

## Aroma Permeability of Hydroxypropyl Maize Starch Films

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In this study, the role of water and the impact of the glass to rubber transition on aroma mass transport through hydroxypropyl maize starch films were followed. The permeability of four aroma compounds (ethanol, pyrazine, menthone, and decanone) was monitored by atmospheric pressure chemical ionization mass spectroscopy. The increase in water content within the film promoted greater water diffusion and film flexibility and resulted in enhanced transport of the four aroma compounds through the film. At low water contents in the glassy state, the permeability of ethanol was much higher than those of the other three compounds, which was attributed to its low molecular volume and greater solubility in starch. The structural changes induced by the glass transition resulted in the hydroxypropyl maize starch films displaying poor barrier behavior in the rubbery state for all the aromas studied.

**KEYWORDS:** Water content; diffusion; glass transition; rubbery state; mechanical properties

### INTRODUCTION

Aroma compounds are often encapsulated by spray drying liquid aromas with a suitable biopolymer. This process produces small aroma droplets coated with a biopolymer film, which protects the aroma droplet by decreasing losses due to volatilization, or through oxidative processes, and therefore improves the shelf life of aromas. The permeability of the biopolymer film to aroma compounds and to oxygen is an important factor determining the shelf life of the encapsulated materials. Encapsulation can be achieved with a range of biopolymers which need to provide protective film properties for storage stability. Gum acacia provides protection as well as assisting in the emulsification stage before spray drying (1), but starch-based materials have become popular due to their lower costs and the ability to modify their properties by chemical or physical means (2).

There have been extensive studies on the volatile permeability of biopolymer films, particularly protein blended films. Studies on starch have been far more limited and have been confined to materials plasticized with substantial quantities of glycerol or other polyols (3). One of the main reasons for this is the poor mechanical properties of starch films, particularly at low relative humidities. Significant quantities of glycerol (~20%) are required to improve the mechanical properties (4), and the presence of this phase in addition to water complicates the interpretation of the data. This can be appreciated from the recent

theoretical study of Habeych et al. (5) where volatile permeation through starch glycerol films was modeled. Another approach is to impregnate filter paper with starch, but this raises questions about the integrity of the starch layer (4).

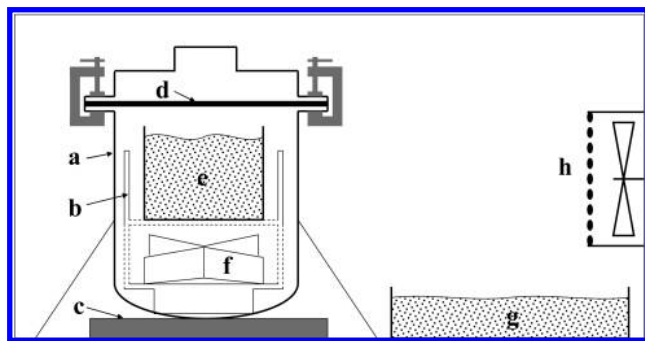
Hydroxypropylated starches produced by the low level etherification of maize starch with propylene oxide are reported to have improved film mechanical strength and cold water solubility and can apparently form flexible films through casting of aqueous dispersions, particularly when prepared from high amylose starch (4, 5). The hydrophilic nature of the hydroxypropyl groups influences the sorption of aroma compounds to the starch interface, resulting in a general decrease in aroma permeability compared with nonpolar polymeric films. However, this polar nature also makes hydroxypropyl starch films poor barriers to water when compared with other polymeric films (7). The material therefore needs testing to determine its suitability as an encapsulating material.

