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Thermal decomposition of dialdehyde cellulose and its nitrogen-containing derivatives

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Abstract

A series of dialdehyde cellulose samples with varied aldehyde content were prepared, and they were further converted to nitrogen-containing derivatives by Schiff base reaction with hydroxylamine or hydrazine. Thermal decomposition of these compounds in nitrogen was studied by thermogravimetry/differential thermal analysis (TG/DTA). While the decomposition of unmodified cellulose in nitrogen started at about 280°C and rapid weight loss occurred at 300–340°C, the introduction of dialdehyde groups to cellulose resulted in significant shifts of decomposition to the lower temperature side. The samples of high degree of substitution showed two-step decomposition at around 220 and 280°C, indicating a basic change in the mode of decomposition. The nitrogen-containing derivatives showed changes in thermal decomposition similar to that of dialdehyde cellulose, but the samples with high degrees of substitution, above ~70%, showed an explosive decomposition at 151–162°C. This anomalous phenomenon seems characteristic to the chemical structures involving C=N–N or C=N–O groups.

Keywords: Periodate oxidation; Dialdehyde cellulose; Oxime; Hydrazone; Thermogravimetry/differential thermal analysis (TG/DTA)

1. Introduction

Cellulose is the most abundant, renewable natural source for organic materials. A variety of cellulose derivatives are produced by chemical modifications, mainly by ester and ether formation under actions of strong acid, alkali or non-aqueous solvents. The periodate oxidation of cellulose, in contrast, proceeds under mild aqueous conditions and is characterized by specific cleavage of the C_2–C_3 bond of glucopyranoside ring, resulting in the formation of two aldehyde groups per unit (dialdehyde cellulose (DAC)) [1–3]. Because of mildness of the reaction conditions, one can easily control the amount of introduced aldehyde groups. Therefore, the dialdehyde cellulose is potentially useful for aqueous chromatography as cellulose-based column packings [4]. The resulting aldehyde can be further modified to carboxylic acid [5–8], primary alcohol [7,8], or imines (Schiff bases) with primary amines [9–11] through its intrinsic reactivity. They can serve as useful intermediates for cellulose-based specialty materials, such as an adsorbent of heavy metals [5,6,9], proteins [10,12] or dyes [13].

Of these, the Schiff bases (imines and oximes, Fig. 1) forming reaction between aldehyde and primary amines is a facile and useful procedure to introduce substituents. Hence, we are interested in periodate oxidation of cellulose and further

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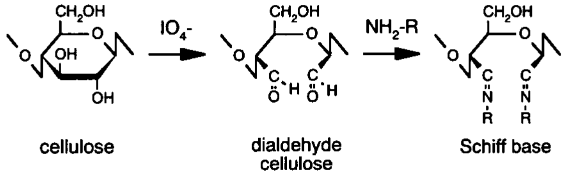

Fig. 1. Scheme of periodate oxidation of cellulose and Schiff base reaction with hydroxylamine ($R = OH$) or hydrazine ($R = NH_2$).

modification of DAC, with the aim of developing useful materials and processes for cellulose utilization. In this study we prepared a series of dialdehyde cellulose and nitrogen-containing compounds derived from it, and found some interesting phenomena in their thermal decomposition behavior.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose powder, Funacel SF (particle size 6–10 µm; Funakoshi Co., Tokyo. This is an acid hydrolysis product of native cellulose similar to Avicel®) was used as cellulose sample. Sodium metaperiodate, hydroxylamine hydrochloride and hydrazine monohydrate were of reagent grade (Wako Chemicals, Tokyo).

2.2. Preparation of dialdehyde cellulose

Desired amount (3.3–16.5 g) of sodium metaperiodate was dissolved in 500 ml of deionized water and 10 g of cellulose powder was added to the solution. The mixture was stirred at room temperature in the dark for 72 h. After the remaining periodate was decomposed by excess ethylene glycol, the product was washed by centrifugation and freeze dried. The periodate consumption was determined by absorbance at 290 nm [5]. The amount of introduced aldehyde was determined by consumption of alkali in Cannizzaro reaction [14,15].

2.3. Schiff base reaction

The DAC samples were converted to nitrogen-containing compounds by Schiff base reaction with hydroxylamine hydrochloride or hydrazine monohydrate. Amine (0.02 mol) was dissolved in 100 ml of 0.1 M acetate buffer (pH 4.4) and added to 100 mg of DAC. The amount of added amine was 16 times of the aldehyde of fully oxidized materials. The mixture was stirred at room temperature for 24 h. The product was recovered by filtration and dried in vacuo.

