Short title: Side-chain motion of partially non-crystallized wood

Title: Side-chain motion of components in wood samples partially non-crystallized using NaOH-water solution

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18 **Abstract**

19 Wood samples (*Picea jezoensis* Carr.) were treated with solutions of aqueous NaOH (0–0.20
20 concentration fraction) and each treated samples evaluated by dynamic mechanical analyses (DMA).
21 NaOH treatment was shown to affect the interactions between microfibrils and the surrounding
22 matrix and, in particular, the dynamics of methylol groups in the microfibrils. The former is not
23 dependent on the degree of crystallization but rather on the eluviation of the matrix. The latter
24 depends on the degree of crystallization. Alkali treatment induces changes in the polymer
25 domains as a result of matrix eluviation. This decreases the dynamics of methylol groups at NaOH
26 concentrations less than 0.11. On the other hand, alkali treatment causes non-crystallization at
27 concentrations greater than 0.11, which quantitatively increases the flexibility of methylol groups.
28 Crystallinity decreased, and main-chain dynamics increased, following treatment with highly
29 concentrated NaOH solutions. The dynamics of lignin also increased due to weakened interactions
30 with microfibrils due to non-crystallization.

31

32 ***Keywords:*** Side-chain, NaOH treatment, Viscoelasticity, Microfibril, Crystallinity

33

1. Introduction

Native cellulose can be transformed into other crystalline forms via NaOH-water treatment [1-6]. In plant cell walls such as wood, native cellulose is mostly found as microfibrils of cellulose aggregate with high crystallinity, which contains two crystalline forms, Iα and Iβ. Recently, the dissolution mechanism of cellulose with NaOH treatment has been reported based on results by various methods. Roy et al. [7] proposed a mechanism for lower temperatures. Cai et al. [8-10] applied the method of Navard et al. [11] to the NaOH/urea system. Additionally, the alkali treatment is applied to various composites in practice and their physical properties are examined [12-15].

This paper discusses the molecular dynamics, especially side-chain motion, of wood components in wood cells that have been non-crystallized by alkali treatment. Nakano [16] reported that wood contracts drastically along its longitudinal axis and demonstrated that this contraction is due to an entropic elastic force caused by the non-crystallization of cellulose microfibrils [17]. Anisotropic dimensional changes have been reported during alkali treatment [18]. Nakano [19] examined this anisotropy based on model analysis.

Changes in dynamics of wood sample during non-crystallization were reported in an analysis of the NaOH concentration ([NaOH]) dependence on stress relaxation [20]. The relaxation modulus and relaxation rate of them were divided into three concentration ranges: less than [NaOH] = 0.10, between 0.11 and 0.14, and greater than 0.15. Changes in relaxation dynamics were due to increases in molecular chain mobility in non-crystallized regions along the longitudinal axis of

53 microfibrils in wood and to lignin swelling as a result of NaOH treatment. That is, the dependence
54 of crystallinity on the relaxation time was related to molecular chain rearrangements required time
55 in this region.

56 This study focuses on changes in non-crystallized cellulose chain dynamics and on the
57 concentration (crystallization) dependence of dynamic viscoelastic behavior, especially side-chain
58 motion. The domains of the cellulose chain and the interactions between cellulose and other wood
59 components are discussed.

60

61 **2. Experimental**

62 **2.1. Materials and NaOH treatment**

63 Wood specimens of 70 (L) × 7.5 (R) × 2 (T) mm were cut from Yezo spruce (*Picea jezoensis Carr.*): L,
64 R, and T are longitudinal, radial, and tangential directions of wood, respectively. The samples were
65 oven-dried at 70°C under vacuum with P_2O_5 overnight. They were then soaked in aqueous NaOH
66 with various concentrations ([NaOH] = 0 to 0.20) for 30 min and stored at room temperature for 2
67 days. The samples were then washed in distilled water for 2 weeks. Washed samples were flash
68 frozen in liquid N_2 and freeze-dried under vacuum for 1 day. The weight and dimensions of the dried
69 samples were measured prior to dynamic mechanical analyses (DMA) and X-ray diffraction
70 measurements.

