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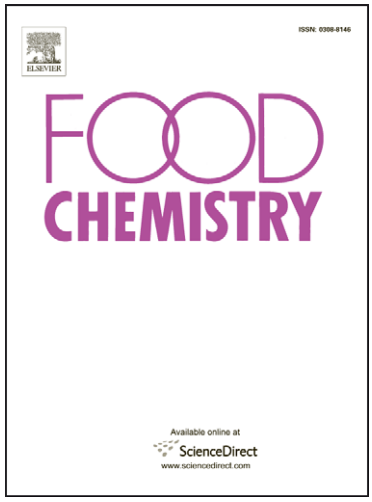

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Food aroma mass transport properties in renewable hydrophilic polymers

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ABSTRACT

The sorption and transport properties of gliadin and chitosan films with respect to four representative food aroma components (ethyl caproate, 1-hexanol, 2-nonanone and α-pinene) have been studied under dry and wet environmental conditions. The partition coefficients (K) of the selected volatiles were also obtained using isooctane and soybean oil as fatty food simulants. The results showed that gliadin and chitosan films have very low capacities for the sorption of volatile compounds, and these capacities are influenced by the nature of the sorbate, the environmental relative humidity and the presence of glycerol as a plasticizer in the polymeric matrix. The volatile compounds also present a low partitioning in the biopolymer film/food stimulant system. Given the low levels of interaction observed with the volatiles, gliadin and chitosan films are of potential interest for the packaging of foods in which aroma is one of the most important quality attributes.

Keywords

Biopolymer films; gliadins; chitosan; aroma compounds; diffusion coefficient; solubility coefficient; partition coefficient

1. Introduction

Plastics obtained from polysaccharides and proteins are attracting considerable interest in food packaging applications. These biopolymers fulfil the criteria of sustainability since they are extracted directly from renewable resources and their biodegradability is in keeping with environmental protection. Whilst the film forming capacity of these biomacromolecules has been employed in the development of edible coatings to preserve the quality of minimally processed foods, these polymers also can be processed into self-standing plastics for food packaging applications. However, major disadvantages of these polymeric films include their solubility in water and the lack of mechanical strength, especially under wet environments, which limits their application as packaging materials (Woerdeman et al., 2004). Water and mechanical resistance however can be improved by blending with higher performance polymers, incorporating fillers or developing polymer nanocomposites, and efforts are currently being made in this direction (Rhim & Ng, 2007). Finally, many natural biopolymers cannot be melt-processed and although some, such as starch and proteins, are thermoplastics their thermal processing presents certain difficulties (Hernandez-Izquierdo & Krochta, 2008).

Whilst synthetic polymers dominate the food packaging market, natural polymers can occupy a niche in this area, replacing the former when packaging is required for just short periods (film wrappings, laminated papers, containers for fast food, bags, etc). In these applications, hydrophilic biopolymers present attractive properties such as good oxygen barrier properties at low and intermediate humidities, grease resistance, and aroma barrier (Bordenave, Grelier, Pichavant & Coma, 2007). It is well known that flavour is a key factor in determining food quality and exerts a direct effect on consumer acceptance. The sorption of aroma compounds into a packaging material that is in contact with a food can produce an imbalance in the food's flavour profile

thereby deteriorating the sensorial quality of the packaged product, a phenomenon known as flavour scalping. Flavour scalping by plastics in contact with foods, particularly polyethylene and polypropylene, is well-documented in the literature (Sajilata, Savitha, Singhal & Kanetkar, 2007). These polymers are usually employed as interior linings in contact with foods but their olefinic structure endows them with a considerable affinity for apolar compounds. In contrast, hydrophilic polymers can be expected to present low affinities for apolar compounds and hence a reduced tendency to cause flavour scalping. There is, however, little information in the literature regarding this issue.

Films made from gliadins, a fraction of wheat gluten soluble in 70% (v/v) ethanol, are glossy, transparent and possess good oxygen barrier properties in low and intermediate relative humidity environments (Hernandez-Munoz, Kanavouras, Ng & Gavara, 2003). Chitosan (poly β-(1,4)N-acetyl-D-glucosamine) is a biodegradable natural polymer produced industrially by the chemical deacetylation of chitin, a major component of crab and shrimp shells and the second most abundant biopolymer present in nature after cellulose. Chitosan is soluble in aqueous acidic solutions, becoming a cationic polyelectrolyte with antimicrobial properties. It also possesses excellent film-forming characteristics, with the resulting films demonstrating good mechanical properties and low permeability to oxygen, a property which (as is the case in protein films) is largely dependent on the relative humidity (Clasen, Wilhelms & Kulicke, 2006).

Given the favourable film-forming and high oxygen barrier properties of gliadins and chitosan they are biopolymers of potential interest for use as food-contact packaging materials. Although the gas and water vapour barrier properties of these polymers have been extensively analysed, no work has been reported in the literature on their interaction with food aroma components.

The aim of the current work has been to study the sorption behaviour of different aroma compounds into gliadin and chitosan films. For this purpose four volatile molecules, ethyl caproate, 1-hexanol, 2-nonanone and α-pinene were chosen to represent the main chemical families of volatile compounds found in foodstuffs. Due to the hydrophilic nature of these biopolymers, the kinetics of aroma sorption were assayed at room temperature at different relative humidities. The partition coefficients for each volatile between a fatty food model and the film were also studied.

