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Thermal analysis of the water uptake by hydrocolloids

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Abstract

Water uptakes by the hydrocolloids gelatin, pectin and sodium carboxymethylcellulose (NaCMC) and their mixtures, following storage at 20°C and 93% relative humidity (RH), were investigated using differential scanning calorimetry. An increase in water uptake was observed for each sample on storage. The majority of the moisture sorption occurred in the initial 2 h. Only non-freezable, bound water was present in gelatin, pectin and gelatin/pectin or NaCMC/pectin/gelatin mixtures during storage for 28 h. Loosely bound freezable and non-freezable, bound water were detected in NaCMC stored for 2 h. Water in mixtures of NaCMC/gelatin or NaCMC/pectin was predominately loosely bound freezable and non-freezable bound. The order of water uptake was gelatin<pectin/gelatin<pectin<NaCMC/pectin/gelatin<NaCMC/gelatin<NaCMC/pectin<NaCMC. © 1998 Elsevier Science B.V.

Keywords: Bound water; DSC; Free water; Gelatin; Hydrocolloids; Pectin; Sodium carboxymethylcellulose; Water uptake

1. Introduction

Gelatin, pectin and sodium carboxymethylcellulose (NaCMC) are examples of hydrocolloids and are integral components of occlusive wound dressings, hydrocolloid gels and ostomy products because of their hygroscopicity. In these preparations, the hydrocolloids are contained within a hydrophobic polymeric matrix. The mode and characterisation of their water absorption are vital to an understanding of the mechanisms by which these products promote wound healing, treat skin disorders and maintain the area surrounding a stoma moisture-free and, consequently, infection-free [1–3].

A variety of hydration techniques, ranging from direct contact between dressing and liquid water to maintaining the dressing in water vapour, has been used to evaluate the water uptakes of hydrocolloid dressings [4,5]. Differential scanning calorimetry (DSC) has been used to confirm the presence of freezable water in a hydrated hydrocolloid dressing [6]. However, the mode and nature of water sorption by hydrocolloids, their blends and simple mixtures of components of such dressings have not been studied.

Water sorption to polymers has been extensively reported. Three types of associated water, namely tightly bound (non-freezing), loosely bound or interfacial (bound freezing) and unbound (freezing), have been reported using thermal and spectroscopic tech-

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niques [7–11]. Eq. (1) may be used to calculate the total bound water (W_b) as follows;

$$W_t = W_f + W_b \quad (1)$$

where W_t is the total water content, and W_f the free (unbound) water. W_b is the sum of non-freezable (W_{nf}) and freezable bound (W_{fb}) water. W_t is evaluated using differential thermal analysis (DTA) or DSC vaporisation curves, W_f and W_b may be estimated using thermal gravimetric analysis (TGA) [12]. The crystallisation peaks corresponding to freezing water (W_f) have been measured by DSC.

Bound water in polymers and polymer complexes was analyzed quantitatively by DSC [12]. A shift in melting temperature may be related to the strength of binding of water molecules to polymer chains. The melting temperature increased with increasing water contents. The bound water was classified into type I (non-freezing with melting temperature below −50°C and for which a melting endotherm was not detected) type II (bound water with a melting point between −50° and 0°C) and type III (bound water with variable melting temperature) [12]. The heat of fusion was constant for bound water with melting temperature between −50° and 0°C. The amount of type I bound water was obtained by extrapolation of the plot of overall heat of fusion and R (weight of water/g÷weight of dry polymer/g) to zero enthalpy.

DSC, in conjunction with pulsed NMR spectroscopy, was used [7,9] to demonstrate different states of water in polyvinylalcohol, poly-(2-hydroxyethylmethacrylate) and poly-(2,3-dihydroxypropylmethylacrylate). Reduced mobility of the water molecules was due to structured ordering of water with the hydrogel matrix. The spin–spin relaxation times, T_2, of water protons were determined and for polymers containing up to 25% w/w water were constant. The T_2 values increased with further increase in water content. This was related to the presence of free and freezable bound water. The results concurred with thermal analysis data confirming the existence of three water phases in the polymers.

The aim of this study was to investigate the water uptake and to characterise the types of water present in single components and in blends of hydrocolloids stored under high relative humidity (93% RH and 20°C). DSC and gravimetry were used to examine the water uptakes.

2. Experimental

2.1. Materials

Throughout this study one batch of each hydrocolloid was used. Citrus pectin (Batch 73173) was used as supplied by Hercules, Lille Skensved, Denmark. The methoxy group content was 9.6%, it had a galacturonic acid content of 91% and a sugar and organic acid content of 10 mg per 125 mg polymer. Porcine gelatin type A (Batch OV321-1) was supplied by Hormel, New Jersey, USA. It had a Bloom strength of 250 g. Sodium carboxymethylcellulose (NaCMC) type 7H3SXF (Batch 46320 6641) (Aqualon Blanose, Salford, UK) was used.

2.2. Gravimetric analysis

Quantities (≈0.5 g) of each of the hydrocolloids, were accurately weighed into pre-tared dried 55 mm pyrex petri-dishes and placed in a vacuum oven (Gallenkamp, Fisons, Loughborough). The dishes were partially covered with lids to allow water vapour to escape and be absorbed by the desiccant. The samples were re-weighed at 2 h intervals or until no further weight loss was observed. The water contents (% w/w), i.e. 'loss on drying,' were calculated using Eq. (2)

$$\text{Water loss } (\%\ \text{w/w}) = \{(a - b) \times 100\} \div a \quad (2)$$

where a is the initial weight of sample (g) and b the weight of sample (g) post-water loss.

Additionally, a similar method was used to determine water sorption (water uptake) by materials. The samples under examination were weighed pre- and post-storage at 93% RH and 20°C after pre-determined times and the water uptakes were determined by Eq. (3)

$$\text{Water uptake } (\%\ \text{w/w}) = \{(c - b) \times 100\} \div b \quad (3)$$

where b is the 'dry' sample weight (g) pre-storage, i.e. moisture free, and c the weight of sample (g) post-storage.

2.3. Karl Fischer coulometric titration analysis

A hyphenated Karl Fischer technique was used to determine the water contents of the hydrocolloids. The

Karl Fischer titrator was linked to an oven to desorb the water and the water vapour was transferred into the reaction chamber using a continuous flow of nitrogen.

