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Vaporization of bound water associated with cellulose fibres

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Abstract

Vaporization of bound water associated with cellulose fibres of natural (cellulose I) and regenerated cellulose (cellulose II) was investigated by differential scanning calorimetry in both dynamic and static conditions. Factors which affect water vaporization, such as sample handling, water content, heating rate, gas flow rate and temperature of holding were examined. It was found that vaporization peak is split into two peaks, one is at around 60°C and the other is at around 120°C, when the samples were measured by slow heating rate (<2.5°C min^{-1}) and low gas flow rate (<30 ml min^{-1}). The high temperature vaporization peak is related with the structural change of amorphous chains of cellulose by desorption of bound water. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Non-freezing water; DSC; Cellulose fibres; Vaporization

1. Introduction

Cellulose is a most abundant biopolymer. Cellulose has a strong interaction with water due to three hydroxyl groups attached to the glucopyranose ring as shown in Scheme 1. Thermal properties of both cellulose and water are markedly influenced through this interaction [1–3]. In spite of recent advance in X-ray crystallography [4], the amorphous structure of cellulose in both natural and regenerated cellulose is not sufficiently understood [5]. In our previous studies [1–3], molecular chains in the amorphous region of natural cellulose take an ordered form when a small amount of water is added. X-ray and heat capacity data indicate that this molecular rearrangement occurs reversibly by absorption and desorption of water [3]. The first-order phase transition of water fractions, closely associated with the cellulose matrix, is usually impossible to observe [6]. Such fractions are referred as non-freezing water. Less closely associated water fractions exhibit melting and crystallization, showing considerable super cooling and significantly smaller enthalpy than that of bulk water. These water fractions are defined as freezing bound water. The sum of the freezing bound and non-freezing water fractions is the bound water content [1,7,8]. In the drying process of hydrophilic polymers, it is difficult to attain a completely dry state in usual conditions. Hence, the dryness of the polymers is not concretely defined due to strong hydrogen bonding established between the hydrophilic groups and water molecules.

As discussed in previous reports [1,2,6,8], the amount of bound water can be estimated by DSC, however, information obtained by thermal analysis

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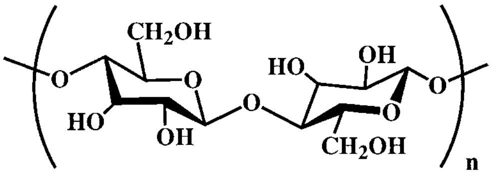

Scheme 1. Chemical structure of cellulose.

concerning bound water is limited. Although proton nuclear magnetic relaxation (NMR) studies provide the relaxation time of bound water, it has a certain technical limitation [9,10]. In this study, vaporization of bound water from cellulose was measured by differential scanning calorimetry (DSC) in order to investigate the nature of bound water, especially non-freezing water.

2. Experimental

2.1. Sample preparation

2.1.1. Dry samples

Natural cellulose (cotton) and two kinds of regenerated cellulose (viscose and cupra rayon) were used. The samples were fabric supplied by Japan Standardization Association as reference materials. Fabrics were cut in a circular shape with a diameter 6 mm using a punching tool.

The sample mass in the dry state was calculated as follows: (1) each sample piece was maintained in a dessicator with P_2O_5 for a month, (2) when the sample was removed from a dessicator, the time was recorded, (3) mass increase of the sample by water sorption from atmosphere (25°C, relative humidity=RH 65%) was monitored using a micro-balance (Sartorius precision $\pm 1\times 10^{-7}$) as a function of time, and (4) dry mass of each sample was obtained by extrapolation to time=0. Five pieces of the sample were weighed in the above procedure and standard deviation (σ) was calculated.