One way to test biopolymers for their encapsulating potential is to measure the permeability of thin biopolymer films to a range of aroma compounds of different polarities. Experimental methods to determine aroma permeability through biopolymer films under controlled conditions (e.g., humidity, temperature, relative humidity) have been reported previously (see, for example, refs 8, 9). The associated mass transfer mechanisms and equations have also been articulated (3, 10–12). Permeability of biopolymer films can also be influenced by the physical state of the material (rubbery or glassy state), and these factors also need to be examined (13, 14). The objective of the present study was to better understand aroma transport through hydroxypropyl maize starch films. To address this, four aromas were selected on the basis of polarity and molecular size and

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**Figure 1.** Apparatus to measure permeation of aroma compounds through starch films: (a) permeation cell; (b) PTFE scaffolding; (c) magnetic stirrer; (d) starch film; (e) aroma solution; (f) PTFE magnetic propeller; (g) saturated salt solution; (h) convection temperature regulator.

shape. Their permeation through free-standing films with different water contents at 30 °C was measured. These observations were then compared with the mechanical characteristics and physical state of the hydroxypropyl maize starch films.

## MATERIALS AND METHODS

**Materials.** Hydroxypropyl maize starch was obtained from National Starch (Bridgwater, USA). Ethanol, pyrazine, decanone, and menthone (Sigma-Aldrich, Poole-Dorset, U.K.) were used as permeate aromas (purity > 98.5%). Ethanol and pyrazine represent linear and cyclic hydrophilic compounds with log  $P$  values of  $-0.14$  and  $-0.06$ , respectively; decanone and menthone are respectively linear and cyclic hydrophobic compounds (log  $P$  values 3.36 and 2.87).

**Film Preparation.** A dispersion of hydroxypropyl maize starch in distilled water (4 g/100 g) was prepared by high shear mixing at 80 °C for 1 h. The dispersion was cast onto polystyrene Petri dishes and dried at 18 °C and room humidity (40–50% RH) for 7 days. The final films showed an average thickness of 124  $\mu\text{m}$  (thickness determined by a 6 point measurement using a micrometer). The water content of films was adjusted to the appropriate value for permeability testing as described below, and film water content was determined gravimetrically (105 °C oven to constant weight).

**Water Diffusion Coefficient Determination.** An estimation of the water diffusion coefficient for a hydroxypropyl maize starch film was performed using dynamic vapor sorption (DVS, Surface Measurement Systems, Middlesex, U.K.). Prior to the tests, hydroxypropyl starch films were ground and sieved to produce particles with an average diameter of  $\approx 115 \pm 10 \mu\text{m}$ ; then they were dried over  $\text{P}_2\text{O}_5$  for 24 h prior to complete drying under DVS conditions. Assuming spherical geometry and a Fickian diffusion mechanism, an estimation of the diffusion coefficient ( $D$ ) was calculated using eq 1 and by measuring the increase in sample mass during hydration at 25 °C over a range of relative humidity from 0 to 95%.  $M_t$  is the mass at time  $t$ ,  $M_\infty$  is the mass at time infinity (the assumed mass when the standard deviation between mass readings is inferior to  $2 \times 10^{-4}\%$ ), and  $R$  is the sphere radius. This model was applied considering  $M_t/M_\infty$  to range between 10% and 60% of the sorption equilibrium (11).

$$\frac{M_t}{M_\infty} \cong \frac{6(D)^{1/2}}{R(\pi)} t^{1/2} \quad (1)$$

In addition to the assumption that the particles are spheres of the same radius, this equation strictly applies only to the early stages of water sorption. Deviations from these assumptions are considered by Peppas and Brannonpeppas (11).

**Aroma Permeability Coefficient Experimental.** The permeability of the four aroma compounds through hydroxypropyl maize starch films was determined using a permeability cell as shown in **Figure 1**. The cell was based on a glass apparatus (QRE-340-B, QAK-520-L, Quickfit, Fisher Scientific, Loughborough, U.K.) with the starch film (d) clamped between the two chambers. The films were equilibrated for 7 days to the desired relative humidity, and the