2.4. Determination of water contents by thermal desorption and Karl Fischer titration

Accurately weighed samples, 50 mg of each hydrocolloid, were weighed into metal sample boats (Metrhom, V.A. Howe, Banbury, UK) which were placed into a 688 KF oven (Metrhom, V.A. Howe, Banbury, UK) set at 150°C and purged with dry nitrogen at 50 ml/min. The 688 KF oven was linked to a 684 coulometer (Metrhom, V.A. Howe, Banbury, UK), 649 stirrer/703 Ti stand (Metrhom, V.A. Howe, Banbury, UK) and an Epson P 40 printer. The water contents (% w/w) of the hydrocolloids were calculated as a percent ratio of the initial sample weights using Eq. (4)

$$\%\,\text{w/w water content of hydrocolloids} = [W_\text{d} \div (W_\text{s} \times 1000)] \times 100 \quad (4)$$

where W_d is the weight of water content (μg) of the sample determined by Karl Fischer methods and W_s the weight of sample (mg).

2.5. Determination of water contents by differential scanning calorimetry

Each sample (3–5 mg) was accurately weighed into an aluminium DSC sample pan (40 μl, Mettler, Leicester, UK). The pan was sealed with a pin-holed lid and the sample was analysed, using a Mettler DSC 30, calibrated with indium, in conjunction with a Mettler TC 11 TA processor (Mettler, Leicester, UK), initially by a cooling scan followed by a heating scan. The cooling scan, from 30° to −85°C at 10°C/min, was linked to a heating scan from −85° to 280°C at 10°C/min. The DSC cell was purged with nitrogen gas at 100 ml/min. Mettler graphware, TA72PS.2 version of the soft-ware package, was used to evaluate the data.

Both exothermic and endothermic transitions were expressed as % w/w water with respect to 'dry' weight sample, determined using Eq. (5);

$$\%\,\text{w/w water by DSC} = (A \times 100) \div (B \times C) \quad (5)$$

where A is the integrated enthalpy under the curve (mJ), B the 'dry' sample weight taken (g) and C the specific enthalpy for the respective transition, i.e. 334 J/g for freezing and melting and 2260 J/g for the vaporisation transitions of water [13].

2.6. Water uptakes by the hydrocolloids

Samples, ≈5 mg of gelatin, pectin or NaCMC or their 1 : 1 or 1 : 1 : 1 mixtures, were accurately weighed into pre-weighed aluminium DSC pans and placed in pre-equilibrated humidity desiccators at 93% RH and 20°C which was generated at 20°C in a closed clear perspex desiccator cabinet (350 mm width, 345 mm depth, 380 mm height, Fisons, Loughborough, UK) using a saturated potassium nitrate solution. The saturated solution was prepared in plastic trays (300 mm×150 mm×50 mm deep) which were placed in the cabinets. The temperature and RH were monitored using a hand-held portable hygrometer (6000 Testoterm, Fisons, Loughborough, UK). Sample pans were removed, after 2, 3, 4, 6.5 and 28 h, re-weighed to determine moisture sorption gravimetrically, then sealed with a pin-hole in the lid and evaluated for water content and the nature of water present by DSC.

3. Results and discussion

In this study:-

1. *Unbound water* refers to *free water* which froze at the same temperature as water samples similarly treated (ca. −22°C at the cooling rate used in this study).
2. *Bound freezable water* refers to water which appeared to crystallise on cooling at <−30°C and was therefore assumed to be *loosely bound water.*
3. *Bound water* was not detected but its presence was assumed because the enthalpies corresponding to freezing water, both unbound or loosely bound, were less than anticipated from the water uptake determined from the volatilization endotherm in the heating curves.
4. The volatilisation endotherms of the heating curves were assumed to represent the total water. The melting endotherm at −10° to 0°C corresponded to water which had recrystallised during the DSC treatment, and was probably the sum of free water and loosely bound water.

5. Water uptakes were calculated as % w/w on the basis of 'dry polymer' weights.
6. Single data points were determined for each sample due to the long storage periods.

3.1. Initial water contents of hydrocolloids

A good correlation was obtained between the initial water contents of the hydrocolloids determined by gravimetric and Karl Fischer methods. The initial water contents of gelatin, pectin and NaCMC were 9.1, 10.9 and 13.8% w/w by gravimetry. Their respective Karl Fischer values were 10.4, 13.3, and 14.3% w/w. The initial water contents were converted to the 'dry weight' values using Eq. (4) and were calculated as 10.0, 12.2 and 16.0% w/w for gelatin, pectin and NaCMC. These 'dry polymer weights' were used to determine the water uptakes by the hydrocolloids.

3.2. Sodium carboxymethylcellulose

A single transition was detected in the DSC cooling scans of NaCMC stored for 3, 4, 6.5 or 28 h (Fig. 1(a)). This was due to the crystallisation of bound freezable water and was detected at ca. −55°C in the samples stored for 3 and 4 h. A gradual movement of the exothermic transition peak to higher temperature at ≈1°C/h, was observed with increased storage time and water content (Table 1). Similar shifts in exothermic peak temperatures were reported in DSC studies on the bound water of cellulose, polyhydroxystyrenes and aqueous solutions of polyelectrolytes [8,14–18]. An increase in the enthalpy of the exothermic transition, with a corresponding shift in the transition peak temperature due to increasing amounts of freezable water, on cooling NaCMC water samples has been reported [16].

In the DSC heating scans, an exothermic transition followed by two endothermic transitions were detected in samples stored from 2 to 28 h (Fig. 1(b)). The exothermic transition was possibly due to the crystallisation of a fraction of water that exist as compartmentalised and/or was trapped water within the network of the material [19,20]. This type of water did not crystallise as the samples were initially cooled from 30° to −85°C. Crystallisation of compartmentalised water during the rewarming of samples is referred to as 'cold crystallisation' [19,20]. Cold crystallisation occurred with peak temperatures between −33° and −23°C (Fig. 1(b)). An increase in the peak transition temperature of cold crystallisation occurred with an increase in water uptake and on prolonged storage (Table 2). The cold crystallised water content was 3–6% w/w for NaCMC stored for 28 h.

The second and third transitions in the heating scans were endotherms corresponding to the melting of the crystallised water and the vaporisation of the total water, respectively. An increase in the peak transition temperature for the melting endotherm of crystallised water was seen with an increase in water content (Table 1 and Fig. 1(c)).

The level of freezable water detected in NaCMC, determined by the enthalpy of the endotherm for the melting of water, increased with an increase in total water uptake and prolonged storage. Differences were detected between the quantity of crystallised water in the cooling scans compared to the corresponding melt of crystallised water (Fig. 2). The enthalpies of the crystal-

Table 1
Evaluation by DSC of water uptake by NaCMC samples stored for 2 to 28 h

Storage in h	Exothermic transitions on cooling stored samples		Exothermic/Endothermic transitions on heating stored samples		
	Peak temperature of crystallisation of water in °C	% w/w crystallised water	Peak temperature of crystallisation of water in °C	% w/w of crystallised water	% w/w total water uptake
2	ND	ND	−12.6	6.4	63.6
2	ND	ND	−11.9	8.1	65.7
3	−54.5	2.4	−9.2	14.7	73.5
4	−53.9	2.9	−9.0	15.4	75.4
6.5	−52.3	4.9	−8.1	18.2	84.9
28	−32.4	21.8	−5.7	32.4	96.3

ND – Not detected.

