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Water absorption and states of water in semicrystalline poly(vinyl alcohol) films

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Thermal analysis of semicrystalline poly(vinyl alcohol) reveals the existence of up to three energetically distinct states of water within the polymer structure. Wide angle X-ray studies indicate that diffusion of water into semicrystalline samples of the polymer gradually destroys the crystalline regions of the polymer, although water is found to not inhabit intact crystallites. The nonfreezing water is responsible for the destruction of crystalline regions by a mechanism of disruption of intermolecular hydrogen bonds in the interface region between the crystalline and swollen amorphous regions. Water does not inhabit the polymer in clusters as freezable water until most of the inter and intra molecular hydrogen bonding has been disrupted by the nonfreezing water. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Differential scanning calorimetry (d.s.c.) has been used previously to obtain quantitative information about the states of water in water-swollen polymers[1-6]. Up to four energetically distinct states of water have been identified in some salt water swollen systems[6], although in systems swollen with pure water, the water usually exists in two or three separate states within the polymer, which can be defined as follows: *free water*, which undergoes similar thermal phase transitions to that of bulk water; *freezable bound water*, which undergoes a thermal phase transition at a temperature shifted with respect to that of bulk water, due to interactions with the polymer chains and/or capillary effects[3,6]; and *nonfreezing water* which is the bound water that does not exhibit a detectable phase transition over the range of temperatures normally associated with bulk water. Poly(vinyl alcohol) (PVA) has been shown[1-3] to contain all three of these separate states of water.

Some researchers[7-10] have claimed that water penetrates the amorphous regions of the polymer only and that the crystalline regions remain unaffected by water at room temperature, whereas other workers[11] have concluded from laser Raman spectroscopy investigations that the crystalline fractions in PVA are in fact affected by water addition.

PVA is usually prepared by hydrolysis of poly(vinyl acetate) (PVAc), where the acetate side groups are progressively replaced by hydroxyls. The structure of crystalline PVA has been determined by other workers[12-14] to be monoclinic. Bunn[13,14] proposed that the high crystallizability of PVA compared with that of the parent polymer, PVAc is due to the fact that the hydroxyl groups are of sufficiently small size to allow the chains to adopt a planar zig-zag conformation. Also, due to the similar radius of the hydroxyl and hydrogen units, Bunn[13,14] explained that stereoregularity has little effect on the crystallizability of PVA and its subsequent X-ray diffraction pattern. The high packing efficiency of the planar zig-zag conformation in crystalline aggregations, coupled with the presence of intermolecular hydrogen bonds between adjacent hydroxyl groups has been widely regarded as a reason for the likely insolubility of PVA crystallites. It has been claimed[11] however, that although the crystallites are, in all likelihood, more resistant to attack from water molecules because of the higher packing efficiency, they are not completely impervious to attack from water in excess quantities.

In earlier work[15], details of the molecular level interactions between PVA and water were reported, mostly relating to the amorphous region in the polymer. In order to fully understand the nature of the molecular interactions of the polymer with water, the influence of water on crystallinity must first be taken into account. Wide angle X-ray diffraction (WAXD) of the polymer samples was used to determine if any variation in crystalline content exists as a result of water addition to the polymer, in conjunction with d.s.c. studies performed on the samples to gather information about the states of water inhabiting semicrystalline film samples of PVA.

EXPERIMENTAL

Materials

The polymer used in the study was Elvanol grade HV

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poly(vinyl alcohol) (PVA) from DuPont chemicals. The material is derived from poly(vinyl acetate) (PVAc) by hydrolysis and is supplied in powder form. The DuPont data sheet states that the degree of hydrolysis for Elvanol HV is 99.8% (0.2% residual acetate groups), and the molecular weight is 105 600–110 000 (weight average). Because of the hydrophilic nature of the polymer, the unprocessed powder contains approximately 6.5 wt% water at ambient temperature[16].

Film preparation

Films were prepared by casting a 10 wt% aqueous solution (mechanically mixed at room temperature) of PVA onto a glass plate at 22°C, followed by conditioning at 22°C for 2 weeks at ambient humidity to allow for the water concentration to equilibrate. Samples were subsequently either dried under vacuum at 55°C to remove residual water or immersed in distilled water at 22°C for various times until samples with a variety of water contents were available for testing. A saturation level of approximately 60% water content was reached after approximately 12 h of immersion. Film thickness in the equilibrium state, i.e. with only residual water remaining, was 0.9 ± 0.1 mm. Surface water was removed from film samples by blotting with filter paper.

