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Assignment of DSC thermograms of wood and its components

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Abstract

Exotherms in the DSC analysis of wood and its components have been assigned using Akamatsu wood (*Pinus densiflora*). Analysis of wood powder indicated two exotherms at around 340 and 475°C. Among isolated components galactoglucomannan has a single exotherm at around 330–360°C, and other commercial amorphous polysaccharides are in the range of 300–370°C. Therefore, the transition at around 340°C in wood thermogram was considered to be due to polysaccharides. On the other hand, the temperature of the exotherm at 475°C in the analysis of wood was similar to that of a lignin–carbohydrate complex (LCC) and not to that of purified lignin (MWL) which was around 530°C. Removing hemicelluloses from LCC by hydrosulphuric acid or cellulase shifted the temperature to around 520°C. It is concluded that the exotherm in wood powder at around 475°C is due to a mixture of lignin and polysaccharides, in which the lignin is closely combined and complexed with the polysaccharides as in LCC. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal analysis is convenient and reproducible, and is a useful method for characterizing heterogeneous organic materials. In past decades, differential thermal analyses (DTA) and a differential scanning calorimetry (DSC) have been used for analyzing biological materials from plants. Mitchell analyzed the plant materials in peat by using DTA [1,2] and investigated humic compounds [3]. Many reports have since estimated the difference in chemical compositions of various plants including alga, cotton, moss, wood and so on [4–12]. In application uses, the evaluation of decayed woods was attempted [13–17]. Cellulose, hemicelluloses and lignin, which are components of plant cell walls, have been analyzed by DTA and DSC from their thermal response [4–7,9,11,12,14,18,19]. However, assignment of the exothermic processes has not been sufficiently rigorous. In this report, we have examined the assignment of the exothermic transition analysis in DSC of wood and its components in order to understand the thermal behaviors of lignocelluloses in more detail.

2. Materials and methods

2.1. Sample preparation

Samples from Japanese gymnospermous wood (Akamatsu, *Pinus densiflora* Sieb et. Zucc.), were used. Wood powder which passed 200 mesh was used

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after extracting with hot water for 1 h and ethanol–benzene solution (1/2=v/v) for 8 h.

Holocellulose, α-cellulose, galactoglucomannan (GM) and milled wood lignin (MWL) were prepared from Akamatsu according to standard procedures. The absence of residual polymeric lignin in the cellulose and hemicellulose was determined by infrared (IR) spectroscopy using a Shimadzu FTIR 8200 spectrometer in KBr discs and also electron magnetic resonance (ESR) spectroscopy using a JEOL JES-TE 300, X-band, 0.2 mW modulation power spectrometer. The isolated MWL was further purified using the procedure of Lundquist and Simonson [20]. A water-soluble lignin–carbohydrate complex (LCC-W) was prepared following the method of Azuma et al. [21].

Dehydrogenation polymeric lignin (DHP: Zutropfverfahren) was synthesized from coniferyl alcohol using a horseradish peroxidase, obtained from Wako Pure, using the method of Tanahashi and Higuchi [22].

Birch xylan from Sigma, cellulose from Whatman CF11 and carboxymethyl cellulose sodium salt (CMC-Na) from Nakalai tesq. and commercial lignin preparations (lignin sulfonate from Tokai Pulp and Indulin AT from Sigma) were used as standard substrates for the purpose of the assignments. Removing residual lignin from commercial xylan was performed using sodium chlorite as an oxidant using the method of Wise et al. [23]. Lignin sulphonate was washed with hot water before use in order to remove residual hemicelluloses. Indulin AT was purified according to the method of Lundquist and Kirk [24].