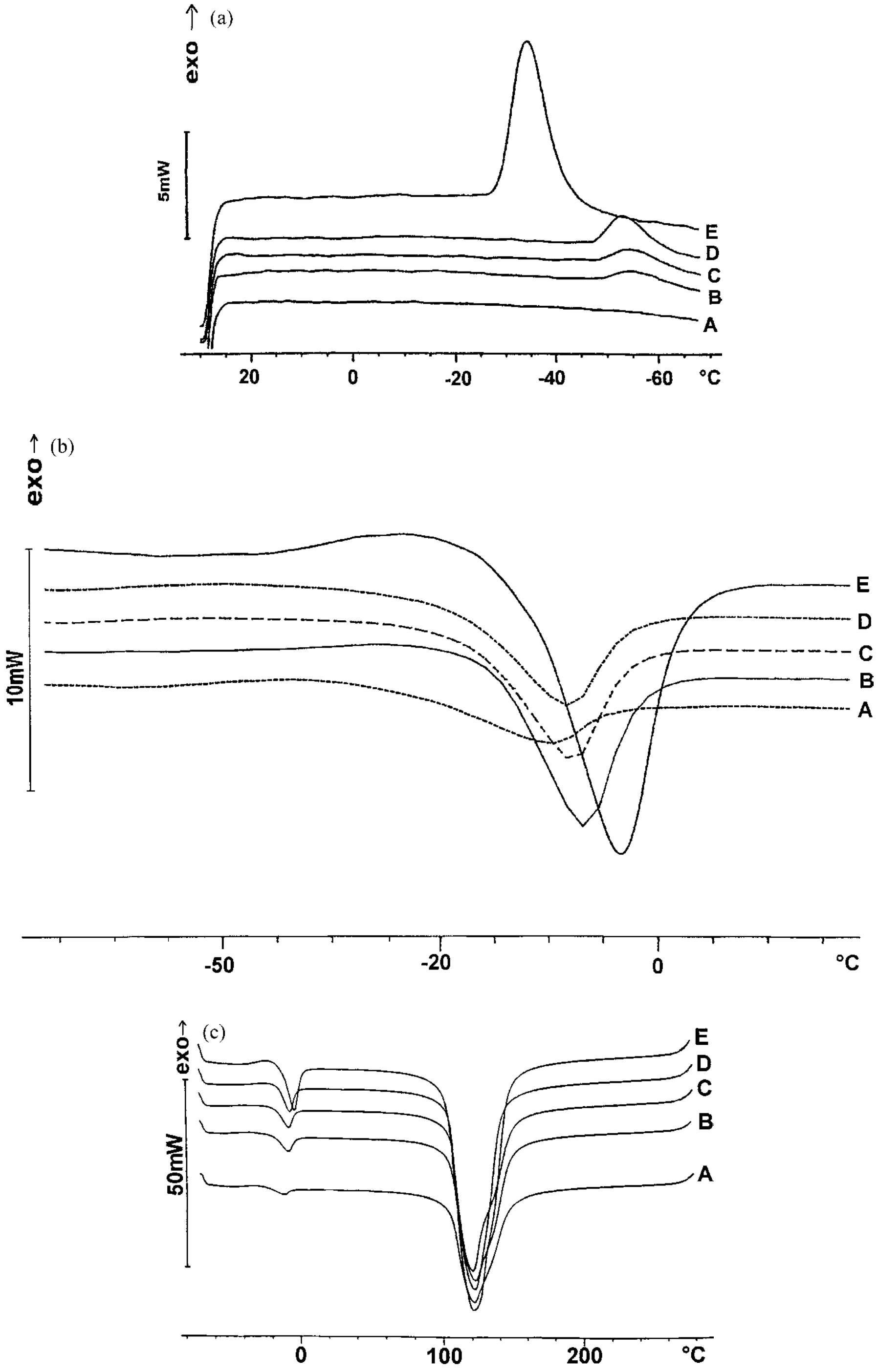

Fig. 1. (a) DSC cooling curves of sodium carboxymethylcellulose samples stored for: A, 2 h; B, 3 h; C, 4 h; D, 6.5 h; E, 28 h. (b) DSC heating curves of sodium carboxymethylcellulose showing cold crystallised water. Key as Fig. 1(a). Curves are expansions of Fig. 1(c). (c) DSC heating curves of sodium carboxymethylcellulose samples. Key as Fig. 1(a).

Table 2
Cold crystallisation of water observed in the heating curves of samples of NaCMC and its 1 : 1 and 1 : 1 : 1 blends with pectin and gelatin stored for 2 to 28 h. Temperature in°C corresponds to peak temperature

Storage time in h	NaCMC		NaCMC : gelatin		NaCMC : pectin		NaCMC : pectin : gelatin	
	°C	% w/w	°C	% w/w	°C	% w/w	°C	% w/w
2	−34.3, −34.7	3.0, 4.5	−35.7	0.6	−31.3	1.3	−31.7	1.0
3	−33.0	4.3	−30.0, −36.6	1.2, 3.3	−34.3	1.3	−30.9	1.0
4	−34.3	5.9	−36.5	1.0	−32.8	0.7	−32.7	1.3
6.5	−23.2	4.3	−38.1	3.4	−31.3, −33.0	2.3, 2.0	−33.5	ND
28	−23.1	5.3	−28.5	4.1	−28.5	4.8	−32.2	2.1

ND: Not determined

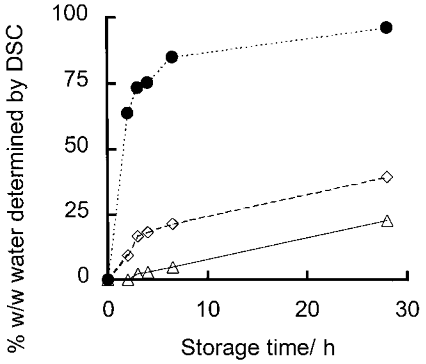

Fig. 2. Total water uptakes and bound freezable water contents of stored NaCMC. Key; ●, % w/w total water uptake; ◇, % w/w melting of crystallised water in DSC heating curves; △, % w/w crystallised water in DSC cooling scans.

