



Investigation of water transfer across thin layer biopolymer films by infrared spectroscopy

Thomas Karbowiak^a, Eric Ferret^b, Frédéric Debeaufort^{a,c,*}, Andrée Voilley^a, Philippe Cayot^a

^a EA 581 EMMA, AgroSup Dijon, 1 esplanade Erasme, Université de Bourgogne, F-21000 Dijon, France

^b GPMA, AgroSup Dijon, 1 esplanade Erasme, Université de Bourgogne, F-21000 Dijon, France

^c IUT-Génie Biologique, Boulevard Dr. Petitjean, BP 17867, F-21000 Dijon, France

ARTICLE INFO

Article history:

Received 1 September 2010

Received in revised form

17 December 2010

Accepted 21 December 2010

Available online 31 December 2010

Keywords:

Polysaccharide

Water diffusion

Interface

FTIR-ATR

ABSTRACT

The investigation of the apparent diffusivity of water in thin layer iota-carrageenan-based films by FTIR-ATR spectroscopy clearly evidences the fundamental role of surface properties on water transfer. Water diffusivity in iota-carrageenan based biopolymer films ranges from 0.3 to $1.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and is thus 10–100 times lower than that in highly hydrated carrageenan gels. The surface heterogeneity and composition when fat is added strongly influence the diffusivity by modifying the liquid water absorption at the inner surface.

This study of diffusing molecules in liquid state is particularly interesting to mimic situations where direct liquid water contact occurs with the film, either liquid water itself or water from a highly hydrated matrix. In such cases, standard gas permeability measurements are inadequate, especially when film properties are modified by the diffusing molecules.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Consumers are increasingly aware of the importance of healthy eating habits, but have less time available for food shopping and preparation. Moreover, for some years, the use of natural polymers coming from renewable sources has greatly increased due to the high amount of waste packaging and dwindling petroleum reserves. Biodegradable polymers known for many decades have been ignored mainly because of the low cost of synthetic polymers. In the same way, the use of edible thin barrier layers to improve food shelf-life by controlling the mass transfers of gas or vapors (oxygen, water vapor, etc.) becomes progressively more economically important for the food industry [1].

Edible coatings have been used to reduce the deleterious effect brought about by minimal processing. The semi-permeable barrier provided by edible coatings aims at extending the shelf-life by reducing moisture and solutes migration, gas exchange, respiration or oxidative reaction rates [2]. The use of edible films to release antimicrobial constituents in food packaging also constitutes a specific case of active packaging [3].

Seaweed hydrocolloids (alginates and carrageenans) are used as edible coatings because of their unique colloidal properties

and their ability to form strong gels or insoluble polymers upon complexation with multivalent metal cations like calcium [4]. Polysaccharide based coatings are expected to be a good oxygen barrier due to their tightly packed, ordered network structure (dipole–dipole interactions) although they do not behave well as moisture barriers because of their hydrophilic residues (hydroxyl and “free” carboxylate or sulphate groups). In addition, plasticizers like glycerol, added to increase film or coating flexibility by reducing the internal dipole–dipole interactions between polymer chains and increasing intermolecular spacing, generally increase film permeability to oxygen and moisture [5].

Carrageenan is a natural gelling polysaccharide extracted from plants or seaweeds, used as a high-value functional ingredient in foods, cosmetics and pharmaceuticals [6]. Iota-carrageenan is a hydrocolloid widely used in the dairy industry. It is used with milk proteins to produce deserts, owing to co-gelation. It is commonly used as a functional ingredient for stabilization or thickening in the preparation of different deserts such as ice cream or custard sauce. Moreover, it is a renewable resource and commercially available at a reasonable cost. The use of carrageenan as edible films and coatings already covers various sectors of the food industry. The applications concern fresh and frozen meat, poultry and fish and generally aim at preventing superficial dehydration, but also manufacturing of soft, especially, non-gelatin capsules [7]. Iota-carrageenan, a water soluble polymer with a linear chain mainly composed of alternated (1,3)-D-galactose-4-sulphate and (1,4)-3,6-anhydro-D-galactose-2-sulphate units, is promising as a film-forming material. In aqueous solutions, iota-carrageenans

* Corresponding author at: EA 581 EMMA, AgroSup Dijon, 1 esplanade Erasme, Université de Bourgogne, F-21000 Dijon, France. Tel.: +33 03 80 77 40 42; fax: +33 03 80 77 40 11.