exposed area was 78.5  $\text{cm}^2$ . A PTFE scaffolding held a magnetic stirrer fitted with a vane to stir the gas phase and maintain a uniform aroma composition within the lower chamber. Aroma was delivered by partition from an aroma solution (50 mL) placed on the PTFE scaffolding below the starch film (e). Aroma was delivered from solutions which maintained the relative humidity within the lower chamber and the water content of the film at the desired level. Solutions used were a (1:1) glycerol/LiCl saturated aqueous solution, a (1:1) glycerol/ $\text{Mg}(\text{NO}_3)_2$  saturated aqueous solution, a (1:1) glycerol/KCl saturated aqueous solution, and a (1:1) glycerol/ aqueous water solution which maintained the water content of the starch films in the chamber at 7.1 g/100 g, 12.6 g/100 g, 16.5 g/100 g, and 29.4 g/100 g (wet weight basis), respectively. Ethanol, pyrazine, decanone, and menthone were dissolved in these solvents to give a solution concentration of 15  $\mu\text{L/L}$ , 30  $\mu\text{L/L}$ , 5  $\mu\text{L/L}$ , and 5  $\mu\text{L/L}$ , respectively. The temperature of the permeability cell was maintained at  $30.0 \pm 0.5$  °C using the heater (h), and the external environment was also maintained at the same humidity as the cell using suitable solutions (g) to avoid any cell humidity changes due to leakage through the film edges.

The aroma concentration in the headspace above the film was determined by direct mass spectroscopy (15) (MS Nose, Micromass, Manchester, U.K.) over a period of 6 h; the headspace concentration below the film was determined in an identical cell with no film in place.

**Aroma Permeability Coefficient Calculation.** Permeabilities of gases, vapors, and aromas through films are frequently compared using the permeability coefficient  $P$  (9, 16). The flux  $J$  of a gas or vapor through a film is related to  $P$  by the equation

$$J = \frac{dM/dt}{A} = \frac{P(p_1 - p_2)}{x} \quad (2)$$

where  $M$  is the mass of material,  $p_1 - p_2$  is the difference in partial pressure between the two film surfaces,  $A$  is the film area, and  $x$  is the film thickness. Since it is assumed that  $x$  and  $A$  are constant, the total mass  $M$  transported across the film in time  $t$  will be given by

$$M = \frac{PA}{x} \int_0^t p_1 - p_2 dt \quad (3)$$

Since, in our experiment (see **Figure 1**), the rate of transport through the film is low compared to the rate of refreshment of the volatile in the headspace below the film, the vapor pressure below the film ( $p_1$ ) was constant. The vapor pressure above the film ( $p_2$ ) was measured as a function of time, and by fitting this relationship to a second order polynomial, eq 3 could be integrated and  $P$  obtained.

Implicit in the use of eq 3 is the assumption that  $P$  is independent of the concentration of the volatile within the film.  $P$  is related to the solubility coefficient  $S$  and the diffusion coefficient  $D$  through the relationship in eq 4.

$$P = DS \quad (4)$$

where  $D$  is the diffusion coefficient and  $S$  is the solubility coefficient. The latter is defined in terms of the concentration  $c$  and partial pressure  $p$  through the Henry's law relationship (eq 5).

$$S = \frac{c}{p} \quad (5)$$

The assumption of linear diffusion (constant  $D$ ) for starch volatile blends at constant relative humidity seems reasonable for nonpolar volatiles, since their solubility in starch matrices is low (3), but we recognize that in our experiments ethanol in particular, though a much less effective plasticizer than water, may contribute an additional polymer plasticization effect, increasing the diffusion coefficient at high concentrations in the film.

**Film Mechanical Properties.** The mechanical properties of the hydroxypropyl maize starch films were measured as a function of water content using a Texture Analyzer (TA.XT plus, Stable Micro Systems, Surrey, U.K.) with a 30 kgf load cell operating in tension at a speed of 12 mm/min. The tests were performed at room temperature (20 °C) using tensile grips. Prior to testing, the starch film strips (thickness =

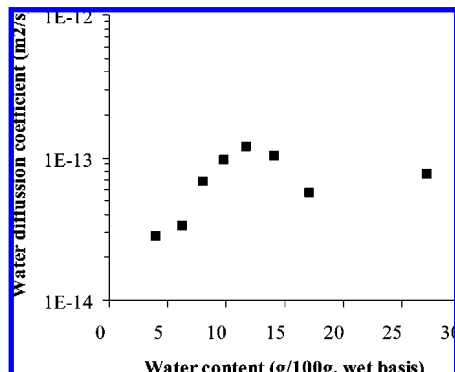


Figure 2. Estimated water diffusion coefficient of hydroxypropyl maize starch films measured by dynamic vapor sorption.