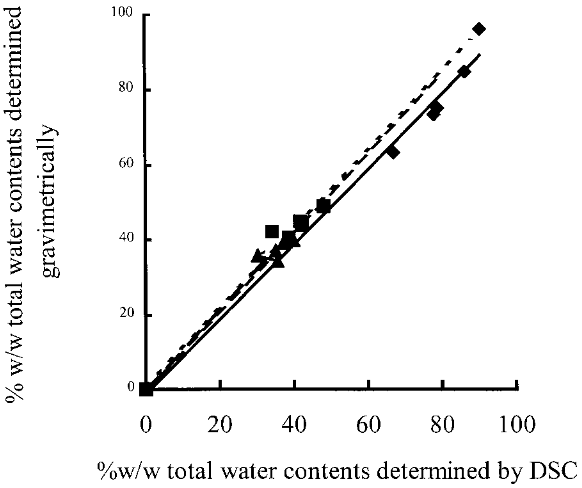

Fig. 3. Comparison of water uptakes by DSC and gravimetry. Correlation coefficients (r^2) were NaCMC=0.9872 (———), pectin=0.9762 (- - -) and gelatin=0.9765 (- · -)

lisation exotherms of water were less than the corresponding melting endotherms. Up to 33% w/w water uptake was detected from the melting enthalpies.

Excellent reproducibility in the evaluation in the DSC heating scans, of the melting endotherms and vaporisation endotherms of water and their corresponding transition temperatures between replicate samples stored for 2 h was observed (Table 1). A straight line relationship between total water uptakes evaluated by DSC and gravimetry was obtained (Fig. 3) for NaCMC and indeed the other two polymers, pectin and gelatin.

DSC analysis of NaCMC stored over 28 h, indicated that the sorbed water existed in different states. Initially non-freezable bound water with a small amount of loosely bound water (exotherm peak temperature at −55°C during the cooling scan) was apparent. With increased uptake of total water on prolonged storage, a large fraction of the sorbed water was present as loosely bound water which crystallised between −54° and −32°C during cooling scans and had melting endotherm transitions from −12° to −6°C on heating. Up to 6% w/w water uptake was observed as cold crystallised water in the DSC heating scans of the cooled samples. The difference between the total water from the DSC heating scans and the crystallised water from the DSC cooling scan was assumed to be non-freezable bound water.

3.3. *Pectin*

The DSC cooling and heating scans of stored pectin are shown in Fig. 4(a) and (b), respectively. No

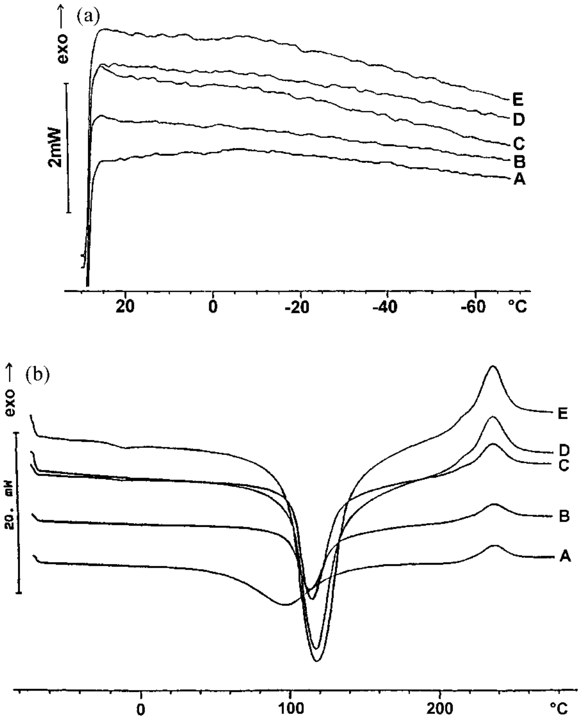

Fig. 4. (a) DSC cooling curves of pectin samples. Key as Fig. 1(a). (b) DSC heating curves of pectin samples. Key as Fig. 1(a).

exothermic transitions for the crystallisation of water were detected in the DSC cooling curves (Fig. 4(a)). With the exception of the sample stored for 28 h, a single endotherm corresponding to the vaporisation of total water, was detected at ca. 115°C in the heating scans (Fig. 4(b)). A second endotherm, at −8.9°C, was seen in the heating scan of the sample stored for 28 h, equivalent to 1% w/w water. Water uptake within the initial 2 h was rapid and was evaluated by DSC to be 42% w/w (Table 3). A further 7% w/w was sorbed by the polymer stored for an additional 26 h (Table 3).

These results showed that the uptake by stored samples of pectin was mainly in the form of non-freezable bound water. A small amount of water, 1% w/w, was present as freezable water on prolonged storage.

3.4. Gelatin

In the DSC cooling scans, there were no exothermic transitions corresponding to the crystallisation of freezable water in stored samples (Fig. 5(a)). Only a single endotherm corresponding to vaporisation of total water was detected in the DSC heating scans of gelatin stored for 2, 4, or 6.5 h (Fig. 5(b)). The peak for vaporisation of water was at times split into two peaks detected at ca. 100° and 130°C (Fig. 5(b)). This peak splitting was unique to gelatin and was not restricted to samples stored over long intervals, i.e. the split was observed in samples stored for 3, 28 and 96 h. The two endotherms indicated the possibility of two types of water present. One of these may be held more tightly within the amorphous structure of gelatin compared to the second type which may be held tightly at the surface. The nature of both types of bonding would be that neither is freezable and would not be detected as exotherms on cooling. The sum of both these transitions was taken as the total for water uptake (Fig. 5(b)).

Endotherms for the melting of water crystallised during the cooling process were not easily detected in the heating scans of any of the stored gelatin samples (Fig. 5(b)). A minor melt transition was apparent at ca. −5°C in samples stored for 3 and 96 h.

In addition to the water loss peak, other peaks were detected at 38° and 55°C in stored samples (Fig. 5(b)).

Table 3
Comparison of water uptakes by the hydrocolloids on basis of dry polymers determined using gravimetry and DSC

Storage time in h	NaCMC		Pectin		Gelatin	
	gravimetric	DSC	gravimetric	DSC	gravimetric	DSC
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	67.1	63.6	34.1	42.3	35.3	37.2
3.0	77.9	73.5	38.8	40.7	37.2	39.4
4.0	78.9	75.4	41.8	45.0	40.0	40.1
6.5	86.4	84.9	42.4	41.0	30.4	36.0
28.0	90.3	96.3	46.1	49.2	35.6	34.6

