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STRUCTURAL CHANGES OF AMORPHOUS CELLULOSE BY THERMAL AND HYDROTHERMAL TREATMENTS

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ABSTRACT: Structural changes of cellulose molecules in non-crystalline region of cellulosic materials by thermal and hydrothermal treatments were studied by using new amorphous cellulose samples, which were prepared from cellulose/SO₂-diethylamine-dimethylsulfoxide solutions. Dry-thermal treatments led to depolymerization of amorphous cellulose and a decrease in moisture contents by forming irreversible hydrogen bonds, and these changes depended on molecular weight of original amorphous samples, heating temperature, and heating time. However, no crystallization was detected by X-ray diffraction analyses. In the case of thermal treatments of amorphous cellulose samples at 80 °C and 80% relative humidity for 1-14 days, no change in amorphous structure, molecular weight, or moisture contents was observed. Hydrothermal treatments of amorphous cellulose samples in water at temperature higher than 100 °C brought about crystallization to cellulose IV, together with depolymerization and a decrease in moisture contents. These structural changes depended on molecular weight of original amorphous celluloses, heating temperature, and heating time. In comparison with the results of dry-thermal treatments, it was shown that the presence of water remarkably enhanced depolymerization and crystallization to cellulose IV.

1. INTRODUCTION

Cellulosic materials consist of crystalline and non-crystalline regions, and hydrophilic properties of cellulosic materials are owing to non-crystalline region. The cellulose I structure in wood does not essentially change during chemical and mechanical pulping, paper making, and other additional processes. On the other hand, cellulose molecules in non-crystalline region may be depolymerized, and may decrease in yields and accessibility during the processes. These microscopic changes in the non-crystalline region must lead to macroscopic changes of cellulose microfibrils and fibers, and furthermore have the influence not only on hydrophilic but also on mechanical properties of cellulosic materials.

Thus, the characterization of non-crystalline region in cellulosic materials is of significance, and many studies concerning thermal, hydrothermal, and pulping treatments of cellulosic materials have been reported from viewpoints of formation of hydrogen

bonds and crystallization by using X-ray diffraction analyses, differential scanning calorimetry, infrared spectroscopy, and others [1-9]. In the case of usual cellulosic materials consisting of both crystalline and non-crystalline regions, it is difficult to characterize only the non-crystalline region in the mixture. Therefore, amorphous cellulose models, which were prepared by ball-milling of cellulosic materials or deacetylation of cellulose acetate under nonaqueous and basic conditions, had also been used for characterization [10-17]. These amorphous cellulose samples, however, are unstable even at room temperature under aqueous conditions to form cellulose II to some extent [10-18], whereas the actual non-crystalline cellulose in cellulosic materials maintains its amorphous structure under these mild aqueous conditions.

On the other hand, we have developed a method of preparing new amorphous cellulose samples, which maintain the amorphous structure even under usual aqueous conditions [19-20]. One of the other features

of this amorphous cellulose is that the molecular weight can be varied by selecting the original cellulose sample for the preparation of the amorphous cellulose. In this paper, therefore, structural changes of these amorphous cellulose samples were studied to elucidate the structural changes of cellulose molecules in the actual non-crystalline region in cellulosic materials under thermal and hydrothermal conditions.

2. EXPERIMENTAL

2.1 Samples

Microcrystalline cellulose powder (Cellulose Powder A, Advantec Toyo Co. Ltd.), filter pulp (Ashless Filter Pulp, Advantec Toyo Co. Ltd.), linter cellulose, and cotton cellulose were used as the original cellulose samples. Degrees of polymerization (DPv) of the above cellulose samples were determined by the capillary viscosity method using Cuen solutions (cupriethylenediamine hydroxide solution) [22], and were 200, 800, 1300, and 1700.

2.2 Preparation of amorphous cellulose

As in previous papers [19-20], regenerated amorphous cellulose samples were prepared from above celluloses by dissolving in the SO_2 -diethylamine-dimethylsulfoxide system and regenerating into water. The regenerated cellulose gel having heterogeneous shape was washed with water several times, and then treated with a blender to form fine gel-particles. The particles thus prepared were washed sufficiently with water, and then freeze-dried. Values of molecular weight of regenerated amorphous cellulose samples were almost equal to those of the original ones.

2.3 Thermal and Hydrothermal Treatments

Thermal treatments of amorphous cellulose samples were carried out in an oven at 100, 120, 140, and 160 °C under dry conditions. Thermal treatments at high humidity were performed at 80 °C and 80% relative humidity for 1-14 days. After these treatments, the samples were weighed, and then conditioned at 20 °C and 65% relative humidity for more than 1 day.

In the case of hydrothermal treatments in water, the samples were heated in water in a stainless steel vessel at 100, 130, 160, and 190 °C. After this treatment, the samples were filtered out, and washed sufficiently with water and finally with acetone. These treated samples were conditioned at 20 °C and 65%

relative humidity for more than 1 day.

All these thermal and hydrothermal treatments were performed in air.

