

Analysis of water binding in starch plasticized films

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Abstract

The water-binding properties of wheat starch films were studied through the determination of water vapour adsorption isotherms at 20 °C. Starch films were obtained by casting after mixing native starch at 95 °C for 15 min with different ratios of plasticizer (glycerol).

Unplasticized starch film was found to adsorb less water than native starch granules. The effect of glycerol on water vapour adsorption by plasticized films depends on equilibrium relative humidity (ERH) value and glycerol content. Below ERH = 44%, plasticized film is less hygroscopic than native starch and above this value, adsorbed water increases with glycerol content. An amount of 20% glycerol seems to be the maximum that can act as plasticizer. Above this percentage, phase separation occurs and the amount of adsorbed water increases as it binds to starch film as well as to “free” glycerol.

The interactions between water, glycerol and starch determined in a wide range of ERH (0–80%) and of plasticizer ratios (0–52.6%) were analysed on a stoichiometric basis. A phase diagram is reported which contains characteristic points distinguished by their composition, stoichiometric ratios and type of phase observed. The phase separation and quantification of free glycerol is particularly discussed. A schematic representation of the different types of binding between starch water and glycerol is given to illustrate our understanding of the molecular interactions in the different phases.

The hydration of plasticized starch films depends on the nature and amount of plasticizer. Water vapour adsorption is proportional to the number of hydrophilic sites (hydroxyl groups) in the plasticizer. Modified starch films adsorb less water than native or plasticized films. The higher the hydrophobicity of substituent, the lower the amount of adsorbed water. Binding of water to starch films influences their thermo-mechanical properties.

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1. Introduction

There was always a need for the modification of starch mechanical properties in order to improve its suitability for both food and non-food applications. To obtain suitable properties, different plasticizers are used

amid which water proves to be the most efficient. Very often water is used in addition to another type of plasticizer. Previous work on starch hydration with and without plasticizer was mainly focused on water–starch interactions, especially as concerns the type of hydration layer (Strauss, Porcja, & Chen, 1990).

Water reacts differently depending on the level of water content in the system. It is successively adsorbed on primary sites (monomolecular layer of water molecules bound via strong H-bonds which is comparable to BET layer (Brunauer, Emmett, & Teller, 1938)),

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followed by multilayers and finally condensed into a liquid phase. The first steps of water adsorption can easily be explained by stoichiometric ratios of water molecules bound to polysaccharide hydroxyls (OHs). It was recently found (Fringant et al., 1996; Joly, Gauthier, & Escoubes, 1996) that water molecules were doubly bound to sorption sites in polysaccharides: (i) the sorption energy determined using microcalorimetry shows a decrease in function of equilibrium relative humidity (ERH); (ii) moreover, the water content at 80% ERH was assigned to the complete saturation of OHs assuming a double bridging mechanism (Fringant et al., 1996).

Unfortunately the real systems are generally formulated using one or more plasticizers beside water. Water vapour sorption isotherms are the best tool to control the level of hydration of the plasticized polysaccharide films. They reveal for example, a particular behaviour of plasticized samples as compared to non-plasticized starch constituents, amylose and amylopectine (Stading, Rindlav-Westling, & Gatenholm, 2001). Two regions of the sorption curve are distinguished:

At constant plasticizer (glycerol) ratio (20%), a minimum of hydration is observed around 60% ERH. Below this ERH value, plasticized samples show a relatively low water content probably due to glycerol competition with water in binding to starch-binding sites. Above 60% ERH, plasticized samples show higher water content values very likely because of glycerol intrinsic hydration. This behaviour seems to be true for plasticizers other than glycerol (Lourdin, Coignard, Bizot, & Colonna, 1997).

At constant ERH (57%), an increase in plasticizer ratio was also found to display a two-step behaviour: below a certain concentration of plasticizer, there is a decrease in water content as a function of plasticizer ratio and above this concentration water content increases.