Experimental measurements

Sample water contents were determined by thermogravimetric analysis (t.g.a.) in continuous heating mode. The thermogravimetric analyser used was a Setaram CS-92 thermal analyzer with the sample maintained in an air atmosphere. Mass loss data were recorded for 30–35 mg samples from 25 to 220°C at a heating rate of 5°C min^{-1}.

Thermal properties were measured on a Perkin-Elmer DSC7 differential scanning calorimeter. Sub-ambient measurements were performed at atmospheric pressure with the differential scanning calorimeter head maintained in a nitrogen atmosphere in a dedicated dry box over the temperature range −40 to 15°C at heating/cooling rates of 5°C min^{-1} in sealed aluminium pans. Samples weighed between 7 and 12 mg. Calibration was performed with distilled water standards. Temperatures quoted are onset temperatures for the transition peaks in the d.s.c. traces.

Wide angle X-ray diffraction (WAXD) patterns were obtained in transmission using a Rigaku Geigerflex X-Ray Diffractometer with Ni filtered CuK$_\alpha$ radiation. Scattering curves were collected from isotropic thin films between $2\theta_B = 5°–80°$ at a scan rate of 2° min^{-1}.

RESULTS AND DISCUSSION

Figure 1 contains the WAXD spectra for samples with a range of water contents. The large peak at $2\theta_B = 19.5°$ corresponds to the (110) reflection, a plane which contains the extended planar zig-zag chain direction of the crystallites[12]. *Figure 1* illustrates that the intensity of the (110) reflection decreases rapidly in response to water addition, virtually disappearing by the time total water content has reached 46%, while the overall intensity of the amorphous halo increases over the same range of water contents. The decrease in intensity of the (110) crystalline reflections and corresponding increase in diffuse intensity clearly indicate that the crystalline fraction decreases as a result of water addition. This interpretation is consistent with the results reported[11] from laser Raman spectroscopy experiments, indicating that water does indeed dissolve PVA crystallites at ambient temperature.

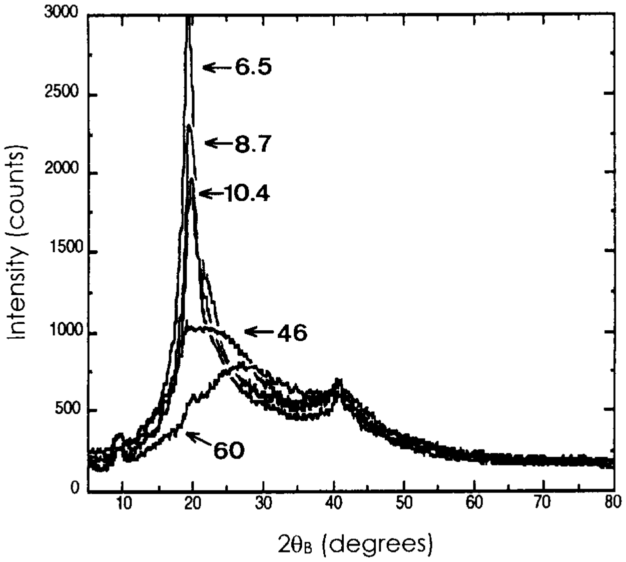

Figure 1 WAXD spectra of water-swollen PVA films. Numbers indicate film water content in wt%. Scanning rate = 2° min^{-1}

The crystalline fractions in the samples were estimated from the ratio of the integrated intensity of peaks associated with crystalline reflections to the total integrated area of the spectrum, i.e.

$$X_C = I_C/I_T \qquad (1)$$

where X_C is the crystalline fraction, and I_T and I_C are the total and crystalline integrated intensities, respectively. Although it is recognized that equation (1) represents a simplification of the true nature of the crystalline variation and does not account for the differences in scattering efficiency of the crystalline and amorphous regions, the simplification is made necessary because of the presence of water in the amorphous region. The classical two-phase method of crystallinity determination described by Alexander[17] assumes a linear relationship between crystalline and amorphous intensities in the samples. The addition of water to the system renders such a treatment inaccurate however, as water has been shown[15] to alter the nature of the amorphous region in a manner specific to the amount and state of water present at any given time, making rigorous calculation of the degree of crystallinity difficult. The computational complexity involved in the X-ray determination of crystallinity in water swollen samples of PVA was recognized by Iwamoto *et al.*[11] who noted that the assumption of the contributions to X-ray scattering intensity of water, amorphous region and crystalline being additive is an oversimplification and 'open to question'.