2. Materials and methods

2.1. Materials

Crude gluten from wheat (80% protein, 7% fat and 8.1% moisture content on a dry weight basis), high molecular weight chitosan, glycerol, ethanol and glacial acetic acid were all of laboratory grade and obtained from Sigma-Aldrich (USA). The aroma compounds ethyl caproate, 1-hexanol, 2-nonanone and α-pinene (each with a minimum purity of 98%) and the fatty food simulants isooctane and soya oil, were also supplied by Sigma-Aldrich (USA).

2.2. Film preparation

Gliadins were extracted from wheat gluten in 70% ethanol solution as described elsewhere (Hernandez-Munoz et al., 2003) and glycerol was added as a plasticizer to the film-forming solution at 25% (g/100 g dry protein). The use of glycerol was necessary to facilitate film handling at 23 ºC and 50% relative humidity (standard conditions). Chitosan was dissolved in 0.5% (w/w) aqueous acetic acid at a concentration of 1.5% (w/w). The solution was filtered with cheesecloth under vacuum to remove residues of insoluble particles. Polymer solution was poured onto a

horizontal flat polystyrene tray and dried at 37 ºC. Chitosan films were neutralized with 0.1 M NaOH.

2.3. Equilibrium distribution of volatile compounds in the film/food simulant system

For equilibrium distribution experiments, 20 cm^2 of film, previously conditioned in standard conditions, was cut into 4 cm^2 squares which were threaded onto a stainless steel wire with alternating glass tube spacers to prevent the films sticking together. The specimens were located in glass vials filled with a solution of isooctane or soybean oil, and the corresponding volatile compound was added at each simulant in a 1% (w/w) concentration. The vials were completely filled with liquid to avoid headspace and hermetically sealed. In order to reach equilibrium samples were stored in the dark at 23 ºC for three months. A blank consisting of the aroma solution without film was prepared to control aroma loss caused by degradation or volatility.

2.4. Vapour phase sorption of volatile organic compounds in films

Dry films were placed in hermetically sealable 250 ml glass jars and conditioned to the desired relative humidity with phosphorus pentoxide (dry environment) or saturated salt solutions of magnesium nitrate (52.9 ± 0.2 RH) and sodium chloride (75.3 ± 0.1 RH); films were allowed to equilibrate for one week at 23 ºC. Thereafter, a 2 ml vial with the corresponding volatile compound was placed in the jar. Equilibrium moisture content of the films was determined by drying moisture-equilibrated samples in a vacuum oven at 70 ºC for 24 h. Uptake of the volatile compound into the polymer film was measured at different times until equilibrium was reached.

2.5. Analysis of volatiles sorbed in a film

The amount of volatile compound sorbed in a film was quantified by thermal desorption using a Dynatherm Thermal Desorber (Supelco Teknokroma, Barcelona, Spain)

coupled to a Hewlett Packard model P5890 gas chromatograph equipped with a flame ionization detector. A strip of the polymer sample was wiped dry with a tissue and placed in the thermal desorption tube, which was inserted in the desorption oven. Tubes were desorbed for 7 minutes at 140 ºC and helium was used as the carrier gas at a flow rate of 1 ml·min^{-1}. Desorbed compounds were transferred from the desorber oven to an Ultra2 column (25m x 0.2 mm x 0.33 µm) through a nickel transfer line maintained at 200 ºC. After desorption, the film sample was recovered and weighed on an analytical balance. The thermal desorption-gas chromatography system was calibrated with polyethylene containing known amounts of the volatile compounds under study (measured independently by gravimetry).

2.6. Analysis of volatiles in food simulants

The amount of volatile compound in a food simulant was measured by gas chromatography with the same chromatograph described above using a HP-1 column (25 m x 0.53 mm x 2.65 µm).

2.7. Solubility parameters

The solubility parameter of a substance (δ) is defined as the square root of the cohesive energy density (CED) (Hildebrand & Scott, 1949):

$$\delta = (CED)^{1/2} = (E_{coh} / V)^{1/2}$$

where E_{coh} is the cohesive energy, and V the molar volume.

Hildebrand et al. (1949) correlated the heat of mixing (ΔH_m) in a binary system with the cohesive energy of the components through the equation:

$$\Delta H_m = V (\delta_1 - \delta_2)^2 \Phi_1 \Phi_2$$

where V is the volume of the mixture and Φ_i the volume fraction of component i in the mixture. A first requirement for the components to be miscible is that the term $(\delta_1 - \delta_2)^2$ be as small as possible. Complete miscibility is expected when $\delta_1 = \delta_2$ and the components present equal degrees of hydrogen bonding. The solubility parameter is widely used for predicting polymer solvent interactions and can thus also be applied to predict the sorption of food aroma compounds into packaging films. The solubility parameters for chitosan and the volatile aroma compounds were obtained by the group contributions to the cohesive energy and molar volume according to Fedors (1974). The solubility parameter for soybean oil (King, 1995) and gliadins (Duclairoir, Nakache, Marchais & Orecchioni, 1998) was obtained from the literature.