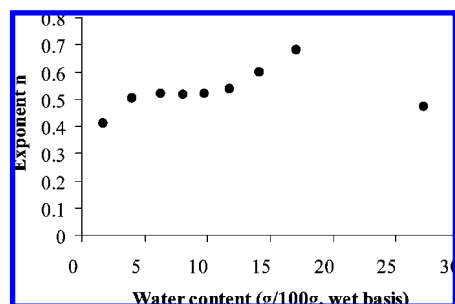


Figure 3. Diffusion exponent  $n$  in eq 6 as a function of the water content of hydroxypropyl maize starch films.

0.12  $\pm$  0.02 mm, width = 10 mm, and length = 100 mm) were equilibrated over saturated salt solutions to produce water contents in the range 2–18 g/100 g (wet weight basis; ww). After mounting in the tensile grips, the starch films were coated with silicon oil to prevent water loss. Stress–strain curves were produced, and values of the Young's modulus (slope of the linear part of the stress–strain curve), strain ( $\epsilon_b$ ), and stress ( $\sigma_b$ ) at break were recorded. Mechanical tests were performed in triplicate for each film sample.

**Glass Transition Determination.** Glass transition temperatures were determined over a range of water contents by differential scanning calorimetry (DSC 7, Perkin-Elmer Ltd., Buckinghamshire, U.K.). Samples were equilibrated over saturated salt solutions to give water contents in the range 5–26 g/100 g (ww). The samples were sealed in 60  $\mu$ L stainless steel pans and submitted to heating, cooling, and reheating stages. A scanning rate of 10  $^{\circ}$ C/min from 5 to 200  $^{\circ}$ C was used.

## RESULTS AND DISCUSSION

**Permeability Cell Performance.** The average standard deviation of the headspace concentration results was 9.8% of the average values, showing a good reproducibility and consistency of the permeability cell.

**Effect of Water Content on Water Diffusion in a Hydroxypropyl Starch Film.** Dynamic vapor sorption was used to measure water diffusion through particles of film at different water contents, based on the hypothesis that diffusion is the major mechanism if the biopolymer is in a fixed (nonmobile) state. It is known that the water content of starch-based materials can affect the physical state of the biopolymer films, and therefore, measuring water diffusion across a range of water contents can indicate if, and where, deviation from the basic Fickian diffusion occurs.

Aroma permeability through starch films is characterized by the partition behavior of the permeate molecule on the film surface (solubility) and the flow of the permeate through the starch polymer matrix (diffusion) (17). Permeate mass transport is affected by factors influencing the structure and chemical