2.4. X-ray diffraction

The X-ray diffractometry profile was recorded for dry pellet of DAC in reflection mode using a Rigaku RINT 2000 at 40 kV and 40 mA, with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm).

2.5. Thermal analysis

Thermal analysis was performed between room temperature and 800°C at heating rate of 10°C min^{-1} in dry nitrogen flow of 200 ml min^{-1}, using a TG/DTA apparatus (TGD 9600, Shinku Riko, Yokohama, Japan). About 20 mg of sample was used in single runs. Aluminum oxide (Al_2O_3) was used as a reference material in all DTA experiments.

2.6. Elemental analysis

Elemental composition of nitrogen-containing derivatives and pyrolysis residue treated up to 800°C was determined for C, H, and N by atomic absorption spectroscopy.

3. Results and discussion

3.1. Degree of oxidation and conversion to nitrogen-containing derivatives

Fig. 2 shows the percentage degree of oxidation (DO) of cellulose as function of added periodate, for 72 h reaction at room temperature. The four curves are based on (i) remaining periodate after oxidation, (ii) alkali consumption in Cannizzaro reaction of the product, (iii) nitrogen content of hydroxylamine derivatives and (iv) nitrogen content of hydrazine derivatives. The values from periodate consumption and Cannizzaro reaction are in good agreement with each other; they are also close to the value for stoichiometric consumption of added periodate for up to 75%

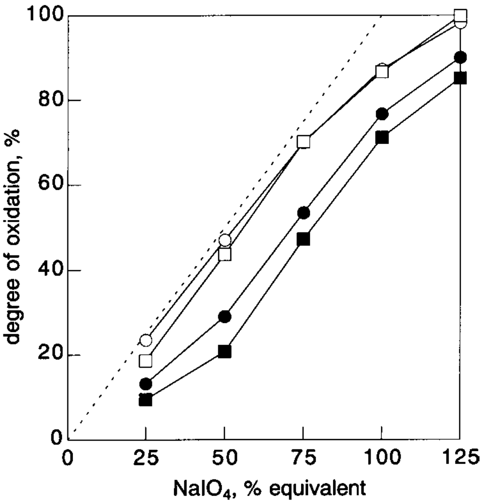

Fig. 2. Degree of oxidation of microcrystalline cellulose as function of added $NaIO_4$, determined by four methods. Oxidation time, 72 h at room temperature. (○) Periodate consumption; (□) alkali consumption in Cannizzaro reaction; (●) nitrogen content of hydroxylamine derivative; (■) nitrogen content of hydrazine derivative. Dotted line shows the level for complete consumption of periodate.

level of periodate addition. These values show some discrepancy from the stoichiometric value at high DO region, probably showing incompleteness of the oxidation reaction under the employed conditions.

The DO values from nitrogen contents of hydroxylamine and hydrazine derivatives are definitely lower than the aforementioned values, indicating that the Schiff base reaction does not proceed stoichiometrically. The ratio of the DO from nitrogen content to that from periodate consumption was 0.6–0.9 for hydroxylamine derivatives, and 0.45–0.85 for hydrazine derivatives. A possible cause of such low reactivities is the limited accessibility of reaction sites on the insoluble dialdehyde cellulose. Thus, the DO of periodate-oxidized cellulose can be evaluated by periodate consumption, the simplest way, with reasonable accuracy. So, the DO values based on periodate consumption are used in the following descriptions.

3.2. Thermal analysis of dialdehyde cellulose

Fig. 3 shows the loss of crystallinity by periodate oxidation of microcrystalline cellulose. The intensity of the crystalline peaks of cellulose diminished with the increase in DO and the product became completely amorphous at DO 87%. The loss of crystallinity apparently results from opening of the glucopyranose ring and destruction of ordered packing of cellulose molecules.

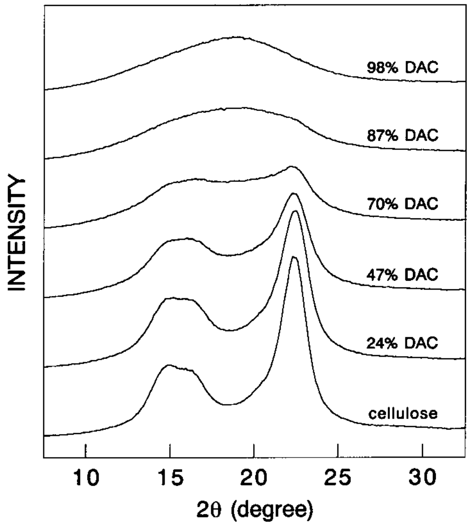

Fig. 3. X-ray diffraction profiles of dialdehyde cellulose. Percentage values show degree of oxidation.

