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Role of bound water on structural change of water insoluble polysaccharides

Tatsuko Hatakeyama [a, *], Mika Iijima [b], Hyoe Hatakeyama [c, 1]

[a] Lignocel Research Co. Ltd, 73-8, Yatsumata, Fukui 910-3558, Japan
[b] Faculty of Education, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki, 852-852, Japan
[c] Graduate School of Engineering, Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505, Japan

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ABSTRACT

In terms of the functionalities of polysaccharides, water molecules play a crucial role. Two kinds of bound water, freezing bound water and non-freezing water have been classified based on the phase transition of water restrained by hydrophilic polymers. In this study, conversion of bound water accompanied with the structural change of two kinds of water insoluble polysaccharides, cellulose and curdlan, is investigated. It was found that bound water is involved in reversible and irreversible structural change of both cellulose and curdlan. Bound water contributes to the reversible structural change of natural cellulose, whose mechanical properties increase in the presence of water. In water-induced crystallization of amorphous cellulose, bound water is excluded from molecular chains and the crystalline region is irreversibly established. Transformation of freezing bound water to non-freezing water was observed when gelation mechanism of curdlan is changed from reversible to irreversible state. Quantification of bound water involved in the above process is described based on the melting enthalpy of ice restrained by cellulose and curdlan.

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1. Introduction

Recently, water molecules directly restrained by the hydrophilic group of biopolymers have received particular attention. Water bound on biopolymer surface is known to be involved with biocompatible function of the polymer (Hatakeyama, Tanaka, & Hatakeyama, 2010a, 2010b; Tanaka, et al., 2000; Tanaka, Mochizuki, Motomura, & Hatakeyama, 2002; Tanaka & Mochizuki, 2004). The above water mediating biopolymer and surrounding media is categorized into bound water. Based on calorimetry, two kinds of bound water are classified (Hatakeyama, Nakamura, & Hatakeyama, 1988; Hatakeyama & Hatakeyama, 1998, 2004; Hatakeyama, Tanaka, Kishi, & Hatakeyama, 2012). The first-order phase transition of water molecules, which are directly restrained by the hydrophilic group, is not detected. This type of bound water is categorized into non-freezing water. The second type of bound water shows the first-order phase transition, however, the transition behaviour is not the same as that of pure water, which is categorized as free water. Accordingly, three kinds of water can be classified in polysaccharide-water systems, i.e. non-freezing, freezing bound and free water. Among two kinds of bound water, the amount of non-freezing water depends on the chemical structure of matrix polysaccharide. In the case of water insoluble polysaccharides, the amount of non-freezing water is determined by the number of hydroxyl groups located in the amorphous region. In contrast, the amount of freezing bound water depends on the higher-order structure of molecular chain.

Nuclear magnetic relaxation time of ^{1}H of water restrained by hydrophilic polymers is also an index indicating restricted molecular motion of water. Relaxation times markedly decrease when free molecular motion is inhibited via hydrogen bonding and/or

* Corresponding author.
E-mail address: lignocel@mx3.fctv.ne.jp (T. Hatakeyama).
[1] Present address: Lignocel Research Co. Ltd.

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ionic interaction (Hatakeyama, Hirose, & Hatakeyama, 1989). Longitudinal and transverse relaxation times (T_1 and T_2) of ^{1}H in the water bound by cellulose molecules were investigated by nuclear magnetic relaxation measurement (Child, 1972; Hsi, Vogt, & Bryant, 1979; Hatakeyama & Hatakeyama, 1990). T_1 is measured by $180 - \tau - 90°$ pulse method and T_2 was measured by Meiboom Gill variant of the Carr-Purcel method or by solid echo method (Farrar & Becker, 1971). ^{1}H T_1 of water restrained by natural cellulose is 1.45 s at water content [W_c = (mass of water/mass of dry sample)] = 0.02 and then T_1 decreases with increasing W_c. T_1 reaches minimum at $W_c = 0.1$ and slightly increases and attains constant value of 0.8 s at around $W_c = 0.4$. T_2 increases with increasing W_c from 0.1 msec ($W_c = 0.02$) to 0.7 msec ($W_c = 0.4$) (Hatakeyama & Hatakeyama, 1990). The T_2 values give an average state of molecular motion of water, on this account, molecular mobility of bound water restrained by cellulose increases with increasing bound water content. Based on several assumptions on different perturbed sites of water and extreme narrowing condition of free water, one average correlation time (τ_c) is calculated (Hatakeyama et al., 1989). The value of τ_c of bound water restrained by cellulose is 6×10^{-7} s ($W_c = 0.02$) to 2×10^{-7} s ($W_c = 0.4$). The above nuclear magnetic relaxation results reveal that molecular motion of bound water is markedly restricted and categorized to non-rigid solid. Nuclear magnetic relaxation measurement is a useful tool for molecular motion of bound water molecule, however, thermal method is advantageous in order to obtain the quantitative data on the amount of each kind bound water. Accordingly, in this study, characteristics of bound water obtained by thermal method will mainly be discussed.