2.1.2. Samples with various water contents

Dessicators maintained at various saturated aqueous solutions of inorganic salts were prepared. RH was changed from 0 to 96% at 25°C. Samples were maintained at each RH for more than a month. The sample mass was weighed in a similar manner as in Section 2.1.1. Mass change occurs when RH was higher or lower than 65%. Mass change was recorded as a function of time and values and extrapolated values to time=0 were obtained. Standard deviation was calculated at time=0. Water contents (W_c=mass of water/mass of dry cellulose) of the conditioned samples were calculated using dry mass obtained in Section 2.1.1 and the sample with W_c's ranged from 0 to 0.3 g g^{-1} were obtained. Standard deviation of W_c thus calculated was within 5%.

2.2. Measurements

2.2.1. Vaporization measurements by DSC

A Seiko DSC 200 equipped with a cooling apparatus was used. The sample mass of cotton was 1.56–1.85 mg, viscose rayon 1.16–1.47 mg and cupra rayon 1.30–1.31 mg, respectively. Heating rate was varied from 2.5 to 40°C min^{-1} and N_2 gas flow rate ranged from 0 to 60 ml min^{-1}. An open type aluminium pan without lid was used. Temperature was varied from −150 to 200°C. Isothermal vaporization was carried out in a temperature at 50, 60, 70 and 80°C. The sample holders were previously maintained at predetermined temperatures and the samples with sorbed water were placed. 30 s after placing the sample. Isothermal condition was obtained. In order to calibrate the mass increase or decrease during handling of the conditioned samples, precise mass change at atmospheric conditions as a function of time (20–120 s) was used as described in Section 2.1. Mass values at an appropriate time were used for W_c determination using a calibration curve.

2.2.2. Heat capacity measurements by DSC

A Perkin-Elmer DSC 2c and 7 were used. Measurement procedure was as reported elsewhere [8,11]. Heat capacities of dry cellulose samples were measured from 50 to 180°C and those of cellulose samples with various W_c's were measured at 47°C.

3. Results and discussion

The maximum amounts of bound water restrained by cellulose samples are 0.16 g g^{-1} for cotton, 0.22 g g^{-1} for cupra rayon and 0.23 g g^{-1} for viscose rayon, respectively [6]. When the bound water is

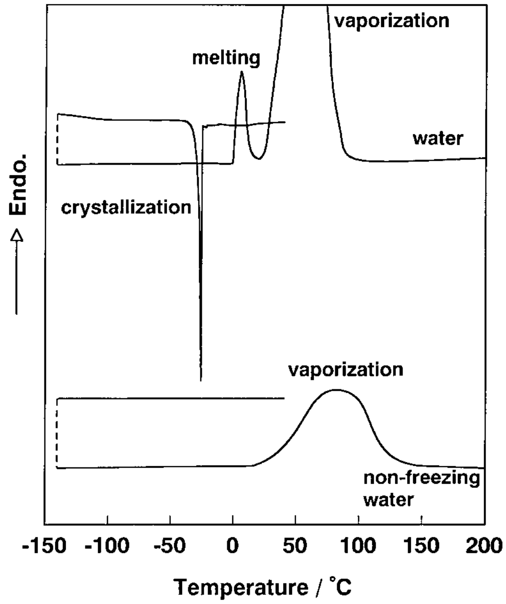

Fig. 1. Schematic DSC curves of water and non-freezing water in a temperature ranging from −150 to 200°C.

estimated by DSC, major part of bound water shows no first-order phase transition and is categorized as non-freezing water. A small amount of freezing bound water, less than 10% of total bound water, shows crystallization and melting, however transition temperatures are lower than those of pure water [1]. On this account, W_c of the samples used in this study is mainly categorized as non-freezing water. Fig. 1 shows schematic DSC curves showing phase transition of water and non-freezing water restrained by cellulose. As already reported, cellulose samples in completely dry state show no first-order phase transition [11]. C_p of cellulose I linearly increases with increasing temperature. $\Delta C_p/\Delta T$ in a temperature ranged from 50 to 180°C was 4.27×10^{-3} J g^{-1} K^{-2} for cellulose I (cotton). On this account, transitions appearing in Fig. 1 are attributable to water restrained by cellulose samples. As shown in Fig. 1, non-freezing water shows neither melting nor crystallization in a temperature from 0 to −150°C. Vaporization of bound water ordinarily terminates at a temperature higher than 100°C. However, it is reported that vaporization is observed at a temperature higher than 100°C when water molecules are strongly restrained by hydrophilic groups [1,12]. Although thermogravimetry was not carried out in this study, a good accordance between vaporization data measured by differential thermal analysis and the mass decrease obtained by TG was already found when vaporization of water from hydrophilic polymers was observed [7]. In order to investigate the characteristics of bound water of cellulose in detail, measurement conditions of vaporization behaviour were analysed by DSC.