The thermal degradation of cellulose and its derivatives has been extensively studied [16–20]. Underivatized cellulose decomposes through the formation of levoglucosan (1,6-anhydro-β-D-glucopyranose) and its further decomposition [21–23]. Chemical modification of cellulose is known to significantly change the thermal decomposition behavior, i.e. the temperature range of decomposition usually shifts to lower temperature side [21,24–26] and the char yield at 500°C increases to 1.5–2.5 times [21,25,26] compared to unmodified cellulose. The dialdehyde cellulose obtained here showed basically the same behavior. The decomposition of unmodified cellulose in nitrogen started at about 280°C and rapid weight loss occurred at 300–340°C. The decomposition temperature of DACs shifted to lower temperature side with increase in the degree of oxidation (Fig. 4). The changes are more clearly seen in the derivative thermogravimetric (DTG) curves, giving two distinct peaks for the samples with DO greater than 70%. The peak positions for fully oxidized samples were 215 and 270°C (Fig. 5). The char yield of DAC

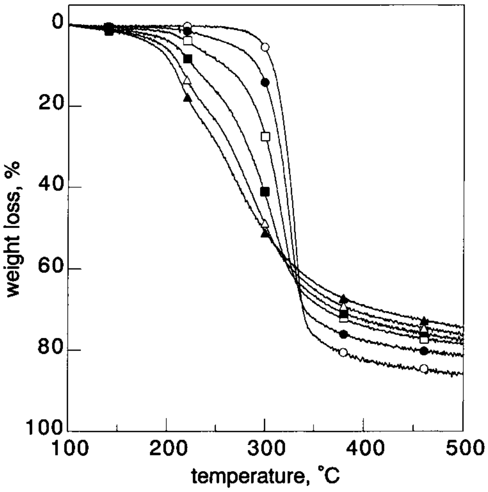

Fig. 4. Thermogravimetric curves of dialdehyde cellulose. (○) Cellulose; (●) 24% DAC; (□) 47% DAC; (■) 70% DAC; (△) 87% DAC; (▲) 98% DAC.

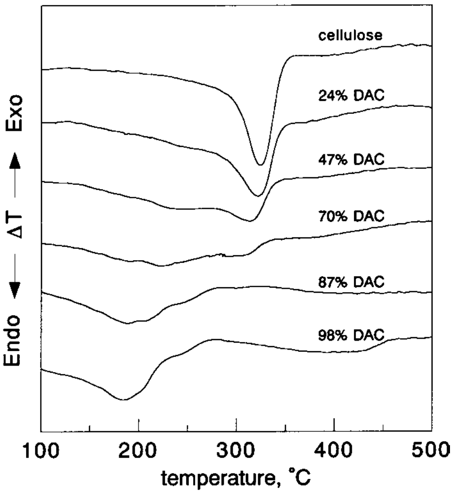

Fig. 6. Differential thermal analysis curves of dialdehyde cellulose.

samples at 500°C increased with increase in DO, being about two times for DO 98% DAC compared to unmodified cellulose.

The DTA curves (Fig. 6) also show a characteristic change by oxidation of cellulose. The large endothermic peak of the original cellulose, apparently corresponding to the rapid weight loss at 300–340°C, gradually diminished and a new, broad endothermic peak appeared at 150–220°C, centered at 185°C for DO 98% DAC. While the peak positions in DTG and DTA curves agree well for original cellulose, they do not agree for dialdehyde cellulose. In the latter, therefore, certain thermochemical changes precede the degradation accompanying weight loss. These changes are likely to be associated with facilitated thermal scission of covalent bonds leading to the generation of volatile substances. Also, some part of curvature around 200°C in DTA profile may be associated with changes in the state of molecular motions of amorphous DAC, such as glass transition.

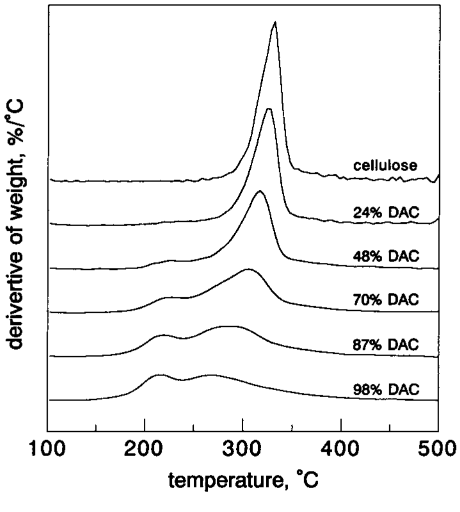

Fig. 5. Derivative thermogravimetric curves of dialdehyde cellulose.