Klason lignin was prepared by acid hydrolysis of LCC-W with 1 N hydrosulfuric acid at 100°C for 1 h. Cellulase treatment of LCC-W was carried out as follows: LCC-W was dissolved in distilled water and treated with Dricellase, obtained from Kyowahakko, at 36°C. Substrate and enzyme concentrations were 1.0 and 0.2% (w/v), respectively. After incubation for 24 h, an equivalent amount of enzyme was added to the reaction mixture, and the incubation continued for 24 h. Precipitate was recovered by centrifugation, washed with water and lyophilized. The recovered precipitate was dissolved in 80% aqueous dioxane. This solution was suspended in distilled water and further treated with Cellulase Onozuka R-10 obtained from Serva Finebiochemica, as described above. Insoluble material was recovered by centrifugation, dissolved in 90% aqueous acetone and centrifuged to remove residual enzyme and polysaccharides. Aqueous acetone-soluble materials were evaporated under reduced pressure. The materials precipitated during removing acetone was recovered by centrifugation, washed with water, and lyophilized.

Alkali-treated LCC was prepared from LCC-W according to the method of Yaku et al. [25]. After reaction, reaction solution was neutralized with acetic acid, dialyzed against a distilled water and then evaporated.

2.2. Differential scanning calorimetric (DSC) analysis

Differential scanning calorimetric (DSC) analysis was carried out as follows: 1.00 mg of wood powder or grounded components were placed in an aluminum pan and dried. Thermal analysis was carried out in an ambient atmosphere using a heat-flux DSC, from Seiko Industry DSC-220, at a constant heating rate of 10°C min^{-1}. Measurements were repeated at least three times.

3. Results and discussion

A typical DSC response from the Akamatsu wood samples is shown in Fig. **1a**. Two main combustion peaks were observed at ca. 340 and 475°C and a small shoulder at 450°C. Reh et al. [14] assigned these transitions to the combustion of carbohydrates and lignin, respectively. In order to examine their assignment, we attempted to analyze the components purified from wood and the commercial substances.

The DSC response with temperature for the celluloses and hemicelluloses are shown in Fig. **1b–g**. Holocellulose **(b)** and α-cellulose **(c)** have two exotherms (340 and 428°C, and 336 and 488°C, respectively) as reported in the earlier study [10], while the main exotherm for GM **(d)** was detected at ca. 330–360°C. Pure cellulose (Whatman CF11) **(e)** had a major sharp exotherm at 351°C and a broader one at around 508°C. Probably the transitions in cellulose are eliminated by the two different regions present crystalline and amorphous, resulting in the appearance of two exotherms. The difference between wood cellulose preparations and pure cellulose is

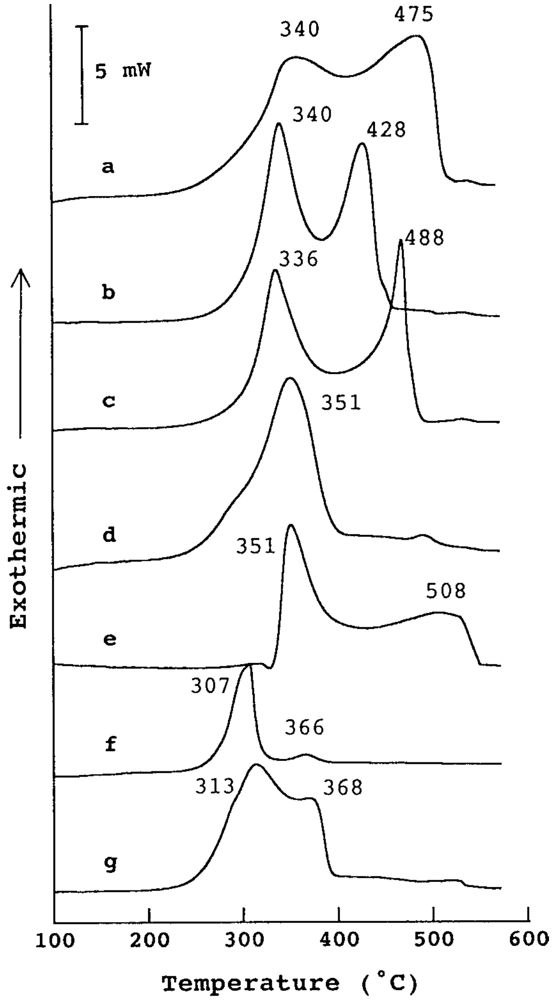

Fig. 1. DSC analysis of cellulose and hemicellulose preparations. (a) Akamatsu wood powder, (b) holocellulose, (c) α-cellulose, (d) galactoglucomannan (GM), (e) Whatman CF11, (f) carbpxymethyl cellulose (CMC), and (g) birch xylan.