3. Results and discussion

3.1. Partition coefficient

The partition coefficient (K) of a volatile compound in a polymer/food simulant system describes the equilibrium distribution of the volatile compound between the polymer and the food simulant, as given in the following expression:

$$K = [S]_p / [S]_s$$

where $[S]_p$ is the equilibrium concentration of the sorbate in the polymer and $[S]_s$ is the equilibrium concentration (w/w) of the sorbate in the food simulant. The partition coefficient determines the extent of the sorption into a polymer film of a compound initially present in food (simulant). In order to minimize the flavour scalping of packaged foods, low values of K are preferred. The magnitude of K is closely related to the relative solubilities of a volatile compound in the polymer and in the food simulant. Figure 1 shows the partition coefficients of volatile aroma compounds in gliadin and

chitosan films using soybean oil or isooctane as fatty food simulants. In general, the partition coefficients of the volatile aroma compounds studied in the polymer/food simulant system were lower than 0.1, which indicates a low affinity of these hydrophilic biopolymers for the aroma compounds. Despite the low volatile aroma sorption capacity of the polymers, the effect of the functional group of the flavour molecule on the resulting K values can be observed. In this regard, molecules carrying the more polar alcohol and ketone groups presented the highest K values whereas the hydrocarbon α-pinene presented the lowest. This behaviour was observed throughout the range of polymer/food simulant systems studied which had similar sorption affinity patterns: 1-hexanol > 2-nonanone > ethyl caproate > α-pinene. With one exception, no significant differences were found in the K values of the volatiles when isooctane or soybean oil was employed as fatty food simulant. The exception was 1-hexanol in gliadin films which presented higher values of K when isooctane was used as the food simulant compared to soybean oil, despite the hydrophobic nature of both simulants. The greater affinity of 1-hexanol for the oil phase could be caused by the development of interactions other than dispersion forces with components of the oil carrying functional groups. With regard to the chemical nature of the polymer, the volatile compounds presented a greater affinity for gliadin proteins than for chitosan, whereas the incorporation of glycerol into gliadin films increased the affinity of volatile compounds for the film, giving rise to higher values of K.

Considering the partitioning of volatiles in gliadin-based films, the chemical and structural diversity of amino acid side chains permits proteins to interact with flavours in different ways. Proteins can interact with non-polar molecules through van der Waals dispersive forces, whereas dipole-dipole, induced dipole-dipole interactions, and hydrogen bonding are also present for molecules carrying functional groups. Carbonyls can be covalently bonded to proteins via condensation with free sulfhydryl groups and free amine groups forming reversible Schiff's bases and Michael addition with

unsaturated aldehydes has also been described (Kühn, Considine & Singh, 2006; Meynier, Rampon, Dalgalarrondo & Genot, 2004). The flavour binding capacity and affinity of proteins depends on their amino acid composition and the physicochemical properties of the sorbate (Tan & Siebert, 2008; van Ruth & Villeneuve, 2002). Protein structure and conformational changes due to environmental factors (media, heat treatment, pressure, pH) will also play roles in determining the extent of binding (Fares, Landy, Guilard & Voilley, 1998; Guichard & Langourieux, 2000). There is considerable work reported in the literature regarding the interaction of flavour compounds with proteins, especially milk and soy proteins since these proteins are incorporated in a great variety of foods. Most of these studies have been carried out with proteins in aqueous media where the binding of most flavours has been primarily attributed to London dispersive forces (Guichard, 2006).

Gliadins present a high content of glutamine (35%), they are rich in non-polar amino acids (~ 20% proline) and contain low levels of residues with charged side chains which contributes to their poor solubility in water. This confers gliadins great potential for hydrogen bonding and hydrophobic interactions. The physicochemical interactions between a volatile compound and a polymer matrix will determine the extent of sorption; however the composition, structure and physicochemical properties of the food matrix will have a considerable effect on the partitioning of the compound in the polymer/food system (Landy, Rogacheva, Lorient & Voilley, 1998).

The effect of fats and oils on the retention of aroma compounds in a food matrix is well known. Riéra, Gouézec, Matthey-Doret, Robert & Blank (2006) reported a considerable retention of hydrophobic compounds such as α-pinene in a fatty food model mainly composed of triacyl glycerol, whereas relatively polar compounds such as 1-hexanol were readily released into the headspace. Schirle-Keller, Reineccius & Hatchwell (1994) also reported the effect of hydrophobicity of the food model system on the

229 retention of volatiles, observing that increasing the content of oil in the liquid phase had
230 a greater effect on the retention of more apolar volatile compounds.

