

DETERMINATION OF BOUND WATER CONTENT IN POLYMERS BY DTA, DSC AND TG *

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(Received 3 February 1987)

ABSTRACT

Various kinds of water sorbed on hydrophilic polymers were analysed using differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetry (TG). From the heat of melting or crystallization of water, the bound water content was calculated using the relationship $W_t = W_f + W_b$, where W_t is the total water content, W_f is the free water content whose phase transition temperatures are similar to those of ordinary water and W_b is bound water. In many hydrophilic polymers, W_b is the sum of the non-freezing water W_{nf} and freezing bound water W_{fb} . From a DTA vaporization curve, the W_t value could be evaluated for a sample containing a large amount of water. At the same time, the W_b value was estimated using TG. In TG curves, a two-step weight loss corresponding to W_f and W_b was observed. By combining DTA, DSC and TG, it becomes possible to evaluate the exact amount of bound water which is tightly attached to the polymer matrix.

INTRODUCTION

It is known that the functional properties of natural polymers can be defined when they coexist with water molecules [1,2]. Biopolymers in the living state generally contain a considerable amount of water, and it is necessary to evaluate the water combined with the polymers in order to

* An application of this method was reported in the Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis, 5–7 November 1986, Hangzhou, People's Republic of China, under the title "DSC Studies on Water Sorbed on Cellulose and Its Derivatives".

elucidate characteristic features of polymer–water systems. Various kinds of techniques have been used to investigate the structure and properties of water sorbed on hydrophilic polymers: nuclear magnetic resonance spectroscopy [3–5], dielectric measurements [6], sorption isotherm techniques [7,8], viscoelastic measurements [9,10], thermal analysis [11–16] etc. Among them, thermal analysis has various advantages, for example, the ability to evaluate qualitatively the water content, the small size of the sample required, rapid measurement etc.

In this report, we intend to establish some thermoanalytical methods of evaluating the bound water content in the hydrophilic polymers. Attention is paid especially to the comparison between the evaluation from the heat of melting or crystallization and that from the heat of evaporation using DSC and DTA. Thermogravimetry is also examined in order to compare the data obtained by DTA and DSC.

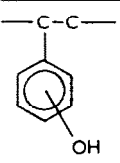
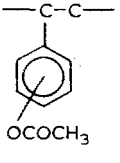
EXPERIMENTAL

Samples

Poly(hydroxystyrene) and its derivatives were chosen, because they were (1) amorphous from X-ray diffractograms [17], (2) synthesized in our laboratory as model polymers related to natural polymers, and (3) well characterized [18,19]. Moreover, the glass transition behaviour of samples had been determined in both dry and wet states [20]. The phase transition

TABLE 1

Chemical structure, molecular weight M_w , molecular weight distribution M_w/M_n and glass transition temperature T_g of the samples

Chemical structure	Sample name	Abbreviation	M_w	M_w/M_n	T_g (K)
	Poly(2-hydroxystyrene)	PoHS	3.4×10^4	2.7	445
	Poly(3-hydroxystyrene)	PmHS	2.1×10^4	2.9	440
	Poly(4-hydroxystyrene)	PpHS	3.6×10^4	3.5	455
	Poly(2-acetoxy-styrene)	PoAS	6.0×10^4	2.7	391
	Poly(3-acetoxy-styrene)	PmAS	4.0×10^4	2.9	345
	Poly(4-acetoxy-styrene)	PpAS	7.2×10^4	3.5	386

behaviour has been examined at a temperature lower than 293 K [19,21]. Table 1 shows the molecular weight M_w and the molecular weight distribution M_w/M_n of the samples used in this experiment.

Cellulose and cellulose derivatives were also used as examples of natural polymers.

Methods

A Perkin-Elmer differential scanning calorimeter DSC II equipped with a cooling apparatus, a Du Pont 910 DSC equipped with a cooling apparatus and a Seiko Denshi data processor, and a Rigaku Denki TG-DSC equipped with an electric heater and an IR radiant heater were used. In this paper, the term DSC indicates the Perkin-Elmer DSC II and DTA indicates the Du Pont DSC.

