

Research paper

Water sorption–desorption behaviour of methyl methacrylate–starch copolymers: effect of hydrophobic graft and drying method

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Abstract

A new family of graft copolymers combining hydrophilic and hydrophobic components have recently been proposed as direct compression excipients. Copolymers were synthesised by free radical copolymerisation of starch derivatives with methyl methacrylate (MMA) and were alternatively dried by oven or freeze-drying techniques. The aim of this study was to investigate the water vapour sorption–desorption behaviour of these copolymers, focusing on the influence of variables such as the hydrophobic component and the drying process.

Moisture sorption and desorption isotherms were measured at 25 °C and analysed according to GAB and Young–Nelson equations, which distinguish between different physical forms of moisture distribution. The Young–Nelson model gave the best fit to the experimental data. The results obtained showed that the presence of the acrylic component modified not only the total hygroscopicity of the copolymers, as compared with the original starch derivatives, but also the water distribution in the solid, which might have an important role in the effect of moisture content on copolymer characteristics. The main water-sorption mechanism seemed to be absorption into the copolymer particles structure, in agreement with their starching nature. In terms of water sorption–desorption characteristics, no marked differences were found between the two drying methods used.

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Keywords: Water vapour sorption–desorption isotherm; Methyl methacrylate; Starch derivatives; Copolymers; Drying method; Water–solid interaction**1. Introduction**

When polymers are exposed to rich water vapour environments, water molecules first interact strongly with polar groups of their backbone, forming a monomolecular layer—Type III water [1,2]. If the vapour pressure is high enough, a multilayer system is created by water–water hydrogen bonds—Type II water [3], which is influenced by the solid, exhibiting a melting/crystallisation temperature different from that of bulk water. Additional water taken up is considered to be bulk or solvent-like water—Type I water [4]. While bonded water molecules show low reactivity, those with a solvent nature can markedly change the physical and chemical properties of solids, not only

influencing their individual characteristics, such as glass transition temperature, flow and compression behaviour, mechanical strength, etc., but also those of the whole formulation [5–7]. Therefore, physicochemical characteristics of excipients and formulations might be protected if moisture levels were held in the range of tight bonds. In this sense, a complete characterisation of water present in the solid is necessary in order to establish the best storage conditions.

Among the current approaches in the development of new polymeric systems, graft copolymerisation is an easy method for modifying the structure of natural polymers [8]. Hydrophobic and hydrophilic components can be copolymerised in order to diminish the important hygroscopic character of some natural products such as starch, improving their technological properties. In this sense, a new generation of copolymers combining semi-synthetic (starch derivatives) and synthetic (methyl methacrylate) polymers have been synthesised by free radical polymerisation, using Ce (IV) as an initiator [9].

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The products obtained were alternatively dried by two different methods: drying in a vacuum oven (6.67–13.33 hPa) at 50 °C until constant weight or freeze drying (freezing process at –20 °C for 24 h and sublimation process at 0.13 hPa and –50 °C) until a powdered product was got. These polymers were thoroughly characterised and their potential value as direct compression excipients for controlled-release matrices were assessed [10–12]. Both polymer composition and drying method used were demonstrated to have an important influence on copolymer properties.

The thermal behaviour of these copolymers–water systems was also investigated for samples previously equilibrated at different relative humidities (RH) from 0% to 97% [13]. Although the thermogravimetric analysis (TGA) showed two types of water associated, no information was provided by differential scanning calorimetry (DSC) studies about the distribution of water in these samples. Furthermore, the plasticisation effect of water was observed in modulated differential scanning calorimetry (MTDSC) scans of the copolymer–water systems under study when sealed 40 µL aluminium pans and covers were used. Generally the temperature range of the glass transition became broader as the RH of the storage conditions, and hence the amount of water contained in the copolymers, increased. In an attempt to find out more about these copolymers–water interactions, the aim of the present work was to study their sorption and desorption characteristics, compared with those of the original carbohydrates, in order to identify the water uptake mechanisms and determine the effect of the hydrophobic component and the drying method used on the water–copolymer interaction. Thus, Guggenheim–Anderson–deBoer (GAB) and Young–Nelson models were used, both broadly applied in the characterisation of water–amorphous products systems [2,14–17].

2. Materials and methods

2.1. Materials

Copolymers (batches SS02) were prepared by free radical copolymerisation of methyl methacrylate (MMA) with hydroxypropylstarch (HS)—Perfectamyl, Avebe, Holland or carboxymethylstarch (CS)—Quicksolan, Avebe, Holland [9]. The products obtained (hydroxypropylstarch methyl methacrylate, HSMMA, and carboxymethylstarch methyl methacrylate, CSMMA) were either dried in a vacuum oven (OD copolymers) or freeze-dried (FD copolymers). OD-CSMMA was crushed in a knives mill (Retsch, Haan, Germany) to obtain powdery samples. Sieve fractions of 25–500 µm were selected for all copolymers.

Before use, the materials were stored at constant relative humidity (40%) and room temperature (25 °C).

2.2. Methods

2.2.1. Surface area measurements

Nitrogen adsorption experiments were carried out in a Quantachrome Nova 2000 apparatus (Boyton Beach, FL, USA) using samples (2–3 g) previously degasified using vacuum and a temperature of 50 °C over 12 h. Nitrogen adsorption at –196 °C was measured over the relative pressure range 0.05–0.95. From the adsorption curve, the specific surface area was estimated from the volume of a nitrogen monolayer using multi-point BET method [18]. From the desorption curve, the mesopore volume was analysed using BJH model [19]. The results are shown as the mean value of two replicates.

2.2.2. Water vapour sorption–desorption isotherm

The original carbohydrates and their corresponding copolymers were kept in vacuum dessicators using silica-gel as dessicant to obtain products dried to constant mass. Samples (1 g) were subsequently equilibrated at different RHs (18.8, 28.0, 37.1, 47.2, 58.3, 70.4, 80.5, 88.8 and 97.5%) using hermetically sealed dessicators containing sulphuric acid solutions of different concentrations [20] to obtain the desired RH conditions. A constant temperature (25 °C) was maintained during equilibration and the samples were regularly weighed on a balance (Mettler Toledo LJ16, Zürich, Switzerland) until constant mass was obtained.

Samples used for sorption isotherms had been previously desiccated and accurately weighed, and samples used for desorption isotherms had been previously desiccated, weighed and hydrated by storage at a relative humidity of 97.5%. Moisture contents were determined on a dry weight basis of the material and the results are shown as the mean value of three replicates. Plots of equilibrium moisture content against relative humidity (RH) were constructed in order to obtain the sorption–desorption isotherms.