231 The hydrophobicity of a compound is commonly expressed by the octanol/water
232 partition coefficient (log $P_{o/w}$). In the present study, volatiles having values of log $P_{o/w}$
233 close to that of the fatty food simulant are expected to have a high degree of retention
234 in the food phase. This is the case of α-pinene with a log $P_{o/w}$ = 4.4, similar to that of
235 isooctane (log $P_{o/w}$ = 4.5). Thus the affinity of the food media for an aroma compound
236 affects the sorption of the latter in the polymer, and it could be expected that an
237 increase in the hydrophobicity of the liquid food phase results in a decrease of the gain
238 of apolar volatile compounds in the film. Hernandez-Muñoz, Catalá & Gavara (2001)
239 observed that the partition coefficients of hexanal, hexanol and 2-phenylethanol in
240 polyethylene terephthalate films decreased, whereas the coefficients of more
241 hydrophobic compounds, namely n-decane, d-limonene and ethyl caproate, increased
242 and achieved greater partitioning in the film than the more polar compounds when
243 isooctane was substituted by ethanol 95% as the liquid food simulant. Landy et al.
244 (1998) also observed that the liquid-liquid partition coefficients of small molecules
245 depend not only on the chemical nature of the molecule but also on the partitioning
246 media.

247 Glycerol presents great compatibility with gliadins and thus at appropriate
248 concentrations it imparts film flexibility and facilitates handling. In addition, it acts to
249 increase the hygroscopicity of the film and consequently the presence of water, which
250 is a strong plasticizer for proteins. Incorporation of glycerol in the gliadin film increased
251 the partition coefficients of the four volatiles studied. The increment in the partitioning
252 was more acute for 1-hexanol (twenty-fold), followed by 2-nonanone and ethyl caproate
253 with increments close to eight and six times respectively, whereas α-pinene doubled its
254 partition coefficient. At appropriate concentrations a plasticizer acts by disrupting
255 intermolecular forces between polymer chains; consequently, the segmental mobility of

256 the peptide backbone as well as the free volume of the protein matrix increases what
257 facilitates sorbate uptake. Glycerol can also modify protein conformation (Lefèvre,
258 Subirade & Pézolet, 2005). As a result the number of available sites in the protein for
259 flavour interactions may increase and hence the number of molecules retained in the
260 film. Glycerol can also act as a binder of relatively polar volatiles such as aldehydes,
261 ketones and alcohols by the formation of hydrogen bonds. Nawar (1971) and
262 Bohnenstengel, Soltani & Baltes (1993) have reported the flavour binding capacity of
263 glycerol in model solutions. The greater capacity of alcohols for hydrogen bonding
264 could contribute to the greater increase in the partitioning of hexanol in films plasticized
265 by glycerol.

266 It is well established that polysaccharides affect the release of volatile compounds in
267 food matrices due to their thickening effect. Moreover, these macromolecules can
268 interact with flavours in several ways, including physical adsorption and hydrogen
269 bonding (Yven, Guichard, Giboreau & Roberts, 1998); and with polysaccharides, such
270 as amylose and cyclodextrins which present three dimensional structures with
271 hydrophobic cavities capable of interacting with flavour compounds via the formation of
272 inclusion complexes (Arvisenet, Le Bail, Voilley & Cayot, 2002). As shown in Figure 1,
273 the capacity of chitosan film to retain volatiles was considerably lower than that of
274 gliadins, the partitioning of 1-hexanol and 2-nonanone being respectively ~ 35 and 10
275 times lower than in gliadin films, whilst for ethyl caproate and α-pinene the retention
276 was 1000 times lower. The greater capacity of proteins compared to polysaccharides to
277 retain flavour compounds is well-known (Schirle-Keller et al., 1994).

278 Considering the hydrophobicity of the volatile compounds and the fatty food simulants,
279 greater partitioning of 1-hexanol in chitosan can be expected due to hexanol's relatively
280 polar nature compared to the other volatiles. However, it is worth noting that though 2-
281 nonanone and ethyl caproate have similar log $P_{o/w}$ values, the partition equilibrium for
282 the former was similar to that for 1-hexanol, whereas ethyl caproate had a partition

coefficient two orders of magnitude smaller and comparable to that of α-pinene. The higher retention of the ketone compared to the ester suggests specific interactions between polar groups in chitosan and the carbonyl group of the ketone. Interaction between polymer primary amine groups and carbonyls via charge transfer, as well as the formation of Schiff's base complexes could also occur.

The solubility parameter approach can be useful to qualitatively predict the extent of flavour sorption into a polymer film. Comparison of the solubility parameter (δ) of a polymer and a sorbate gives information on their compatibility. The smaller the difference between the solubility parameters of the polymer and the flavour compound having similar hydrogen bonding degree, the greater the magnitude of sorption will be. The solubility parameters of the substances in the present study are listed in Table 1, whereas Figure 2 shows a plot of the partition coefficients of the volatile compounds versus the difference in the solubility parameter value between them and the polymers. It can be observed that partitioning increased when the difference between the solubility parameters of the aroma compound and the film decreased.

3.2. Sorption kinetics of vapour phase compounds in polymer films

Figure 3 shows the sorption curves of different volatile compounds in gliadin films both unplasticized or plasticized with glycerol measured at 23 ºC and at different relative humidities of 0%, 50% and 75%. Experimentally derived sorbate uptake curves were well-fitted by the model based on the one-dimensional solution of Fick's second law of diffusion in a plane sheet, considering that the diffusion coefficient is independent of concentration the sorbed compound and assuming the initial/boundary conditions:

$$t = 0 \qquad 0 < x < L \qquad c = c_0$$

$$t \geq 0 \qquad x = 0, \qquad x = L \qquad c = c_\infty$$

where c_0 is the initial concentration of sorbate in the polymer ($c_0 = 0$) and c_∞ is the concentration of the sorbate in both surfaces of the plane sheet which is assumed to be constant throughout the experiment.

