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

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ABSTRACT

Wood samples (*Picea jezoensis* Carr.) were treated with solutions of aqueous NaOH (0–0.20 concentration fraction) and each treated samples evaluated by dynamic mechanical analyses (DMA). NaOH treatment was shown to affect the interactions between microfibrils and the surrounding matrix and, in particular, 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. Alkali treatment induces changes in the polymer domains as a result of matrix eluviation. This decreases the dynamics of methylol groups at NaOH concentrations less than 0.11. On the other hand, alkali treatment causes non-crystallization at concentrations greater than 0.11, which quantitatively increases the flexibility of methylol groups. Crystallinity decreased, and main-chain dynamics increased, following treatment with highly concentrated NaOH solutions. The dynamics of lignin also increased due to weakened interactions with microfibrils due to non-crystallization.

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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 Roy et al. [7,11] 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 microfibrils in wood and to lignin swelling as a result of NaOH treatment. That is, the dependence of crystallinity on the relaxation time was related to molecular chain rearrangements required time in this region.

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

2. Experimental

2.1. Materials and NaOH treatment

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

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2.2. Dynamic mechanical analyses and X-ray diffraction measurements

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

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

3. Results and discussion

3.1. Relative crystallinity and dimensional changes

Figs. 1 and 2 show the changes in dimension along the longitudinal direction of wood sample and relative crystallinity observed during NaOH treatment. Wood sample length characteristically decreased with increasing in NaOH concentration. The relative crystallinity was nearly constant for less than [NaOH] = 0.10 but started to decrease at 0.11. Crystallinity decreased drastically between [NaOH] = 0.11 and 0.13 and slightly for concentrations greater than 0.14. The concentration-dependence of dimensional changes along the longitudinal direction of each sample was similar to that of the crystallinity change. This indicates that the dimensional changes were due to non-crystallization with NaOH treatment. Fig. 2 suggests a linear relationship between both of these variables for concentrations greater than 0.11. These changes during NaOH treatment are consistent with our previous reports and indicate satisfactorily non-crystallization.

3.2. Changes in molecular dynamics of non-crystallized wood

Fig. 3(b) shows the variation of tanδ as a function of temperature for treatments with [NaOH] = 0 and 0.20. Three characteristic relaxations were identified in the untreated ([NaOH] = 0) sample. These relaxations were labeled α, β, and γ in the order of decreasing temperature. The β relaxation was obscured in the fully dried samples. The α dispersion was attributed to micro-Brownian motion of the cell wall polymers in the non-crystallized regions, the β dispersion was attributed to the motion of the absorbed water itself or the segmental motions associated with it, and the γ dispersion was attributed to the motion of methylol
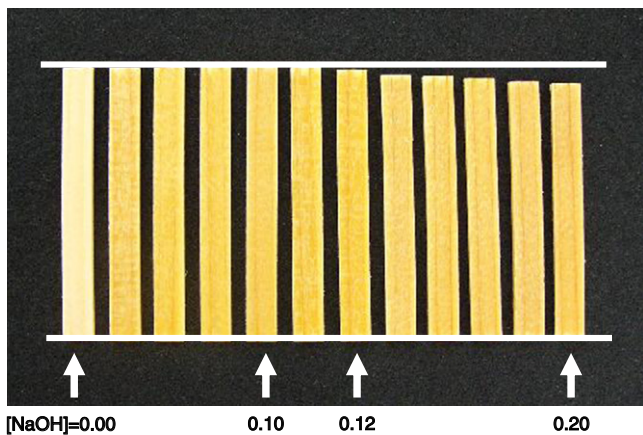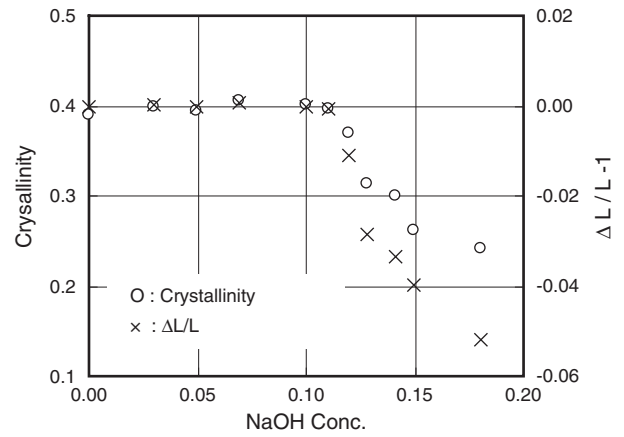

Fig. 2. Crystallinity and relative dimensional changes along the longitudinal axis (ΔL/L-1) of wood samples as a function of NaOH concentration.

groups according to a previous study [21,22]. These three relaxations of the untreated sample were identified at roughly the same temperatures for a sample treated with [NaOH] = 0.20. Therefore, the relaxations in the sample that had been treated with [NaOH] = 0.20 were attributed to the same causes as those in the untreated sample. However, their intensities and temperatures of tanδ have the characteristic concentration-dependence of NaOH solution.

The temperature dependence of tanδ in the untreated sample was generally similar to that of the treated wood studied by other researchers and cellulose filaments [23]. However, tanδ intensity of both the α and γ
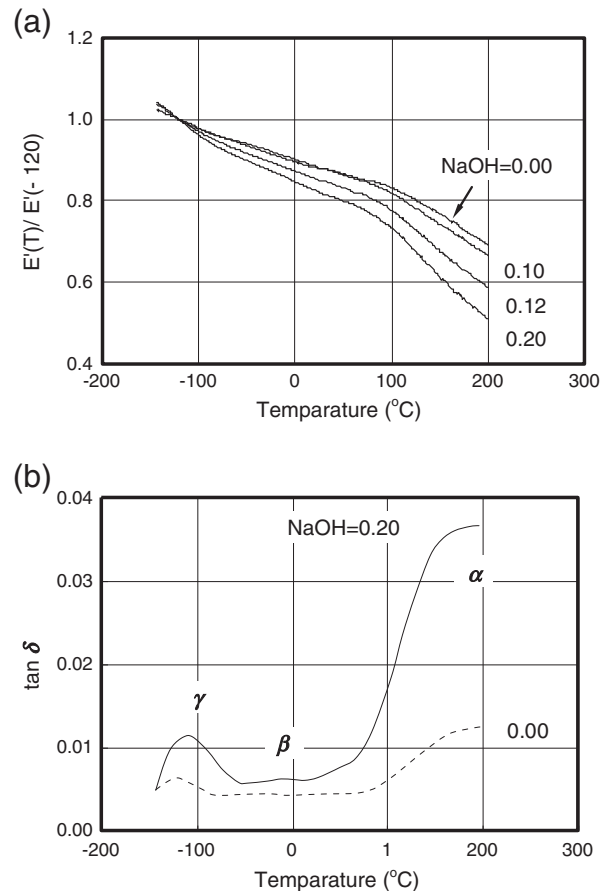

Fig. 3. The typical temperature dispersion of the relative dynamic modulus normalized to its value at −120 °C (a) and tanδ (b) under dry condition for samples treated with various aqueous NaOH solutions.

Fig. 1. Dimensional changes under wet condition along the longitudinal axis of wood samples Yezo spruce (*Picea jezoensis* Carr.) as a function of NaOH concentration.