The explanation of this two-step phenomenon involves specific binding of the plasticizer in the first step and phase separation in the second. This implies also that the special concentration between the two steps very likely corresponds to saturation of polymer sites with plasticizer. This saturation was found to affect other properties of starch and constituents (amylose and amylopectine) plasticized films. This is the case for strain at break which shows a minimum at saturation for plasticized starch film with glycerol at constant ERH (Myllärinen, Partanen, Seppälä, & Forssell, 2002; Lourdin, Bizot, & Colonna, 1997). Oxygen permeability shows a minimum for sorbitol-plasticized starch films. Such a behaviour was described as an anti-plasticizing effect of the additive and correlated with an increase in β -transition temperature of starch-plasticized samples (Gaudin, Lourdin, Forssell, & Colonna, 2000; Gaudin et al., 1999). The β -transition temperature reaches a plateau around a plasticizer concentration cor-

responding to saturation (Lourdin, Coignard et al., 1997).

The plasticizer concentration at saturation was found different by the different authors (Lourdin, Coignard et al., 1997; Myllärinen et al., 2002). For glycerol, values between 10% and 20% (w/w) were reported. The possible origin of this variation can be attributed to the change of ERH, the type of property considered or to starch crystallinity rate.

We now approach the hydration of plasticized starch films using the stoichiometric ratios as was applied to starch–water binary system. The level of hydration was systematically determined over a wide range equilibrium relative humidity and plasticizer ratios. The aim was to ascertain that plasticizer saturation concentration is a function of both water and plasticizer ratio. Simple stoichiometric calculations suppose that all starch-binding sites are available. According to Van Soest, Hulleman, de Wit, and Vliegenthart (1996), up to the value of 60% relative humidity (RH), only 5% of crystallinity remains after 2 weeks of conditioning of starch films. This level of crystallinity increases to reach 35% after 7 days at 90% RH and 25% after 7 days at 70% RH. In this work, the experimental conditions were set in order to maintain the amorphous state of the studied starch films and hence conform with the stoichiometric binding ratio approach.

2. Materials and methods

2.1. Materials

Native wheat starch complimentary supplied by Chamtor (Bazancourt) was used for the preparation of films. Glycerol was a Sigma product with a purity >99% used without further purification. Doubly distilled deionized water (HPLC quality) was used for sample preparation. Reagent grade mineral salts (Sigma products) were used to prepare saturated aqueous solutions destined to obtain constant equilibrium relative humidity (ERH).

2.2. Preparation of starch films

Starch films were prepared by the casting method. After heating from ambient temperature to 95 °C (3 °C/min) and mixing 15 min at 95 °C, the liquefied aqueous suspension (4% (w/w)) was spread on Petri dish. Water was then evaporated under controlled low ERH (=11%). After 24 h of drying, a film of about 200 μ m thickness is obtained. Plasticized films were obtained using the same method and adding precise weight ratios of glycerol to the suspension. After drying the films (7–8% water content), the concentration of glycerol in the film was checked chromatographically

(HPLC; Dionex) and the absence of crystallinity microscopically observed under polarized light.

2.3. Conditioning of films at different ERH

Starch films were dried in a desiccator in presence of P_2O_5 and their water content was determined using Karl Fischer titration method. Samples (3–4 mg) of dried film were equilibrated at constant temperature (20 °C) during 158 h (nearly 1 week) with ERH fixed by saturated salt solutions. The salts used were LiCl (11%); $MgCl_2$ (33%); K_2CO_3 (44%); $CuCl_2$ (68%); NaCl (75%) and $(NH_4)_2SO_4$ (80%). After equilibration, precise weighing of samples allowed obtaining of water content and establishing of water vapour sorption isotherms.

3. Results and discussion

3.1. Water vapour adsorption isotherms

Fig. 1 shows the water vapour adsorption isotherms of wheat starch films with and without plasticizer. The ratio of plasticizer (glycerol) was varied between 0% and 52.63% (g glycerol/g dry starch). As already mentioned, a change in adsorption of water occurs around 50% ERH. Below this value, the increase of glycerol content leads to a decrease in water content of plasticized film as compared to non-plasticized. Above 50% ERH, the level of hydration which increases rapidly in function of ERH shows a clearer difference between plasticized and non-plasticized samples. Composition