71

72

73 **2.2. Dynamic mechanical analyses and X-ray diffraction measurements**

74 DMA measurements were acquired in dired-air with a dynamic mechanical analyzer DMA50
75 (METRAVIB). In the chamber of DMA, dried-air was flowed before measurement. The moisture
76 content of the samples was confirmed to be negligible small for each measurement. The
77 measurement was performed with 5 μm of tensile forced oscillation over a 40-mm span from –150 to
78 200°C at 1 Hz. The programmed heating rate was 3°C /min.

79 Crystallinity measurements were performed with an X-ray diffractometer RINT-UltimaIV
80 (Rigaku). Diffractograms were obtained for the LR-plane at room temperature over a range of 5–35°.
81 The measurements were performed at 40 kV and 40 mA at a scan rate of 2°/min. The relative
82 crystallinity of the samples was calculated as the ratio between the area of the crystalline
83 contribution and the total area in the range of 10–28°.

84

85 **3. Results and Discussion**

86 **3.1. Relative crystallinity and dimensional changes**

87 **Figures 1 and 2** shows the changes in dimension along the longitudinal direction of wood sample
88 and relative crystallinity observed during NaOH treatment. Wood sample length characteristically
89 decreased with increasing in NaOH concentration. The relative crystallinity was nearly constant for
90 less than [NaOH] = 0.10 but started to decrease at 0.11. Crystallinity decreased drastically between

91 [NaOH] = 0.11 and 0.13 and slightly for concentrations greater than 0.14. The
92 concentration-dependence of dimensional changes along the longitudinal direction of each sample
93 were similar to that of the crystallinity change. This indicates that the dimensional changes were
94 due to non-crystallization with NaOH treatment. **Figure 2** suggests a linear relationship between
95 both of these variables for concentrations greater than 0.11. These changes during NaOH treatment
96 are consistent with our previous reports and indicate satisfactorily non-crystallization.
97
98 **3.2. Changes in molecular dynamics of non-crystallized wood**
99 **Figure 3(b)** shows the variation of tanδ as a function of temperature for treatments with [NaOH]=0
100 and 0.20. Three characteristic relaxations were identified in the untreated ([NaOH] = 0) sample.
101 These relaxations were labeled α, β, and γ in the order of decreasing temperature. The β relaxation
102 was obscured in the fully dried samples. The α dispersion was attributed to micro-Brownian motion
103 of the cell wall polymers in the non-crystallized regions, the β dispersion was attributed to the
104 motion of the absorbed water itself or the segmental motions associated with it, and the γ dispersion
105 was attributed to the motion of methylol groups according to a previous study **[21], [22]**. These three
106 relaxations of the untreated sample were identified at roughly the same temperatures for a sample
107 treated with [NaOH] = 0.20. Therefore, the relaxations in the sample that had been treated with
108 [NaOH] = 0.20 were attributed to the same causes as those in the untreated sample. However, their
109 intensities and temperatures of tanδ have the characteristic concentration-dependence of NaOH

110 solution.

111 The temperature dependence of tanδ in the untreated sample was generally similar to that of
112 the treated wood studied by other researchers and cellulose filaments **[23]**. However, tanδ intensity
113 of both the α and γ relaxations in samples that had been treated with NaOH 0.20 were much higher
114 than those of the untreated sample.

115 The cause of the β relaxation has been discussed in several independent studies. Obataya *et al.*
116 **[22]** assigned this relaxation to the absorbed water itself. Montés *et al.* **[24]** acquired DMA data on
117 amorphous cellulose and other polysaccharides and reported that the β relaxation had a moisture
118 dependence. In the current study, the β relaxation was indistinct in fully dried samples, which
119 confirms a relationship to absorbed water but not to the absorbed water itself. The α and γ
120 relaxations, which were observed in the current study, are discussed below.

121 **Figure 4** shows detailed profiles of tanδ of γ relaxation and exhibits characteristic changes in
122 peak location and intensity during NaOH treatment. **Figures 5(a) and (b)** shows the peak intensity
123 and location of tanδ for γ relaxation during NaOH treatments. Its dependence on NaOH
124 concentration can be divided into three distinct ranges. Tanδ was nearly constant for NaOH
125 concentrations between [NaOH] = 0.00 and 0.10, then increased considerably between 0.10 and 0.14,
126 and maintained a nearly constant value at NaOH concentrations greater than 0.15. The peak
127 shifted to a higher temperature range in the region below [NaOH] = 0.10 and remained constant
128 above [NaOH] = 011.