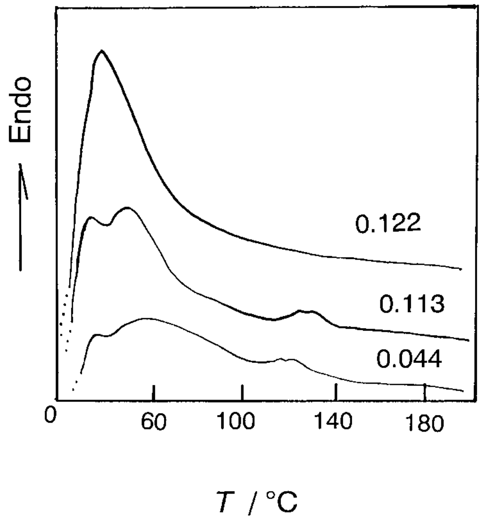

Fig. 2. DSC heating curves of bound water sorbed on cellulose I (cotton). Numerals in the figure shows water content (W_c, g g^{-1}) heating rate=10 C min^{-1}, N_2 flowing rate=0.

Fig. 2 shows representative DSC curves of vaporization of water restrained by cellulose I (cotton) with W_c's of 0.044, 0.113 and 0.122 g g^{-1}. When heating rate was 10°C min^{-1} and no N_2 gas flows, two broad endothermic peaks with a shoulder were observed for the samples with W_c=0.044 and 0.113 g g^{-1}. The low temperature peak with a shoulder (T_{pl}) is broad. The endothermic deviation starts at around 0°C and terminates at around 100°C. The high temperature (T_{ph}) peak with a shoulder is observed from 100 to 150°C. Two groups of vaporization peaks were observed for cotton samples with W_c's less than 0.113 g g^{-1}. Vaporization finishes at 150°C. When W_c exceeds 0.122 g g^{-1}, a small peak at 120°C was masked with the baseline and disappeared. As shown in Fig. 3, regenerated cellulose (viscose rayon) showed a similar behaviour, although peak temperatures were different from those of natural cellulose. Two peaks were only observed for viscose rayon when W_c was 0.032 g g^{-1}.

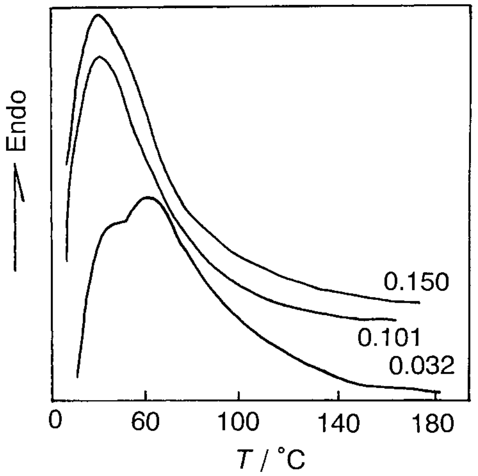

Fig. 3. DSC heating curves of bound water sorbed on cellulose II (viscose rayon). Numerals in the figure shows water content (W_c, g g^{-1}) heating rate=10°C min^{-1}, N_2 flowing rate=0.

