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Solubilization of dialdehyde cellulose by hot water

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Abstract

We found that dialdehyde cellulose (DAC) prepared by periodate oxidation of cellulose dissolves in hot water, and examined the extent of decomposition during solubilization. The degree of polymerization and aldehyde content of DAC did not show significant decreases during treatments of 80 °C for 4 h or 100 °C for 1 h, but underwent increasingly severe degradation at elevated temperatures and longer times. The aqueous DAC solution is possibly useful for mild aqueous processes utilizing aldehyde reactivity.

Keywords: Cellulose; Periodate oxidation; Solubilization

1. Introduction

Periodate oxidation of cellulose cleaves the C2–C3 bond of anhydro-glucopyranoside ring, forming a pair of aldehyde groups (Gal'braikh & Rogovin, 1971). The product is commonly referred to as dialdehyde cellulose (DAC). Because of rich reactivity of aldehyde group, DAC can serve as intermediates for derivatization of cellulose. Since the degree of oxidation can be readily controlled by the amount of periodate added, functional utilization of partially oxidized materials have been explored as column packings (Boeden et al., 1991; Kim & Kuga, 2001a; 2002), drug release (Liu, Nishi, Tokura, & Sakairi, 2001) and an adsorbent of heavy metal ions (Bhattacharyya et al., 1998; Koshijima, Tanaka, Muraki, Yamada, & Yaku, 1973; Maekawa, & Koshijima, 1984) and protein (Varavinit, Chaokasem, & Shobsngob, 2001; Villalonga, Villalonga, & Gomez, 2000).

One notable feature of DAC is that it is not soluble in water or common organic solvents, even after complete oxidation; the product becomes water-soluble only after reduction of its aldehyde groups to primary alcohols (Casu et al., 1985; Rahn & Heinze, 1998), or to carboxylic acid groups by chlorite oxidation (Chavan, Sarwade, & Varma, 2002; Varma, Chavan, Rajmohanan, & Ganapathy, 1997). This insolubility has been ascribed to hemiacetal formation of aldehyde groups with cellulose's remaining hydroxyl groups (Gal'braikh & Rogovin, 1971; Mester, 1955). While water-solubility is advantageous for utilizing the aldehyde reactivity of DAC, we found that the fully oxidized DAC can be easily solubilized in water by simple heating. In view of the known susceptibility of (original) glycosidic bonds of DAC under both acidic and alkaline conditions, its chemical stability by the solubilization process is of major concern. Therefore, we examined the extent of chemical degradation of DAC during hot-water solubilization.

2. Experimental

2.1. Materials

Microcrystalline cellulose powder, Funacel SF (particle size 6–10 μm; Funakoshi Co., Tokyo.) was used as cellulose sample. The weight-average molecular weight (M_w) was 42,700 ($M_w/M_n = 3.49$) by size-exclusion chromatography (Shibazaki, Kuga, & Okano, 1997). Sodium metaperiodate, hydroxylamine hydrochloride and others were of reagent grade (Wako Chemicals, Tokyo). Distilled or deionized water was used throughout.

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2.2. Preparation of dialdehyde cellulose

To 10 g of cellulose suspended in 500 ml of water (molar ratio of oxidant to glycoside residue, 1.25) 16.5 g of sodium metaperiodate was added. The mixture was stirred at room temperature in the dark for 72 h (Kim & Kuga, 2001b). After the remaining periodate was decomposed by adding of excess ethylene glycol, the product was washed by centrifugation. The periodate consumption was determined by absorbance at 290 nm (Maekawa & Koshijima, 1984).

2.3. Solubilization of dialdehyde cellulose

Never-dried DAC suspension (0.8 g solid in 40 ml water) was gently stirred at 80 or 100 °C in an oil-bath. After the desired time, the sample was quickly cooled in running water and centrifuged at 200,000 g for 10 min to remove residual solid (negligible in amount). The supernatant was collected and dialyzed in distilled water using cellulose membrane (MW cutoff 13000) to neutrality. The recovery was determined by weighing the remaining solid after drying at 105 °C.

2.4. Determination of aldehyde content

The suspension (before solubilization) or solution of dialdehyde cellulose, both 0.1 g solid in 30 ml water, was adjusted to pH 4.50 with HCl. Hydroxylamine hydrochloride solution (0.43 g in 20 ml water, adjusted to pH 4.50) was added to the DAC suspension/solution. The mixture was stirred at room temperature for 24 h. The conversion of aldehyde to oxime was determined by the consumption of 0.1 N NaOH (Veelart, Wit, Gotlieb, & Verhe, 1997).