129 Side-chain relaxation generally depends on the dynamics of localized regions of molecular
130 chains. Nakano [21] and Nakano et al. [25, 26] performed DMA on chemically modified wood,
131 introducing various lengths of acyl groups, and reported that the dispersions assigned to side-chain
132 motion depended on both the interactions between the side chains and the free volume created by
133 the introduction of the acyl groups into wood substance. In the previous report, it was demonstrated
134 that side-chain dispersion depends characteristically on the number of methylene group carbon.
135 This result agrees with similar results obtained with PMMA [27]. While side-chain dynamics
136 increases with increasing side-chain length for short side chains, it decreases in motion due to
137 self-entanglement occurred for chain lengths more than 5 or 6 carbon atoms. Additionally, as for
138 wood sample introduced dissociative side chains, the side-chain motion changes drastically by
139 cross-linking with a metal ion [28, 29]. Considering these results in the previous work, changes in
140 the intensity and location of the γ relaxation in the current study, which is due to the motion of side
141 chains, also reflect changes in the methylol group domains during NaOH treatment.

142 The α dispersion in wood is assigned to micro-Brownian motion in non-crystalline regions of
143 wood components [30], which is influenced by environmental condition. For example, the α
144 dispersion shifts to lower temperatures with increasing moisture content and shows a clear peak
145 below 100°C at high moisture content [31, 32]. The moisture dependence on peak location roughly
146 corresponds with that of the glass transition temperature (Tg) of isolated lignin [32-34]. The α
147 dispersion in the current study appeared as a shoulder. Thus, as the NaOH concentration

148 dependence on the α peak location cannot be addressed here, the intensity of tanδ at 200°C, which is
149 used as tanδ(200°C), is discussed in the following discussion. **Figure 6** shows the relationship
150 between α intensity and NaOH concentration. Tanδ(200°C) was nearly constant for concentrations
151 less than NaOH 0.10 and increased at concentrations greater than 0.11. This result clearly
152 corresponds to that shown in Figure 1.
153
154 **3.3. Changes in storage modulus**
155 **Figure 3(a)** shows the variation in relative storage modulus, normalized to –120°C. The storage
156 modulus was nearly constant for NaOH concentrations less than [NaOH] = 0.10 and showed a
157 characteristic decrease at concentrations greater than 0.11. Changes in storage modulus at greater
158 than [NaOH] = 0.11 were composed of two processes. The first process caused a slight decrease
159 between –120 and –70°C; the other process resulted in a drastic decrease above 100°C. The former
160 and latter correspond to changes in the γ dispersion, as shown in **Figure 4** and in the α dispersion
161 shown in **Figure 3(b)**, respectively.
162 **Figure 7** shows the concentration dependence on relative modulus at –70, 100, and 200°C. At all
163 temperatures, the relative modulus decreased drastically at concentration 0.10. The decrease at
164 –70°C was less than that at the other two temperatures. However, a clear decrease was observed at
165 concentrations greater than 0.11. The observed decrease in relative modulus was more clear at
166 200°C than at 100°C at greater than [NaOH] = 0.11. This effect might be due to a glass transition in

dry lignin in this temperature region [35]. While the relative modulus at –70°C is nearly constant at less than [NaOH] = 0.10, and then decreased at greater than [NaOH] = 0.10. This difference in temperature dependence of the storage modulus agrees with the concentration dependencies of tanδ of the α and γ dispersions.

3.4. Crystallinity dependence on γ and α dispersions

The aforementioned characteristic concentration dependence on the γ dispersion is due to a change in methylol group domains, according to viscoelasticity measurements of chemically modified wood [21], [25, 26]. This concentration dependence may be discussed in terms of relative crystallinity. **Figures 8(a) and (b)** show the dependence of crystallinity on the tanδ intensity and the peak position of the γ dispersion, respectively. The tanδ increased slightly with near constant crystallinity at less than [NaOH] = 0.11. The trend then leveled off after a drastic increase with a decrease in crystallinity at greater than [NaOH] = 0.11 (**Figure 8(a)**). The peak corresponding to the γ dispersion shifted to higher temperatures with increasing NaOH concentration for samples with constant crystallinity at less than [NaOH] = 0.11, while it did not shift with a decrease in crystallinity at higher concentration (**Figure 8(b)**).