3.3. Thermal analysis of nitrogen-containing derivatives

Fig. 7 shows the TG curves of the hydroxylamine derivative of dialdehyde cellulose (DAC oxime) of varied degree of oxidation. The decomposition temperature shifted to lower side with increasing DO as in the case of dialdehyde cellulose, but showed an anomalous transition in decomposition behavior at high DO; i.e. the samples with DO greater than 70% showed a sudden weight loss at 156–162°C, apparently a kind of explosion. DO of 70% seems to be the critical level, since this sample showed two-step decomposition at 160 and 300–350°C, the latter being the decomposition range for unmodified cellulose.

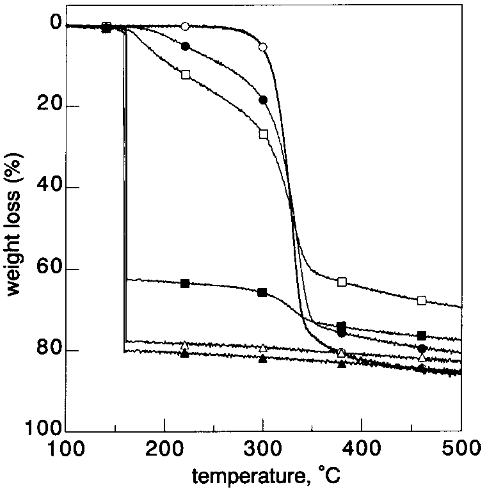

Fig. 7. Thermogravimetric curves of dialdehyde cellulose oxime. (○) cellulose; (●) 24% DAC oxime; (□) 47% DAC oxime; (■) 70% DAC oxime; (△) 87% DAC oxime; (▲) 98% DAC oxime.

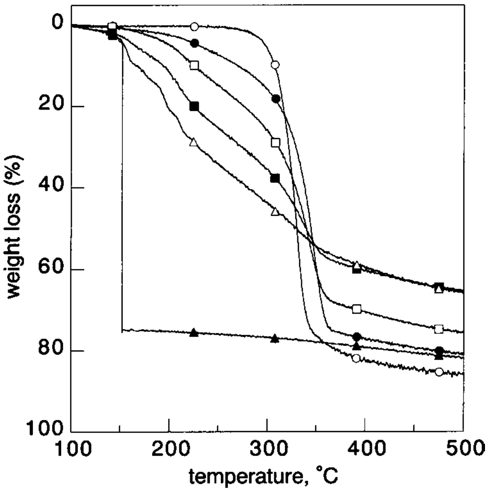

Fig. 9. Thermogravimetric curves of dialdehyde cellulose hydrazone. (○) cellulose; (●) 24% DAC hydrazone; (□) 47% DAC hydrazone; (■) 70% DAC hydrazone; (△) 87% DAC hydrazone; (▲) 98% DAC hydrazone.

The char yield from high DO samples at 500°C was 15–17%, remarkably lower than that of low DO materials and close to that of unmodified cellulose. The residue of DO 98% DAC oxime immediately after the explosive decomposition was totally black, and elemental analysis of the 800°C char gave a weight composition of 81% carbon, 10% nitrogen. Thus, the incorporation of C=N–O moiety greatly facilitates the formation of volatile compounds and non-carbon elements from cellulose.

The DTA curves (Fig. 8) showed a change correlated to TG, i.e. the explosion at 156–162°C is accompanied by a sharp exothermic peak. The DTA curve, however, shows small exothermic peaks

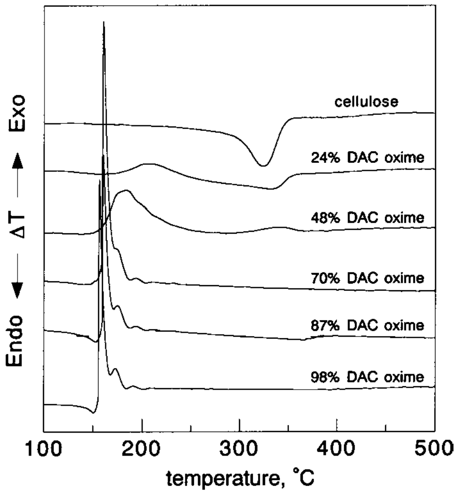

Fig. 8. Differential thermal analysis curves of dialdehyde cellulose oxime.

