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Comparison of measurement techniques for the identification of bound water restrained by polymers

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ABSTRACT

We attempted to compare the measurement methods concerning characterization of bound water restrained by hydrophilic polymers having biocompatibility, since the structural change of water on the surface of bio-membranes has attracted considerable attentions. In particular, calorimetry that has been used for quantitative analysis of bound water in bio-membranes has been criticised in terms of the results obtained by nuclear magnetic resonance spectrometry, infrared/Raman spectrometry, X-ray analysis, and neutron scattering measurements. Based on the identical definition of bound water, and by using biocompatible polymers, the present status of calorimetry is investigated in order to identify and quantify the bound water restrained by bio-membranes.

1. Introduction

According to Vogler, "Water is truly an intimate structural element of terrestrial perhaps universal, biology" [1]. When functionalities of biological materials are investigated, water molecules play a crucial role [2]. New bio-mediated polymers have been designed and adsorption of protein at polymer surface in aqueous media has attracted special attention from bio-medical aspects. It is generally accepted that the chemical structure, especially molecular balance of hydrophilic and hydrophobic groups in a polymer is an important factor in developing a synthetic biocompatible polymers. Biological properties of water on the surface of polymers have been investigated by various analytical techniques. Recent infrared (IR) and Raman spectroscopic studies have elucidated the structure of single water molecule directly attached with a certain hydrophilic group on the surface of hydrophilic polymers [3,4]. At the same time, recent studies suggest that water molecules surrounded by water bonded directly to matrix polymer act to mediate protein and polymer surface [5–7]

A molecular model of water surrounding cell organ has been suggested by many researchers over the last 50 years [8], i.e. correlation time calculated from nuclear magnetic relaxation study of water molecules surrounding organs is 10^{-5}–10^{-6} s and that of water molecules inside of cell wall is in the range 10^{-7}–10^{-8} s. The above kinds of water having longer correlation times are considered to be categorized as bound water, although the terminology of bound water is also not standardized and the exact meaning of "bound water" depends on researchers utilizing different experimental techniques, such as NMR, thermal analysis, dielectric measurement, viscoelastic measurement and so on. Recent studies of water coexisting with bio-compatible polymers, that have been carried out using Raman and FTIR spectrometry, have shown a precise procedure during water contact that is followed via a time resolved method using a newly developed sample holder [3,4]. A recent study on Raman spectroscopy presented important evidence for understanding the monomolecular water in hydrophobic polymer, such as polystyrene [9].

Thermal analysis (TA) has been used for these 40 years for the estimation of bound water restrained by various kinds of polymeric materials and biomaterials. TA is an advantageous method compared with other rheological and spectroscopic methods, when samples with a broad range of water content are investigated quantitatively [10,11]. At the same time, it is known that various factors, such as calibration methods, data analysis, and sample preparations affect the reliability of results. Since the molecular relaxation phenomena of matrix polymer must be taken into consideration, the variations of the higher order structure of matrix as a function of time and temperature necessarily accompany the structural change of water molecules [12]. On this account, it is necessary to reexamine the thermal method for the determination of bound water restrained at synthetic biopolymers and natural polymers which are mainly targeted for using biomedical applications. In this study,

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the analytical method of TA for the determination of bound water is examined by comparison with other experimental techniques such as X-ray-TA simultaneous measurements, NMR and IR/Raman spectroscopy.

2. Experimental

2.1. Samples

A series of two representative water-insoluble polymers were used. One is natural polymer cellulose from various kinds of plants and chemically modified cellulose, and the other a synthetic poly(methyl methacrylate) (PMMA) group.

2.2. Measurements

A Seiko Instruments, Ltd. differential scanning calorimeter DSC 200C, equipped with a cooling apparatus was used. Nitrogen gas flow rate was 30 ml min^{-1}. The samples were heated to 80 °C, and then cooled to −150 °C at 10 °C min^{-1} (1st cooling run). The samples were held at −150 °C for 10 min and heated to 100 °C at 10 °C min^{-1} (1st heating run). The samples were cooled to −150 °C at 10 °C min^{-1} (2nd cooling run), and then heated at 10 or 2 °C min^{-1} (2nd heating run).