2.5. Size-exclusion chromatography

Size-exclusion chromatography (SEC) was carried out using an aqueous size exclusion column (PL-aquagel-OH 30, 300 × 6 mm I.D., Polymer Laboratories Ltd, UK) at a flow rate of 1 ml/min. The sample was injected from a 120 μl sample loop after filtration through a 0.45 μm membrane filter. Elution of solute was monitored by an optical rotation detector (OR-990. Jasco, Tokyo) and a refractive index detector at room temperature (Yang, Du, Wen, Li, & Hu, 2003). A pullulan standard was used to determine weight- and number-average molecular weights (Standard P-82. Showa Denko, Co., Tokyo).

2.6. FTIR spectroscopy

FTIR spectra were recorded by a Nicolet Magna 860 with accumulation of 64 scans and resolution of 4 cm^{-1}.

Table 1
The dissolution condition of dialdehyde cellulose and recovery, molecular weight and aldehyde content of solubilized dialdehyde cellulose

Condition	Recovery (%)	Weight-average molecular weight[a]	Polydispersity index	Aldehyde content[b] (mmol/g)
80 °C 4 h	92	41,200	1.81	10.3
80 °C 6 h	84	39,200	1.97	10.1
100 °C 1 h	90	42,000	1.81	10.4
100 °C 2 h	80	30,400	2.02	9.7

[a] By size-exclusion chromatography.

[b] Formula value for dialdehyde cellulose is 12.5 mmol/g.

3. Results and discussion

The aldehyde content of DAC obtained was 12.2 mmol/g from consumption of sodium periodate, and 11.2 mmol/g from titration by alkali, corresponding to 98 and 90% of the aldehyde content of fully oxidized cellulose, respectively. Thus, the periodate oxidation was almost complete. When heated in water, the aqueous suspension of DAC gave a transparent solution, which did not give any apparent precipitation on cooling to room temperature and standing thereafter.

Table 1 shows the dissolution conditions, recovery, average molecular weight (MW) and aldehyde content of solubilized DAC. The amount of undissolved part was approximately 1% for all samples. Fig. 1 shows the chromatogram of solubilized DAC after 3-day standing of aqueous solution at room temperature. The amount of recovered DAC after dialyzing with water corresponded 80–92%. This discrepancy could be ascribed to the formation of low-molecular weight fragments. The molecular weight of DAC treated at 80 °C for 4 h or at 100 °C for 1 h decreased by about 5% from that of

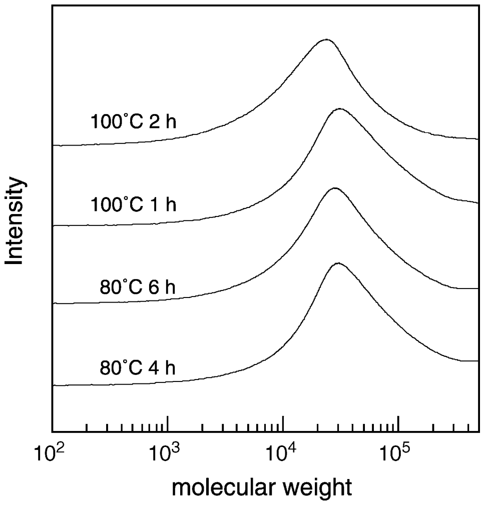

Fig. 1. Chromatogram of dialdehyde cellulose solubilized by hot water after 3 days.

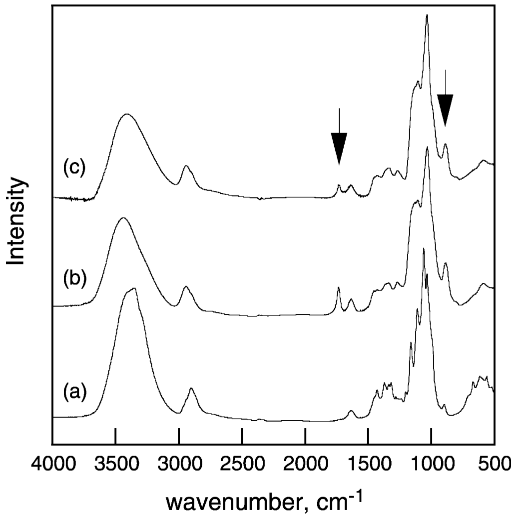

Fig. 2. FTIR spectra of cellulose (a) and dialdehyde cellulose before (b) and after (c) dissolution in hot water (at 100 °C for 1 h).

the original cellulose. On the other hand, the MW of the material treated at 100 °C for 2 h was decreased by about 30%. The aldehyde content showed the same tendency, being about 8 or 14% lower after treatment at 80 °C for 4 h or at 100 °C for 2 h, respectively. This degradation seems to have resulted from thermally induced chain scission and formation of low-molecular weight products. (Veelart et al., 1997).