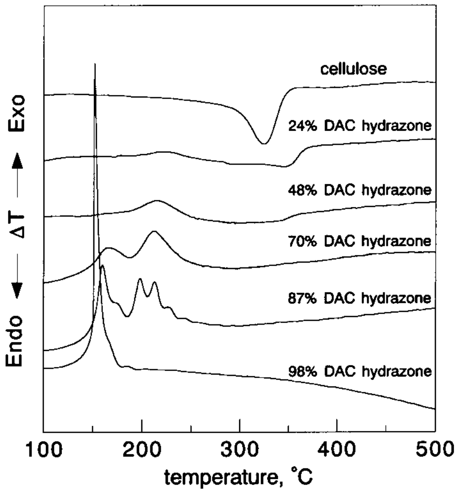

Fig. 10. Differential thermal analysis curves of dialdehyde cellulose hydrazone.

Table 1
Activation energy E_a (kJ mol^{-1}) of decomposition of dialdehyde cellulose, its oxime and hydrazone

DO (%)	DAC		DAC oxime		DAC hydrazone	
	E_a (kJ mol^{-1})	Temperature range (°C)	E_a (kJ mol^{-1})	Temperature range (°C)	E_a (kJ mol^{-1})	Temperature range (°C)
0	240	280–340	–	–	–	–
24	49	220–260	40	210–240	39	190–250
	137	280–340	122	300–350	106	310–360
47	59	210–240	64	175–190	48	180–240
	101	280–330	77	300–350	65	300–350
70	64	200–240	1182	160–162	40	150–230
	59	270–320	1182	160–162	34	300–350
87	70	190–230	1534	160–162	115	150–165
	41	250–310	1534	160–162	36	180–220
98	74	190–220	1564	156–158	1312	151–153
	32	240–300	1564	156–158	1312	151–153

at 170–185°C that has no corresponding weight loss in TG curve.

Basically the same features were observed in TG and DTA curves of hydrazine derivative of dialdehyde cellulose (DAC hydrazone) (Figs. 9 and 10). The explosion temperature was slightly lower than that of DAC oxime, being 151°C. In this case, the transition with increasing DO is more gradual, and the DO 87% hydrazone showed small stepwise decrease at 160–220°C in TG curve, accompanied by sharp exothermic peaks in DTA curve.

Though both hydroxylamine and hydrazine are explosive compounds, they simply evaporate below boiling points of 57 and 114°C, respectively. Also the extent of weight loss of DAC oxime and hydrazone is much greater than the amount of bound hydroxylamine or hydrazine. Therefore, this remarkable phenomenon of explosive decomposition seems to result from the chemical association of the nitrogen-containing moieties and oxidized cellulose, i.e. C=N–N or C=N–O groups.

3.4. Activation energy of decomposition

The process of thermal decomposition can be analyzed in more detail by the non-isothermal integral method of Coats and Redfern [27,28], which gives the activation energy (E_a) of reaction in selected temperature ranges. We applied this method to the TG data of DAC, DAC oxime and DAC hydrazone by assuming first-order reactions. The results are listed in Table 1.

In the Coats–Redfern method, different reactions in decomposition give separate linear regions in the analyzing plot. The plots for DAC samples and the DAC oxime/hydrazone samples with low DO gave two distinct linear ranges for each TG curve, the lower-temperature reaction and the higher-temperature reaction. The E_as are, therefore, given for the two temperature ranges indicated in parentheses. The E_a values for DAC are significantly smaller than that of unmodified cellulose. The reduced E_a can be ascribed to facilitated cleavage of covalent bonds that leads to generation of volatile compounds, possibly water, carbon oxides and small aldehydes.

The explosive decomposition observed with DAC oxime/hydrazone gave very large E_as, about 1180–1560 kJ mol^{-1}. Such large activation energies seem to be characteristic of thermally induced chain reactions. This explosive reaction, however, proceeds in a very narrow temperature range and is sensitive to the heating rate; therefore, the activation energy obtained here should be taken as semiquantitative ones. More details, including the influence of heating rate and comparison with behavior of other nitrogen-rich cellulose derivatives, have yet to be investigated.

4. Conclusion

The explosive nature of nitrogen-rich organic compounds is a classic chemical knowledge. This feature is generally considered to be related with the thermodynamic stability of the produced nitrogen compounds, such as N_2, NO, or NO_2. While the explosive nature of cellulose nitrate is well known, that of oxime and hydrazone of dialdehyde cellulose does not seem to be noted so far. It is likely that other organic compounds having aldehyde groups exhibit the same behavior. Since the features of this anomalous decomposition are sensitive to the chemical structure of the material, this phenomenon can be useful in thermal analysis of aldehyde-containing materials.

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