assumed to be due to contamination with hemicelluloses. The main transition of other polysaccharide preparations were observed at 300–370°C (CMC (**f**): 307 and 366°C; birch xylan (**g**): 313 and 368°C). Therefore, main exotherm in amorphous polysaccharides appeared at ca. 300–370°C. Some reports have proposed that the hemicelluloses have several transitions at 300–350 and 450–500°C [11,13,15,18], but highly purified GM and birch xylan (**d** and **g**) had an exotherm at around 300–360°C as shown in this study. The exotherms observed in the range 450–500°C in hemicellulose is affected by residual lignin as shown below.

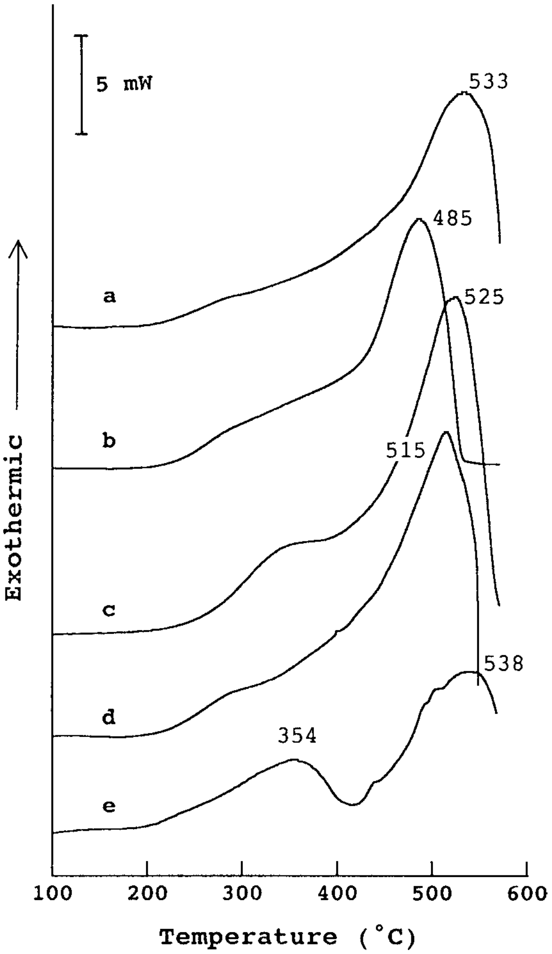

Fig. 2. DSC analysis of lignin preparations. (a) Milled wood lignin (MWL), (b) lignin–carbohydrate complex (LCC), (c) klason lignin, (d) cellulase-treated LCC, and (e) alkali-treated LCC.

The DSC analyses of the lignin preparations are shown in Fig. 2. Earlier studies reported that MWL and other lignin preparations had several exotherms at 270–555°C [7,10,12,14,15,19]. But, in our study, MWL had one at 533°C (see Fig. **2a**) and lignin–carbohydrate complex (LCC) also had one at 485°C (see Fig. **2b**), which was lower than that of MWL but similar to the higher-temperature exotherm in the wood powder. This disappeared on treatments with hydrosuphuric acid or cellulase, and a new exotherm occurred at a higher temperature (**c**: 525 and **d**: 515°C, respectively). Reh et al. [14] estimated that exotherm above 500°C in klason lignin thermogram was caused by the preparation-mediated artifacts such as condensation products. It is true that acid treatment caused the appearance of exotherm at higher temperatures, around 520°C (**c**), but even cellulase treatment, which cannot cause lignin to condense, shifted it to higher temperatures (**d**). Therefore, the exotherm at 520°C is assigned not to condensation products of lignin but to the lignin purified by removal of hemicelluloses. In fact, in this study, crude MWL was observed to have two exotherms at 350 and 490°C as reported earlier [7,14,19], but on purification MWL one exotherm at 533°C was found indicating that the exotherms at 350°C was due to hemicelluloses and the one at 490°C shifted to higher temperatures, 533°C by removal of hemicelluloses. Alkali-treatment of LCC are separated one into two exotherms at 354 and 538°C (**e**), which could be assigned to carbohydrates and lignin, respectively, on the basis of the above results. Alkali-treatment of LCC split hemicellulose from lignin *via* α-ether cleavage [26], resulting in the observation of two exotherms due to hemicellulose and lignin.