Both open- and sealed-type aluminium sample pans were used. The aluminium sealed sample pans were previously exposed to steam in an autoclave at 393 K for 3 h to eliminate the formation of aluminium hydroxide while measurements were being taken. The samples were first dried in a vacuum desiccator for about one week and then about a 5 mg sample was weighed. For the measurement of polymers containing sorbed water, small amounts of water were added with a microsyringe and the total weight was then measured on a microbalance (Sartorius 708501; accuracy, ± 0.001 mg). If the water content exceeded the predetermined amount, the sample pan was allowed to stand for a few minutes until the water evaporated. The water content (g g^{-1}) was calculated from the following equation:

$$\text{water content}(W_t) = \text{added water}(w_w) / \text{dry sample}(w_s) \quad (1)$$

In order to avoid experimental errors, DSC runs were repeated three times in each experiment. The DSC curves were obtained at a scanning rate of 10 K min^{-1} . The temperature of the apparatus was calibrated using the extrapolated starting temperature of melting of indium (purity, 99.999%) and that of pure water. The heats of melting, crystallization and vaporization were calculated by reference to the enthalpy of pure water. When the sample containing water was measured using an open aluminium pan, the sample was frozen in liquid nitrogen to avoid vaporization during sample handling. In this case, the sample was weighed after the DTA or TG measurements.

RESULTS AND DISCUSSION

Figure 1 shows typical DSC crystallization curves of water sorbed on poly(4-hydroxystyrene) containing various amounts of water. The samples were packed into a sealed sample pan and no water evaporated before or

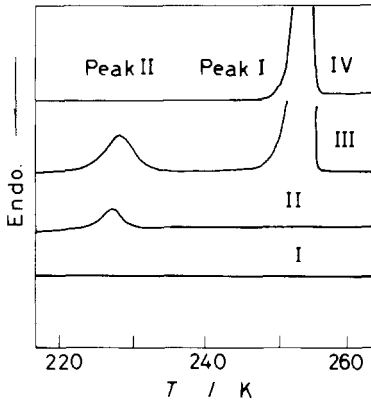


Fig. 1. DSC crystallization curves for water sorbed on poly(4-hydroxystyrene): curve I, $W_t = 0.079$; curve II, $W_t = 0.107$; curve III, $W_t = 0.263$; curve IV, pure water.

after the measurements. The first-order transition of water was not observed at first unless the water content exceeded a certain amount (curve I). The amount was 0.08 g g^{-1} for this sample. The critical amount of water varied according to the chemical structure and/or the higher-order structure of each sample. After this water content was exceeded, a small broad crystallization peak (peak II) appeared at about 235 K (curve II). This small peak shifted to a higher temperature range with increasing amount of water, and then reached an upper temperature limit. The heat of crystallization for peak II also increased in the initial stage and then attained a constant value. A new sharp peak (peak I) appears when the amount of water in each sample exceeds that needed to show a constant heat of crystallization for peak II (curve III). The shape of peak I and the temperature at which it occurs agree well with the shape and temperature range of the peak for the crystallization of pure water (curve IV), although peak I becomes slightly wider at low temperatures. When the hydrophobic polymers co-exist with water, only a DTA or DSC curve similar to curve IV is generally observed. This suggests that non-freezing water and water observed as peak II are affected by the polymer matrix.

In heating curves, the melting peak was not as clearly separated as the crystallization peaks. However, melting started at a temperature lower than the melting temperature of pure water.

On the basis of the DTA and DSC data measured at a temperature lower than 393 K, the following equation can be applied to water sorbed on the samples:

$$W_t = W_f + W_{fb} + W_{nf} \quad (2)$$

W_t is the total weight of water added to a sample, W_f is the weight of water calculated from the heat of crystallization (peak I), W_{fb} is the weight calculated from the heat of crystallization (peak II) and W_{nf} is the weight of

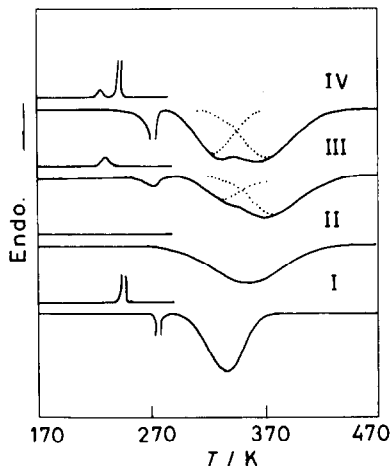


Fig. 2. DTA vaporization curve for cellulose diacetate film: curve I, pure water; curve II, $W_t = 0.171$ (W_{nf}); curve III, $W_t = 0.206$ ($W_{nf} + W_{fb}$); curve IV, $W_t = 0.293$ ($W_{nf} + W_{fb} + W_f$).

non-freezing water. The weight of bound water can be defined as follows:

$$W_b = W_{fb} + W_{nf} \quad (3)$$

As reported previously [12,13], W_{fb} amounts to a few percent of the total W_b and in some cases it is very difficult to detect [17,18].