2.2.3. Mathematical modelling

2.2.3.1. GAB equation. The GAB equation can be described by the following expression:

$$Y = \frac{Y_m C K a_w}{(1 - K a_w)(1 + (C - 1) K a_w)} \quad (1)$$

where Y is the moisture content of the solid on a dry basis, Y_m the monolayer moisture content, a_w the water activity and C and K are energetic constants related to the heat of sorption.

This model has been recommended by the European Project Group COST 90 on physical properties of foods [21] as the fundamental equation for the characterisation of water sorption by food materials.

The estimation of the parameters in the GAB model (C , K and Y_m) was carried out by multiple linear regression of Eq. (1) (Microsoft® Excel 97).

2.2.3.2. *Young–Nelson model.* The Young–Nelson model [22] fits experimental sorption and desorption data to equations of the form

$$M_s = A(\beta + \theta) + B\theta RH \quad (2)$$

$$M_d = A(\beta + \theta) + B\theta RH_{\max} \quad (3)$$

where M_s and M_d are, respectively, the amount of water sorbed and desorbed at each RH (used as per unit), expressed as a fraction of the dry mass of the polymer.

A and B are constants characteristic of each material:

$$A = \frac{\rho_w \text{Vol}_M}{W_m} \quad (4)$$

$$B = \frac{\rho_w \text{Vol}_A}{W_m} \quad (5)$$

where ρ_w is the water density, Vol_M and Vol_A are, respectively, the adsorbed and absorbed water volumes and W_m is the weight of dry material. In this model, θ is the fraction of the material surface covered by at least one layer of water molecules, and $A\theta$ is the mass of water in a complete adsorbed monolayer expressed, like all masses in the model, as a fraction of the dry mass of the polymer. Therefore, this term would be equivalent to Y_m in the GAB equation. $A(\beta + \theta)$ is the total amount of adsorbed water, and $A\beta$ is the mass of water which is adsorbed beyond the mass of the monolayer, that is, in multilayer. B is the mass of absorbed water at 100% RH, and, hence, $B\theta RH$ is the mass of absorbed water when the monolayer coverage is θ and the relative humidity is RH.

θ and β include the following mathematical expressions:

$$\theta = \frac{RH}{RH + E(1 - RH)} \quad (6)$$

$$\beta = -\frac{ERH}{E - (E - 1)RH} + \frac{E^2}{(E - 1)} \ln \left[\frac{E - (E - 1)RH}{E} \right] - (E + 1) \ln(1 - RH) \quad (7)$$

where E is an equilibrium constant between monolayer water and the ‘normally condensed’ water adsorbed externally to the monolayer. E is equivalent to C in the GAB Equation [14].

$$E = e^{-\left[\frac{q_1 - q_L}{k_B T} \right]} \quad (8)$$

where q_1 (J/mol) is the heat of adsorption of water on the polymer, q_L (J/mol) the heat of condensation of water molecules, k_B the Boltzmann’s constant (1.38×10^{-23} J/K) and T (K) the temperature.

The experimental data were fitted to Eq. (2) and (3) by means of an iterative multiple linear regression using, as fitting criteria, the sum of the squares of the residuals

between the experimental and the calculated values [22]. The degree of adjustment was expressed by the multiple correlation coefficient (Microsoft® Excel 97). According to the model characteristics, from the estimated values of A , B , θ and β , the corresponding profiles of water adsorbed in monolayer ($A\theta$), absorbed water ($B\theta$) and multilayer adsorbed water ($A\beta$) were obtained.

2.2.4. IR balance moisture determination

The moisture content in the sorbed and desorbed samples was analysed using an infrared balance (Mettler Toledo LJ16, Zürich, Switzerland). Samples (500 mg) were tested at 50 °C until constant weight (weight variation less than 0.2 mg/s) was achieved. The results are shown as the mean value of three replicates.

3. Results and discussion

3.1. Surface area measurements

The analysis of the nitrogen adsorption and desorption over bulk solids allows rapid and cheap measurements of surface parameters such as specific surface area, total pore volume and mean pore radius. The specific surface area is considered in this assay as the total surface where the nitrogen molecules can be adsorbed, which covers not only the external particle surface but also the available surface of macropores, mesopores and micropores [23]. However, there are important disadvantages and limitations to these studies; for example, the great molecular volume of nitrogen makes its access to small pores impossible, which must be taken into account in the evaluation of microporous results [24]. The sample pre-treatment [25] is also extremely important; it may be the cause of the great disparity found in the literature for specific surface area data of similar products [24]. In order to avoid this problem, and to compare the results of the different products under study, the samples were degasified in exactly the same conditions.

When evaluating HS products, data given in Table 1 show no great variations in specific surface area values concerning the copolymerisation process and drying method used. The slightly smaller specific surface area for HS particles could be due to their rounded and even surfaces, in contrast to the lobe masses typical of HSMMA particles [9, 11]. In case of CS products, the copolymerisation process led to a substantial increase in the specific surface area, in agreement with the decrease in particle size observed when compared with the original carbohydrate [9]. A higher specific surface area was observed for FD-CSMMA, in accordance with the spongy particle structure, with significant hollow regions. The smaller surface area detected for OD-CSMMA might be due to the milling process carried out after drying, which created smooth particle surfaces [11].

Table 1

Nitrogen adsorption–desorption results for the original carbohydrates and their corresponding copolymers ($n=2$)