The solution under these conditions is (Crank, 1975):

$$c_t = c_\infty \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left[\frac{1}{(2n+1)^2} exp\left\{ \frac{-\pi^2 \cdot D \cdot (2n+1)^2 \cdot t}{L^2} \right\} \right] \right)$$

where c_t is the concentration of the sorbate in the polymer (kg/m^3) at time t (s), and c_∞ is the concentration of the sorbate in the polymer at equilibrium (kg/m^3), L is the thickness of the film (m) and D the diffusion coefficient (m^2/s).

3.2.1. Solubility coefficient

The estimated solubility coefficient of volatiles in both glycerol-plasticized and non-plasticized gliadin films conditioned at different relative humidities is presented in Table 2. Glycerol-plasticized gliadin films showed poor affinities for volatile organic compounds as revealed by the low values obtained for their solubility coefficients. Under each relative humidity condition studied, the solubility coefficients followed the order: 1-hexanol > 2-nonanone > ethyl caproate > α-pinene, and this pattern was similar to that found for the liquid fatty food simulant/polymer systems tested. The binding strength was greater for the alcohol 1-hexanol while the hydrocarbon α-pinene interacted only weakly with gliadins. Zhou et al. (2006) also reported a decrease in the sorption of volatile compounds in dry soy protein in the following order: 1-hexanol > hexanal > 2-hexanone > ethyl butyrate > hexane.

As can be seen in Table 2 when glycerol was not present in the film, the solubility of the volatiles decreased considerably as compared to glycerol-plasticized gliadin films. This behaviour was similar to that previously described in the liquid fatty food simulant/polymer system. Moreover the addition of glycerol promoted a greater

increase in the solubility of the more polar molecule 1-hexanol compared to ethyl caproate. Thus, glycerol not only plasticizes the film favouring the sorption of organic volatiles, it also increases the affinity of the protein for relatively polar compounds.

The effect of relative humidity on the sorption of volatile compounds was only evaluated in gliadins plasticized with glycerol. The composition (wet basis) of gliadin films plasticized with 25% glycerol and when conditioned at 53% RH was 70.2% protein, 17.5% glycerol and 12.3% water, whereas for films kept at 75% RH this was 63% protein, 16% glycerol and 21% water. The solubility coefficients of the volatiles were affected by the relative humidity in different manners depending on their polarity. In this regard, humidity had a negative effect on the binding of 1-hexanol to gliadin films plasticized with glycerol. Compared to dry environments, when films are exposed to 53% and 75% RH, the solubility coefficient values were reduced by 50% and 85%, respectively. Gliadins present a great affinity to water, which is even increased by the high hygroscopicity of glycerol incorporated to the film. Water molecules interact strongly with the polar groups from proteins and glycerol, and thus reduce the number of free sites for 1-hexanol-film interactions. The decrease in the sorption of 1-hexanol in the hydrated matrix indicates that its retention involves hydrogen bonding and dipole-dipole interactions through the hydroxyl group of the alcohol. At 53% RH the hydration of films slightly increased the solubility coefficients of the volatiles ethyl caproate and 2-nonanone, whereas the solubility coefficient of the weakly retained volatile α-pinene was practically unaffected. Protein hydration confers flexibility to the polypeptide chains and promotes protein conformational changes (Lefèvre et al., 2005) which can modify the binding of volatile compounds depending on their molecular structure and chemical nature. A further increase in the RH to 75% gave rise to lower retention of the four volatiles studied. At high RH, gliadin films containing 25% glycerol are highly plasticized by water imbibed by the protein matrix, which could hinder the accessibility of protein binding sites for interaction with weakly retained compounds.

Several authors have reported the effect of the degree of protein hydration on the binding of volatile aroma compounds. In this sense Seuvre et al. (2000) examined the importance of beta-lactoglobulin hydration for the binding of 2-nonanone and linalool, and the authors found that the retention of these two flavour molecules did not increase significantly at humidities across the range of 11% to 43%. These volatiles were however, highly retained when the protein was present at 3% in an aqueous solution. Zhou et al. (2006) reported that the weak interactions of the apolar compounds hexane, 1-hexene and limonene with soy protein isolate were not affected by the environmental relative humidity tested across the range 0-50%, whereas the sorption of the relatively polar compounds hexanol, trans-2-hexen-1-ol and cis-3-hexen-1-ol tested at high partial vapour pressure increased gradually when the RH was increased from 30% to 50%. However at low partial vapour pressures the sorption of the three alcohols decreased in the humidity range 0-50%, suggesting competition for protein binding sites between flavour compounds and water.

3.2.2. Diffusion coefficient

The diffusion coefficients of volatile compounds in gliadin films are given in Table 2. In general, the diffusion coefficients of volatiles through protein films were found to be much lower than those for conventional films used in contact with foodstuffs (Hernandez-Munoz, Gavara & Hernandez, 1999).