The data of the γ dispersion in **Figures 8(a) and (b)** imply a change in the methylol domains during NaOH treatment. An initial change of tanδ with almost constant crystallinity is not due to change in the microfibrils themselves, because the shift in peak position occurred with no changes

186 in crystallinity. NaOH treatment induces two changes in wood. The first is a structural change of
187 cellulose, the main ingredient in wood, known as mercerization. The second is the eluviation of wood
188 components. NaOH treatment eluviate hemicellulose and some lignin **[36-38]**. Therefore, it may be
189 inferred that a change occurring at constant crystallinity is due to this eluviation. An average
190 weight loss of approximately 6% was observed in samples treated with NaOH at the concentrations
191 used in this study.

192 Furthermore, it may be inferred that the methylol domains experienced restricted flexibility as
193 they approached each other as a result of hemicellulose eluviation and the partial eluviation of
194 lignin. This decreased flexibility, in turn, resulted in a peak shift to higher temperatures and a
195 decrease in tanδ. This restriction effect is manifested in the concentration dependence of the relative
196 modulus at –70°C in **Figure 6**. Relative modulus did not decrease but constant at less than [NaOH]
197 = 0.10 at this temperature, comparing with the other temperature.

198 The minimal crystallinity dependence of the tanδ peak position at greater than [NaOH] = 0.11
199 shown in **Figure 8(b)** indicates a negligible change in the flexibility of the methylol groups. Note,
200 however, that tanδ increased with decreasing in crystallinity (**Figure 8(a)**), and the dispersion of the
201 peak widened (**Figure 4**). This result strongly suggests an increase in the relative proportion of
202 regions that contribute to the relaxation process. In other words, results of the γ dispersion shown in
203 **Figures 8(a) and (b)** show that the relative number of methylol groups affecting relaxation increased
204 due to an increase in amorphous domains. Nakano **[21]** pointed out that an increase in the amount

of side chains introduced during esterification caused an increase in the free volume. This increased the flexibility of both the side chains themselves and the main chains. However, the effect was smaller for shorter side chains. Additionally, effects due to hydrogen bonding with the hydroxyl group can be expected with methylol groups. Therefore, contributions restricting flexibility were larger at –70°C, comparing with the other temperatures 100 and 200 °C (**Figure 7**).

The tanδ at 100 and 200°C increase increased drastically between [NaOH] = 0 and 0.12 and then gradually increased at greater than [NaOH] = 0.12. Considering that the α dispersion is assigned to main-chain motion of lignin by which hemicellulose and cellulose microfibril surface are bonded, **Figure 9(a)** suggests that the interaction between the both is weaken by the eluviation of the matrix in wood with NaOH treatment.

The crystallinity dependence of the storage modulus shown in **Figure 9(b)** corresponds roughly with that of tanδ in **Figure 9(a)**. **Figure 9(b)**shows the dependence of the relative modulus on the degree of crystallinity at 100 and 200°C. The relative modulus decreased drastically between [NaOH] = 0.11 and 0.12, was nearly constant between 0.12 and 0.15, and then decreased again at greater than [NaOH] = 0.15. This dependence is similar to that of the relaxation modulus, which measures stress relaxation, in our previous study **[20]**. This is because a decrease in the storage modulus at high concentrations is related to the main chain and not to the dynamics of the side chains.

4. Conclusions

Changes in molecular dynamics in wood as the result of NaOH treatment were examined using DMA measurements. It was shown that NaOH treatment affects the interactions between microfibrils and the surrounding matrix and the dynamics of methylol groups in the microfibrils. The former is not dependent on the degree of crystallization but rather on the eluviation of the matrix. The latter depends on the degree of crystallization. Low-concentration NaOH treatment induces changes in the polymer domains through the eluviation of the matrix material. Conversely, at high alkali concentrations, the proportion of domains that are involved in methylol group dynamics increases quantitatively, indicating significant non-crystallization. In addition, main-chain dynamics in wood increased with decreasing crystallinity. The interactions between microfibrils and matrix are believed to be weakened by the swelling of matrix and the shrinkage of microfibrils, thereby increasing the flexibility of matrix.