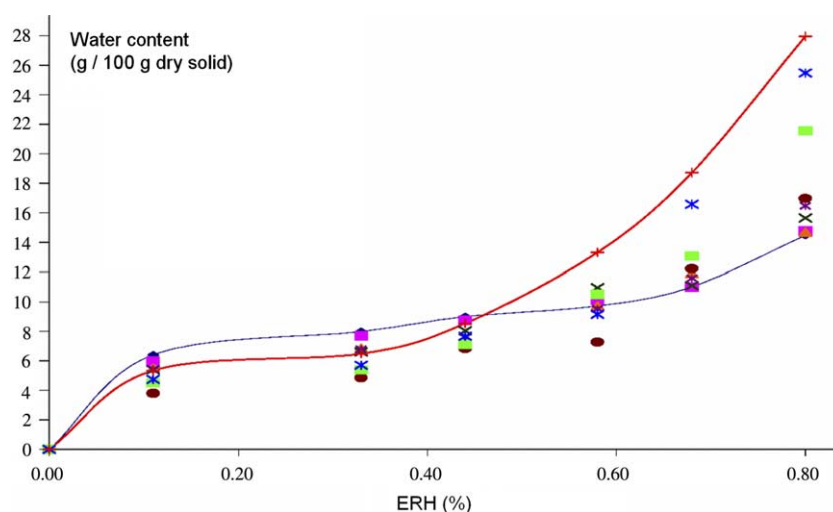


Fig. 1. Water vapour sorption isotherms of wheat starch film without (—) and with (—) different % of plasticizer (glycerol — 0%, — 4.8%, — 8.3%, — 12.4%, — 14.8%, — 20.6%, — 28.6%, — 37.8%, — 52.6%.

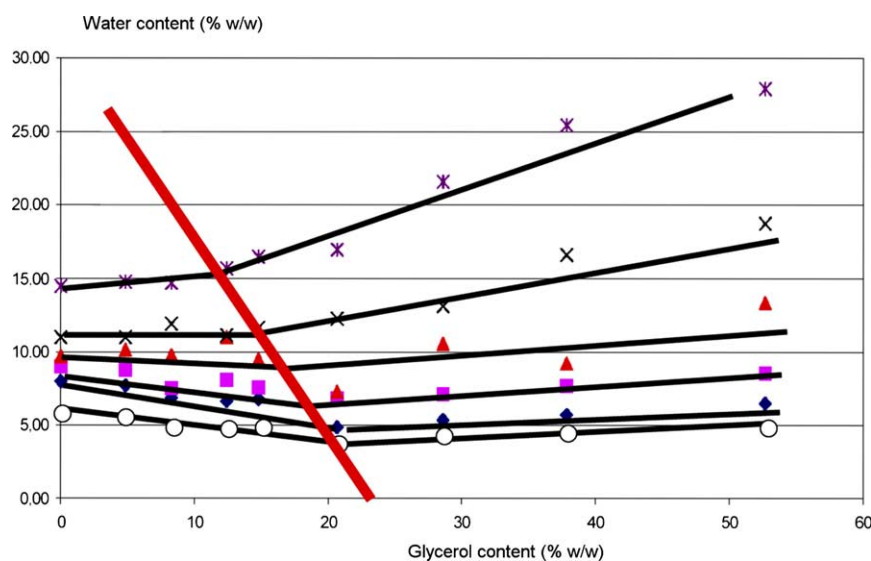


Fig. 2. Representation of water sorption isotherms (water content) as a function of glycerol percentage at different ERH (○ 11%, ◆ 33% ERH, ◆ 44%, ▲ 58%, × 68%, * 80%).