Peak temperatures of the exotherm of lignin preparations (including DHP, Indulin AT, and lignin sulfonate) are summarized in Table 1. These have only one exotherm, and each except for LCC was detected at higher temperature than that of the wood powder. Accordingly, pure polymeric lignin is concluded to have the main exotherm at around 530°C in DSC thermogram. Therefore, the exotherm at around 475°C in DSC analysis of wood is due to the lignin containing large amounts of hemicelluloses, not to the pure lignin alone.

Table 1
Peak temperature of lignin preparations

Sample	Peak temperature (°C)
MWL	533
LCC-W	485
Klason ligning	525
Cellulase-treated LCC	515
Alkali-treated LCC	354 and 538
DHP	560
Indulin AT	513
Ligning sulfonate	528
Wood powder	340 and 470

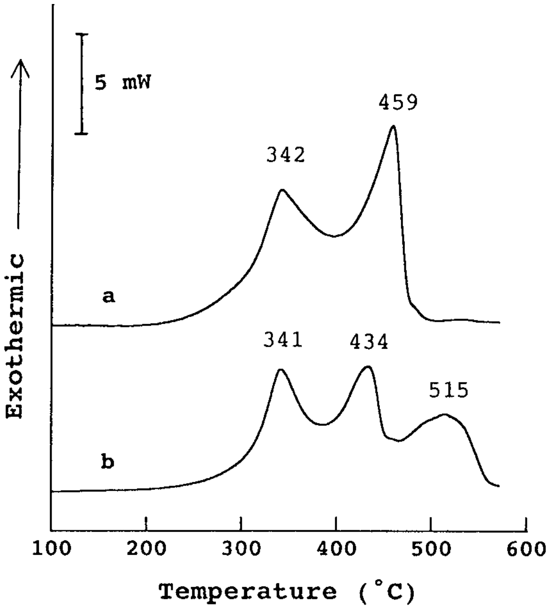

Fig. 3. DSC analysis of mixtures of holocellulose and lignin (MWL). (a) A mixture in which lignin was impregnated into holocellulose, (b) a simple mixture of holocellulose and lignin.

Mixtures of holocellulose and MWL (7/3=w/w) were also analyzed (Fig. 3); a sample **a**: a mixture which was impregnated lignin solution (80% aqueous dioxane) into holocellulose and dried up, and a sample **b**: a simple mixture of both grounded powders. Mixture **a** produced two endotherms similar to the wood powder, while mixture **b** indicated three peaks due to each sample. In mixture **a**, lignin penetrates into the swollen part of the holocellulose and coats the holocellulose fibres. This increases the carbohydrate content and lowers the exotherm temperature of lignin. Although Arseneau considered that the interaction between the wood components has little effect on the DSC analysis [4], our results suggest that the components are not present independently of the thermal analysis.

Based on the above results the two main exotherms observed in the DSC analysis of wood at 350 and 475°C were assigned to amorphous polysaccharides and to mixtures of lignin and polysaccharides, respectively. From the ultrastructural model of wood cell wall proposed by Kerr and Goring [27], this mixture may be regarded as the lignin–hemicellulose matrix. However, the possibility that cellulose might participate in the higher temperature exotherms remains, because pure cellulose has broad exotherms at ca. 460–500°C. In wood cell walls, cellulose forms bundles called microfibrils, and these are coated with hemicelluloses as a cellulose–hemicellulose complex [27]. If the interaction between the components is not negligible in the thermal analysis, DISC profil of the cellulose–hemicellulose complex will be similar to holocellulose and will have exotherm at different temperatures from the pure cellulose. In the formation of the secondary tissue, the deposition of lignin into the cellulose–hemicellulose matrix during ligninification results in the production of complicated mixtures of lignin and polysaccharides. Therefore, it is concluded that the higher temperature exotherm in the DSC analysis of wood is due to presence of mixtures of lignin and polysaccharides and not lignin as above suggested by Reh et al. [14].