2.4 Analyses

Yields, moisture contents, X-ray diffraction patterns, and DPv of treated samples were measured.

X-ray diffraction patterns of pellet samples were recorded on a JEOL JDX-5B diffractometer equipped with a reflection type goniometer, using Ni filtered CuK_α radiation.

Intrinsic viscosities of cellulose samples were measured using 0.5 mol Cuen solution and a capillary type viscometer [21]. DPv values were calculated from the intrinsic viscosity, according to the following formula [22].

$$[\eta] = 0.57 \times \text{DPv}^{1.0}$$

3. RESULTS AND DISCUSSION

3.1 Dry-thermal Treatments

Fig. 1 shows X-ray diffraction patterns of the original cellulose samples and the corresponding regenerated ones. All these regenerated celluloses had the amorphous pattern, irrespective of the molecular weight and the crystallinity of the original cellulose samples. Since these amorphous cellulose samples

Fig. 1. X-ray diffraction patterns of the original (a - d) and the corresponding regenerated (a' - d') celluloses. a; Microcrystalline cellulose powder, b; filter pulp, c; linter cellulose, and d; cotton.

Fig. 2. Degree of polymerization of amorphous cellulose samples subjected to dry-thermal treatments at 100 °C.

Fig. 3. Degree of polymerization of amorphous cellulose samples subjected to dry-thermal treatments at 100, 120, 140, and 160 °C for 12 h.

prepared from microcrystalline cellulose powder, filter pulp, linter cellulose, and cotton had different DPv values, these were named amorphous cellulose 1, 2, 3, and 4, respectively. These four amorphous cellulose samples were treated at 100, 120, 140, and 160 °C for 3, 6, 12, and 24 h in a drying oven.

Fig. 2 shows DPv values of four amorphous cellulose samples treated at 100 °C. Depolymerization at this temperature was negligible even after the treatment for 24 h. DPv values of the samples treated at 120 °C or higher for 12 h were shown in Fig. 3. Cellulose molecules in the samples were depolymerized

Fig. 4. Moisture contents of amorphous cellulose samples subjected to dry-thermal treatments. Measured after conditioning at 20 °C and 65% relative humidity.

as a result of the dry-thermal treatment at 120 °C, and DPv values decreased with an increase in the heating temperature. Weight-loss of the samples after these treatments was almost negligible for all the samples.

Fig. 4 illustrates the moisture contents of the heated and then conditioned samples, which were prepared from amorphous cellulose 1. The crystalline cellulose samples used for preparing the amorphous samples had moisture contents of 4.4–5.5%, and the corresponding amorphous cellulose samples had those of 10.9–11.4%. The dry-thermal treatments led to a decrease in moisture contents. Amorphous cellulose 2, 3, and 4 also had similar patterns of moisture contents to that of amorphous cellulose 1. The moisture contents of the samples treated at 100 °C increased at the initial stage, and then decreased. This finding suggests that the accessibility of the amorphous cellulose samples increases at the initial stage of the dry-thermal treatment and then decreases with an increase in the heating time. This phenomenon at the initial stage may not correspond to the thermal behavior of the actual non-crystalline region in cellulosic materials, but may be observed particularly on the amorphous cellulose samples used in this study. However, the trend of the decrease in moisture contents of the model samples, thus observed in this study, indicates that formation of hydrogen bonds, a part of which are stable and uncleaved during conditioning treatments,

Fig. 5. X-ray diffraction patterns of amorphous cellulose samples subjected to dry-thermal treatments.

proceeds in non-crystalline region under dry-thermal conditions.

X-ray diffraction patterns of the treated samples are shown in Fig. 5. No crystallization was detected for all the samples and the amorphous structure was maintained, although depolymerization and a decrease in the accessibility took place on the samples under the dry-thermal conditions.

These findings indicate that the structural changes of cellulose molecules in non-crystalline region in cellulosic materials under the dry-thermal conditions are depolymerization and the formation of intra- and/or inter-molecular hydrogen bonds without crystallization. These changes depend on heating temperature and heating time.

The dry-thermal treatments were also performed on wet amorphous cellulose samples, in order to examine the structural changes of cellulose molecules in non-crystalline region in cellulosic materials during drying processes from wet state. The temperature in the oven was 105°C and the heating time was less than 30 min. Consequently, neither depolymerization nor crystallization took place on cellulose molecules of the samples under these conditions.

3.2 Thermal Treatments at High Humidity

Thermal treatments of cellulosic materials under high humidity conditions have been often carried out, associated with accelerated aging of paper [23]. However, even after the treatments at 80°C and 80%

relative humidity for 14 days, X-ray diffraction analyses showed that all the samples kept the amorphous structure. Furthermore, neither depolymerization nor a decrease in moisture content after conditioning was observed. Thus no structural changes of cellulose molecules in the actual non-crystalline region are plausible to take place under these conditions.

3.3 Hydrothermal Treatments in Water

Wood chips undergo hydrothermal treatments during auto-hydrolysis or prehydrolysis of kraft pulping. During the hydrothermal process, some structural changes including depolymerization may occur on accessible parts such as non-crystalline cellulose and hemicellulose. Then the structural changes of cellulose molecules in non-crystalline cellulose region under these conditions were examined using the amorphous cellulose samples.