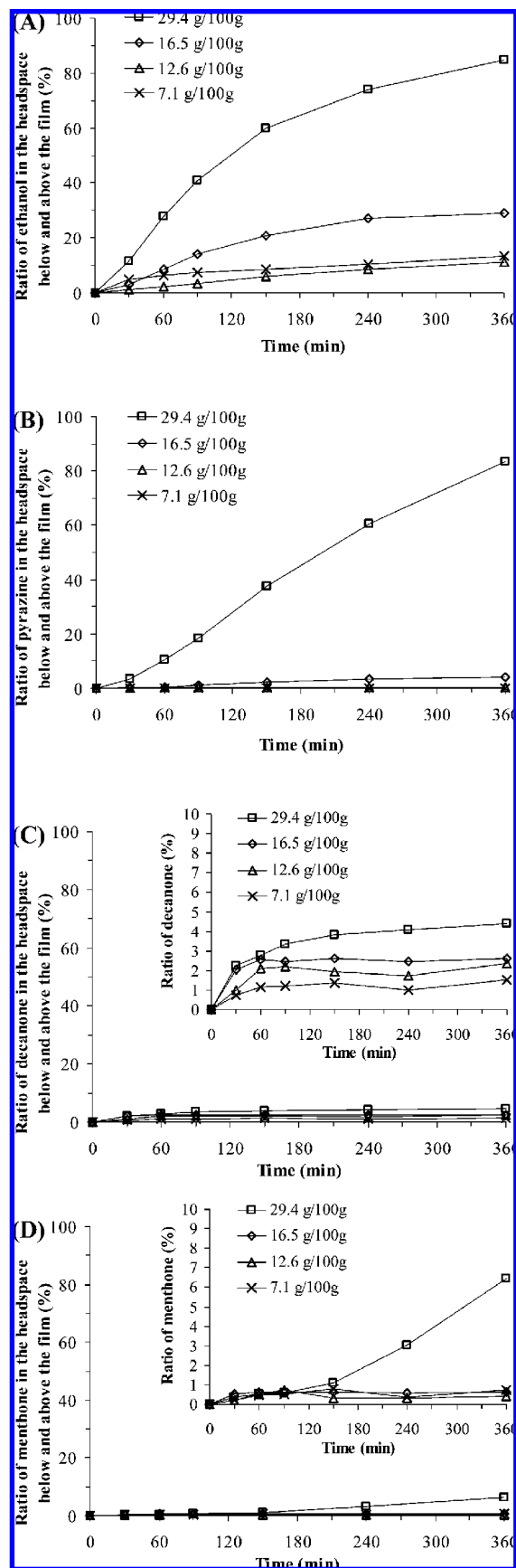
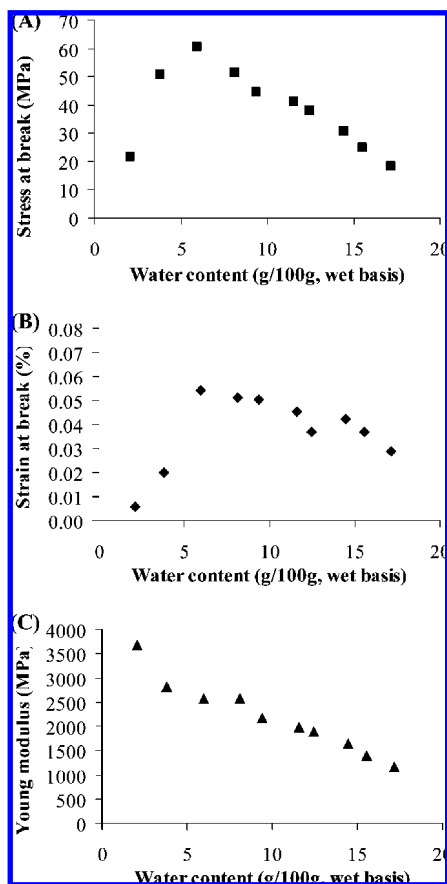


Figure 4. Aroma transport through hydroxypropyl maize starch films equilibrated to different water contents (g/100 g, ww): (A) ethanol; (B) pyrazine; (C) decanone; (D) menthone.

properties of the polymer/permeate system such as the following: polymer cross-linking and crystallinity, polymer free volume



**Figure 5.** Mechanical properties of hydroxypropyl maize starch films: (A) stress at break; (B) strain at break; (C) Young modulus.

(volume not occupied by the polymer molecules), polymer polarity, chemical structure and level of additives, and permeate molecular size, shape, and polarity (10, 18–21).

Water content has a direct impact on permeability due to its role in plasticizing the starch matrix. Plasticization enhances polymer chain mobility, which affects permeate solubility and polymer free volume (21–23). This increase of molecular mobility in the film can be observed by following the changes in the water diffusion coefficient measured by DVS. **Figure 2** shows a progressive increase in estimated water diffusion coefficients with water content.