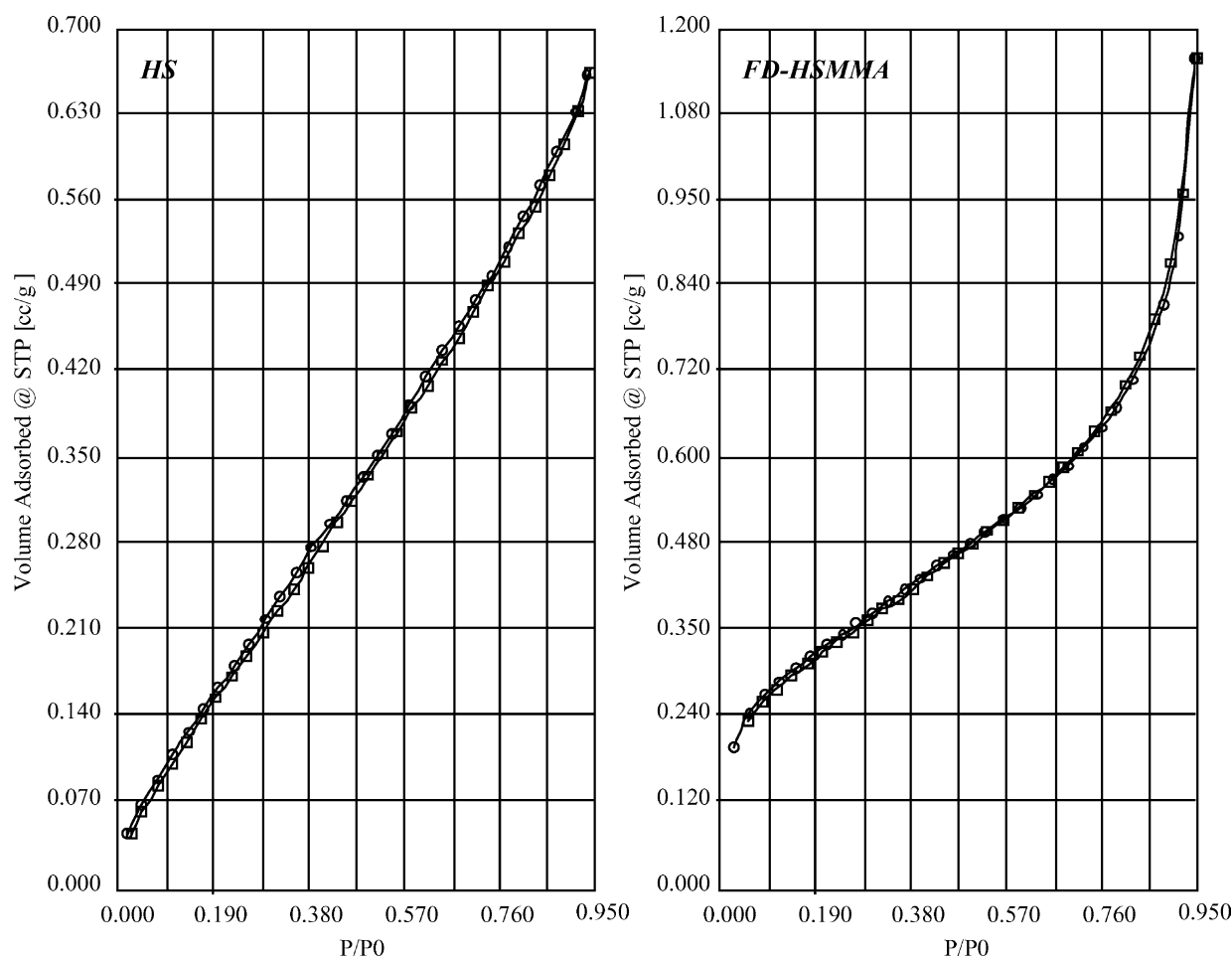
Polymer	C_{BET}	Specific surface area (m^2/g) (BET method)	BJH method	
			Total volume of mesopores ($\text{cm}^3/\text{g } 10^{-3}$)	Mean mesopore diameter (nm)
HS	8.54 (0.43)	1.06 (0.32)	1.21 (0.25)	4.60 (0.40)
OD-HSMMA	34.39 (1.89)	1.36 (0.12)	2.61 (0.30)	7.66 (0.17)
FD-HSMMA	66.47 (3.91)	1.28 (0.13)	1.90 (0.17)	5.95 (0.07)
CS	5.73 (0.70)	0.64 (0.23)	0.80 (0.19)	5.04 (0.70)
OD-CSMMA	61.70 (25.47)	4.83 (0.40)	9.12 (1.32)	6.47 (0.70)
FD-CSMMA	91.19 (26.46)	5.45 (0.33)	8.05 (1.19)	5.91 (0.61)

Correlation coefficient for nitrogen adsorption data: 0.9829–0.9999.

C_{BET} constant is closely related to the state of the adsorbate associated with the solid. The higher values of freeze-dried products (Table 1) denote a stronger interaction of these derivatives due to the structural differences induced during the drying process [26].

Fig. 1 shows two examples of the nitrogen adsorption–desorption isotherms found for the original carbohydrates and their homologous copolymers. Whereas the carbohydrates showed a linear nitrogen adsorption–desorption

behaviour throughout the range of partial pressures (Langmuir isotherms type III), in case of copolymers, typical Langmuir curves type II were found. These sigmoidal profiles are representative of monolayer formation at low adsorbate partial pressures, as has already been noticed for other starch derivatives [23]. This fact, together with the absence of hysteresis, confirmed the limited importance of micropores in these particles. Once the monolayer was formed, the nitrogen condensed in

Fig. 1. Nitrogen adsorption–desorption isotherms (-196°C) corresponding to HS (a) and FD-HSMMA (b).

mesopores (50–2 nm pore radius) until high nitrogen partial pressure was achieved; at that point, a strong increase in the slope denoted the abundant presence of macropores (pore radius higher than 50 nm). The linear adsorption–desorption behaviour perceived in the original carbohydrates, without a differential point for the monolayer formation, might be because the adsorption energy (solid–gas interaction) was lower than the condensation energy (gas–gas interaction). This was also seen in the low C_{BET} values (Table 1), which might limit the reliability of specific surface area data obtained for these products by this method [27].

The relationship established by Oscik between nitrogen adsorption–desorption profiles and pore shape [28] leads us to consider the presence of conic mesopores in the copolymers under study. Both the presence of macropores and the conical shape proposed for the pores limit the reliability of the results obtained by the BJH method, which considers a system with cylindrical pores only in the mesopore range. Taking these limitations into account, the results of the mesopore analysis presented in Table 1 denoted a higher volume of mesopores for CSMMA copolymers, in agreement with their higher values of specific surface area. The collapse of small pores, which

typically occurs during the oven-drying process [24], was noticed in higher mean mesopore diameter data, in contrast to the unaltered structure obtained after freeze-drying.

3.2. Water vapour sorption–desorption isotherm

Following Callahan's classification [29], the copolymers might be catalogued as 'moderated hygroscopic products', whereas the carbohydrates would fall between this denomination and that of 'very hygroscopic' because, although their weight did not increase 50% in the first week of storage at 80% RH, they exhibited a considerable water uptake (5.65% w/w for HS and 9.57% w/w for CS) after equilibration at RHs lower than 40–50% [28].