Cupra rayon showed no T_{ph}. The above facts suggest that the vaporization curve is strongly influenced by crystallinity and higher order structure of amorphous region of the samples.

Fig. 4 shows the relationships between peak temperature of vaporization and W_c. As shown in Fig. 2, T_{pl}'s are observed at around 50°C regardless of bound water content and T_{ph}'s are found at around 125°C. T_{ph} of viscose rayon was not observed. Although data points are scattered, standard deviation caused by sample handling is represented with the size of each symbol. It is reported that water molecules restrained by cyclodextrin evaporated at around 150°C by TG–Fourier transformed infrared spectroscopy (TG–FTIR) [12]. The above facts indicate that water molecules evaporated at a temperature higher than 100°C when the intermolecular bonding was established between the hydroxyl group and water molecules. It is considered that the higher order structure of matrix molecules seems to affect the vaporization temperature.

As clearly seen in Fig. 2, a part of the bound water vaporizes at a temperature higher than 100°C, however it is thought that the appearance of the peak is markedly affected by measurement conditions. Among various factors affecting the vaporization behaviour of bound water restrained by cellulose, atmospheric conditions and heating velocity are considered to be important [12]. Fig. 5 shows the relationship between T_{pl} (°C) and N_2 flow rate (ml min^{-1}). The sample used was cotton with W_c=0.044 g g^{-1}. This amount of water corresponds to less than one water molecule attached to the hydroxyl group of cellulose repeating unit in the amorphous region [1]. By rapid N_2 flow rate, vaporization is completed

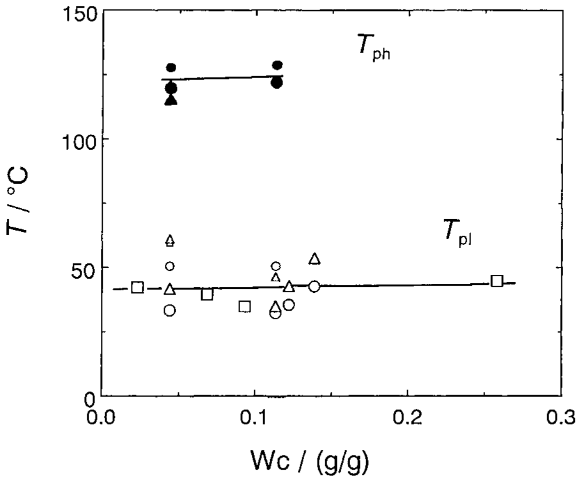

Fig. 4. Relationships between peak temperature of vaporization and water content (W_c g g^{-1}). (○, ●) cellulose I (cotton); (□;) cellulose II (cupra rayon); (△,▲;) cellulose II (viscose rayon); heating rate=10°C min^{-1}; N_2 flow rate=0 ml min^{-1}; T_{ph}: high peak temperature; T_{pl}: low peak temperature.

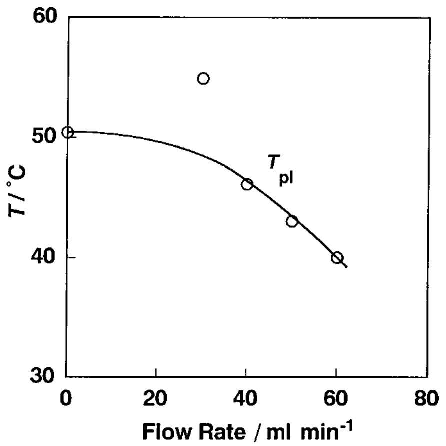

Fig. 5. Relationship between main peak temperature of vaporization (T_{pl}) and N_2 flow rate of water sorbed on cellulose I (cotton) W_c=0.044 g g^{-1}, heating rate=10°C min^{-1}.