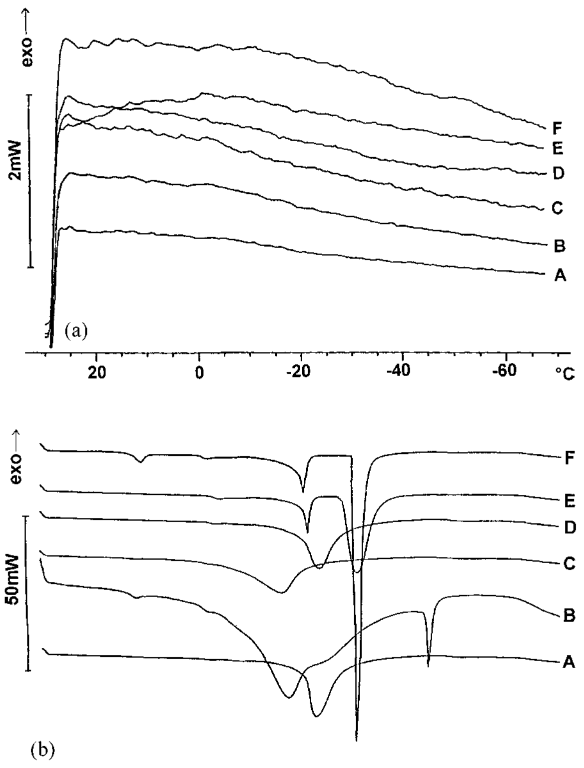

Fig. 5. (a) DSC cooling curves of gelatin samples. Key as Fig. 1(a); F, 96 h. (b) DSC heating curves of gelatin samples. Key as Fig. 5(a).

Although, these transitions were at lower temperatures than the glass transition of gelatin [21] they probably corresponded to glass transitions. The glass transition (T_g) of gelatin was determined by annealing a 5 mg sample of gelatin at 70°C for 2 h in the DSC cell prior to heating scan (Fig. 6). The T_g of gelatin varies with moisture content [21,22]. In order to determine accurately the T_g of polymers, excess water must be removed without degrading the sample prior to the DSC heating scan [21,22].

The water uptake by gelatin was lower than that of NaCMC or pectin. The difference in maximal water uptake by gelatin compared to pectin was ca. 9% w/w. Water uptake by gelatin was rapid up to 3 h and then a steady state was reached where no further water uptake occurred with storage (Table 4).

The absence of exotherms for the crystallisation of freezable water in the cooling scans and the presence of a single endotherm due to the vaporisation of total water in the heating scan indicated that the majority of uptake by gelatin was non-freezable bound water.

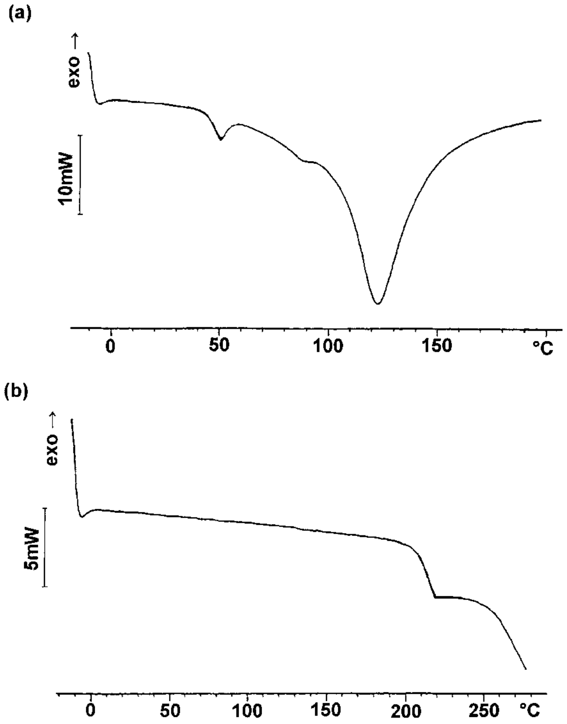

Fig. 6. (a) DSC heating curve of gelatin sample stored for 4 h, (b) DSC heating curve of gelatin sample stored for 4 h and annealed at 70°C for 2 h.

3.5. Pectin : gelatin (1 : 1)

No exothermic transitions were detected in the cooling scans of the stored pectin/gelatin samples (Fig. 7(a)), but four transitions were detected on the heating in each sample (Fig. 7(b)). Two minor endothermic transitions were detected at 41° and 58°C which were probably due to the glass transitions of gelatin. The main endothermic transition was detected at 100–115°C, due to the vaporisation of water (Fig. 6). An exotherm detected at ca. 250°C (Fig. 7(b)) was due to conformational changes in the structure of pectin (see also Fig. 4(b)). The absence of exotherms for the crystallisation of water during cooling and a single endotherm corresponding to water vaporisation in each stored sample, indicated that the uptake by pectin : gelatin blends was non-freezable bound water.

Table 4
DSC evaluation of water uptakes of the hydrocolloid blends

Hydrocolloid blends	% w/w Hpothetical water uptakes/h						% w/ww Actual water uptakes/h					
	0	2	3	4	6.5	28	0	2	3	4	6.5	28
1 : 1 Pectin/gelatin	0	39.8	40.1	42.6	38.5	41.9	0	34.2	31.6	34.9	38.6	39.5
1 : 1 Pectin/NaCMC	0	53.0	57.1	59.0	61.7	69.1	0	49.3	47.6	43.2	47.7	64.7
1 : 1 NaCMC/gelatin	0	50.4	56.5	57.8	60.5	65.5	0	42.9	50.8	51.8	49.7	51.3
1 : 1 : 1 NaCMC/pectin/gelatin	0	47.7	51.2	53.5	54.0	60.0	0	41.7	43.0	38.0	41.1	48.5

The water uptake by the mixture was intermediate to the individual components and was lower than the predicted theoretical values (Table 4). As was the case for both pectin and gelatin, a rapid rate of water uptake occurred within the first 2 h, equivalent to 34% w/w (Table 4). Although, further increase in water uptake was observed with prolonged storage, it was at a much reduced rate, i.e. only 5% w/w more water was sorbed by samples stored for a further 26 h (Table 4).

3.6. *Pectin : sodium carboxymethylcellulose (1 : 1)*

In the DSC cooling curves of stored pectin/NaCMC blends, freezable water was detected as exotherm transitions at −53°C to −48°C in samples stored for 6.5 and 28 h, respectively (Fig. 8(a)). A peak transition temperature shift was exhibited with increased water uptake. A similar shift in peak tem-