In order to have samples with various water contents, the following procedure was used: (1) 3–5 mg samples were placed in pans and a small amount of deionized water was added using a micro-syringe, (2) the water was evaporated until a predetermined mass of water was attained, (3) the sample pans were sealed hermetically using an auto-sealer, (4) samples with added water were weighed, and (5) samples were kept at room temperature overnight, and weighed again in order to confirm no mass loss occurred. After DSC measurement, the pan was pierced, annealed at 110 °C over 2 h in an electric oven and then weighed. The amount of water was evaluated using Eq. (1). Although the water content (W_c) of hydrated polymers has been defined in various equations, in this study, W_c is defined as follows

$$W_c = \frac{m_w}{m_s} \quad (1)$$

where m_s is the mass of dry sample and m_w is the mass of water in the system [13,14].

Glass transition temperature (T_g) was defined as the temperature at which the extrapolated baseline before the transition intersects the tangent drawn at the point of greatest slope on the step of heat capacity change due to glass transition [15]. Temperature and enthalpy of transition was calibrated using pure water as a standard material.

Peak temperature of melting was assigned as T_m. When two melting peaks of water were observed, the high temperature side peak was designated as T_{mh} and low temperature side peak as T_{ml}. In this study, cold crystallization was observed as an exothermic transition that occurred in a temperature range between T_g and T_m. Peak temperature of exotherm was defined as T_{cc} [16]. Melting enthalpy (ΔH_m, J g^{-1}), and cold-crystallization enthalpy (ΔH_{cc}, J g^{-1}) were calculated. Enthalpy of melting of ice (334 J g^{-1}) was used for calculation. The amount of freezing water was calculated from ΔH_m calculated from the 2nd heating curve.

As described above, enthalpies of transitions were calculated from the peak area of each transition. When the two melting peaks were observed, the enthalpy of each peak was calculated. In this study, bound water was calculated as follows.

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

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

where W_f is the amount of free water calculated from ΔH_m of the high temperature side melting peak, W_{fb} is the freezing bound water calculated from ΔH_m of the low temperature side melting peak, and W_b is the total amount of bound water. The amount of non-freezing water (W_{nf}) can be calculated by Eq. (2), since W_c was obtained from Eq. (1).

3. Results and discussion

3.1. Non-freezing water and water-vapour sorption

The thermal data indicate that water restrained by hydrophilic polymers can be categorized into three groups: non-freezing, freezing bound and free water which can be calculated from Eqs. (2) and (3). The amount of non-freezing water depends principally on the chemical structure of polymer matrix, however the value also varies according to the conformational change of polymer. Molecular relaxation of polysaccharides directly reflects the number of non-freezing water molecules. Molecular equilibration procedure of polysaccharide chains in aqueous media is indirectly proved by the fluctuation of W_{nf} values [17,18].

Historically, water sorption (for example [19]) and swelling properties of polymeric materials has been investigated by mass measurement as a function of time and temperature at well defined humid conditions. Early theoretical approaches established by Brunauer, Emett and Teller concerning the first and second layer water on polymeric matrix based on sorption isotherm obtained by mass measurement have been used by many researchers [20]. Generally, the following results can be obtained by mass measurements, (1) equilibrium swelling and water holding capability (EWC), (2) diffusion and permeation constant, and (3) activation energy of the first layer sorption. In the initial stage of water sorption on polymers, recently, the IR and Raman spectroscopic approach to single water molecule restrained by a specific functional group of biopolymers has attracted special attention. Kitano and his research group, and Morita have extensively carried out time-resolved ATR-FTIR and Raman spectroscopic measurements sorbed on biopolymers using a sample holder which they improved [3,4]. The number of water molecules involved in the initial stage of water sorption can be measured. With their methods, experimental errors that are always taken into consideration by traditional measuring techniques can be avoided. For example, as shown in Fig. 1, by modern methods carried out in a completely sealed system, mass change can be measured after several seconds, however, by traditional batch system, the early stage of sorption data could not