Note that the DSC analysis of wood powder which has not been ball-milled to pass 200 mesh, did not change before and after extraction with 80% aqueous dioxane for 48 h (data not shown) as the lignin could not be extracted from this wood powder. Evidence for the covalent bonding has been shown by other investigators [26,28,29]. These chemical bonds, between lignin and hemicelluloses, have to be broken by ball-milling for the lignin to be extracted [30]. Therefore, the higher temperature exotherm in wood is due to a mixture of lignin and polysaccharides that is neither combined nor simply mixed with each other, but which forms a matrix involving chemical bonding between the lignin and the hemicelluloses as in LCC.

References

[1] B.D. Mitchell, Nature 180 (1957) 1414.
[2] B.D. Mitchell, Sci. Proc. R. Dublin Soc. A 1 (1960) 105.
[3] J.M. Stewart, A.C. Birnie, B.D. Mitchell, Agrochimica 11 (1966) 92.
[4] D.F. Arseneau, Can. J. Chem. 39 (1961) 1915.
[5] W. Sandermann, H. Augustin, Holz Roh- u. Werkst. 21 (1963) 305.
[6] B.D. Mitchell, A.H. Knight, J. Exp. Bot. 16 (1965) 1.
[7] F. Abe, Mokuzai Gakkaishi 14 (1968) 98.
[8] F. Beall, Wood Sci. Technol. 5 (1971) 159.
[9] T. Arima, Mokuzai Gakkaishi 19 (1973) 435.
[10] T. Arima, Mokuzai Gakkaishi 19 (1973) 443.
[11] M.Z. Sefain, S.F. El-Kalyoubi, N. Shukry, J. Polym. Sci., Polym. Chem. Ed. 231 (1985) 1569.
[12] S.K. Bhaduri, M.D. Mathew, A. Day, S.N. Pandey, Cellulose Chem. Technol. 28 (1994) 391.
[13] F. Abe, Mokuzai Gakkaishi 17 (1971) 335.
[14] U. Reh, G. Kraepelin, I. Lamprecht, Appl. Environ. Microbiol. 52 (1986) 1101.
[15] U. Reh, G. Kraepelin, I. Lamprecht, Thermochim. Acta 119 (1987) 143.
[16] U. Reh, G. Kraepelin, U. Schulze, Lignin enzymic and microbial degradation, INRA Publications, 1987, 291 pp.
[17] C.S. Knoll, B.M. Wong, D.N. Roy, Wood Sci. Technol. 27 (1993) 439.
[18] M.V. Ramiah, J. Appl. Polym. Sci. 14 (1970) 1323.
[19] J. Kaloustian, A.M. Pauli, J. Pator, J. Them. Anal. 46 (1996) 91.
[20] K. Lundquist, R. Simonson, Svensk Papperstidn. 78 (1975) 390.
[21] J. Azuma, N. Takahashi, T. Koshijima, Carbohydr. Res. 93 (1981) 91.
[22] M. Tanahashi, T. Higuchi, Wood Res. 67 (1981) 29.
[23] L.E. Wise, M. Murphy, A.A. D'Addieco, Paper Trade J. 122 (1946) 35.
[24] K. Lundquist, T.K. Kirk, Tappi 63 (1970) 80.
[25] F. Yaku, Y. Yamada, T. Koshijima, Holzforschung 30 (1976) 148.
[26] T. Iversen, Wood Sci. Technol. 19 (1985) 243.
[27] A.J. Kerr, D.A.I. Goring, Cellulose Chem. Technol. 9 (1975) 563.
[28] Ö. Eriksson, D.A.I. Goring, B.O. Lindgren, Wood Sci. Technol. 14 (1980) 267.
[29] T. Watanabe, Wood Res. 76 (1989) 59.
[30] A. Björkman, Svensk Papperstidn. 60 (1957) 243.