During the storage at different RHs, the samples gradually changed their physical aspect, showing a cohesive behaviour at high RHs. These changes were particularly evident for the carbohydrates, especially for CS, where the sorbed water promoted the transition of samples to a rubbery state when the water uptake was higher than 30%.

As Fig. 2 shows, although the sorption behaviour of the carbohydrates and their copolymers were qualitatively similar, the water sorption was more marked in the absence

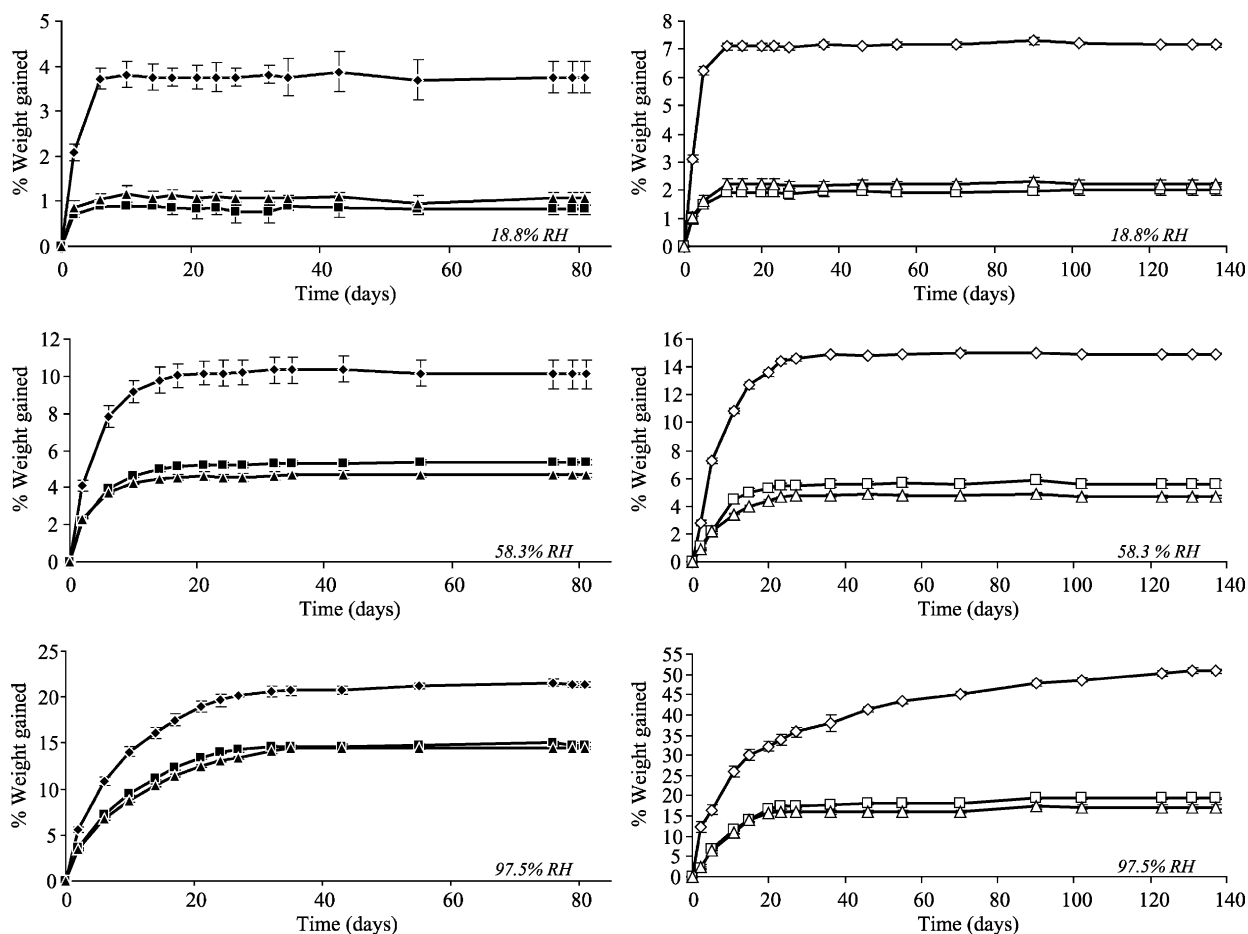


Fig. 2. Percentage of weight gained based on dry mass of HS (◆), OD-HSMMA (■), FD-HSMMA (▲), CS (◇), OD-CSMMA (□) and FD-CSMMA (△) at low (18.8%), intermediate (58.3%) and high (97.5%) RHs.

Table 2

Ratio of weight gained by the carbohydrates and their corresponding copolymers at low (18.8%), intermediate (58.3%) and high (97.5%) RH conditions ($n=3$)

% RH	HS/OD-HSMMA	HS/FD-HSMMA	CS/OD-CSMMA	CS/FD-CSMMA
18.8	4.3	3.6	3.7	3.2
58.3	1.9	2.2	2.7	3.1
97.5	1.4	1.5	2.9	3.1

of methyl methacrylate, since the hydrophobic graft might diminish the polarity and water solubility of the copolymer and, hence, its water uptake. However, from the results in Table 2, we see that for hydroxypropyl derivatives the differences in weight gained due to water sorption were less and less important with the increase in RH, while they remained relatively constant in case of carboxymethyl derivatives. This behaviour could be explained on the basis of the grafting yields of the copolymers [9], which revealed the presence of 70% w/w of acrylic component in CSMMA copolymers. However, most of this MMA polymerised as poly-methyl methacrylate (PMMA) and only 10% w/w was grafted on CS. The low percentage of acrylic graft might not dramatically change the carbohydrate backbone structure, leading to similar ratios of weight gained with the different RH conditions. This hypothesis was corroborated by the fact that the proportion of water sorption percentage between CS and CSMMA was practically the same as the carbohydrate proportion (30% w/w) in the copolymer.

The behaviour of OD-HSMMA and FD-HSMMA was not so clear. Although the percentage of methyl methacrylate in the copolymer (60% w/w) was in the same range as in CS copolymers, almost the 70% w/w of this acrylic component was grafted on the carbohydrate backbone. In this situation, acrylic chains might prevent the direct hydration of the carbohydrate backbone, which might

promote water–water interactions, making these products more sensitive to the water plasticisation effect.