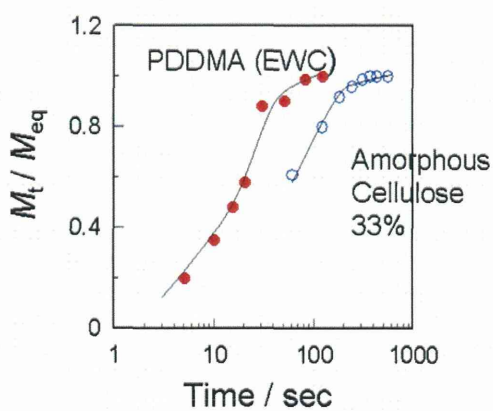

Fig. 1. Normalized sorption curves of representative two polymers at 25 °C. Filled circle (red); poly(N,N-dimethylacrylamide) (PDMMA), Open circle (blue); amorphous cellulose. M_t: mass at time t; M_{eq}: mass at equilibrium state. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

be obtained. By traditional batch system, the mass of equilibrium state (M_{eq}) was obtained at the time where no mass change was observed, when the sample was maintained in a humid condition [10]. The mass at time t (M_t) was obtained by weighing the sample at each time t. It takes at least several minutes for sample handling. By spectroscopy, M_{eq} was determined from spectra in which the specific band is saturated after a certain time of water vapour introduction. M_t was obtained from absorbance of specific band at each time period. This blank time in the initial stage of sorption by traditional batch system has made it difficult to calculate the diffusion rate of water by sorption. Traditionally, Fickian type diffusion has been postulated for analysis of this kind of sorption isotherm, if border conditions to solve the equation are known. This calculation can be carried out in recent studies when the hydrophobicity of matrix polymers is high, such the poly(methyl methacrylate) (PMMA) family having a stable higher order structure [21]. By IR and Raman spectroscopy, (1) location of water molecules in single polymer molecule, (2) identification of dry or wet state of samples, and (3) sorption and desorption mechanism in molecular level, can be obtained.

By NMR relaxation measurements, ^{1}H correlation time of water restrained by polymers calculated from longitudinal and transverse relaxation time, is reported as 10^{-7}–10^{-6} s which are close to those of "rigid solid" (for example, [22]). By NMR relaxation, the following result can be obtainable, (1) identification of different type of water from relaxation times, (2) molecular motion of bonded water as functions of temperature and time, and (3) interaction between water and specific group of polymer chain.

By DSC, no thermodynamic first-order phase transition of water can be detected in the water content range mentioned above. Due to this characteristic feature, the above kind of water is thermally defined as non-freezing water. We have reported the results of poly(2-hydroxylethyl methacrylate) (PHEMA) and poly(2-methoxyethyl acrylate) (PMEA) (PMMA group) measured X-ray diffractometry (XRD)-DSC simultaneous measurement as a function of temperature. When the sample restrains non-freezing water, no X-ray diffraction pattern of ice could be detected [23].

Although no first order thermodynamic phase transition is observed, non-freezing water affects the molecular motion of matrix polymer which can be detected as shift of glass transition temperature (T_g) and heat capacity difference (ΔC_p) at T_g as reported previously [24]. We reported that T_g of polysaccharide–water systems in non-freezing water content range is markedly affected by a small amount of water by breaking of inter-molecular hydrogen bonding of polysaccharides. In contrast, in the sample whose major constituent is the hydrophobic group, such as PMEA, T_g maintains a constant value regardless of W_c [5]. This indicates that hydrophobic groups stabilize the higher order structure. When the hydrophilic polymer is investigated, it is unavoidable that the higher-order structure of matrix polymer varies as functions of temperature and time [12,24,25]. Changes in W_{nf} values caused by the structural change of matrix will be described in Section 3.2 related with the variation of freezing bound water.

