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Thermal decomposition of native cellulose: Influence on crystallite size

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ABSTRACT

The thermal degradation behavior of crystalline cellulose has been investigated using thermogravimetry, differential thermal analysis, and derivative thermogravimetry in a nitrogen atmosphere. Three cellulose samples, *Halocynthia*, cotton, and commercial microcrystalline cellulose Funacel, were used in this study to analyze the influence on crystallite size. They all belongs to cellulose I_β type and those crystallite sizes calculated from the X-ray diffractometry profiles by Scherrer equation were very different in the order *Halocynthia* > cotton > Funacel. The thermal decomposition of cellulose shifted to higher temperatures with increasing crystallite size. However, activation energies for the thermal degradation were the almost the same among the samples: 159–166 kJ mol^{-1}. These results indicated that the crystal structure does not affect the activation energy of the thermal degradation but the crystallite size affects the thermal degradation temperature.

1. Introduction

Cellulose is a linear β-1,4-glucan, and is the most abundant polymer available worldwide. In nature, it occurs as crystalline fiber called microfibril that is a few nanometers across. Dimensions of crystalline microfibril depend on cellulose origins [1] and thus the surface of microfibril can only be regard as an amorphous region [2]. There are two naturally occurring forms of cellulose: cellulose I_α and I_β. Although cellulose I_α is a rather rare form, cellulose I_β, which originates from higher plants, is the major form. The crystal structure and hydrogen-bonding system of cellulose I_β have been determined based on a two-chain monoclinic unit cell ($a = 0.7784$ nm, $b = 0.8201$ nm, $c = 1.0380$ nm, and $\gamma = 96.5°$) with $P2_1$ symmetry [3]. Cellulose I_β consists of parallel chains forming hydrogen-bonded sheets that stack with an alternating shear running parallel to the chain axis ($\pm c/4$) through van der Waals interactions [3,4].

Many studies on the effect of heat on the structure of cellulose have been carried out to understand the pyrolytic process for controlling thermal stability, mainly for wooden, paper, and textile materials: (a) the initial rapid weight loss was related to the percentage of less-ordered regions under vacuum conditions at 251 °C [5], (b) amorphous (ball-milled) cotton decomposed faster in a vacuum than crystalline cotton did [6], (c) the oxidative degradation in air took place in the amorphous regions of cellulose [7], (d) the initial decomposition occurred at the crystalline–amorphous boundaries [8]. Although many other recent studies on the thermal degradation of cellulose have been carried out [9–12], the detailed pathway of this process is not understood clearly. Because the thermal degradation of cellulose occurs through a series of complex features, it is difficult to evaluate the mechanism of pyrolysis.

The aim of this study was to elucidate how the thermal decomposition of crystalline native cellulose occurred. For this purpose, three types of cellulose with very different crystallite size from different sources, but having the same I_β crystalline form, were prepared from wood, cotton, and *Halocynthia* (a highly crystalline form of cellulose obtained from animal). In this study, we focused on the changes in peak temperatures in the derivative thermogravimetric curves during the course of thermal decomposition in an inert atmosphere.

2. Materials and methods

2.1. Materials

Cellulose samples from different sources were used in this study: *Halocynthia roretzi* (animal), cotton linter ACALA SJ-2, and Funacel SF (microcrystalline cellulose powder, particle size = 6–10 μm, Funakoshi Co., Tokyo, Japan. This is an acid hydrolysis product of

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wood cellulose). *Halocynthia* and cotton linter were treated repeatedly with a 5% KOH and 0.3% sodium chloride solution until they became perfectly white as previously described [4]. The purified *Halocynthia* and cotton celluloses were dispersed with a double-cylinder-type homogenizer into submillimeter-size fragments, and then freeze-dried *in vacuo*.

2.2. Gel permeation chromatography

The freeze-dried cellulose samples were converted to cellulose trinitrate by treating them with a mixture of nitric acid and phosphorous pentoxide for a period of 30 min. The derivatized cellulose was washed with cold distilled water until all the residual acid was removed. The dried samples were dissolved in tetrahydrofuran and analyzed using size exclusion chromatography, TSK GMHXL and TSK G2500H6 columns, connected in this order, each had dimensions of 300 × 7.5 mm I.D. The elution was detected from the UV adsorption at 254 nm. The degree of polymerization was obtained from the chromatogram after calibration using polystyrene standards, as described in a previous publication [13].

2.3. X-ray diffractometry

Approximately 100 mg of the freeze-dried samples were pressed into disks at 200 kgf cm^{-2} for 30 s. X-ray diffractometry in reflection mode was carried out using a diffractometer (Rigaku, RINT2000), with monochromatic Cu Kα radiation ($\lambda = 0.15418$ nm), generated at 38 kV and 50 mA, by using the following optical slit system: divergence slit = 0.5°; scattering slit = 0.5°; and receiving slit = 0.15 mm. The scanning was performed as follows: scattering angle, $2\theta = 10$–30°; step in 2θ of $\Delta 2\theta = 0.1°$; accumulation time for each step, $t = 20$ s.