Moreover, a clearly higher tendency to sorb water was observed (Fig. 2) for CS (7.16% w/w at 18.8% RH, 14.96% w/w at 58.3% RH and 50.76% w/w at 97.5% RH) than for HS (3.71% w/w at 18.8% RH, 10.50% w/w at 58.3% RH and 23.63% w/w at 97.5% RH). This behaviour was also seen for the copolymers, as CSMMA derivatives showed a higher water uptake than HSMMA ones. The reason might be the higher hydrophilicity of the former, which might counteract its minor presence in the copolymer (30% w/w of CS in CSMMA and 40% w/w of HS in HSMMA) [9].

With regard to drying methods, no important differences were detected (Fig. 2) between OD and FD products for each copolymer, except a slightly higher water uptake capacity for FD products at low RH conditions and for OD derivatives at intermediate and high RHs.

Desorption profiles at low and intermediate RHs are presented in Fig. 3. As might be expected, none of the samples desorbed 100% of water sorbed. It is important to point out that the percentage of water desorbed by HS was lower compared with HSMMA, where the high presence of methyl methacrylate graft might prevent the formation of carbohydrate–water bindings, providing easier water desorption. This phenomenon was less obvious for carboxymethyl derivatives.

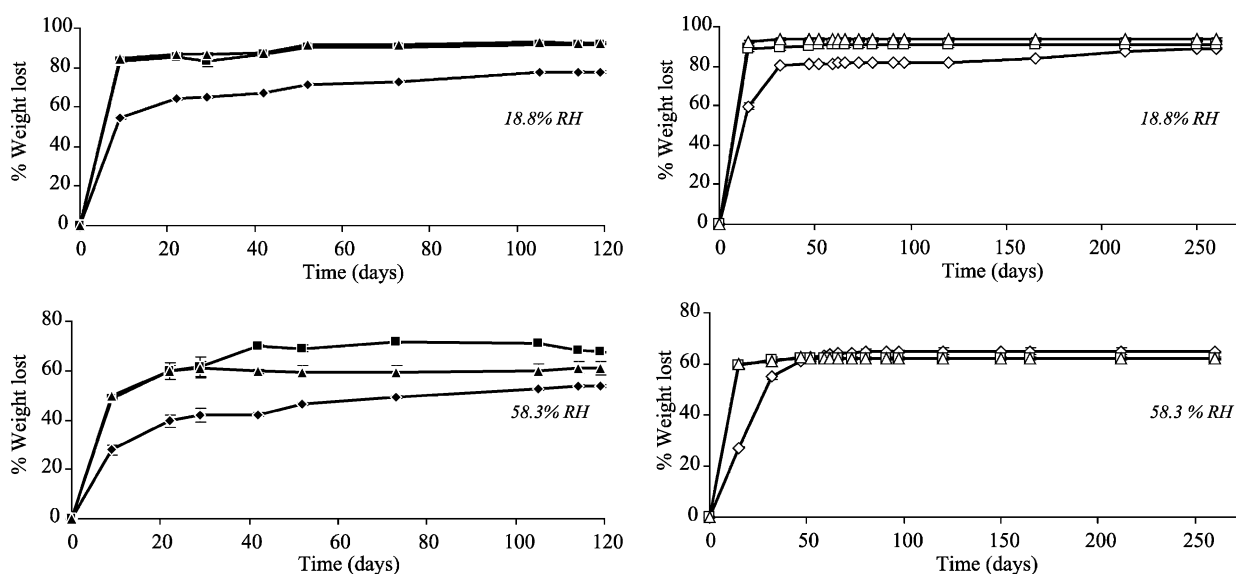


Fig. 3. Percentage of weight lost based on dry mass of HS (◆), OD-HSMMA (■), FD-HSMMA (▲), CS (◇), OD-CSMMA (□) and FD-CSMMA (△) at low (18.8%) and intermediate (58.3%) RHs.