Molecular enhancement of polysaccharides in the presence of water affects the ΔC_p value at T_g. We have suggested that modified Gordon–Teller equation can be applied for ΔC_p of polysaccharide and water if we assume the presence of amorphous ice in the system. Heat capacity (C_p) of polymer–water systems has been investigated by DSC in an appropriate temperature range [26]. It is thought that difference between experimental values and calculated values assuming additivity of C_p values of water and polymer is closely related with the molecular relaxation of matrix polymers and further investigation is necessary.

Fig. 2 shows EWC and bound water content calculated based on ice-melting enthalpy measured by DSC for PMMA and cellulose group. Both sample groups are water insoluble. PMMA group is amorphous and the cellulose group is crystalline whose crystallinity depends on original plant species from which cellulose was extracted. The crystallinity estimated by X-ray diffractometry is in a range from 28 to 70%. It is clear that W_b values of PMMA group are smaller than EWC. On the other hand, Fig. 2 clearly shows that water sorbed on cellulose group at the equilibrium water condition, is categorized into non-freezing water.

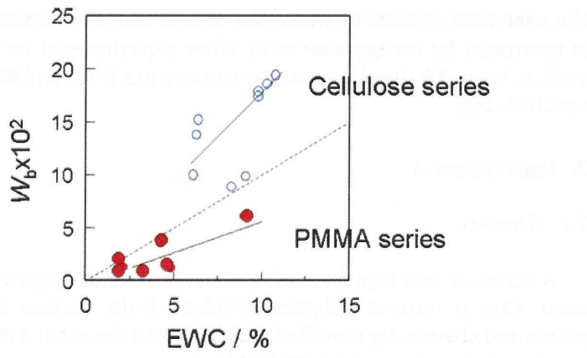

Fig. 2. Relationships between bound water content and EWC. Broken line shows W_b = EWC

Recent IR and Raman spectroscopic results at least ascertain the dry condition of hydrophilic polymers, which concludes a long-term discussion concerning the initial stage of water sorption. TA is not a suitable technique to investigate the molecular level of the water sorption process. The most advantageous point of DSC is that the W_{nf} value can quantitatively be calculated using Eqs. (2) and (3) if experimental conditions are well defined. Furthermore, when chemical structure and crystallinity of the sample are known, the number of water molecules restrained by each functional group can be calculated from the W_{nf} value [10]. A detectable amount of non-freezing water was also observed in various types of synthetic membranes (for example, [27]).

3.2. Freezing bound water

Beside non-freezing water, most hydrophilic polymers restrain freezing bound water, which shows the thermodynamic first order phase transition whose transition temperature is not the same as that of the free water. Recent studies on freezing bound water of poly(2-methoxyethyl acrylate) (PMEA) and related polymers [5–7] indicate that biocompatibility is correlated with the amount and ratio of freezing bound water on the surface of the above polymers. It is also suggested that functional properties of membranes are closely related with the characteristic amount of bound water [28,29].

When W_c exceeds the characteristic value (the maximum value of W_{nf}) of each polymer, ^{1}H NMR correlation times decrease continuously with increasing W_c [30]. This suggests that there are another kinds of water molecules which form a second or third layer in the system. By NMR, the quantitative amount of different kind of water cannot be calculated, and accordingly a distinct border of different kinds of water is difficult to estimate. When a sufficient number of water molecules is assembled on the surface of polymer, ice is formed in the system [31]. Ordinarily, melting of most polymers belonging to the PMMA group showed a ice-melting peak at the same temperature of free water even at EWC. By DSC, PMEA exceptionally shows cold-crystallization and two melting peaks, T_{ml} and T_{mh} [5]. As described in Section 2.2, T_{ml} is observed at a temperature lower than 0 °C. Similarly, a low temperature side melting peak is observed in various kinds of polysaccharides, such as cellulose.