The variation in the degree of crystallinity of the samples calculated using equation (1) and the data from *Figure 1* is shown in *Figure 2*. This clearly indicates that water dissolves crystallites when present in excess quantities. The angular position of the (110) reflection—and thus the spacing of the planar zig-zag chains—is unaltered by water addition, indicating that the crystallites are not swollen by the diffusing solvent, but dissolve gradually, with a decreasing amount of intact crystalline

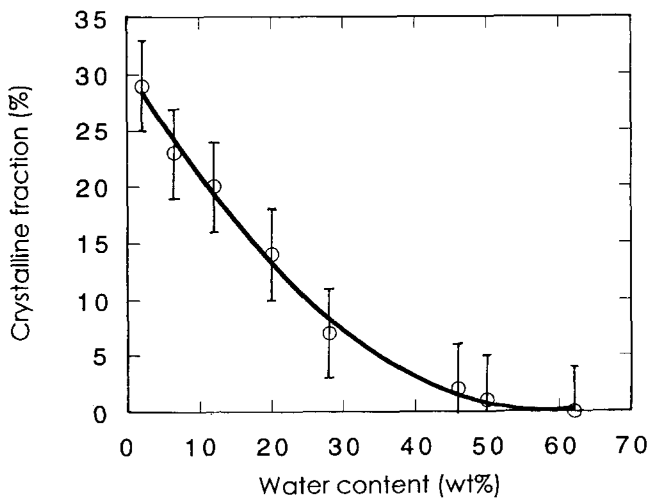

Figure 2 Variation in crystalline fraction with water content for water swollen PVA films

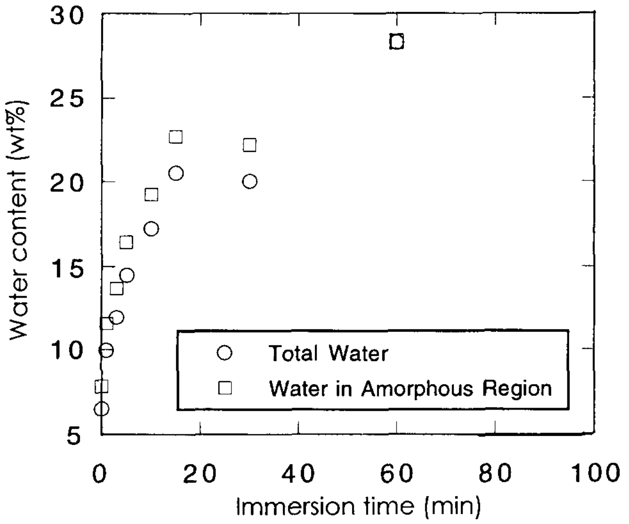

Figure 3 Comparison in water uptake characteristics for water swollen PVA film

region remaining as water molecules diffuse down the concentration gradient through the swollen amorphous region to the newly dissolved, prior crystalline regions.

Using the relationship illustrated in *Figure 2*, the total amount of water absorbed into PVA samples can be corrected for crystallinity using equation (2), namely

$$W_A = W_T(1 - X_C) \qquad (2)$$

where W_A and W_T are the water contents of the amorphous region and whole sample, respectively. The simplest example of the results of this correction is shown in *Figure 3*, which compares the water absorption characteristics of a typical PVA thin film sample with and without the application of the correction described in equation (2). Note that for high water contents, the total water content approaches that of the water contained in the amorphous region, as crystallites are dissolved and the sample becomes totally swollen, tending towards 100% amorphous content. This correction therefore accounts not only for the fact that water occupies only the amorphous region, but that it progressively destroys crystallites, increasing the amount of amorphous region present in the samples.