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278

279 **Figure captions**

280 Figure 1. Dimensional changes under wet condition along the longitudinal axis of wood samples

281 Yezo spruce (*Picea jezoensis Carr.*) as a function of NaOH concentration.

282

283 Figure 2. Crystallinity and relative dimensional changes along the longitudinal axis (ΔL/L) of wood

284 samples as a function of NaOH concentration.

285

286 Figure 3. The typical temperature dispersion of the relative dynamic modulus normalized to its

287 value at –120°C (a) and tanδ (b) under dry condition for samples treated with various aqueous

288 NaOH solutions.

289

290 Figure 4. The NaOH concentration dependence of tanδ assigned to methylol groups in wood for

291 samples treated with NaOH treatment.

292

293 Figure 5. The NaOH concentration dependence of tanδ(γ) and temperature (T γ) of the γ

294 dispersion assigned to methylol groups.

295

296 Figure 6. Tanδ intensity at 200°C as a function of NaOH concentration.

297

298 Figure 7. The relative dynamic modulus at various temperatures normalized to its value at 120°C

299 as a function of NaOH concentration.

300

301 Figure 8. The crystallinity dependence of the peak intensity and temperature of tanδ for methylol

302 groups in wood.

303

304 Figure 9. The crystallinity dependence of the tanδ intensity at 200°C and the relative dynamic

305 modulus at 100 and 200°C.

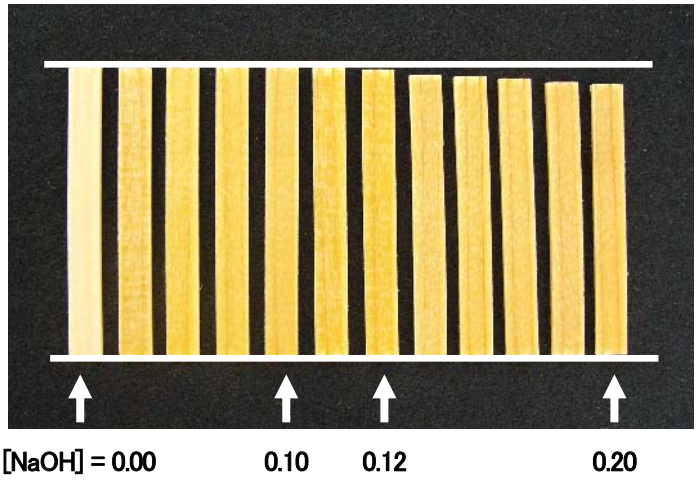

Figure 1

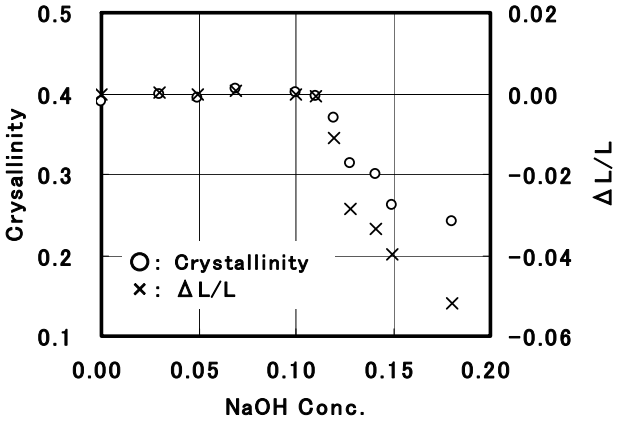
0.5
0.4
0.3
0.2
0.1
Crysallinity
0.02
0.00
−0.02
−0.04
−0.06
ΔL/L
○: Crystallinity
×: ΔL/L
0.00
0.05
0.10
0.15
0.20
NaOH Conc.