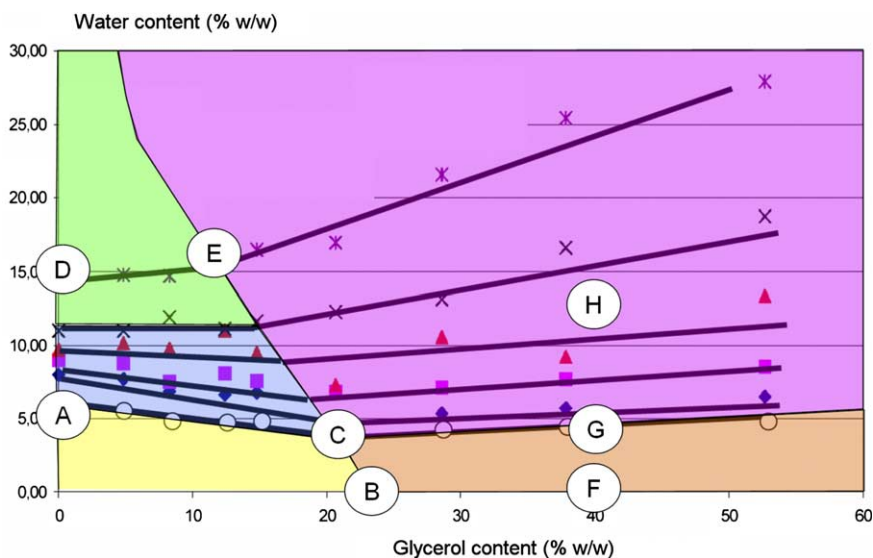


Fig. 3. Representation of Fig. 2 as a phase diagram with characteristic points (for significance of A, B, C, ..., see text).




and the physical state of starch sample influence its water content at a given ERH. For example, non-plasticized native wheat starch film was found to adsorb less water than native starch granules.









Another way of representation of water adsorption by starch films which takes into account the ratio of plasticizer is reported in Fig. 2. Previous results reported by different authors (Lourdin, Coignard et al., 1997; Myllärinen et al., 2002) for the hydration at constant ERH (50%), evoke the presence of a minimum of water content in the plasticized starch films around 20% of glycerol. In our work, this finding is confirmed (see Fig. 2). Moreover, it seems to depend on ERH. If as already proposed, this minimum corresponds to the saturation of starch-binding sites, it is obvious that it depends on the availability of these sites. As a consequence, the saturation of sites should correspond to the combination of H-bonding of starch with water on the one hand and with both water and glycerol on the other. Thus, when glycerol is preponderant, the amount of water bound to starch is low. Conversely, the saturation of starch sites with glycerol occurs with low glycerol concentration when ERH is high. To account for this ternary hydrogen bonded system, the data reported in Fig. 2 were redrawn in Fig. 3 with characteristic points discussed in terms of phase diagram.

3.2. Phase diagram

Fig. 3 represents the characteristic points of the phase diagram which we propose to comment on a stoichiometric basis. The schematic representation of the binding between starch, glycerol and water is given in Table 1. A model of starch representation involving a series of equivalent monomers of an hydro-glucose with three-

Table 1

schematic representation of the binding of water , glycerol  and starch 

A	
B	
C	
D	
E	
F	
G	
H	

binding sites one of which having a stronger binding capacity (CH_2OH) is proposed as well as models for water and glycerol.

Point A corresponds to the monomolecular layer of starch primary hydration (BET layer). Water content at this point is around 5.5%. The calculated stoichiometric ratio at 5.5% of water is equal to 0.5 (mol H₂O/mol anhydro-glucose).

Point B is a graphical extrapolation to zero water content of the line crossing the minima of hydration corresponding to glycerol saturation concentration at the different ERHs experimented (Fig. 3). Glycerol concentration at B is 23%, which is equivalent to a stoichiometric ratio of 0.5 (mol glycerol/mol anhydro-glucose). In other words, at this point a molecule of glycerol binds to 2 glucoses (Table 1).

Point C is an experimental point at 11% ERH corresponding to minimum hydration of starch plasticized with 20% glycerol. C is a good illustration of an intermediate state of double binding (water + glycerol) to starch (Table 1). It corresponds to the progressive substitution of glycerol by water in occupying the primary hydroxyls of starch.

Point D is obtained assuming a complete saturation of the 3OHs in anhydro-glucose (starch) with water, i.e. $3 \times 5.5\% = 16.5\%$ (w/w), or a stoichiometric ratio of 1.5 (Table 1). This point is close to the level of hydration experimentally obtained at 80% RH (Fig. 2). Fringant et al. (1996) propose a limit of binding (double bonding) of water to starch at the same ERH (80%).