The data contained in this investigation support the conclusion that water inhabits only the amorphous regions of the polymer, but also destroys crystallinity, presumably by attacking crystallites at the crystalline/amorphous interface. At this interfacial region, the chain configuration is in transition between the tightly packed planar zig-zag, where access to the hydroxyl groups is restricted, and the swollen amorphous region, where more free volume is available and the water molecules encounter less resistance to diffusion. The driving force for the diffusion of water molecules is provided by the concentration gradient between the amorphous region, where there are few available hydroxyl groups, and the newly dissolved transition region at the surface of the crystallites, where more potential bonding sites exist for the diffusing water molecules. As the water molecules penetrate the transitional region at the interface between crystallite and amorphous region, the structure is forced open by the water molecules disrupting intermolecular hydrogen bonds and attaching themselves to the available hydroxyl groups. This would cause the associated planar zig-zag to collapse into an amorphous structure as the effective size of the side groups including water is too great for the chains to maintain the high-efficiency planar zig-zag conformation. As a result, fresh areas of the crystallites are exposed to attack from the water molecules, and the crystalline regions are progressively dissolved.

The above interpretation is consistent with the contentions of Iwamoto *et al.*[11], who concluded that water destroys crystallinity in PVA, but also with those of other workers[7–10] who have claimed that water inhabits only the amorphous regions in PVA. When interpreting the data however, it is important to make a

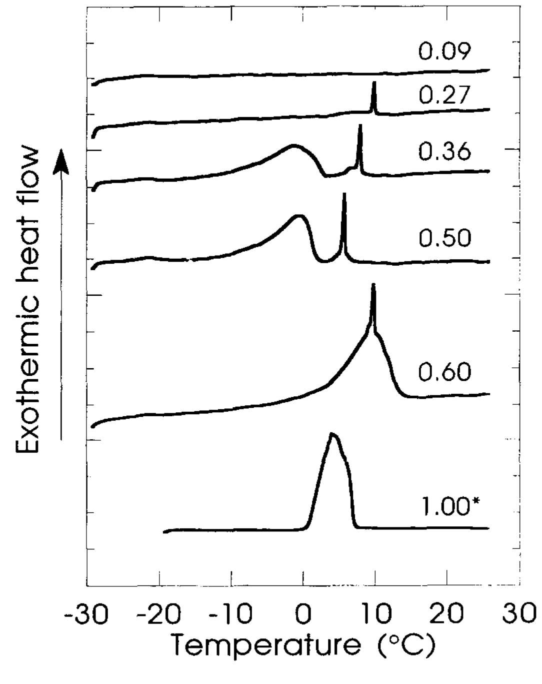

Figure 4 D.s.c. heating thermograms for water swollen PVA films. Numbers indicate the mass fraction of water in the amorphous region. *The vertical scale of the pure water trace has been reduced for clarity. Scanning rate = 5° min^{-1}

clear distinction between water not inhabiting crystallites, and not affecting crystallinity. Although water has been clearly shown in this investigation to destroy crystallinity in PVA, the data also indicate that in the intermediate stages of water absorption where some crystallinity remains, the remaining intact crystallites do not contain any water themselves, but instead are dissolved gradually by attack at the surface by water molecules.

The curves representing d.s.c. heating traces are shown in *Figure 4*. No peaks are evident in the d.s.c. heating traces until the water content in the amorphous region has reached approximately 22%, above which a single, narrow peak appears. This peak increases in size until the water content in the amorphous region has reached approximately 28%, and remains constant for higher water content. Additionally, at approximately 28% water in the amorphous region, a second, broad peak appears in the heating traces. The size of this peak does not reach a maximum, but increases monotonically until the room temperature saturation level of ~60% water content is reached. The general form of these curves is qualitatively similar to that reported for PVA by other workers[1–3]. A similar notation to that of Higuchi and Iijima[1] will be used to identify the two peaks observed in *Figure 4*. The first peak to appear will be denoted peak 1^{h}, and the second (broad) peak will be denoted peak 2^{h}.

Figure 5 shows the corresponding cooling traces for the water swollen PVA thin films. In this case, the higher temperature (narrow) peak is denoted peak 1^{c} and the lower temperature (broad) peak as peak 2^{c}. The trends closely follow those described for the heating traces in *Figure 4*, although the threshold water contents for the appearance of each peak varies slightly from those of the heating data. The onset temperature of the second peak (peak 2^{c}) ranges between −25° and −19°C, compared with the freezing onset temperature of the distilled water calibration sample of −21°C.