A small decrease in water diffusion coefficients was observed at high water contents and was interpreted and as a deviation from a Fickian diffusion mechanism accompanied by an association of particles. A semiempirical model has been proposed by Peppas and Sinclair (12) to characterize the transport mechanism in glassy polymers.

$$\frac{M_t}{M_\infty} \cong kt^n \quad (6)$$

where  $M_t$  corresponds to the mass at time  $t$ ,  $M_\infty$  corresponds to the mass at time infinity,  $k$  is a constant related to the molecular network system, and  $n$  is a diffusion exponent.

Peppas and Brannonpeppas (11) established for spherical particles with values of  $n = 0.5$  that the system diffusion mechanism can be regarded as Fickian. An increase in  $n$  above this value as shown in **Figure 3** is evidence that molecular relaxation processes make an important contribution to the water transport kinetics.

The influence of water on molecular mobility within the starch matrix had a direct impact on aroma mass transport through

**Table 1.** Aroma Permeability Coefficients ( $\text{g} \cdot \text{m}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ ) of Hydroxypropyl Maize Starch Films as a Function of Water Content

water content (g/100 g, wet basis)	ethanol	pyrazine	decanone	menthone
7.1	$1.97 \times 10^{-16}$	$2.08 \times 10^{-18}$	$7.49 \times 10^{-17}$	$2.30 \times 10^{-17}$
12.6	$1.62 \times 10^{-16}$	$1.13 \times 10^{-17}$	$1.03 \times 10^{-16}$	$2.21 \times 10^{-17}$
16.5	$4.09 \times 10^{-16}$	$1.10 \times 10^{-16}$	$1.17 \times 10^{-16}$	$2.98 \times 10^{-17}$
29.4	$1.26 \times 10^{-15}$	$1.70 \times 10^{-15}$	$2.20 \times 10^{-16}$	$3.16 \times 10^{-16}$

the film, expressed in terms of the ratio of aroma concentration in the headspace above and below the film (**Figure 4**). With an increase of the water content of hydroxypropyl maize starch films, an increase in aroma transport was observed for all the compounds tested.

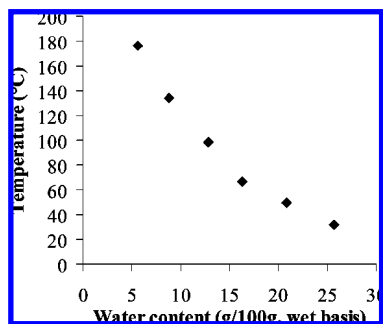
The plasticizing role of water in the film also influenced the film's mechanical properties. **Figure 5A** shows that below 4 g/100 g (wwb) a brittle film was generated (break stress was low) but increasing water content initially increased break stress and then decreased it to initial levels so the break stress at 2 and 17 g/100 g (wwb) was comparable. The strain at break point (**Figure 5B**) also changed with water content. Below 5 g/100 g (wwb) the strain values were low but then increased and decreased to a small extent up to 17 g/100 g (wwb), showing the film had some elastic properties (**Figure 5C**). Above 6 g/100 g water content (wwb), film toughness was enhanced, as can be seen by the increase in strain at break (**Figure 5B**). In this region, the films showed plastic behavior, as evidenced by a plateau in the stress–strain relationship followed by abrupt fracture (results not shown). These plastic films showed a reduction in the Young modulus with increased water content (**Figure 5C**). At high water levels, above 15.5 g/100 g (wwb), a further reduction in film toughness was observed (**Figure 5C**).

This change in the film's mechanical behavior had an impact on the mass transport of ethanol. In the case of plastic films with water content between 7.1 g/100 g and 12.6 g/100 g (wwb), almost no change in ethanol transport through the film was observed, but for higher water levels, a substantial increase in ethanol transport occurred (**Figure 4A**). The reason why such a clear distinction in transport was not seen for the other compounds is probably due, in part, to the molecular affinity of ethanol for water.