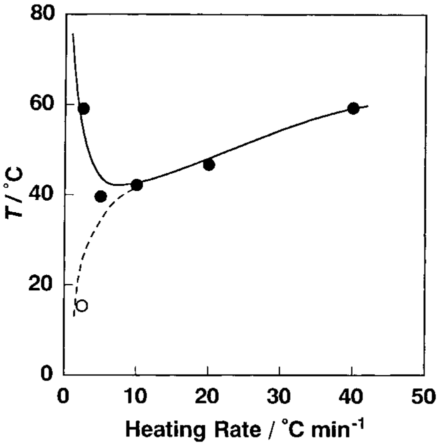

Fig. 6. Heating rate dependency of peak temperature of vaporization of water sorbed on cellulose I (cotton), W_c=0.044 g g^{-1}, N_2 flow rate=30 ml min^{-1}; (○) shoulder peak; (●) major peak.

quickly. Fig. 6 shows the effect of heating rate on T_{pl}. When the heating rate was slow, the shoulder of the major peak was clearly observed.

In order to investigate the time dependency of vaporization, isothermal vaporization was carried out at various temperatures. As described in Section 2, the sample holder was maintained at a constant temperature (50, 60, 70 and 80°C) and the sample was placed in the holder. Endothermic deviation was monitored as a function of time. Fig. 7 shows a representative vaporization curve of cotton with W_c=0.044 g g^{-1}, N_2 flow rate=30 ml min^{-1}. In the initial 20–30 s, isothermal condition was not attained. On this account, starting time t_0 was defined as indicated in Fig. 7. However, vaporization occurs during initial non-isothermal stage, where calibration techniques as described in Section 2.1.2 cannot cover. On this account, the results obtained especially at 80°C, were less reliable. t_p values were almost constant regardless of isothermal temperature. This result suggests that a certain degree of experimental errors is present in the data. However, as shown in Fig. 7, isothermal vaporization curves show long trains and it takes a certain time interval in order to recover the flat baseline. Termination time of isothermal vaporization is defined as t_e as indicated in Fig. 7. t_e values depend on W_c and isothermal temperature.

Fig. 8 shows the relationships between t_e and W_c at 50, 60 and 70°C of cellulose I (cotton). t_e increases

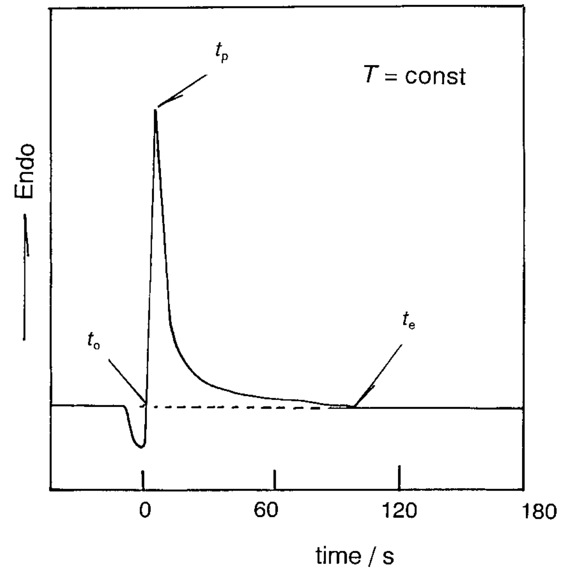

Fig. 7. Representative isothermal vaporization curve of water restrained by cellulose I (cotton). T=50°C, W_c=0.044 g g^{-1}, N_2 flow rate=30 ml min^{-1}; (●) main peak; (○) shoulder peak.

with increasing W_c and decreases with isothermal temperature.