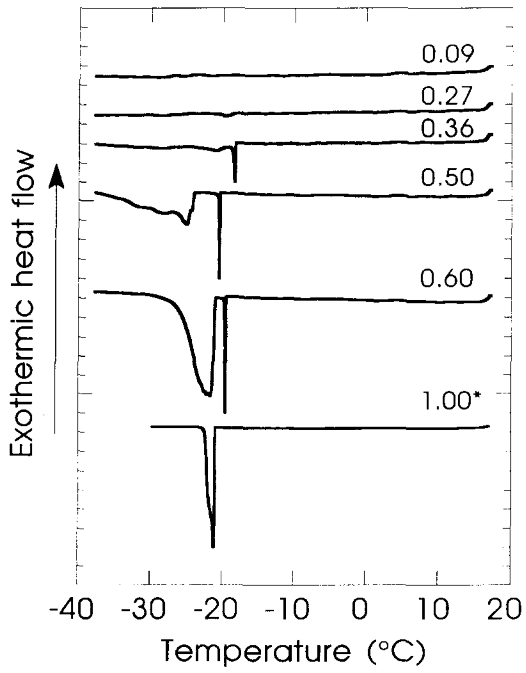

Figure 5 D.s.c. cooling thermograms for water swollen PVA films. Numbers indicate the mass fraction of water in the amorphous region. *The vertical scale of the pure water trace has been reduced for clarity. Scanning rate = 5° min^{-1}

The onset temperature for the phase transition associated with peak 2^{h} varies between −8 and 0°C, which compares to that of the pure water internal calibration value of 0°C. The similarity of the phase transitions observed for peak 2^{h} and pure water indicate that peak 2^{h} is associated with the melting transition of free water within the samples. In addition, the magnitude of peak 2^{h} does not reach a plateau, but increases in height in proportion to the amount of water progressively added to the system, further confirming this association. Peak 1^{h} can therefore be ascribed to phase transitions occurring in water clusters that are influenced by interactions with the macromolecular chains. The narrow temperature range over which this transition occurs in each sample suggests that it is associated with molecules in a correspondingly narrow range of environments within the polymer and thus a well defined range of energetic states. Such a narrow range would be expected to occur in water molecule clusters closely associated with the hydroxyl side groups. These clusters are proposed to be of sufficient size to form a crystalline array, yet not be sufficiently large to escape the influence of the binding environment associated with the hydroxyl side groups. This influence explains the difference in the positions of peak 1^{h} and peak 2^{h}, along with the narrow temperature range over which peak 1^{h} occurs.

The broad temperature range over which peak 2^{h} is observed is believed to arise from the fact that the free water occupies available free space in the polymer, in the form of voids and free volume with a range of sizes, as discussed elsewhere[15], and therefore freezes into crystals with a corresponding range of sizes and melting temperatures, due to surface energy effects.

The amount of each state of freezable water may be calculated from the melting traces by using equation (3)

$$W_i^{\mathrm{h}} = 100\left(\frac{Q_i^{\mathrm{h}}}{\Delta H_{\mathrm{f}}^{\mathrm{h}}}\right) \qquad (3)$$

where W_i^{h} is the weight percent of each state of water calculated from the individual peaks (i.e. $i = 1$ or 2), Q_i^{h} is the measured heat of transition of each peak, and $\Delta H_{\mathrm{f}}^{\mathrm{h}}$ is the enthalpy of the ice–water transition ($\Delta H_{\mathrm{f}}^{\mathrm{h}} = 293.6\,\mathrm{J\,g^{-1}}$ for 100% water, experimentally determined in this work). The amount of nonfreezing water may be calculated by subtracting the total amount of freezing water from the total water content according to the equation

$$W_{\mathrm{nf}}^{\mathrm{h}} = W_{\mathrm{T}} - (W_{\mathrm{f}} + W_{\mathrm{fb}}) = W_{\mathrm{T}} - \sum_{i=1}^{2}\left(\frac{100Q_i^{\mathrm{h}}}{\Delta H_{\mathrm{f}}^{\mathrm{h}}}\right) \qquad (4)$$

where $W_{\mathrm{nf}}^{\mathrm{h}}$, W_{fb} and W_{f} are the nonfreezing, freezable bound and free components, respectively, of the water in wt%, and W_{T} is the total water content, as determined by t.g.a. The calculated proportions of the bound states of water are limited in their accuracy by the assumption that the heat of fusion for the water–ice transition is identical for each state of freezable water. Since each state of water is, by definition, in a different bonding environment, it is reasonable to expect that the heats of fusion for each state would in fact be different. This issue has previously been addressed at some length[1] by applying a series of empirical corrections to data collected for samples with water contents below 46%, where corrections are necessary as transitions occurred in their investigation below 250 K—where the heat capacities of the different states of water differ significantly—over this range of water contents. In the current investigation, all transitions occurred at temperatures in excess of 250 K, and so no corrections will be applied to the data and ΔH_f will be assumed to be constant for each state of water in the data calculated from equations (3) and (4).