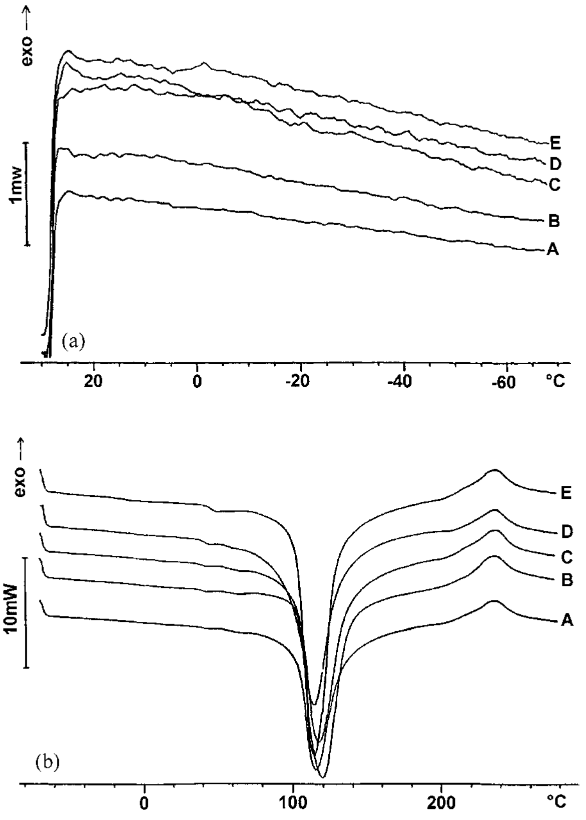

Fig. 7. (a) DSC cooling curves of 1 : 1 pectin : gelatin samples. Key as Fig. 1(a). (b) DSC heating curves of 1 : 1 pectin : gelatin samples. Key as Fig. 1(a).

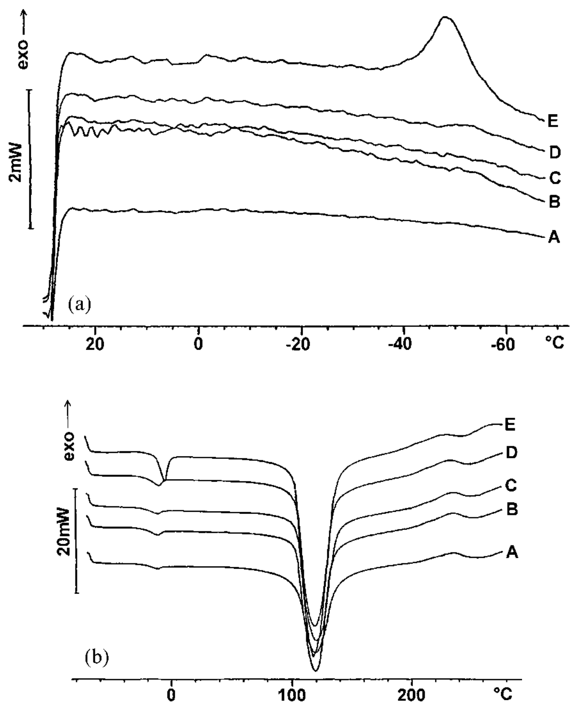

Fig. 8. (a) DSC cooling curves 1 : 1 NaCMC : pectin samples. Key as Fig. 1(a). (b) DSC heating curves 1 : 1 NaCMC : pectin samples. Key as Fig. 1(a).

perature was observed in stored samples of NaCMC alone (Table 1). The enthalpy of exotherms of crystallisation of this bound freezable water was calculated as 0.2 and 4.7% w/w in the samples stored for 6.5 and 28 h, respectively. Thus, a 23-fold increase in loosely bound water was found on prolonged storage. Exothermic transitions corresponding to crystallisation of water were not detected in 2, 3 and 4 h old samples.

Four transitions were detected in the heating scans of the stored blends (Fig. 8(b)). The first transition was an exotherm due to cold crystallisation of water with peak temperature from −31.3° to −28.5°C (Table 2). The amount of freezing water corresponding to the enthalpy of this exotherm in the heating scan was from 0.7 to 4.8% w/w. There was no correlation between the amount of water uptake, which was rapid in the initial 4 h, and the enthalpy of cold crystallisation of samples stored for 4 h. An increase in cold crystallised water was observed for samples stored for 6.5–28 h, compared to samples stored for up to 4 h or less. A slight increase in peak transition temperature was observed for this exotherm on prolonged storage.

The second transition, an endotherm, with a peak temperature at −12° to −6.5°C was seen in the heating scans of the stored samples. This transition was due to the melting of crystallised water and its enthalpy was evaluated for blends stored for 2–6.5 h as 4–6% w/w water content. A further 3.5-fold increase was detected in the enthalpy of pectin/NaCMC stored for 28 h.

The third transition was an endotherm corresponding to the vaporisation of total water. The endotherm had a peak temperature of 113–118°C (Table 3). A fourth transition detected as an exotherm during the heating scans with a peak temperature of 250°C was due to structural conformational changes in pectin (Fig. 4(b)). Approximately 75% of the water uptake was complete within the initial 2 h storage period. The remainder was at a slower rate on prolonged storage over the further 26 h (Table 5).

The difference between the bound freezable water detected as an exotherm in the DSC cooling scans and the endotherm corresponding to the vaporisation total water uptake in the DSC heating scan was assumed to be bound and non-freezable, i.e. tightly bound water within the polymer blends.

3.7. *Sodium carboxymethylcellulose : gelatin (1 : 1)*

An exotherm was detected at ca. −55°C in samples stored for 4 and 28 h on cooling. This exotherm was again due to the crystallisation of bound freezable water. The enthalpy of the exotherm corresponded to 0.4–0.7% w/w moisture. Exotherms for the crystallisation of bound freezable water were not detected in samples stored for 2, 3, or 6.5 h (Fig. 9(a)).

On rewarming the cooled samples, an exothermic transition for cold crystallisation was observed (Table 2; Fig. 9(b)). These exotherms were detected in samples stored from 2 to 28 h with transition peak temperatures from −36.6° to −28.3°C. An increase in storage did not result in a marked increase in peak transition temperature compared to NaCMC alone. Evaluation of the exothermic enthalpies showed that there was no increase in samples stored from 2 to 4 h. A fourfold increase in cold crystallised water was observed as storage increased from 4 to 28 h. The cold crystallised water content was lower for NaCMC/gelatin blends compared to NaCMC alone.

The glass transition for gelatin was detected in the heating scans of the blends. The glass transition peak temperature was 46°C followed by recrystallisation

Table 5
Endotherm peak temperatures and % w/w water uptakes using DSC on the basis of dry blends of pectin: NaCMC (1 : 1) stored at 20°C and 93% RH (ND: not detected)

Storage time in h	Peak temperature of melt of crystallised water in °C	% w/w crystallised water by melt endotherm	Peak temperature of vaporisation of total water in °C	% w/w Total water uptake
0	ND	0.0	ND	0.0
2	−11.9	4.5	116.4	49.3
3	−12.1	4.4	115.0	38.9
4	−11.9	4.0	117.9	43.2
6.5	−10.5	6.0	116.1	47.7
28	−6.4	16.5	113.5	64.7