**Influence of the Glass to Rubber Transition and Nature of the Permeate on the Films Permeability.** A similar progressive increase in molecular transport with increasing water contents was observed by Forssell et al. (23) in their study of oxygen permeability through amylose and amylopectin films at 20 °C. In fact, at high water contents (above 20 g/100 g, wwb), a dramatic increase in oxygen permeability was observed. Similarly, when analyzing the ethanol, pyrazine, and menthone systems, a similar dramatic increase in aroma permeability coefficient was observed for films with 29.4 g/100 g water content (wwb) (**Table 1**). This drastic deterioration in the film's barrier properties at the highest water content was a result of the film's phase transition from a glass to a rubbery state (**Figure 6**).

In the glassy state, the free volume within the polymer matrix is reduced and the ability of the polymers to flex allowing the permeate to diffuse through the matrix is restricted (20, 24). Therefore, this lower polymer flexibility can in part account for the higher permeabilities observed for ethanol and decanone (linear molecules with low cross section) than those for their hydrophilic/hydrophobic counterparts pyrazine and menthone, which are cyclic molecules with respectively higher cross sections (**Table 1**). Also, the higher polarity of ethanol in relation





**Figure 6.** Glass transition temperature of hydroxypropyl maize starch as a function of water content.

to pyrazine enhances permeate mass transport as a result of its solubility in the hydrophilic starch environment. Moreover, at low humidity (7.1 and 12.6 g/100 g water content, wwb), where the influence of water in permeate diffusion is reduced, as is the solubility of hydrophilic molecules in the film, decanone and menthone showed higher permeability values than pyrazine (Table 1). But with a further increase in water content promoting a simultaneous increase in free volume and the enhancement of hydrophilic compounds adsorption to the film interface (3), an inversion in aroma permeability was observed, with pyrazine displaying higher values than decanone and menthone (Table 1).

To our knowledge, there are no previously reported data on the permeability coefficients for volatiles through hydroxypropylated starch films, or indeed other free-standing starch films, in the absence of plasticizers. As would be expected, the values obtained are substantially lower than the water vapor permeabilities through hydroxypropylated starch films. Values of  $1.1 \times 10^{-10} \text{ g}\cdot\text{m}/(\text{m}^2\cdot\text{s}\cdot\text{Pa})$  have been reported by Azemi et al. (24) for hydroxypropylated rice starch (RH gradient 100%) and  $3 \times 10^{-12} \text{ g}\cdot\text{m}/(\text{m}^2\cdot\text{s}\cdot\text{Pa})$  for hydroxypropylated potato starch in the presence of 8% glycerol (4), but ones of a similar order of magnitude have been reported for limonene permeability through whey protein films (7).

Once above the glass transition, where particle volume restrictions to diffusion are mitigated and molecular mobility is greatly enhanced, an increase in bonding between the linear aromas (ethanol and decanone) and the starch molecules appeared to occur. This bonding is characterized by the entrapment of the volatile compound in the amylose complex through hydrophobic bonding or by polar interactions through hydrogen bonding between hydroxyl groups. This possible molecular bonding had an impact on ethanol and decanone mobility in the film (20, 26–28), with lower permeability values observed for these compounds with respect to the cyclic pyrazine and menthone compounds (Table 1). Ethanol displayed an overall higher permeability at the water levels tested (Table 1). This might be attributed, as suggested by Menting et al. (10), to the linear polar characteristics and small molecular volume of the ethanol molecule, which appeared to substantially enhance its mass transport through the hydroxypropyl maize starch films.

In conclusion, water content and the glass to rubber transition played an important role in aroma permeability through hydroxypropyl maize starch films. Water content directly affected polymer free volume within the films, resulting in changes in permeate mobility. Low water content starch films in the glassy state displayed restricted molecular transport for the aromas tested. The progressive increase in molecular motion, film mechanical flexibility, and solubility

promoted by an increase in water content resulted in an increase of 3 orders of magnitude for the permeability of pyrazine as the film's water level changed within the tested range. The results showed that, although a general increase in aroma permeability with the increase in water content was observed for films in the glassy state, a major increase in permeability was recorded as the system moved to the rubbery state. In fact, hydroxypropyl maize starch films showed poor barrier behavior to all aromas studied above its glass transition temperature.

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