Point E is situated on the glycerol saturation line (Fig. 3). The corresponding concentration of glycerol is 12% (w/w) which means 1 glycerol for 4 anhydro-glucoses. At this point, water content is nearly 16%, close to

the stoichiometric ratio 1.5 as in Point D. This situation implies multi-layer, multi-plasticizer binding as schematically represented in Table 1. We suppose that water molecules saturating the primary hydroxyls are the preferred sites for glycerol binding.

Point F is found in a region of excess in glycerol. Phase separation can occur. For example at 40% glycerol (0% water), we could obtain the schematic binding represented in Table 1. Part of glycerol binds to the primary hydroxyls of starch and the excess separates as free glycerol. Likewise, glycerol–glycerol bridges can take place on the glycerol bound to starch.

Point G corresponds to 40% glycerol and water content at 11% ERH. At this level, water can be associated by H-bonds either to starch or to glycerol (free or multi-layer). The preponderance of glycerol implies a preference for starch–glycerol binding (Table 1).

Point H is situated on the hydration curve corresponding to 58% ERH. At this level, the increase of water content leads to a complex hydrogen bonding in the ternary system. Water can either bind to starch primary or secondary hydroxyls in association with glycerol or not. It can also bind directly to free glycerol. In such conditions a question worth asking is how much is there free glycerol?

3.3. Free glycerol

A method of estimation (overestimation) of free glycerol is proposed in Fig. 4. After phase separation, all water molecules are supposed to bind to free glycerol.

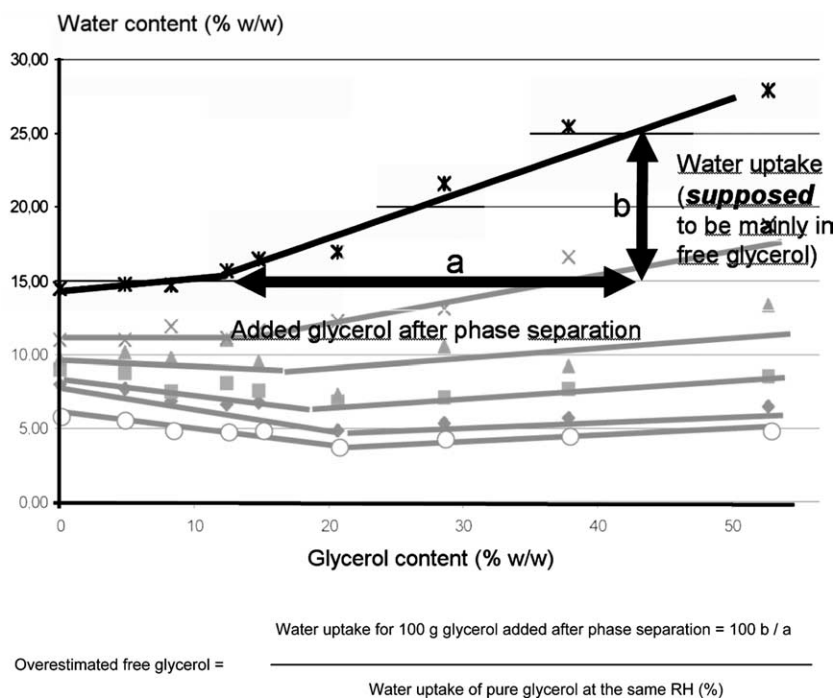


Fig. 4. Method applied to estimation of free glycerol in the ternary system starch–water–glycerol (equation used and the schematic representation of a and b on Fig. 2).

Theoretical water uptake by glycerol can be obtained from water vapour sorption isotherm of pure glycerol (Sloan, Waletzko, & Labuza, 1976). Of course, the amount of water practically bound to free glycerol in our experimental conditions is lower. The ratio of practical to theoretical water uptake allows calculation of free glycerol. We are aware that this is an overestimation because water can bind either to free or multi-layer glycerol. Fig. 4 shows the graphical overestimation method used to calculate free glycerol as a function of ERH. Results are represented in Fig. 5. At 11% ERH, we found 100% of free glycerol. As ERH is increased, a decrease in free glycerol is observed with a minimum at 58% ERH.