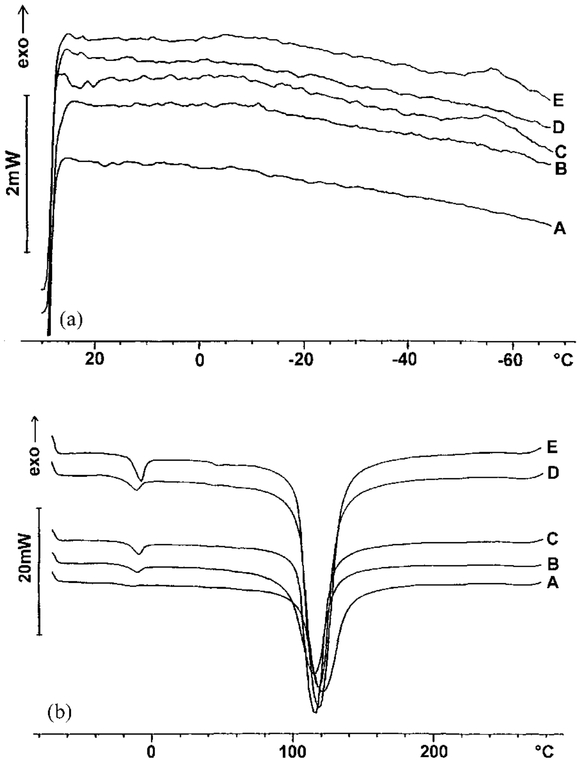

Fig. 9. (a) DSC cooling curves 1 : 1 NaCMC : gelatin samples. Key as Fig. 1(a). (b) DSC heating curves 1 : 1 NaCMC : gelatin samples. Key as Fig. 1(a).

with peak temperature of 58°C (Fig. 9(b)). An endotherm corresponding to the melting of frozen water was detected between -11° and -8°C in the heating scans (Fig. 9(b)). An increase in the peak transition temperature for the melting endotherm of frozen water was observed with an increase in water uptake. An increase in the melting enthalpy of frozen water, equivalent to 1% to 11% w/w, was observed as storage increased to 28 h (Fig. 10). The plot of % w/w water against storage time (Fig. 10) showed an initial increase in freezable water content in the stored samples and a maximal value was obtained after 4 h.

The endotherm, for the vaporisation of total water, was detected in stored samples at ca. 112°C (Fig. 9(b)). Total water uptake was evaluated quantitatively between 42 and 52% w/w in samples stored for up to 28 h (Fig. 10). Water uptake was rapid in the initial 4 h and there was no major increase in water uptake with a further 24 h storage as evaluated by the enthalpy of endotherms for the vaporisation of total water.

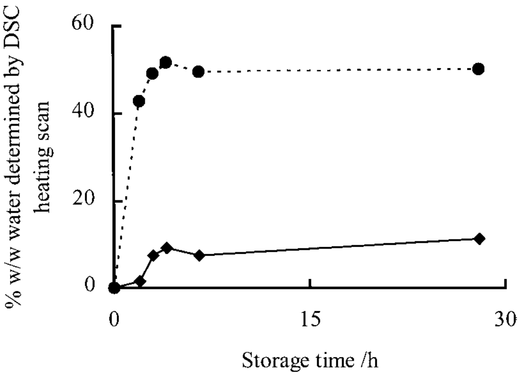

Fig. 10. Total water uptakes (●) and bound freezable water contents (◆) determined from DSC heating curves of 1 : 1 NaCMC : gelatin samples.

The majority of the water uptake by NaCMC/gelatin was non-freezable tightly bound water although a small quantity of loosely bound water was detected as crystallisation in the DSC cooling scans and as cold crystallised water in the heating scans of some stored samples. Gelatin reduced the cold crystallised water content of NaCMC.

The total water uptake by the polymer blends was lower than the hypothetical value. The presence of gelatin in the stored blends of NaCMC/gelatin was detrimental to the water uptake capacity of NaCMC (Table 4).

3.8. Sodium carboxymethylcellulose : pectin : gelatin (1 : 1 : 1)

Freezable water was not detected in the cooling scans of the stored 1 : 1 : 1 samples, confirmed by the absence of exothermic transitions (Fig. 11(a)). Exotherms for the cold crystallisation of freezable water, endotherms for the peaks for melting of crystallised water and vaporisation of total water were detected in the heating scans of the stored samples (Fig. 11(b)). Cold crystallisation of free freezable water was detected as an exotherm at -33.5° to -31.7°C and the enthalpy of the exotherm was evaluated to be equivalent to 0.6–4% w/w water. Although, there was no marked increase in peak transition temperature of the exotherms observed with

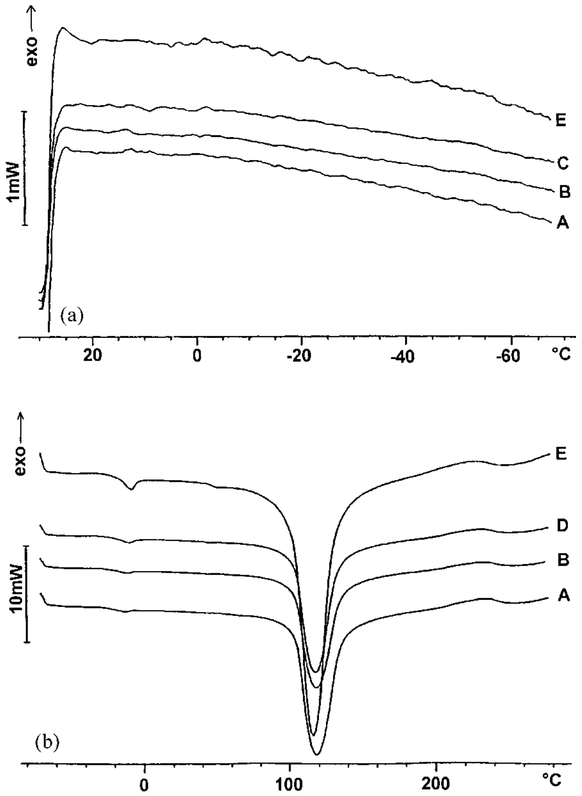

Fig. 11. (a) DSC cooling curves 1 : 1 : 1 NaCMC : pectin : gelatin samples. Key as Fig. 1(a). (b) DSC heating curves 1 : 1 : 1 NaCMC : pectin : gelatin samples. Key as Fig. 1(a).