Peak separations of the profiles were carried out using the nonlinear least squares fitting program, where a pseudo-Voigt function for each crystalline peak and a fifth-degree polynomial function for the background profile were used, as described in previous paper [1]. The *d*-spacings were calculated using the Bragg's equation and the crystallite sizes of cellulose were calculated using the Scherrer equation:

$$L = 0.9\lambda/(H \cos\theta),$$

where L is the crystallite size perpendicular to the plane; λ is the X-ray wavelength; H is the full-width at half-maximum in radians; and θ is the Bragg angle. The crystallinity index (CI) was determined from the ratio of the separated peak area to the total area.

2.4. Thermal analysis

Thermal analysis was performed between room temperature and 500 °C at heating rates of 2, 5, 10, and 20 °C min^{-1} in dry nitrogen with a flow rate of 200 ml min^{-1} in a thermogravimetric (TG)/differential thermal analysis (DTA) apparatus (TGD 9600, Shinku Riko, Yokohama, Japan). Each cellulose sample, weight = 5 ± 0.1 mg, was used in a single run and the thermal profile of each sample was measured three times. Aluminum oxide (Al_2O_3) was used as a reference material in all the DTA experiments.

3. Results and discussion

3.1. Characteristics of cellulose

Fig. 1 shows X-ray diffractometry profiles of native cellulose samples used in this study. In each profile, three crystalline peaks that could be index as 1$\bar{1}$0, 110, and 200 from the lowest angle in this order were observed. These peaks were separated by a least squares method, and the following were calculated: the *d*-spacings, crystallite size, and crystallinity indices. Results are tabulated in Table 1 with the values of degree of polymerization (DP). The calculated *d*-spacings clearly indicated that the cellulose samples used in this study are all cellulose I_β type [14]. The cellulose samples that exhibited same crystal type but different crystallite size, crystallinity indices and DP were suitable to investigate the relationship between the thermal degradation behavior and the structure of the cellulose. The three structural factors (crystallite size, crystallinity index and DP) of the three cellulose samples showed values increasing in the order: Funacel < cotton < *Halocynthia*. Crystallinity indices increased with increasing crystallite sizes because the crystallites surface corresponding to amorphous region diminished. This is consistent with the ^{13}C NMR result that the amorphous signal in the spectra could be considered to be due to the chain conformation on the crystallite surface [2]. Thus, the thermal degradation behavior with relation to crystallite size will be discussed in the following sections.

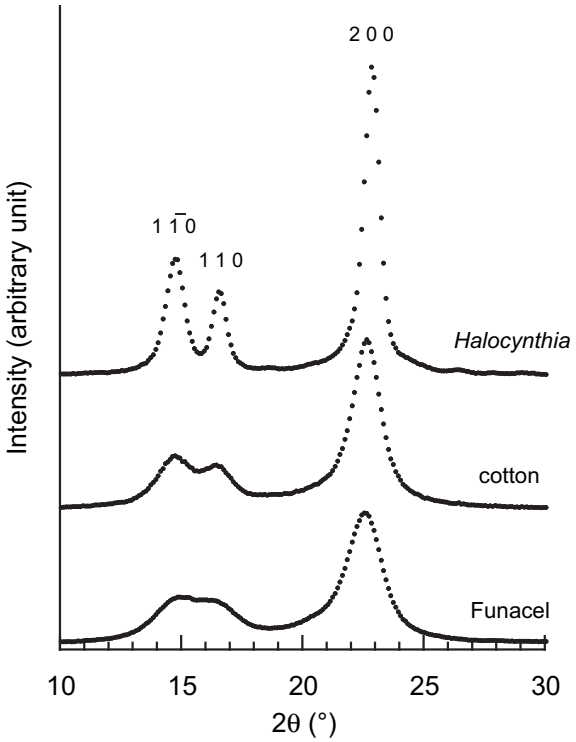

Fig. 1. X-ray diffractometry profiles of native cellulose samples.

Table 1
The degree of polymerization, *d*-spacings, crystallite sizes, and crystallinity indices of native cellulose samples.

	DP[a]	*d*-spacings (nm)[b]			*L* (nm)[c]			CI[d]
		(1$\bar{1}$0)	(110)	(200)	(1$\bar{1}$0)	(110)	(200)	
Funacel	520	0.597	0.536	0.395	3.9	5.5	4.5	0.54
Cotton	4300	0.623	0.539	0.394	4.9	6.5	5.8	0.58
Halocynthia	19,000	0.603	0.536	0.390	8.7	11.7	10.6	0.74

[a] Degree of polymerization.
[b] *d*-Spacings of typical three equatorial peaks of cellulose in Fig. 1.
[c] Crystallite size perpendicular to each plane.
[d] Crystallinity index.