When the phase transition behaviour of the water combined with the hydrophilic sample is measured, one of the difficulties is to determine the exact weight of a dry sample. A water molecule restrained directly by the hydrophilic group via hydrogen bonding remains bound even at a temperature higher than 373 K under reduced pressure. Ambiguous values of the sample weight lead to difficulties in the calculation of the heat of transition. In our previous reports, we defined a dry sample as one which showed no endothermic deviation caused by the vaporization of water up to the decomposition temperature in DTA or DSC curves [19,22,23]. The heat of vaporization is large enough to detect a trace of water in the sample. It was also suggested that there was a possibility of evaluating the bound water content of hydrophilic samples using the heat of vaporization.

When the same sample shown in Fig. 1 was measured in an open-type pan and heated up to a temperature lower than the decomposition temperature, a vaporization curve could be observed. Figure 2 shows the DTA curve for water sorbed on cellulose diacetate containing various amounts of water. The water content of the sample shown in curve II corresponds to W_{nf} . The peak temperature is higher than that of pure water (curve I). Curve III corresponds to the sample containing W_{nf} and W_{fb} . The peak temperature shifts to a lower temperature range and the peak shape becomes slightly

distorted. Curve IV corresponds to the sample containing W_{nf} , W_{fb} and W_f . Two peaks are clearly observed in this case.

As shown in Fig. 2, vaporization of pure water was complete at 370 K, but water restrained by the polymer remained up to 450 K. If the peak is resolved assuming the gaussian distribution, two or three peaks can be obtained as projected in Fig. 2. From the high temperature side, we can distinguish non-freezing water, freezing bound water and free water respectively. The resolution of the vaporization peaks contains various kinds of errors. However, the advantage of this method is that an exact value for W_t can be determined. In the case of synthetic polymers, it is not so difficult to estimate W_t . Natural polymers, especially biopolymers, however, contain a large amount of water and it is difficult to evaluate the water content before the measurement. This difficulty arises because, when the sample is dried completely in order to estimate the dry weight (eqn. (1)), the characteristic structure of the sample is damaged and the original state is not recovered by adding water. The evaporation method is useful for calculating W_t in the samples containing a large amount of water, even if the peaks (W_f and W_b) are not completely resolved. In order to calculate W_b , W_f evaluated from crystallization or melting was subtracted from W_t obtained by the evaporation method:

$$W_b = W_t(\text{DTA vaporization}) - W_f(\text{DSC/DTA melting or crystallization}) \quad (4)$$

To determine the optimum experimental conditions for the vaporization method, several experimental factors were examined; the sample weight was varied from 0.1 to 10 mg, the scanning rate from 0.5 to 40 K min⁻¹, the gas flow rate from 5 to 50 cm min⁻¹ and the water content W_t from 0.01 to 2.0. Although the phase transition temperatures were considerably affected by the above factors, the heat of vaporization stayed almost constant when the calibration was carried out under the same conditions.

Figure 3 shows the DTA vaporization curves for water sorbed on various poly(hydroxystyrene) compounds. The peak temperature for W_b varied in the order poly(3-hydroxystyrene) > poly(4-hydroxystyrene) > poly(2-hydroxystyrene). This order agrees with the order of hydrogen-bond formation in the samples [19].

As shown in Figs. 2 and 3, vaporization of water started as soon as the ice melted. This fact suggests some difficulty in using TG to determine W_t . Typical TG curves for the water-sorbing sample are shown in the right upper part of Fig. 4. TG curves were measured at a temperature higher than 393 K but a weight loss occurred unavoidably during the sample handling. Therefore the TG data for the W_t determination were less reliable than the DSC and DTA data. In TG curves, the weight of the sample decreased in two steps. As indicated in Fig. 4, line A shows the total weight of dry sample and water $w_s + w_w$ (see eqn. (1)). Line A includes the weight loss during the

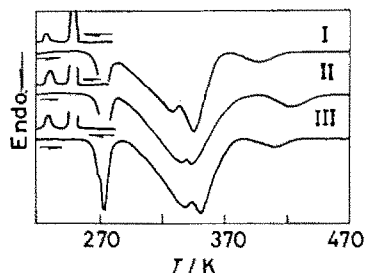


Fig. 3. DTA vaporization curves for various poly(hydroxystyrene) compounds ($W_t = 0.20$): curve I, PoHS; curve II, PmHS; curve III, PpHS (see Table 1).