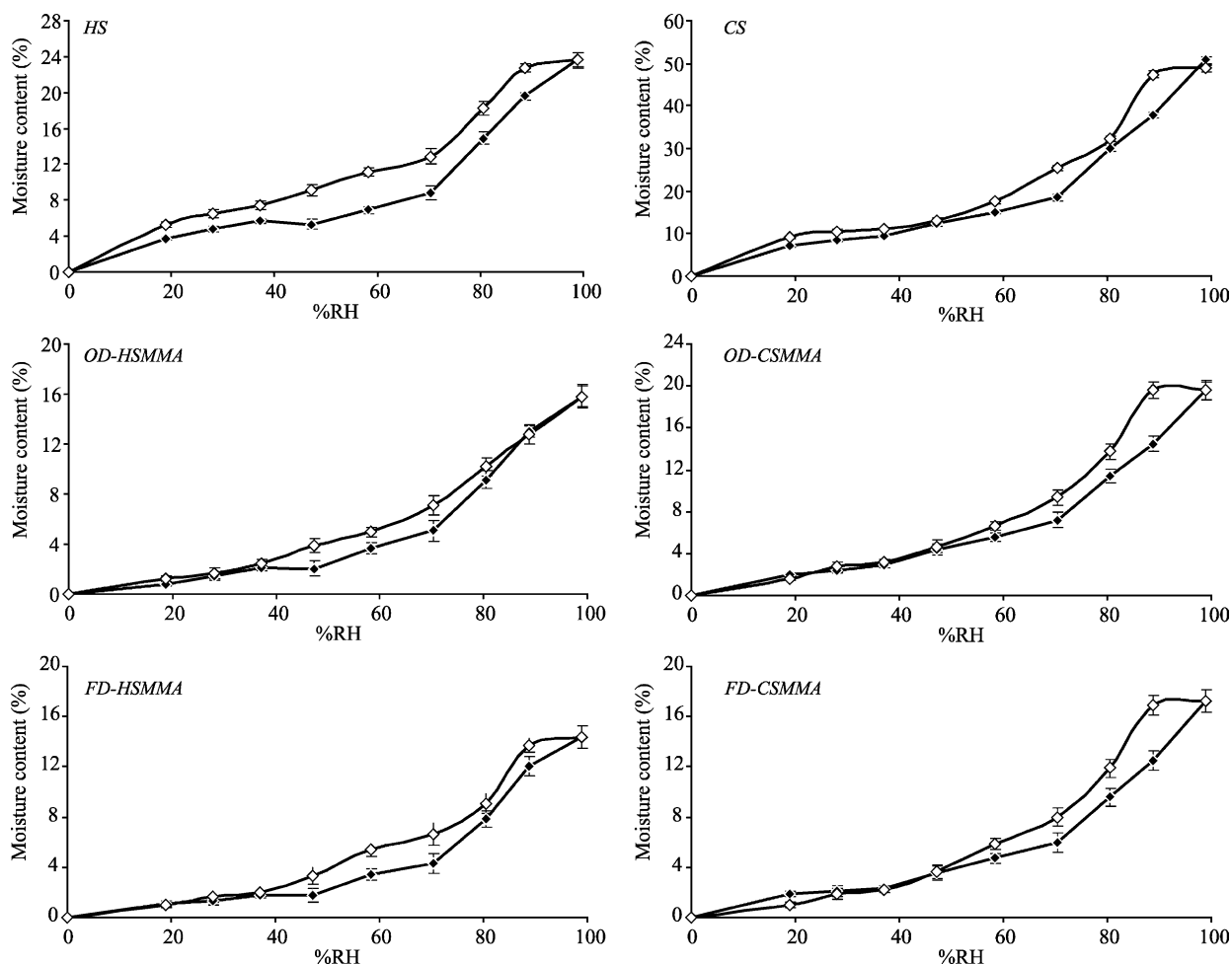


Fig. 4. Water sorption (black symbols)–desorption (white symbols) isotherms at 25 °C of products under study.

While there was no difference in the desorption behaviour between OD-CSMMA and FD-CSMMA, a higher percent of water desorbed was noted for OD-HSMMA than for FD-HSMMA at intermediate RH conditions.

The differences between sorption and desorption behaviour were observed in the isotherm plots (Fig. 4), where hysteresis was clearly demonstrated. This phenomenon could be attributed, for starch products, to a structural change promoted by the establishment of water molecules among the glucose chains [30]. In this regard, Nokhodchi et al. [14] pointed out that the plasticisation effect that water performs over certain products might limit the dehydration process due to a permanent deformation in the polymeric structure. It is also interesting to note that neither the presence of methyl methacrylate nor the drying method induced deep changes in isotherm profiles, as all of them showed the typical sigmoidal shape of starch related products [2,31], which sorb relatively small amounts of water at low water activities and large amounts at high relative humidities.

In order to evaluate the topological distribution of water in these samples, experimental moisture

sorption–desorption data were fitted to GAB and Young–Nelson equations. Table 3 shows the estimated parameters for both models.

3.2.1. GAB equation

C_{GAB} values obtained for carbohydrates (Table 3) were in the range of those found by other authors for starch products [2,6,15,27] and were clearly higher than the ones obtained for the copolymers. This behaviour might be related to a weaker water–copolymer interaction caused by the presence of methyl methacrylate. It is worth pointing out the higher C_{GAB} values for FD products compared with those for OD derivatives. A possible explanation could be the sequentiation of the oven-drying process, which would tend to dehydrate the hydrophobic component of the copolymer first, creating an external and hydrophobic layer over the powder [32]. In contrast, the freeze-drying process provides a dry product with porous structure and little or no shrinkage, thus improving the accessibility of water molecules to the carbohydrate chains. That would induce the formation of more energetic bindings than in case of OD products.

Table 3

Correlation coefficients (r) and parameters values estimated from GAB equation and Young–Nelson model for the different products under study

Polymer	C_{GAB}	K_{GAB}	Monolayer-GAB (%)	r_{GAB}	$A_{\text{Y\&N}}$	$B_{\text{Y\&N}}$	$E_{\text{Y\&N}}$	Monolayer-Y\&N (%)	$r_{\text{Y\&N}}$
HS	35.45	0.912	3.78	0.879	1.913	11.992	0.312	1.9	0.966
OD-HSMMA	1.85	0.909	2.60	0.979	0.024	16.231	1.800	0.02	0.989
FD-HSMMA	4.53	0.953	1.64	0.907	0.027	14.733	1.900	0.02	0.985
CS	10.22	0.942	8.70	0.966	4.698	21.122	0.321	4.68	0.984
OD-CSMMA	4.05	0.892	3.42	0.953	1.653	8.742	0.405	1.64	0.990
FD-CSMMA	5.66	0.913	2.53	0.922	1.346	8.010	0.530	1.33	0.989

That the K_{GAB} values were so close to one, might be interpreted as due to the existence of little energetic differences between monolayer and multilayer water [33].

3.2.2. Young–Nelson model

The GAB model does not consider the possibility for water to be absorbed into the particle, which is one of the main water sorption mechanisms in amorphous

solid–water systems. For this reason, the percentage of water needed to form the monolayer onto the solid was higher than that calculated by the Young–Nelson model (Table 3). Data obtained from this model offer more reliable information about the distribution of water in the solid, as was denoted by the better correlation coefficient values obtained with this model compared with the GAB equation.