Because the amount of free glycerol is almost negligible at 58% ERH, the complex binding of water and glycerol to starch implies mainly multi-layer multi-plasticizer mechanism (Table 1). This point H is an example of the numerous types of bindings one can imagine in such a complex medium. Above 58% ERH, the calculated free glycerol increases (Fig. 5). On the other hand, it was found (Van Soest et al., 1996) that retrogradation of glycerol-plasticized starch (with 20% glycerol) occurs above 60%

ERH. Obviously, the retrogradation of starch yields a release of bound glycerol into the liquid disordered medium where it becomes largely in excess.

4. Conclusion

Results presented in this work cover a wide range of glycerol ratios used in glycerol-plasticized starch films as well as the whole range of ERH to which they might be submitted. This is an advantage if we compare our systematic approach to that reported in literature at constant RH (50–60%) or constant glycerol rate. Stoichiometric ratios were found useful to describe the interactions (H-bonding) between water and starch and their fitting was good especially at 11% ERH or 80% ERH. At 58% ERH the saturation concentration of glycerol was found equal to 17%. Such a plasticizer rate although not fitting with a simple stoichiometric ratio, should be taken into account in starch plasticizing strategy for films exposed to average ERH encountered under our climates.

Commenting of the hydration levels obtained by water vapour adsorption isotherms for the plasticized starch films with different ratios of glycerol on a stoichiometric basis allowed clarification of the understanding of the interactions between the three molecules. A phase diagram is proposed in which characteristic points are reported and their binding to starch hydroxyls schematically represented. The dependency of glycerol concentration needed to saturate starch-binding sites on ERH is evidenced and the complexity of molecular association in the ternary system at 58% ERH demonstrated. Such complexity can originate from the beginning of starch retrogradation at that level of hydration as well as from glycerol availability. It was indeed shown that this ERH corresponds to a minimum of free glycerol.

We intend to use this stoichiometric approach to the study of hydration behaviour of plasticized starch using other plasticizers or modified starches.

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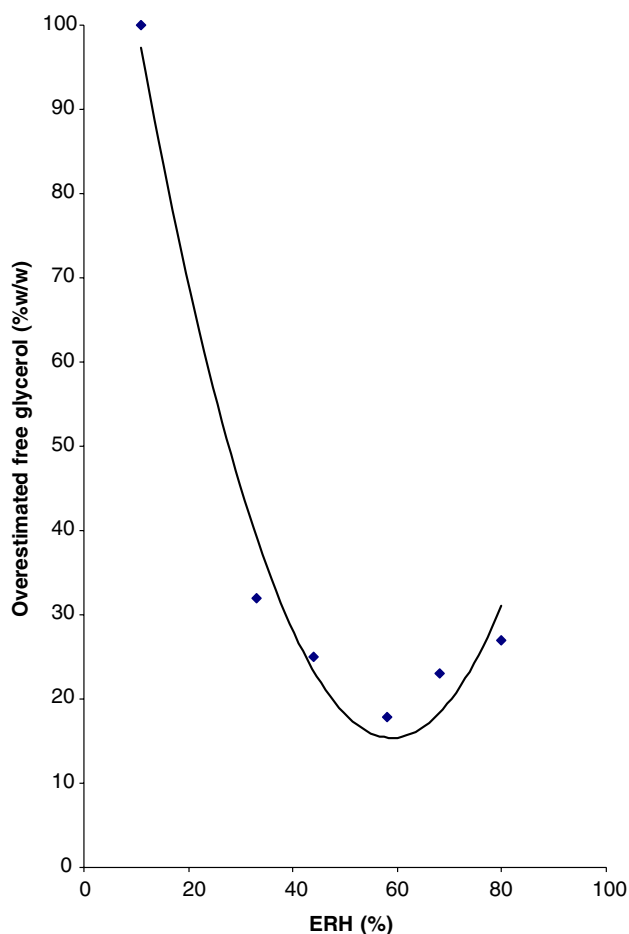


Fig. 5. Overestimated free glycerol percentage variation with ERH in the ternary system glycerol-plasticized starch and water.

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