When W_c of water soluble polysaccharides and several kinds of synthetic biopolymers exceeds the maximum value of W_{nf}, glass

transition, cold crystallization and melting of ice are observed in DSC curve. The temperature range of cold crystallization of various kinds of polysaccharide and representative synthetic biocompatible polymers has been reported previously [11]. We have suggested in our previous papers [32] that a part of water is glassified in amorphous ice [24,32–34] when the water–polymer system is frozen at the conditions described in Section 2. By heating, amorphous ice transforms into ice at a temperature range of cold crystallization. By XRD-DSC simultaneous measurement, we reported that crystallization of water in PMEA occurs at a temperature range of cold crystallization [23]. It is also reported that the crystalline structure of ice formed at cold-crystallization temperature range belongs to hexagonal ice (Ih). Zhang reported that cubic ice is formed in a temperature range where cold crystallization occurs if the size of ice is less than ca. 10 nm [35]. By atomic force microscopy (AFM), we reported the size of molecular bundles of various kinds of polysaccharide [36–38]. It is thought that the space 10–20 nm is acceptable size for ice crystallization even if we take into consideration the fact that the higher-order structure depends on sample preparation conditions [39]. However, the melting temperature of cubic ice is almost the same as that of hexagonal ice [35]. Accordingly, it is thought that the ice formed at cold crystallization is hexagonal ice with defects, since T_m observed in our samples is always found at a temperature lower than 0 °C. This can be confirmed from the following facts that equilibrium melting temperature obtained by Hoffman–Weeks plots is reported to be −20 to −10 °C depending on W_c of each system [40]. By the Avrami equation, nucleation of freezing bound water is conducted two dimensionally [40,41]. The rate of crystallization is calculated from Cohen–Turnbull equations, the crystallization rate of bound water is far slower than that of free water. This suggests that freezing bound water is in a non-equilibrium state and time for attaining a stable state is markedly retarded, i.e. thermal history markedly affects the temperature and ice-melting enthalpy for the freezing bond water. When the sample is subjected to repeat freezing and thawing cycles by DSC, the amount of freezing bound water varies reflecting the change of higher order structure of matrix polymers [12].

It is reported that T_{ml} of PMEA is found to be constant regardless of W_c, in contrast T_{ml} of the cellulose group shifts to the high temperature side with increasing W_c [5,10]. The difference seems to come from the hydrophobicity of PMMA group. In contrast molecular relaxation of natural polymers is enhanced in the presence of water. We reported that inter-molecular hydrogen bonding of regenerated cellulose breaks at around RH = 50–60% and the higher-order structure changes through the molecular rearrangement which is observed by dynamic viscoelastic measurement, X-ray analysis and nuclear magnetic resonance spectrometry [25].

An example of the structural change of cellulose in the humid conditions is found in amorphous cellulose. It is known that cellulose is polymorph and that amorphous cellulose forms cellulose II type crystal in the presence of water [42]. Fig. 3 shows the crystallinity of amorphous cellulose kept in 100% relative humidity at 25 °C as a function of holding time. The calculated was calculated from wide angle X-ray diffractograms. Water plays a catalytic role in breaking and reforming intermolecular hydrogen bonding and crystalline region is gradually formed as a function of time. Structural change of water occurs simultaneously as shown in Fig. 4. W_b(=W_{nf} + W_{fb}) decreases with increasing holding time. In the initial stage of crystallization, W_{fb} is mainly excluded from the amorphous region, which is followed by a decrease of W_{nf}. Figs. 3 and 4 strongly indicate that the crystalline region is simultaneously formed when two types of bound waters are excluded. If we assume that non-freezing water is restrained only in amorphous region, ca. 3 H_2O molecules are restrained in a repeating unit of glucopyranose unit [10]. This suggests that one hydroxyl group in the amorphous region restrains 1 H_2O of non-freezing water molecule.

