.

186   The former increases the region reacting to deformation promptly, namely the

187   non-crystallized region.   That is, the decrease in the relaxation modulus at ln(t) = 0 with increasing

188   NaOH concentration was due to a decrease in the fraction of the crystallized region (Fig. 4), which was

189   rigid, and an increase in the fraction of the non-crystallized region, which was flexible.   Another

190   factor is a decrease in the contribution of lignin, which binds microfibrils.   The interaction between

191   microfibrils and lignin is believed to have been weakened by swelling during alkali treatment.   Alkali

192   solution causes dissolution of hemicellulose, but dissolution was nearly complete at a NaOH

193   concentration of 0.05 and did not increase for concentrations greater than 0.05.   Thus, dissolution

194   scarcely affected the mechanical properties.

195   The relaxation rate depended on the response of molecular chain rearrangement.   Figure 6

196   shows that the crystallinity dependence on the relaxation rate increased with increasing $\ln(t)$,

197   suggesting that molecular chain rearrangement required time, and that the change in the relaxation

198   rate related to the restricted molecular chain motion.   Furthermore, the relaxation rate did not

199   change for relative crystallinities greater than 0.33 but did change for relative crystallinities less than

200   0.33, suggesting that the molecular chain response required a large non-crystallization region.   Thus,

201   non-crystallized regions formed along the microfibril longitudinal axis.   The motion of

202   non-crystallized regions around the microfibrils appears to be restricted by crystalline regions parallel

203   to the longitudinal axis.

204   Nakano et al. (2000) proposed that a reduction in the end-to-end distance of the chain

205   segments in the amorphous regions was due to longitudinal contraction of microfibrils caused by

206   alkali solution penetrating the defects in the microfibrils longitudinal direction.   For the

207   experimental method used in this study (three-point bending tests), contractive and tensional stress

208   occurred.   The S2-layer, which is about 0.80 fraction occupation of the cell wall, so that it dominates

209   the mechanical properties of wood.   The result shown in Figure 4 suggests that the alkali solution

210   penetrated the defects in the microfibril longitudinal direction, and that a non-crystallized region was

211   formed along the longitudinal axis for softwood, in which the fibril angle of the S2-layer is small.

212   Furthermore, molecular chain rearrangement in this region requires time; thus, the crystallinity

213   dependence on the longer time relaxation rate (Fig. 6) was evident.

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216   **Conclusion**

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218   The effect of the crystallinity change induced by NaOH treatment on the mechanical relaxation

219   behavior of wood was investigated.   The relaxation modulus and relaxation rate were divided into

220   three concentration ranges.   Both decreased slightly for NaOH concentrations less than 0.10,

221   decreased markedly for concentrations between 0.11 and 0.14, and decreased slightly for

222   concentrations greater than 0.15.   This was due to an increase in the molecular chain mobility in

223   non-crystallized regions along the microfibril longitudinal axis in wood and lignin swelling due to the

224   NaOH treatment.   Furthermore, molecular chain rearrangement in this region requires time; thus,

225   the crystallinity dependence on the longer time relaxation rate was apparent.

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267   **Figure captions**

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269   Figure 1. Typical X-ray diffractograms of untreated and treated wood using aqueous NaOH solutions.

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271   Figure 2. Relationship between crystallinity and NaOH concentration.

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273   Figure 3. Stress relaxation curves of samples treated with various NaOH solutions. Note: numbers

274   indicate NaOH concentration fractions.

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276   Figure 4. Dependence of the relaxation modulus at ln(t/s) = 0 and the dimensional change along the

277   longitudinal direction on NaOH concentration and relative crystallinity.

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279   Figure 5. Relaxation rate, $d \ln E(t) / d \ln[t]$, of samples treated with various NaOH concentrations.

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281   Figure 6. Dependence of the relaxation rate at ln(t/s) = 3, 8, and 11 on relative crystallinity.

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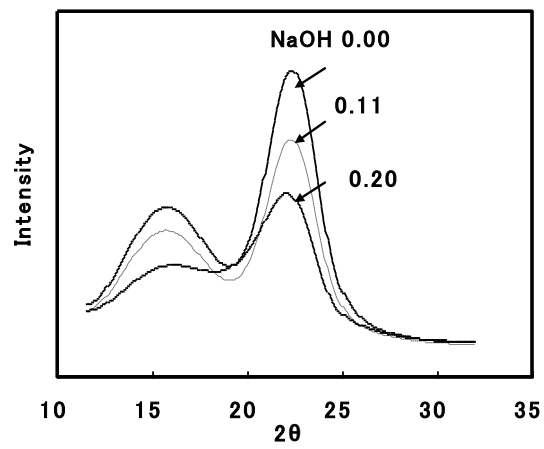
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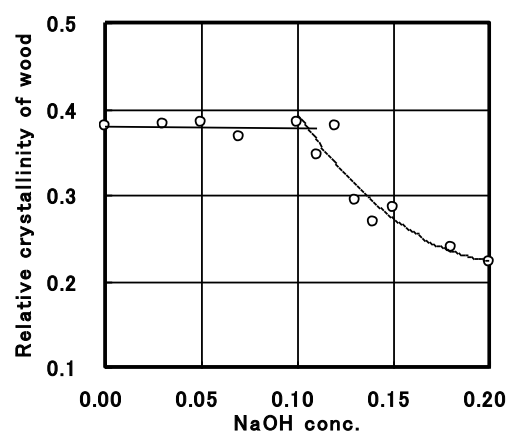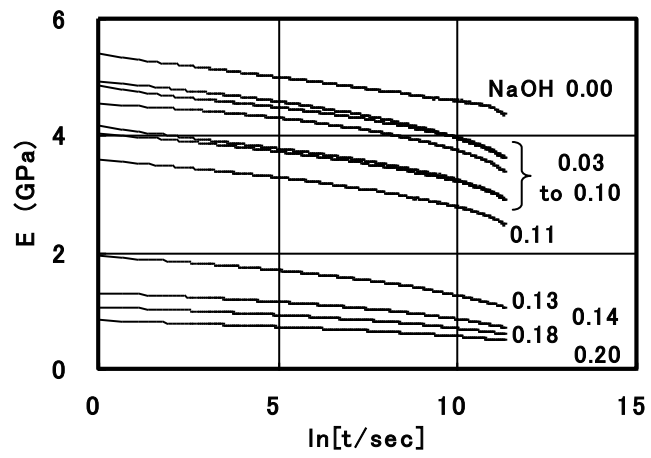
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Figure 2. Relationship between crystallinity and NaOH concentration.