The chemical structure and the free volume of a polymer play a major role in the diffusion behaviour of small organic molecules. Increasing the free volume of a polymer by plasticization or swelling is expected to increase diffusion. As can be observed in Table 2, for films kept in a dry environment plasticization of gliadins with 25% glycerol provoked a slight increase in the diffusivity of the volatiles evaluated under these conditions (1-hexanol and ethyl caproate) compared to films without glycerol. The diffusion coefficient experienced a further increase with the incorporation of water in the

384 films. At intermediate and high relative humidities, moisture acts as a strong plasticizer
385 in protein films, disrupting hydrogen bonds between polypeptide chain segments giving
386 rise to an increase in chain mobility and free volume for mass transport.

387 The diffusion coefficient is also affected by the shape, size and chemical nature of the
388 diffusing molecule, as shown in Table 2. For the same film and environmental
389 conditions, variations in the diffusivity should be related to the penetrant including
390 molecular geometry, molar volume and penetrant-penetrant and polymer-penetrant
391 specific interactions. The effect of penetrant size and shape on diffusion in a polymer
392 has been the object of numerous studies. Although most of these have been carried
393 out using alkanes, in general, it has been found that for a homologous series of linear
394 molecules diffusivity decreases with increasing molecular weight and molar volume
395 (Kwan, Subramaniam & Ward, 2003), whereas rigid molecules with cyclic and
396 branched geometries are expected to diffuse more slowly compared to flexible and
397 linear ones (Sakellariou & Kapadia, 1996). In the present study, it is difficult to compare
398 the diffusivity of molecules belonging to different series of compounds, and although
399 differences in the diffusion coefficients were not great, the lower diffusion coefficient
400 was obtained for α-pinene because of the rigid bicyclic backbone and despite
401 possessing a lower molar volume than ethyl caproate and 2-nonanone. This behaviour
402 was maintained in all the relative humidity environments evaluated. Regarding
403 elongated molecules, the diffusion coefficient could be expected to increase as the
404 molar volume decreases if the functional group of the molecule is not taken into
405 account; however, 2-nonanone presented a lower diffusion coefficient than 1-hexanol
406 whereas ethyl caproate diffusivity was similar to the alcohol. Clustering of 1-hexanol
407 and specific interactions with the film could have decreased its diffusivity in the film.

408 The sorption kinetics of the compounds in the chitosan film could not be accomplished
409 since the experimental method used was not sensitive enough to discern differences in
410 the initial sorption values. Thus, only sorption values at equilibrium were obtained and

411 these are shown in Table 2. The results reveal the low affinity of chitosan films for the
412 organic vapours and a preference for alcohols and ketones. The retention of the
413 volatiles studied was greater under humid conditions. The moisture content of the
414 chitosan films at 50% and 75% RH was 16.5% and 22.4% (g water/g dry film)
415 respectively. Since chitosan films were not plasticized with glycerol, the effect of the
416 humidity on the retention of volatiles varies with respect to the effect observed in gliadin
417 films incorporating glycerol. As can be seen in Table 2, the solubility coefficients of the
418 volatiles increased considerably when dry films were conditioned at 75% RH, whilst
419 sorption was not affected at a moderate humidity level of 50%. At low to moderate
420 humidities water molecules are strongly adsorbed as monolayers through specific
421 interactions with the hydroxyl and amine groups of chitosan. At 75% HR the water
422 content in the film exerts a plasticizing effect favouring the sorption of vapours,
423 especially those carrying highly polar functional groups.

424 **4. Conclusions**

425 The results from this study show that hydrophilic biobased films made from gliadins or
426 chitosan have low sorption capacities for aroma compounds. The extent of sorption
427 depends on several factors including the chemical structure of the volatile organic
428 compound, the film composition, and the degree of film hydration. It has also been
429 shown that aroma compounds have a low partitioning in gliadin and chitosan
430 bioplastics employing soybean oil and isooctane as fatty food simulants. Given the low
431 levels of interaction observed with the organic volatiles studied, gliadins and chitosan
432 show great potential for use in the packaging of foods in which aroma is one of the
433 most important quality attributes.

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533 **Figure captions**

534

535 **Figure 1**

536 Partition coefficients of volatile aroma compounds between films and fatty food

537 simulants measured at 23 ºC

538

539 **Figure 2**

540 Partition coefficients of volatile aroma compounds in several film/fatty food simulant

541 systems *vs.* the difference in Hildebrand solubility parameters between volatile and film

542

543 **Figure 3**

544 Kinetics of sorption of several volatile aroma compounds in gliadin films plasticized with

545 glycerol or unplasticized measured at different relative humidities of 0%, 50% and 75%

546 and 23 ºC. (●) 1-hexanol, (■) ethyl caproate, (▲) 2-nonanone and (▼) α-pinene

547

548 **Tables**

549 **Table 1** Hildebrand´s Solubility Parameters
550

Compound	δ ($MPa^{1/2}$)
Chitosan	41.0
Gliadins[a]	34.5
Glycerol plasticized gliadins	34.3
Glycerol	33.5
1-Hexanol	21.9
Soybean oil[b]	18.2
2-Nonanone	18.0
Ethyl caproate	17.7
α-Pinene	17.3
Isooctane	14.3

