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Food aroma mass transport properties in renewable hydrophilic polymers

M. Pau Balaguer, Rafael Gavara, Pilar Hernández-Muñoz *

Institute of Agrochemistry and Food Technology (IATA), CSIC, Avda. Agustín Escardino 7, 46980 Paterna, Valencia, Spain

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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.

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

* Corresponding author. Tel.: +34 96 3900022; fax: +34 96 3636301.
E-mail address: phernan@iata.csic.es (P. Hernández-Muñoz).

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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 °C 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 °C. 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 °C for 3 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 1 week at 23 °C. 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 °C 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 min at 140 °C 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 (25 m × 0.2 mm × 0.33 μm) through a nickel transfer line maintained at 200 °C. 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 × 0.53 mm × 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):

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

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

Hildebrand and Scott (1949) correlated the heat of mixing ($+H_{\mathrm{m}}$) in a binary system with the cohesive energy of the components through the equation:

$$+H_{\mathrm{m}} = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2$$

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.