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Figure 3. Stress relaxation curves of samples treated with various NaOH solutions. Note: numbers indicate NaOH concentration fractions.

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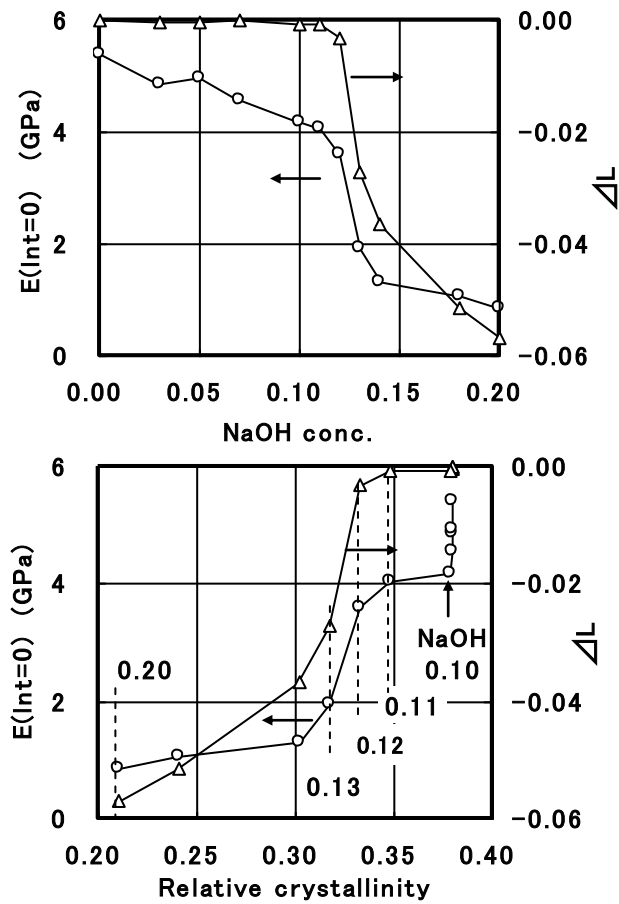374

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Figure 4. Dependence of the relaxation modulus at ln(t/s) = 0 and the dimensional change along the

longitudinal direction on NaOH concentration and relative crystallinity.

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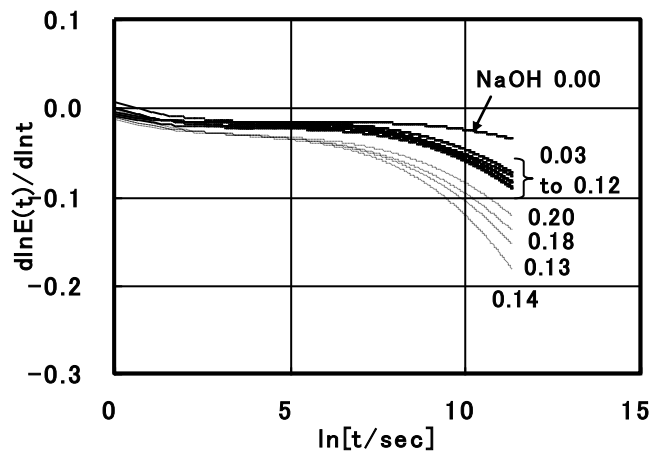399

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402 Figure 5. Relaxation rate, $d \ln E(t) / d \ln[t]$, of samples treated with various NaOH concentrations.

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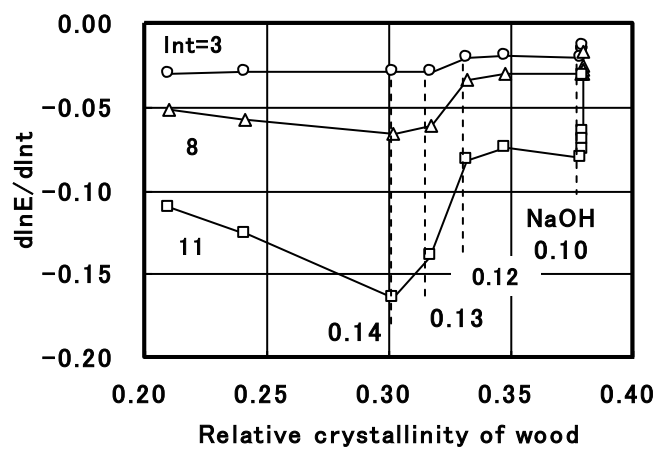413

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Figure 6. Dependence of the relaxation rate at ln(t/s) = 3, 8, and 11 on relative crystallinity.

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