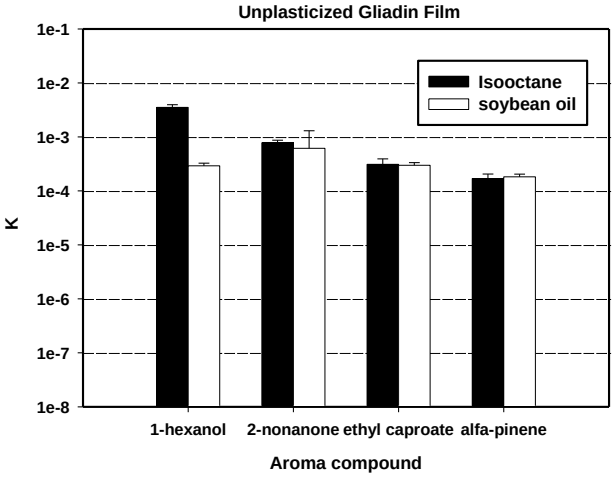
551 a: (Duclairoir et al., 1998); b: (King, 1995)

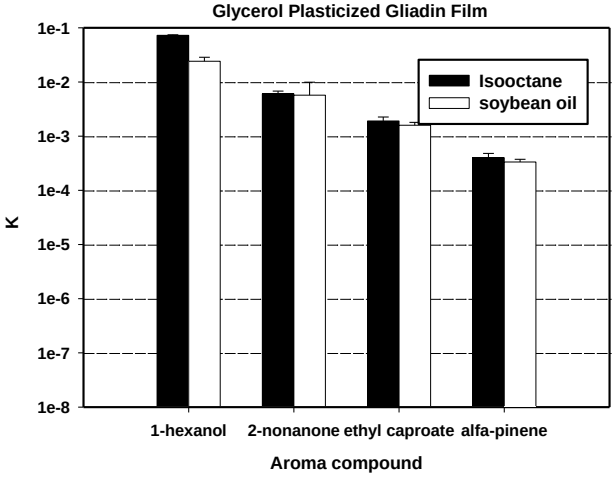
552
553 **Table 2** Solubility (S in $g_{volatile}/(g_{dry\ film} \cdot atm)$), and diffusion (D in m^2/s) coefficients of
554 organic volatile compounds in gliadin and chitosan films evaluated at 23 ºC. Films were
555 conditioned at 0%, 50% or 75% RH.

		Gliadin films	Gliadins films with 25% glycerol			Chitosan films		
		0% RH	0% RH	50% RH	75% RH	0% RH	50% RH	75% RH
1-hexanol	S	$7.5 \cdot 10^{-5}$ ($2.3 \cdot 10^{-5}$)	34 (1)	18 (3)	5.0 (1.0)	0.0008 (0.0003)	0.005 (0.002)	0.03 (0.01)
	$D \cdot 10^{16}$	0.38 (0.10)	0.72 (0.20)	1.2 (0.4)	1.5 (0.2)	-	-	-
2-nonanone	S	-	1.92 (0.04)	3.3 (0.3)	2.7 (0.2)	0.004 (0.002)	0.004 (0.002)	0.013 (0.008)
	$D \cdot 10^{16}$	-	0.35 (0.10)	0.66 (0.30)	0.95 (0.10)	-	-	-
ethyl caproate	S	$7.7 \cdot 10^{-6}$ ($3.5 \cdot 10^{-6}$)	0.55 (0.03)	0.82 (0.02)	0.14 (0.05)	0.0017 (0.0011)	0.0017 (0.0012)	0.0033 (0.0015)
	$D \cdot 10^{16}$	0.33 (0.10)	0.55 (0.15)	1.6 (0.8)	2.2 (0.7)	-	-	-
α-pinene	S	-	0.15 (0.04)	0.16 (0.04)	0.05 (0.02)	0.0003 (0.0001)	0.0003 (0.0001)	0.003 (0.001)
	$D \cdot 10^{16}$	-	0.21 (0.12)	0.50 (0.22)	0.71 (0.20)	-	-	-

556
557 Values reported are the means and in parenthesis the standard deviations.