Figure 2

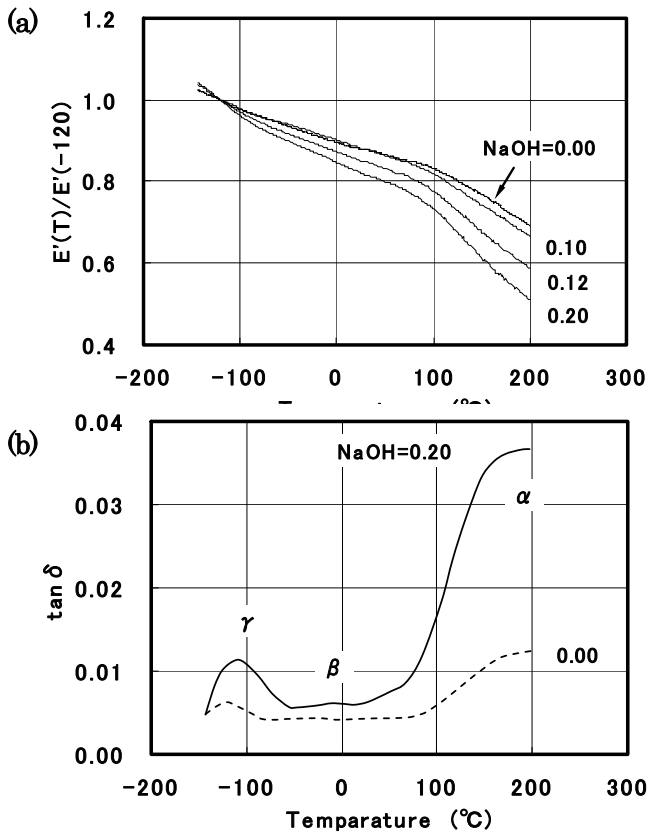
(a)
1.2
1.0
0.8
0.6
0.4
E'(T)/E'(-120)
NaOH=0.00
0.10
0.12
0.20
-200
-100
0
100
200
300
(b)
0.04
0.03
0.02
0.01
0.00
tan δ
NaOH=0.20
α
γ
β
0.00
-200
-100
0
100
200
300
Temparature (℃)

Figure 3

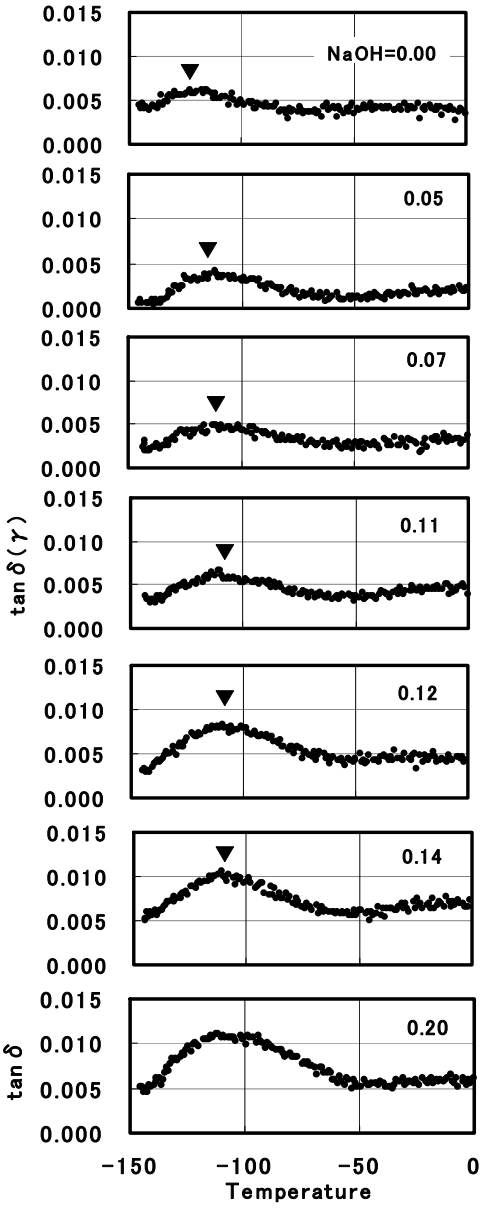
NaOH=0.00
0.05
0.07
0.11
0.12
0.14
0.20
tan δ (γ)
tan δ
0.015
0.010
0.005
0.000
−150
−100
−50
0
Temperature