Fig. 6 shows DP_v values of the samples treated at 100°C. The amorphous cellulose samples were evidently hydrolyzed even at this temperature in the presence of water, and this phenomenon was different from that observed under the dry-thermal conditions. Furthermore, as shown in Fig. 7, cellulose molecules in the samples were remarkably depolymerized with an increase in heating temperature. Yields after hydrothermal treatments began to decrease at temperature higher than 160°C for all the amorphous cellulose samples (Table 1). Fig. 7 and Table 1 show that

Fig. 6. Degree of polymerization of amorphous cellulose samples subjected to hydrothermal treatments at 100°C in water.

Table 1 Yields after Hydrothermal Treatments of Amorphous Cellulose Samples

DPv of amorphous cellulose sample	Time (h)	Yield (%)		
		130 °C	160 °C	190 °C
200	2	100	100	77
	4	100	98	70
	8	100	95	59
800	2	100	99	89
	4	100	97	56
	8	100	97	51
1300	2	100	100	82
	4	100	100	80
	8	100	100	62
1700	2	100	100	90
	4	100	95	69
	8	100	94	55

Fig. 7. Degree of polymerization of amorphous cellulose samples subjected to hydrothermal treatments at 100, 130, 160, and 190 °C for 8 h in water.

the yields and DPv values after the hydrothermal treatments at 190 °C for 8 h were 51–62% and 30–40, respectively, for all the samples.

Fig. 8 shows moisture contents of hydrothermally treated and conditioned amorphous cellulose 1, and the other three amorphous cellulose samples had almost identical patterns of amorphous cellulose 1. The moisture contents decreased with an increase in the heating temperature and the heating time, and these changes were more remarkable than those for the dry-thermal treatments. These observations indi-

Fig. 8. Moisture contents of amorphous cellulose samples subjected to hydrothermal treatments in water. Measured after conditioning at 20 °C and 65% relative humidity. **Fig. 9.** X-ray diffraction patterns of amorphous cellulose 1 (original DPv = 200) heated in water.

cate that the hydrogen bonds, which are stable and uncleaved during conditioning treatments, are formed in non-crystalline region during the thermal treatments.

Fig. 9 and 10 show X-ray diffraction patterns of the treated amorphous cellulose 1 and 4, respectively. These patterns revealed that the crystallization from

Fig. 10. X-ray diffraction patterns of amorphous cellulose 4 (original DP_v = 1700) heated in water.

Table 2 Rate Constants to Form Cellulose IV from Amorphous Celluloses by Hydrothermal Treatments

DP _v of amorphous cellulose sample	Crystallization rate constants to cellulose IV (h ⁻¹)		
	100 °C	130 °C	160 °C
200	0.009	0.025	0.070
800	0.006	0.020	0.050
1300	0.006	0.020	0.043
1700	0.006	0.020	0.048

the amorphous structure to cellulose IV takes place on cellulose molecules in the samples under the hydrothermal conditions. Cellulose IV was slightly detected on the samples treated even at 100 °C, and was evidently detected for all the samples treated at 130 °C. Thus, in the case of the hydrothermal treatments of the amorphous cellulose samples in water, the clear crystallization from the amorphous structure to cellulose IV proceeds with an increase in the heating temperature and the heating time, and these changes are associated with depolymerization and the decreases in yields and accessibility. Amorphous cellulose samples with higher molecular weight have higher resistance to the structural changes.

The crystallinities of cellulose IV were calculated from the X-ray diffraction patterns using the following formula, according to a modified method of measuring crystallinity of cellulose I and II [24].

$$\text{Crystallinity of cellulose IV} = \frac{I_p - I_b}{I_p} \times 100(\%)$$

Where, I_p is the peak intensity at $2\theta = 15.56^\circ$ due to $1\bar{1}0$, 110 , and the amorphous region. I_b is the intensity of the slope-base-line at $2\theta = 15.56^\circ$ due to the amorphous region (Fig. 9). The crystallization to cellulose IV was estimated to proceed according to the pseudo-first-order reaction rate expressions for the treatments at 100, 130, and 160 °C, where the yield loss was negligible. Then the rate constants of the crystallization were obtained from the slopes of the plots, which were illustrated in terms of the logarithms of the crystallinities against the treatment time. The results were shown in Table 2.

On the basis of these constants, we can estimate the structural changes of cellulose molecules in the actual non-crystalline region in cellulosic materials during these treatments under various conditions. The amorphous cellulose samples used in this work have the properties close to those of the actual non-crystalline cellulose, in terms of the stability of the amorphous structure under aqueous conditions. However, some essential differences in the amorphous structure between regenerated amorphous cellulose samples and the actual non-crystalline cellulose in cellulosic materials may be still present. It is also unknown which amorphous cellulose sample has the most representing molecular weight to cellulose molecules in the actual non-crystalline region. Therefore, further experiments are necessary to solve these problems.

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