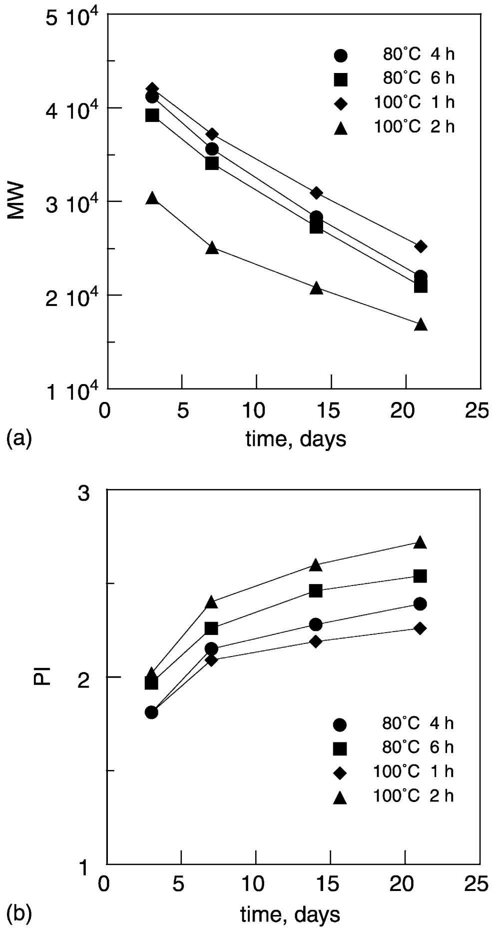

Fig. 3. Change in (a) average molecular weight (MW) and (b) polydispersity index (PI) of solubilized dialdehyde cellulose during room-temperature standing of an aqueous solution.

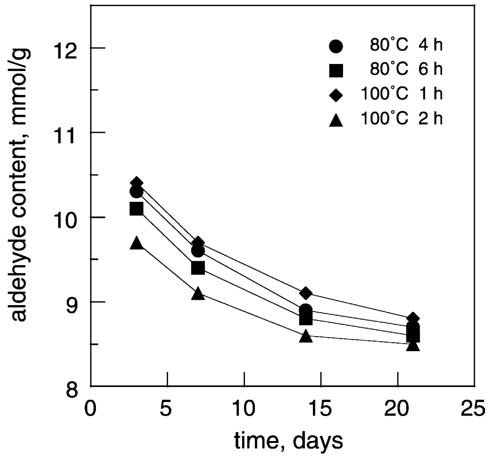

Fig. 4. Change in aldehyde content of solubilized dialdehyde cellulose during room-temperature standing of an aqueous solution.

Fig. 2 shows the FTIR spectra of DAC before and after hot-water solubilization. The FTIR spectra of all solubilized DACs showed the same pattern without regard to solubilization conditions. Both samples showed absorption bands characteristic of dialdehyde cellulose at around 1740 and 880 cm^{-1}. The former is assigned to the C=O stretching of free aldehyde (Fan, Lewis, & Tapley, 2001) and the latter to hemiacetal structure (Gal'braikh & Rogovin, 1971; Mester, 1955).

The long-term stability of solubilized DAC was examined in terms of chain length (Fig. 3) and aldehyde content (Fig. 4). Standing at room temperature as aqueous solution caused significant decrease in average molecular weight and increase in polydispersity index. After 3 weeks the molecular weight decreased by about 50%, and the polydispersity index increased by about 40% for all the samples. The aldehyde content also decreased by 10–15%. These changes can be ascribed to chain scission due to hydrolysis.

The DACs having degree of oxidation lower than 75% did not completely dissolve in water even by elongated treatments at 100 °C. This behavior is probably due to high heterogeneity in the mode of reaction, which leaves isolated unreacted cellulose crystallites (Kim, Kuga, Wada, Okano, & Kondo, 2000).

4. Conclusion

Dialdehyde cellulose obtained by complete oxidation with periodate dissolves in hot water. Though the material is not highly stable during solubilization in water and standing of the aqueous solution at room temperature, its aqueous solution is expected to be useful as a reducing or crosslinking agent.

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