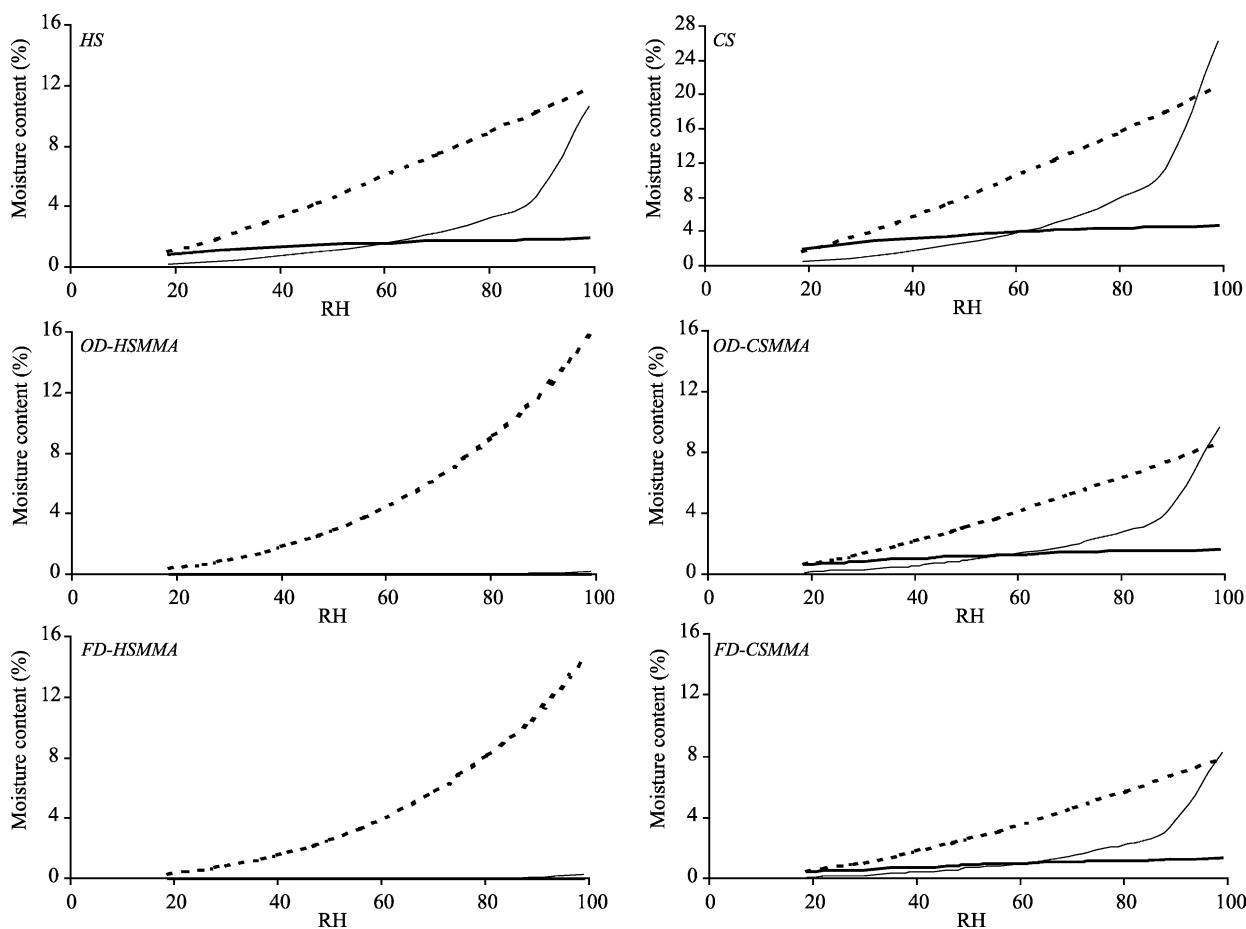


Fig. 5. Water distribution, following the Young–Nelson model, in monolayer adsorbed water (—), multilayer adsorbed water (---) and absorbed water (· · ·), for products under study.

As Table 3 shows, $E_{Y\&N}$ values were higher than one for OD-HSMMA and FD-HSMMA, that is, the heat of adsorption was less than the heat of condensation, which might be related to a very low tendency for water to be adsorbed onto the particles for these copolymers.

For amorphous products, the monolayer water is related to the amount of water that directly hydrates the solid, thus forming water–solid unions [1]. In this context, the lower values of monolayer water (0.02%) obtained for both OD-HSMMA and FD-HSMMA products might be explained by the presence of few hydrophilic groups available to directly interact with water molecules. So, for HSMMA copolymers (Fig. 5), absorption might represent, according to this model, the main, almost only, way for water to be taken up, as can be confirmed by the low values of the $A_{Y\&N}$ parameter, compared with those of the $B_{Y\&N}$ parameter (Table 3). It is assumed therefore that the majority of water that interacted with these copolymers penetrated and established water–water interactions [3,34].

On the other hand, for CSMMA copolymers, adsorbed water appeared mainly after storage under RHs higher than 80% (Fig. 5). Again, the similar water distribution of CSMMA copolymers compared with the homologous carbohydrate would support the idea of a less altered carbohydrate structure in these products. Like HSMMA products, OD-CSMMA and FD-CSMMA had similar $E_{Y\&N}$, $A_{Y\&N}$ and $B_{Y\&N}$ values, showing the OD derivative a slightly higher tendency to absorb water than the FD one. This could be related to the higher volume of mesopores and mean mesopore diameter reported for OD products (Table 1).

CS and the copolymers were proved to be fundamentally amorphous [35], while HS was slightly more crystalline. According to the results obtained, for the materials used in this study, the accessibility of the polar sites, rather than the

degree of crystallinity, seems to govern the solid–water interactions.

3.2.3. Water uptake kinetics

When evaluating the water uptake kinetics of the products under study, a linear relationship was found between the logarithms of percentage of sorbed water, based on dry mass, and time before achieving the equilibrium:

$$\ln\% = A + n \ln t \quad (9)$$

This relationship could be similar to the one established by Michailova et al. [36,37] to study water penetration in HPMC-amylopectine matrices and by Katime et al. [38] in their study of water penetration into acrylic hydrogels. According to these authors, n values could be indicative of the water uptake mechanism and K (antlog A) of the water uptake rate.

Regarding these sorption kinetic data (Table 4), first of all, it is necessary to point out the low values of water uptake rate constant (K) found for these products. This is in accordance with the behaviour of other starch products such as potato starch and maltodextrins, which have a high capacity for water sorption but a slow penetration rate due to their amorphous structure [29].

This water uptake rate constant became higher with an increase in RH, and this behaviour was clearer for the carbohydrates than for their respective copolymers, which demonstrated the effect of methyl methacrylate on this parameter [38]. The plasticisation effect of water, which improved the water penetration, was again evident for HSMMA, showing more important changes with an increase in RH, as compared to CSMMA.

Regarding the mechanism of water uptake, a clearly different behaviour was observed depending on the type of carbohydrate present in the copolymer. Thus, for

Table 4
Kinetic data of sorption study of the different products at three levels of RH (18.8%; 58.3%; 97.5%)

Polymer	% RH	n	K (days ^{−n})	r^2
HS	18.8	0.68	1.144	0.974
	58.3	0.74	2.164	0.977
	97.5	0.72	3.086	0.988
OD-HSMMA	18.8	0.70	0.377	0.975
	58.3	0.61	0.995	0.928
	97.5	0.66	2.061	0.927
FD-HSMMA	18.8	0.68	0.473	0.991
	58.3	0.64	1.250	0.939
	97.5	0.61	2.077	0.979
CS	18.8	0.87	1.572	0.992
	58.3	0.67	2.761	0.996
	97.5	0.49	7.524	0.973
OD-CSMMA	18.8	0.72	0.501	0.953
	58.3	0.89	0.541	0.997
	97.5	1.19	1.002	0.994
FD-CSMMA	18.8	0.77	0.503	0.957
	58.3	0.92	0.503	0.999
	97.5	1.05	1.204	0.999