Water soluble polysaccharides change their molecular conformation in aqueous media as a function of temperature. In contrast, it has been recognized that molecular conformation of water insoluble polysaccharide is stable since the crystalline region restricts molecular rearrangement even in the presence of water. However, it has been found that the conformation of water insoluble polysaccharides, such as cellulose and curdlan, varies in the presence of water. Cellulose is a representative water insoluble polysaccharide. It is one of the most abundant organic compounds and shows unique properties in the presence of water, although characteristic features caused by water have been accepted as an ordinary feature since cellulose is usually utilized in humid circumstances (Hatakeyama & Hatakeyama, 1998, 2004). Curdlan is a unique gel forming polysaccharide (Fulton & Atkins, 1980; Funami, Funami, Yada, & Nakao, 1999a, 2000; Harada, Masada, Fujimori, & Maeda, 1966; Harada, Misaki, & Saito, 1968) that is widely used in the food industry, as an ingredient in various types of processed foods (Funami, Yada, & Nakao, 1998; Miwa, Nakao, & Nara, 1994). Curdlan is also known as a water insoluble saccharide. Aqueous dispersion of curdlan forms two types of heat induced gel depending on temperature (Harada et al., 1968; Kanzawa, Harada, Koreeda, Harada, & Okuyama, 1989; Kanzawa, Koreda, Harada, & Harada, 1989; Nishinari & Zhang, 2004; Saito et al., 1987) According to previous studies, curdlan forms thermo-reversible hydrogels when aqueous suspension is heated to ca. 60 °C. When the suspension is treated at a temperature higher than 60 °C, the obtained hydrogel is thermo-irreversible (Hatakeyama, Ueda, & Hatakeyama, 2006).

In this study, two types of water insoluble polysaccharides, poly(β-1,4 D-glucose) (cellulose) and poly(β-1,3 D-glucose) (curdlan), were selected and the structural change of the above two kinds of polysaccharides were investigated by introduction of a small amount of water. In the equilibrium conditions of polysaccharides, the amount of non-freezing water is defined basically by the chemical structure of each polysaccharide. However, in transient state, a part of the non-freezing water converts to freezing bound water, or in some cases decrease in the amount of bound water is observed. The amount of freezing bound water changes when gelation or crystallization occurs. In this study, conversion of bound water from freezing bound water to free water, or from non-freezing water to freezing bound water accompanied with the structural change of cellulose and curdlan is discussed.

2. Materials and methods

2.1. Materials

Natural cellulose obtained from cotton lint and cotton cloth was used. (Hatakeyama & Hatakeyama, 2004; Hatakeyama et al., 1988; Hatakeyama, Nakamura, & Hatakeyama, 2000). The samples were washed with ethanol-benzene solution using a Soxhlet extractor. Samples were dried under reduced pressure for 24 h at room temperature and placed in a vacuum oven (1.33 Pa) whose temperature was maintained at 105 °C for 5 h. For differential scanning calorimetry (DSC) and X-ray diffractometry, the cotton lint and cloth samples were powdered to eliminate the effect of fibre orientation. Besides the above natural cellulose samples, amorphous cellulose was prepared by deacetylation in completely dry conditions as reported previously (Hatakeyama & Hatakeyama, 2004). Curdlan granules (Wako Pure Chemicals) were ground and filtered and 9 fractions with diameter from 15 to 100 μm were obtained.

2.2. Methods

2.2.1. Differential scanning calorimetry

An SII Nanotechnology, differential scanning calorimeter DSC200C, equipped with a cooling apparatus was used. Nitrogen gas flow rate was 30 ml min^{-1}. Sample mass was ca. 5 mg, heating and cooling rate 10 °C min^{-1} and temperature varied from −150 to 80 °C. The 2nd heating was used for analysis. Detailed conditions are found in our previous papers (Hatakeyama et al., 2010a; Hatakeyama et al., 2012). In order to have natural cellulose and curdlan particles with various water contents, the following procedure was carried out. i.e. (1) 3–5 mg samples were placed in pans and a small amount of deionized water was added using a micro-syringe, (2) the above water was evaporated until a pre-determined mass of water was attained, (3) the sample pans were sealed hermetically using an auto-sealer, (4) samples with added water were weighed, (5) samples were kept at room temperature overnight and weighed again in order to confirm that no mass loss occurred. After DSC measurement, the pan was pierced, annealed at 110 °C over 2 h in an electric oven and finally weighed. In order to have amorphous cellulose treated in a humid condition with various times, the following procedure was conducted, (1) a number of sample films was placed in a desiccator with 100 %RH at 25 °C, (2) each sample piece was removed at a pre-determined time from 10 to 10^5 min, immediately sealed and weighed, (3) dry sample mass was determined after measurements. The amount of water was evaluated by Eq. (1). Although the water content (W_c) of hydrated polymers has been defined in various equations, in this study, W_c is defined as follows:

$$W_c = m_w/m_s \quad (1)$$

where m_s is the mass of dry sample and m_w is the mass of water in the system. In this study, samples showing no heat of vaporization on thermogravimetric (TG) curve from room temperature to 200 °C were defined as dry samples. The sample prepared as described in 2.1 was designated as a dry sample.

2.2.2. Wide angle X-ray diffractometry

A Rigaku Denki Co. x-ray diffractometer Rotaflex RU-100-PL was used to evaluate the degree of crystallinity (X_c). The detailed

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