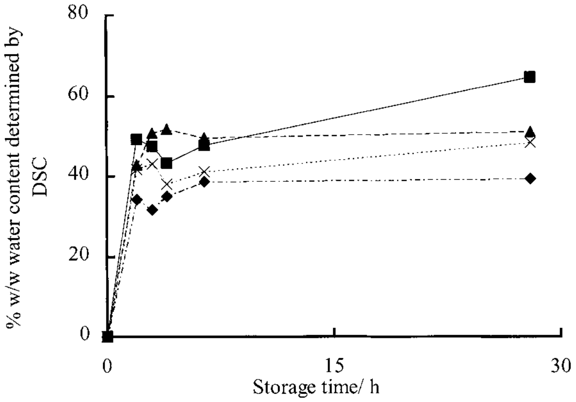

Fig. 12. Comparison of total water uptake profiles of ◆, 1 : 1 gelatin : pectin; ■, 1 : 1 pectin : NaCMC; ▲, 1 : 1 NaCMC : gelatin; and ×, 1 : 1 : 1 NaCMC : pectin : gelatin samples stored at 20°C and 93% RH.

prolonged storage of the samples, a fourfold increase in cold crystallised water content was observed for samples stored from 4 to 28 h.

The endotherms for the melting of crystallised water were detected between −13° and −9°C; their position was dependent on the total water uptake by the blends. The enthalpy of the melt transition increased with an increase in overall water content. The endotherm peaks corresponding to the vaporisation of total water in the heating scans were at ca. 114°C.

The water uptake by the 1 : 1 : 1 polymer blends evaluated by the enthalpy of vaporisation was initially rapid and a plateau was observed after 2 h (Fig. 12). An increase in water uptake of only 7% was observed with the further 26 h storage. Additional endotherms corresponding to the glass transition of gelatin were detected in the heating curves of stored samples with temperatures of 39.5° and 55°C. An exotherm with a peak temperature of ca. 230° to 250°C was due to structural changes within gelatin and pectin (Fig. 11(b)).

It was assumed that majority of the water uptake by the NaCMC/pectin/gelatin blend was non-freezable bound water on the basis of the absence of exotherms in the cooling scans. A small fraction of the water uptake was possibly present as free freezable water but was difficult to distinguish. In addition to this, a small quantity of water was detected as cold crystallised water which was present as compartmentalised water within the NaCMC matrix. Both pectin and gelatin reduced the cold crystallised water capacity of NaCMC alone. There was no correlation between the initial increase in total water uptake and the cold crystallised water content. The total water uptake was less than the hypothetical value (Table 4). Non-freezable, tightly bound water was apparently present in stored mixtures of pectin/gelatin, whereas blends of NaCMC had both bound freezable and bound non-freezable water. Cold crystallised water was observed in NaCMC and in blends of hydrocolloids containing NaCMC. The order of water uptake was pectin/gelatin<NaCMC/pectin/gelatin<NaCMC/gelatin<NaCMC/pectin. Similarly, the bound freezable water content was NaCMC/gelatin<NaCMC/pectin (Figs. 10 and 12; Table 4). Water uptakes of the stored blends were lower than the theoretical mean values of the individual components (Table 4).

4. Conclusions

Only tightly bound, non-freezable water present as demonstrated during the cooling of gelatin, pectin, gelatin : pectin and NaCMC/pectin/gelatin samples following storage at 20°C and 93% RH. Both tightly bound non-freezable and bound freezable water, i.e. loosely bound water, were present in NaCMC samples stored for 28 h. Initial water uptakes by the 1 : 1 NaCMC/gelatin and 1 : 1 NaCMC/pectin blends were bound and non-freezable. Following storage for 28 h, bound freezable water was detected in both mixtures. The majority of the water uptake occurred within 2 h of storage for all samples examined. Cold crystallised water was observed in stored NaCMC and the hydrocolloid blends containing NaCMC. With the exception of NaCMC, there was no marked increase in their cold crystallised water content during the initial rapid water uptake phase (0–4 h). An increase in cold crystallised water content was observed in NaCMC on further storage up to 28 h. Both gelatin and pectin affected the cold crystallised water content of NaCMC. The order of water uptake was pectin/gelatin<gelatin<NaCMC/pectin/gelatin<pectin<NaCMC/gelatin<NaCMC/pectin<NaCMC. The water taken up by the blends was less than the theoretical water sorption values based on the individual components.

References

[1] J.E. Fairbrother, Beyond occlusion and back again, in: Beyond occlusion: Dermatology proceedings, T.J. Ryan (Ed.), ICSS 137, 1987, p. 3.
[2] D.A. Hollingsbee, P. Timmins, Bioadhesion-possibilities and future trends, R. Gurney, H.E. Junginger (Eds.), WIS. Verl.-Ges, Stuttgart, 1990, p. 140.
[3] J. Horncastle, Medical Device Technology, Jan/Feb (1995) 30.
[4] F. Ferrari, M. Bertoni, C. Cammella, M. Waring, M.E. Aulton, Proceedings of wound care international conference, Harrogate, UK (1993) 167.
[5] British Pharmacopoeia. II, HMSO (1993) A218.
[6] D. Bloor, An investigation of physical properties of hydrocolloid wound care materials, MSc thesis, Manchester University, 1992.
[7] T. Hatakeyama, A. Yamauchi, H. Hatakeyama, Eur. Polym. J. 20 (1984) 61.
[8] S. Deodhar, P. Luner, Water in polymers, ACS (1980) 273.
[9] Y.K. Sung, Polym. Kor. 6 (1986) 576.
[10] V. Renugopalakrishnan, G. Chandrakasan, S. Moore, B. Hutson, R.S. Bhatnagar, Macromol. 22 (1989) 4121.
[11] W.-Z. Zang, M. Satoh, J. Komiyama, J. Memb. Sci. 42 (1989) 303.
[12] T. Hatakeyama, K. Nakamura, H. Hatakeyma, Thermochim. Acta 123 (1988) 153.
[13] Merck Index, 10th edition, M. Windholtz, S. Budavari, R.F. Blumetti, E.S. Otterbein (Eds.), Merck and Co., Inc., 1983, p. 9860.
[14] H. Ohno, M. Shibayama, E. Tsuchida, Makromol. Chem. 184 (1983) 1017.
[15] H. Hatakeyama, T. Hatakeyma, K. Nakamura, Appl. Polym. Symp. 37 (1983) 979.
[16] T. Hatakeyama, K. Nakamura, H. Yoshida, H. Hatakeyama, Food Hydrocoll. 3 (1989) 301.
[17] K. Nakamura., T. Hatakeyama, H. Hatakeyma, Tex. Res. J. (1981) 607.
[18] K. Nakamura, T. Hatakeyama, H. Hatakeyama, Polym. 24 (1983) 871.
[19] N. Murase, K. Gonda, J. Phys. Chem. 90 (1986) 5420.
[20] N. Murase, T. Watanbe, Physics and Chemistry of Ice, N. Maeno, T. Hondoh (Eds.), Hokkaido University press, Sapporo, 1992, p. 249.
[21] A.S. Marshall, S.E.B. Petrie, J. Phot. Sci. 28 (1980) 128.
[22] G.I. Tsereteli, O.I. Smirnova, Polym. Sci. 33 (1991) 2119.