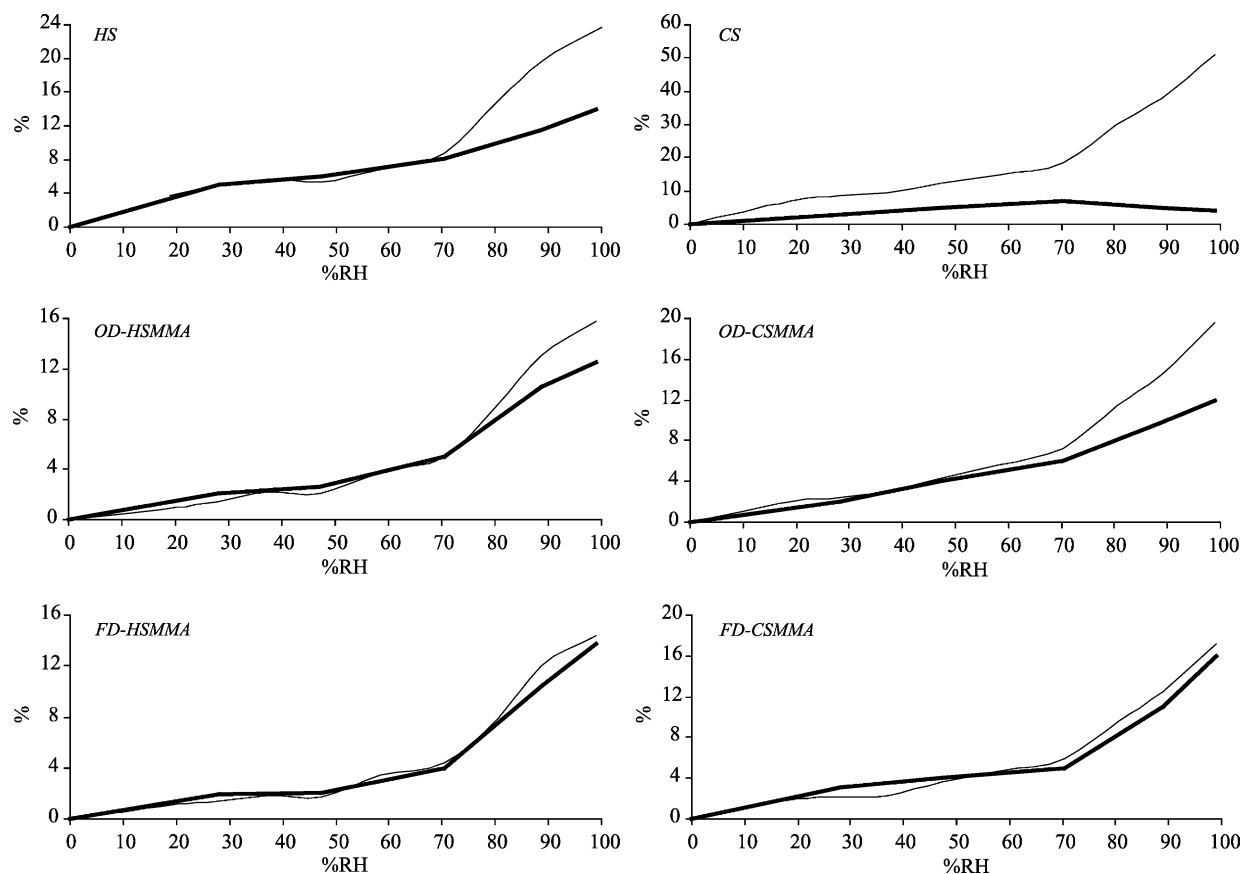


Fig. 6. Comparison of water isotherm sorption by gravimetric method (—) and by weight loss at 50 °C in IR balance (—) for samples stored at 18.8%; 28.0%; 37.1%; 47.2%; 58.3%; 70.4%; 80.5%; 88.8%; 97.5% RH for each product under study.

HS-products, $n=0.61$ – 0.74 throughout the range of RH, which implies a water uptake mechanism independent of RH. However, for CS-MMA derivatives, n values showed a progressive change in the water uptake mechanism, approaching one as RH increased.

According to Young–Nelson model results (Table 3, Fig. 5) and kinetic parameters (Table 4), an internal diffusion or absorption process can be postulated as the main water uptake mechanism for HS-derivatives. This phenomenon might be enhanced by a limited chains relaxation due to the plasticisation effect of water molecules, as it was reported for other starch products [34]. On the other hand, the change in the water uptake mechanism observed for OD-CSMMA and FD-CSMMA might be explained by the increase in externally adsorbed water at high levels of RH (Fig. 5), which might promote the water uptake due to interparticular capillarity, improved by the higher specific surface area and roughness observed for these derivatives [11].

3.3. IR balance moisture determination

In an attempt to find out more about the interaction of water with these products, the sorbed samples were analysed

in an IR moisture balance to evaluate the weight loss at 50 °C.

As Fig. 6 shows, using this technique, all products under study, except CS, lost practically all sorbed water if stored at RHs lower than 70%. The only partial loss of water by CS in these conditions might be attributed to the high amount of water in the sample along with a slow desorption rate. The physical changes undergone by CS samples slowed down the kinetic of water evaporation from this product, greatly affecting the water loss determination by means of this technique.

When copolymers stored at RHs higher than 70% were analysed, a difference in behaviour was noted between OD and FD samples. While freeze-dried products lost all sorbed water, the OD ones kept a fraction of water, which might be in accordance with the more homogeneous structure obtained after freeze-drying.

4. Conclusions

The presence of methyl methacrylate diminished the water sorption of the copolymers, so they might be catalogued as ‘moderated hygroscopic products’, while the original carbohydrates might be considered ‘very

hygroscopic'. Furthermore, the polymerisation process protected CSMMA derivatives from the change to a rubbery aspect at 25 °C and high levels of RH.

The Young–Nelson model fitted the moisture sorption and desorption profiles of the products under study better than the GAB model. This implies that the water vapour is not merely adsorbed onto the particle surface, but is also internally absorbed.

The presence of a high percentage of acrylic component grafted limited the direct hydration of the carbohydrate chains in HSMMA products; thus, the water molecules were absorbed into the material by water–water interactions, promoting its plasticisation effect. However, CSMMA derivatives adsorbed more water molecules directly onto the hydrophilic sites, due to their higher hydrophilicity and also to the fact that the carbohydrate backbone structure was altered less than in case of HSMMA.

The drying method did not significantly affect the sorption capacity of the dry product; however, a slightly greater tendency to forced desorption was observed for FD products, due to their more homogeneous structure.

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