Figure 4

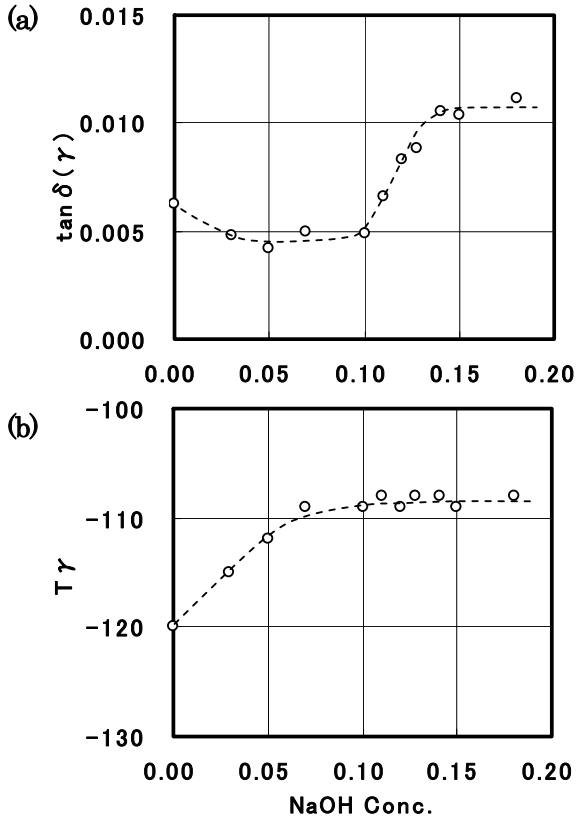
(a)
0.015
0.010
0.005
0.000
tan δ(γ)
0.00
0.05
0.10
0.15
0.20
(b)
−100
−110
−120
−130
Tγ
0.00
0.05
0.10
0.15
0.20
NaOH Conc.

Figure 5

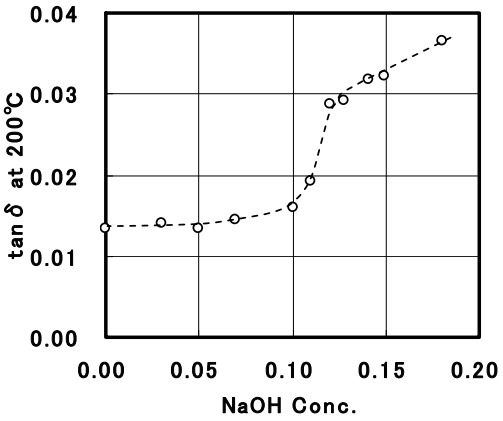

Figure 6

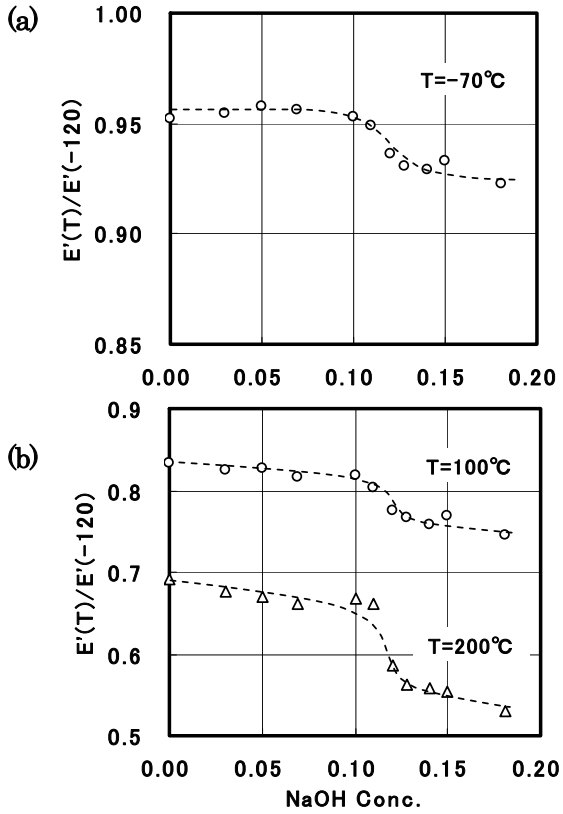
(a)
1.00
0.95
0.90
0.85
E'(T)/E'(-120)
T=-70℃
0.00
0.05
0.10
0.15
0.20
(b)
0.9
0.8
0.7
0.6
0.5
E'(T)/E'(-120)
T=100℃
T=200℃
0.00
0.05
0.10
0.15
0.20
NaOH Conc.