The data represented in *Figure 6* show the amount of each state of water calculated from equations (3) and (4) at various stages of water absorption. *Figure 6* shows that for total water contents less than 22%, all the water is completely contained in the polymer as nonfreezing water. Above this total water content a constant, maximum value of nonfreezing water is reached, and freezable bound water appears, increasing rapidly before plateauing at a value of about 2.5% by mass. At around 27% total water content, free water appears in the polymer, increasing in a linear fashion up to the saturation level of about 60% total water.

The fact that the amounts of freezable bound and nonfreezing water states reach constant maximum values is an indication that there are a finite number of available binding sites to which water molecules may attach themselves, which can be explained by the finite number of hydroxyl side groups in the polymer. Based on the simple assumption that a single water molecule attaches itself to every hydroxyl side group in the polymer as nonfreezing water (i.e. one water molecule for every monomer unit), the expected level at which site saturation would be achieved (i.e. the maximum possible amount of nonfreezing water) is 29 wt%. This of course assumes that only a single water molecule attaches itself to each hydroxyl group, and that all such possible attachments are achieved before subsequent molecules attach themselves as freezable bound water. In reality, some overlap between the point at which hydroxyl site saturation occurs and the onset of the appearance of freezable bound water would be expected.

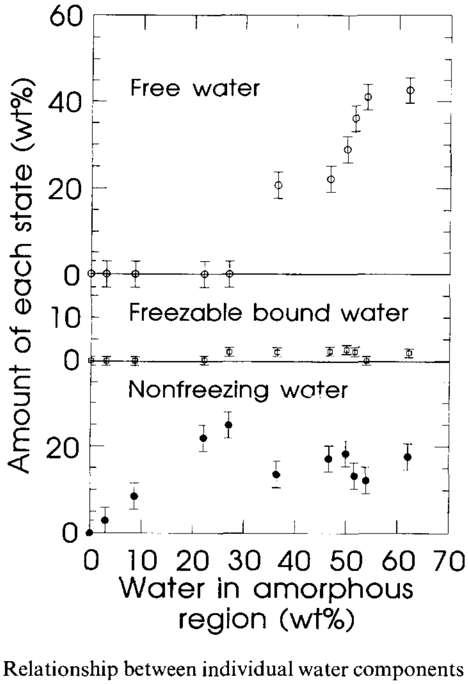

Figure 6 Relationship between individual water components and total water content in amorphous region of water swollen PVA films determined from heating (melting) d.s.c. traces

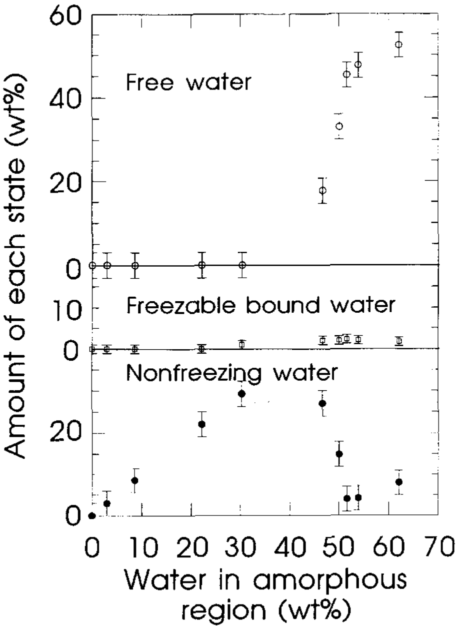

Figure 7 Relationship between individual water components and total water content in amorphous region of water swollen PVA films determined from cooling (freezing) d.s.c. traces