From the above results, it can be said that thermal behaviour of non-freezing water can be investigated

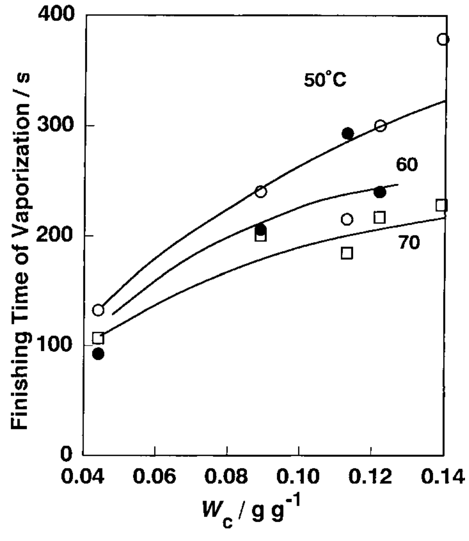

Fig. 8. Relationships between finishing time of vaporization and water content of cellulose I (cotton) held at various temperatures. Numerals in the figure show holding temperatures. N_2 flow rate=30 ml min^{-1}; (○) 50°C; (●) 60°C; (□) 70°C.

by vaporization technique if the appropriate experimental condition is selected. It is known that water molecules directly attached to the hydroxyl group in the amorphous region are non-freezing. As reported in our previous studies, the amorphous structure of natural cellulose is not completely random, but molecular chains are arranged unidirectional along fibre axis. Molecular chains in the intermediate region reversibly change from regular structure to random molecular arrangement in the presence of a trace amount of water. The reversible change can be estimated by X-ray diffractometry as change of crystal size. This change can also be evaluated by the C_p change of cellulose I in the presence of water.

Fig. 9 shows C_p of cellulose I–water systems in a W_c from 0 to 0.3 g g^{-1}. Although data is limited, it can be said that C_p decreases when cellulose restrains a small amount of non-freezing water. In the case of cotton cellulose, crystallinity measured by X-ray was 54% and changes of crystal size of cellulose I as a function of W_c is reported elsewhere [6]. The maximum amount of bound water of cellulose fibre used in this study was 0.16 g^{-1}. This amount corresponds to that where one hydroxyl group in the amorphous region attracts ca. one water molecule. The minimum C_p is observed at around 0.05–0.10 g g^{-1}. This W_c range is accorded with vaporization curves where the high temperature vaporization peak is observed. The vaporization and C_p data suggest that structural change of the amorphous region concerns the above unusual thermal behaviour. As shown in Fig. 9, the higher order structure of amorphous cellulose chains convert to a more random form by loosing a small amount of non-freezing water.

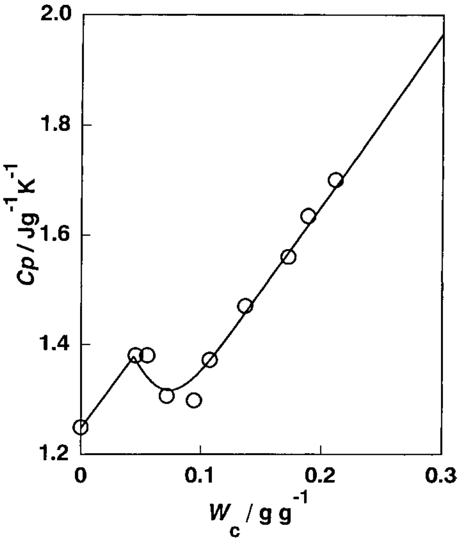

Fig. 9. Heat capacities of cellulose I (cotton) and water systems.

It is considered that water molecules coexist with cellulose molecules in the biosynthetic path way, when cellulose is formed in plant tissue. If we considered that cellulose I is synthesized in cell membranes in living plants, it is appropriate to assume that the molecular chain takes an extended form. During the transient state when cellulose molecules gather, excess free water molecules which are bound to the hydroxyl groups of cellulose are excluded from the system. During this process, water molecules take a catalytic role in order to from inter-molecular hydrogen bonding in the crystalline region. This process is considered to start randomly along the molecular chain. It is reasonable that a part of the molecular chains remains distorted and strained, when they form and extended chain structure. In the completely dry state of cellulose I, this area is detected as the amorphous region. Once-dried systems used in this study are considered to follow a similar drying procedure as mentioned above, although higher order structure of the wet state is more restricted compared with that of never-dried systems.

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