sample handling. Line B shows the weight loss of water in the second step. This kind of water is thought to be bound water W_b . The reliability of the weight calculated from line B is much higher than that from line A. Line C shows the weight of dry sample w_s . In order to obtain the exact w_s , it is necessary to obtain a flat TG baseline at a temperature in the range 10–30 K before thermal decomposition of the sample. By TG, the bound water content can be obtained as follows;

$$W_b(\text{TG}) = \text{line B}/\text{line C} \quad (5)$$

Figure 4 indicates that bound water W_b could be separated from free water W_f . When the TG curve was differentiated, two peaks could be clearly separated. As mentioned previously, W_b consists mostly of W_{nf} , and the amount of W_{fb} is only a few percent. In the TG method, the separation of W_{fb} from W_b was difficult as shown in the second-step weight loss in Fig. 4.

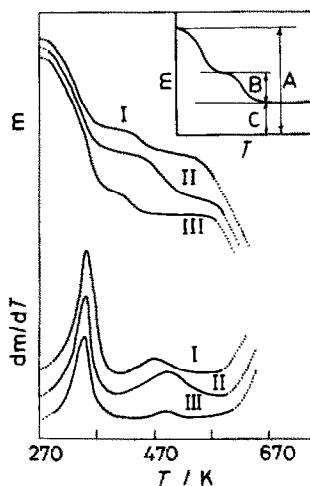


Fig. 4. TG curves for various poly(hydroxystyrene) compounds ($W_t = 0.20$): curve I, PoHS; curve II, PmHS; curve III, PpHS (see Table 1).

TABLE 2

Bound water content W_b evaluated from DSC, DTA and TG

Sample	DTA and DSC		DTA Vaporization	TG
	Melting	Crystallization		
PoHS	0.080	0.084	0.102	0.081
PmHS	0.111	0.127	0.122	0.127
PpHS	0.100	0.103	0.133	0.114
PoAS	0.026	0.029	0.010	0.020
PmAS	0.044	0.049	0.010	0.027
PpAS	0.030	0.036	0.025	0.023

It seems to be difficult to distinguish W_{fb} from the total experimental error.

We tried to measure the isothermal evaporation curves using TG. However, evaporation of water from the sample started during sample handling. Moreover, it took a certain time for the apparatus to reach an isothermal state, even when we used an IR radiant heater instead of a standard electric heater. We chose the fixed temperatures 333, 343, 353, 363, 373 and 393 K. The duration of vaporization in an isothermal state varied from about 1 to 8 min. However, the results we obtained were not as expected, since two-step curves were scarcely observed. Our results may be explained by losses during the time required for the stabilization of the apparatus.

Figure 4 also shows TG vaporization curves for poly(4-hydroxystyrene) and its related polymers (see Table 1). The hydroxyl group is introduced into different positions in the aromatic ring of the sample. The intermolecular hydrogen bonding between the hydroxyl group and a water molecule depends on the position of the hydroxyl group. This means that the TG vaporization curve reflects the degree of hydrogen bonding. The second step of the weight loss corresponds to W_b , and the amount varied in the order poly(3-hydroxystyrene) > poly(4-hydroxystyrene) > poly(2-hydroxystyrene). This order agrees with the order of hydrogen-bond formation in the samples [19]. Similar results were also obtained by DTA.

The calculated values of W_b from the TG curve are listed in Table 2 together with those obtained by DTA and DSC. The W_b values obtained from crystallization and melting peaks were calculated using eqns. (2) and (3). In these cases, the W_t value was obtained by weighing. The W_b value obtained from the DTA vaporization curve was calculated using eqn. (4). W_b from the TG curve was calculated using eqn. (5). For the sample with a strong hydrophilic group such as the hydroxyl group (poly(hydroxystyrene)), the amount of W_b is comparatively high, and the values obtained by different methods agree fairly well (upper column in Table 2). However, in the sample with a very weak hydrophilic group such as an acetoxyl group (poly(acetoxystyrene)), the W_b values as obtained by DTA, DSC and TG vary (lower column in Table 2).

From the results obtained in this experiment, it can be said that water molecules sorbed on hydrophilic polymers can be detected by DTA, DSC and TG. By combining the three methods, it becomes possible to evaluate the exact amount of bound water which was tightly attached to the matrix. At the same time, the exact amount of dry sample can be evaluated. In the past, it was difficult to define the exact water content of a sample containing a large amount of water, for example, biomaterial.

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