Figure 7 shows the amount of each state of water calculated from the cooling d.s.c. traces (equivalent to the data represented in *Figure 6*). The trends shown in *Figure 7* are similar to those contained in *Figure 6*, although the threshold moisture content for the appearance of each state of water is slightly higher. Similar discrepancies in the amount of water calculated from exothermic and endothermic enthalpies have been previously observed and discussed elsewhere[1]. Once again, no transition peaks are evident in the initial stages of water absorption, before a single peak—denoted peak 1^c—appears, defined over a narrow temperature range. Peak 1^c increases in magnitude with water addition until the total water content has reached approximately 32%, at which point its magnitude reaches an approximately constant value and peak 2^c appears, defined over a wider temperature range and occurring at lower temperatures than peak 1^c. Peak 2^c increases continuously in magnitude over all subsequent water contents. As with the heating traces, the first peak is assigned to freezable bound water and the second, broad peak is assigned to free water. Using equations (3) and (4), but substituting cooling components for the respective heating components, the amount of each state of water observed (or deduced in the case of nonfreezing water) can be calculated and presented in similar manner to *Figure 6*. The results are shown in *Figure 7* which presents the amounts of each state of water calculated from the freezing traces at various stages of water absorption. In this case, ΔH_f was taken as 219.1 J g^{-1} (enthalpy of fusion for the water–ice transition, experimentally determined in this work from pure water).

The data contained in *Figure 7* reveal similar trends for the cooling components of free water and freezable bound water to those for the heating traces. The nonfreezing water component is seen to initially increase in magnitude in the early stages of water absorption before reaching a maximum of approximately 30%, thereafter decreasing steadily for subsequent water addition. This decreasing trend at higher water contents seems at odds with the contention that a fixed and finite amount of water—related to the number of hydroxyl groups in the polymer available to act as binding sites for the water molecules—would be expected to remain in the polymer as nonfreezing water.

The form of the free and nonfreezing water curves in *Figure 7* implies, with increasing amounts of free water, that the free water causes the water molecules previously in the highly bound nonfreezing state to change state to free water (indicated by progressively less nonfreezing water being evident at higher total water content). The reason for such a transfer in state is not readily apparent, and the situation is further complicated by the observation that the water molecules have apparently re-distributed, as shown in *Figure 6* (which contains data from the melting curves, which were recorded following the cooling curves), to a stage where the amount of nonfreezing water is approximately constant and unaffected by the free water content. This effect is not observed in the results from heating scans shown in *Figure 6*.

In addition to the differences in heat evolved during cooling and that absorbed during heating, some workers[18–20] have shown that the properties and characteristics of water-swollen PVA films such as water retention and the position of phase transition temperatures in d.s.c. traces are sensitive to the order and number of melting/freezing cycles. These effects, along with the fact that the freezing point of water in the samples in this investigation is measured under non-equilibrium conditions—with significant supercooling—may account for the observed differences between the position of the transition temperatures in the melting and freezing traces shown in *Figures 6* and *7*.

Consideration of the transition temperatures in both sets of curves reveals a systematic shift to lower temperatures with increasing water content in all peaks except the saturation level (60% water) samples, which indicate a shift to higher temperatures relative to the previous curve. The systematic downward shift in temperature was also observed by other workers[1], and probably arises from freezing point depression due to interactions between the water molecules and polymer chains. The seemingly anomalous shift to higher temperature in the saturated samples is believed to occur because when the water aggregations have grown to a sufficient size so that volumetric effects dominate over interfacial effects between the water aggregations and the macromolecular structure, the number of water molecules in the aggregation that undergo interaction with the macromolecules becomes small compared with the number contained in the bulk of the aggregation which experience no such interaction and instead behave essentially as bulk water. The tendency towards bulk-like behaviour therefore predominates over effects arising from interactions with the surface of the clusters when the water aggregations are sufficiently large, and the associated phase transition shifts towards that of bulk water.

This investigation indicates that water molecules diffuse initially through the amorphous region of the polymer and attach themselves to hydroxyl side groups, disrupting inter and intra molecular hydrogen bonding, and swelling the polymer. In the initial stages of water absorption, the water molecules are directly attached one each to the hydroxyl side groups and do not possess sufficient structural order to undergo a thermal phase transition. Such molecules are contained in the polymer as nonfreezing water. Subsequent diffusion results in a small amount of water molecules consolidating themselves in aggregations with sufficient structural order that they undergo a thermal phase transition, yet still small enough as to be influenced by interactions with the polymer macromolecules, and the resulting phase transition of these aggregations is shifted with respect to that of bulk water. In the latter stages of water absorption, water enters the polymer and exists within the polymer structure as free water, which is presumably located in free volume within the polymer. The action of water molecules attaching to the hydroxyl groups on the macromolecules destroys crystallinity by forcing the chains to change configuration from the crystalline planar zig-zag into an amorphous configuration in order to accommodate the effective increase in size of the side group, and because of the destruction of hydrogen bonding in the system which acts to hold the chains together in a tight, crystalline array.

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