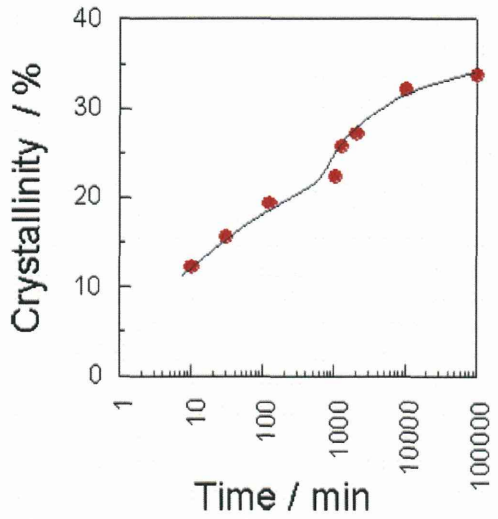

Fig. 3. Change of crystallinity of amorphous cellulose maintained at relative humidity 100% at 25 °C as a function of time.

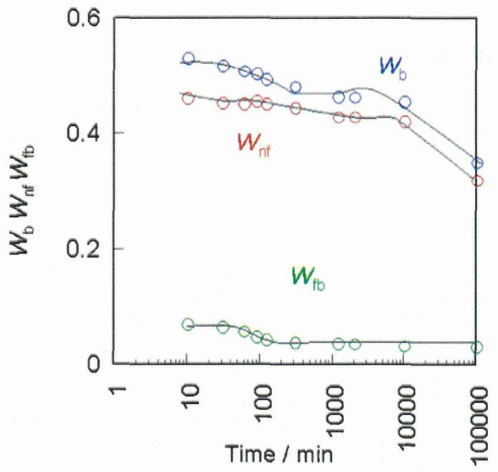

Fig. 4. Change of amount of non-freezing water (W_{nf}), freezing bound water (W_{fb}) and total amount of bound water (W_b) of amorphous cellulose maintained at 100% relative humidity at 25 °C as a function time.

The above results show that location of bound water varies according to the change of higher order structure of matrix polymer. Small angle neutron scattering shows the different type of water in amorphous or crystalline region of cellulose based on the Hosemann type para-crystalline concept. [43]

Characteristic features of freezing bound water are, (1) amorphous ice coexisting with polymer matrix crystallizes at temperature range of cold crystallization, (2) ice-melting temperature of freezing bound water is observed at a temperature lower than 0 °C, (3) ice-melting temperature of freezing bound water depends on chemical structure of matrix polymer and also its higher order structure, (4) the crystalline structure of the freezing bound water is categorized to be hexagonal, and (5) the freezing bound water is in unequilibrium state and the amount depends on both a time and a temperature range where the samples are maintained.

4. Conclusions

The present stage of identification of water restrained by hydrophilic polymers is summarized as follows. The amount of non-freezing water can be obtained by calorimetry. XRD-DSC simultaneous measurement confirms that non-freezing water is in amorphous state. Spectrometry is useful to investigate molec-

ular conformation in the initial stage of water sorption on the surface of polymers. Kinetic data can also be obtained by spectroscopic results. By NMR relaxation measurement, relaxation time of sorbed water is obtained. By viscoelastic measurement, non-freezing water is indirectly observed as temperature shift of main chain motion.

DSC is the most useful tool to investigate freezing bound water which is in a non-equilibrium state, accordingly, well-defined conditions controlling the temperature and time are crucial factors of the investigation. Reorganization of molecular chain reflects sensitively the amount of freezing bound water. Molecular relaxation of matrix polymer is also concerned with the amount of non-freezing water. The equilibration condition should be defined when bound water content is compared with each other. The following technical matters are also necessary for further investigation; melting peak of freezing bound water frequently merges with melting of free water, and peak separation of DSC is not theoretically ascertained, a certain error necessarily exist for the calculation of the amount of freezing bound water. According to the relaxation time of matrix polymers, the amount of freezing bound water is always accompanies a certain fluctuation. On this account, it is important to define the thermal history of the sample in a rigorous manner.

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