Figure 7

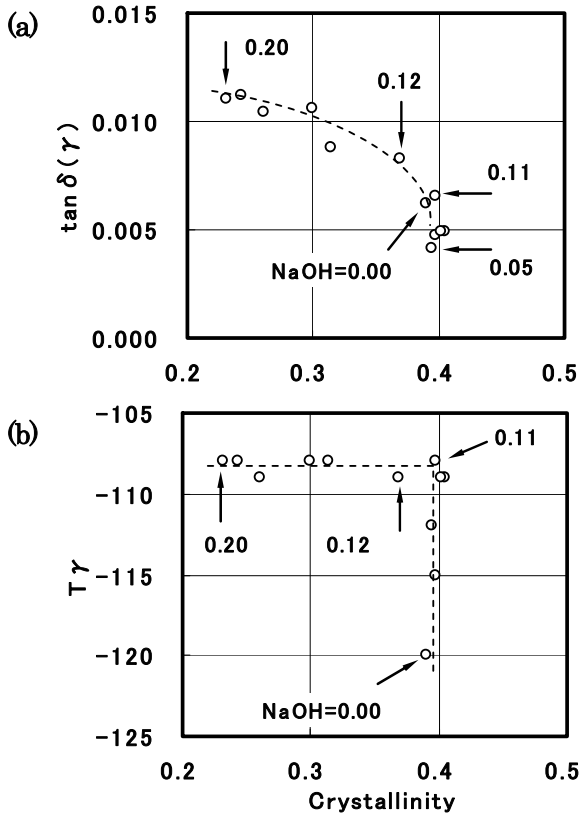
(a)
0.015
0.010
0.005
0.000
tan δ(γ)
0.20
0.12
0.11
0.05
NaOH=0.00
0.2
0.3
0.4
0.5
(b)
-105
-110
-115
-120
-125
Tγ
0.11
0.20
0.12
NaOH=0.00
0.2
0.3
0.4
0.5
Crystallinity

Figure 8

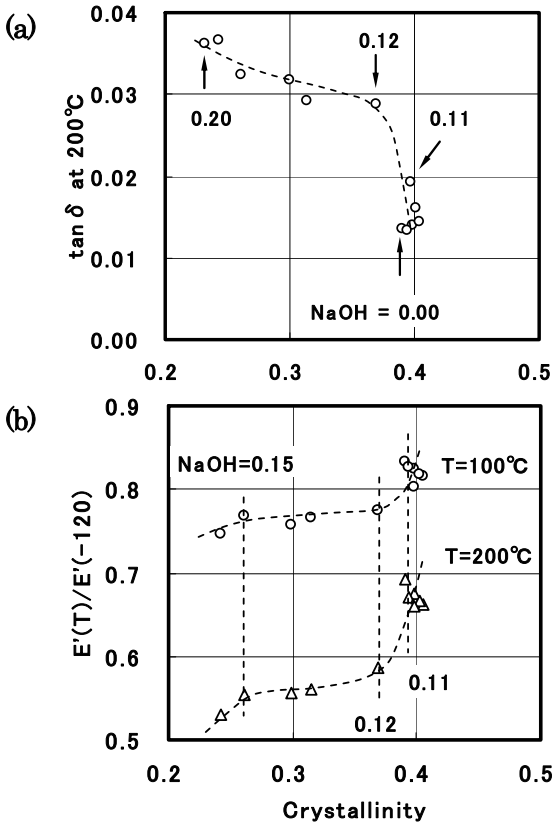
(a)
tan δ at 200℃
0.04
0.03
0.02
0.01
0.00
0.12
0.20
0.11
NaOH = 0.00
0.2
0.3
0.4
0.5
(b)
E'(T)/E'(−120)
0.9
0.8
0.7
0.6
0.5
NaOH=0.15
T=100℃
T=200℃
0.11
0.12
0.2
0.3
0.4
0.5
Crystallinity

Figure 9