Figure 1





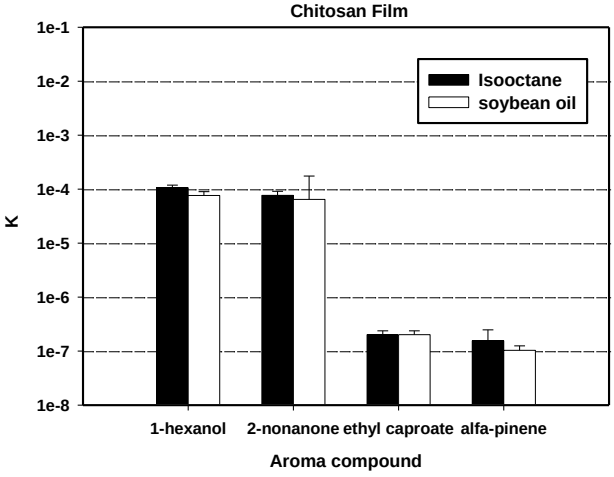


Figure 2

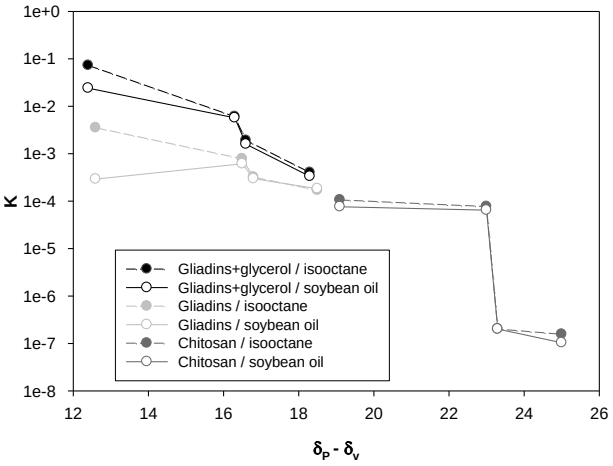
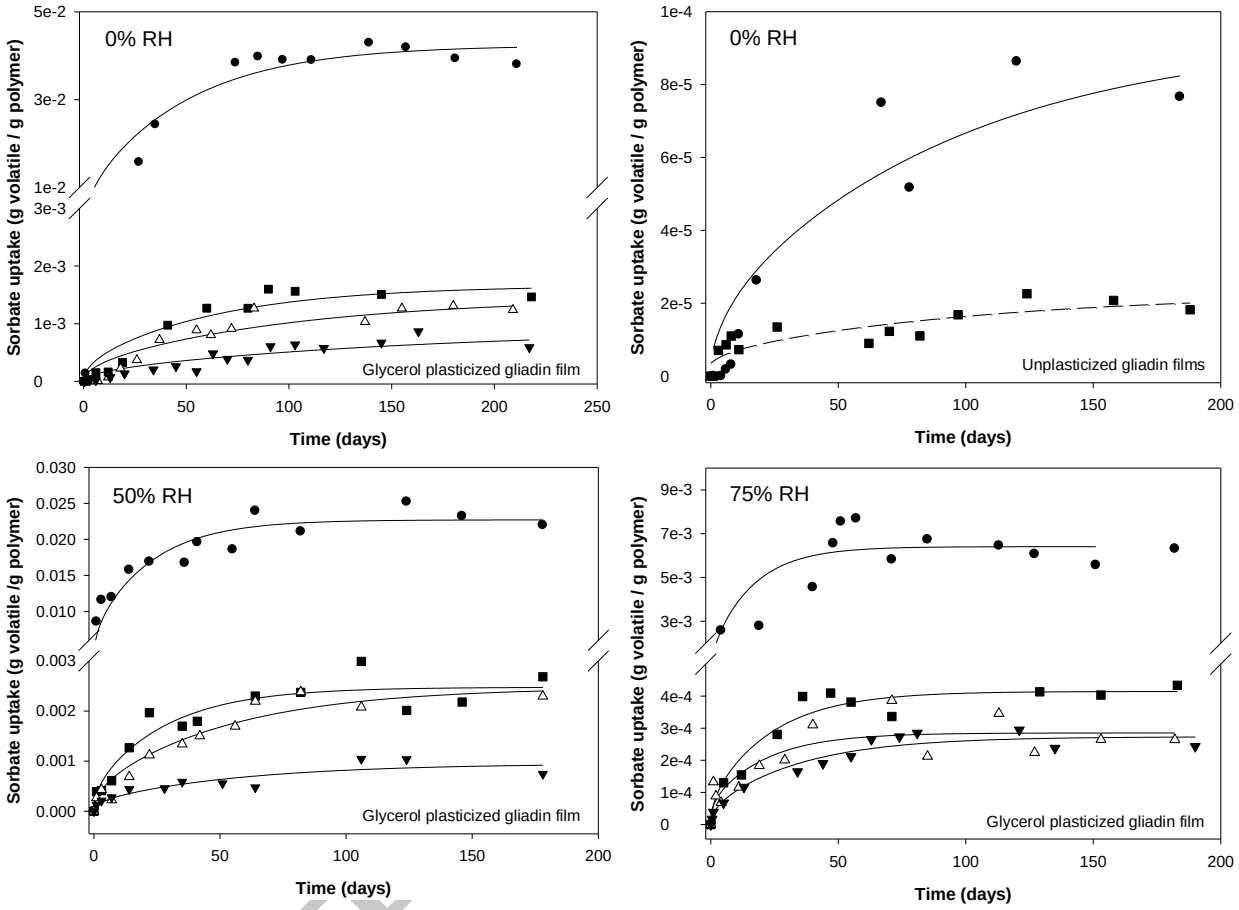


Figure 3



RESEARCH HIGHLIGHTS

- Sorption kinetics and equilibrium partitioning of food aroma compounds in bioplastics.
- Gliadin and chitosan films show low sorption and partitioning capacities of food aroma compounds.
- Sorption and diffusion depend on volatile chemical structure, film composition and moisture.
- Great potential in packaging of foods in which aroma is an important quality attribute.