E-mail address: frederic.debeaufort@u-bourgogne.fr (F. Debeaufort).

produce thermo-reversible gels on cooling below the critical temperature. The conformation then changes from random coiled single chain to the formation of double-helices of carrageenan chain [8]. This three-dimensional network formed by the polysaccharide double helices in a gel state is then dried to obtain a compact solid film. The use of iota-carrageenan as edible films or coatings is related to controlling the mass transfer of small molecules [9]. With the addition of lipids to form emulsified films, they can also be used to encapsulate active molecules such as aroma compounds [10].

Barrier properties of films as thin layer materials are usually described by their permeability value. This corresponds to stationary state of the mass transfer of a small molecule in gas phase through the membrane. Some standard methods are established for these measurements, such as ASTM E96 [11] for water vapor or ASTM D3895 [12] for oxygen. Recently, an original approach to study mass transfers through films was first proposed by Fieldson and Barbari [13], who used Fourier transform infrared (FTIR) spectroscopy with attenuated total reflection (ATR) technique. They studied water diffusion in polyacrylonitrile by following a specific infrared absorption band of water molecules. The evolution of its intensity ratio with time can then be used for data analysis assuming a Fickian diffusion model to determine a diffusion coefficient. Such diffusivity values obtained by this method are in accordance with those obtained from gravimetric measurements [14,15]. Diffusivities of various compounds, such as acetone or methanol, but also aroma compounds, were also studied by this technique, but mainly in synthetic packaging materials [15–18]. However, the main drawback of the FTIR technique to study mass transfer lies in the overlapping of absorption bands in case of multi-component diffusion or interaction with the polymer (hydroxyl group of galactosyl residues in our study), making identification and analysis difficult. Although still rather unusual, this method appears to be very promising to precisely and non-destructively determine the apparent diffusivity of small molecules, which are easily characterized by infrared spectroscopy, through thin layer materials. This technique allows measuring the diffusivity in a thin layer whatever the state (liquid or gas) of the diffusing molecule in contact with the barrier layer.

This study focuses on the set up of a new method for measuring diffusivity of small molecules across thin barrier layers such as biopolymer-based films, membranes or coatings, and on the better understanding of the influence of both structure and composition of the barrier film on moisture diffusivity.

2. Experimental

2.1. Materials

Iota-carrageenan, supplied by Degussa Texturant Systems (DTS, Baupre, France, now Cargill), constituted the continuous matrix of films. The extract used was 95.4% pure and had a mean molar mass of $690\,000\text{ g mol}^{-1}$, a 30.6 wt% sulphate content, and 3.2 and 6.8 wt% (dry basis) of Na^+ and K^+ , respectively (data from supplier). Anhydrous glycerol, purchased from Fluka (98% purity, Fluka Chemical, Germany), was used as plasticizer in order to improve mechanical properties of iota-carrageenan films. Fat used in this study, Grindsted Barrier System 2000 (GBS), supplied by Danisco (Bradbrand, Denmark), was an acetic acid ester of mono- and diglycerides made from edible, fully hydrogenated vegetable oil blended with beeswax. It had a melting point of 57°C , a saponification value around 280 (consistent with short chain length fatty acid residues) and is constituted of 97% saturated fatty acid residues. Glycerol monostearate (GMS), purchased from Prolabo (99% purity, Merck Eurolab, Fontenay-sous-Bois, France), was used as an emulsifier.

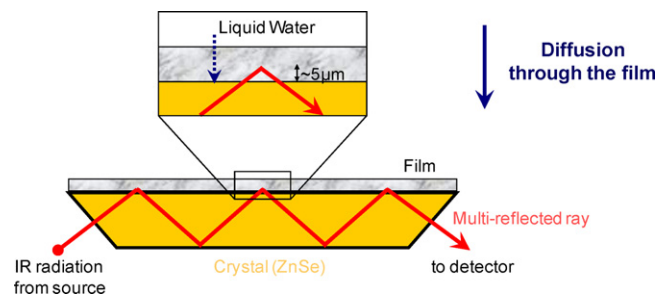


Fig. 1. Attenuated total reflectance (ATR) sampling unit.

2.2. Preparation of iota-carrageenan-based thin layers

Iota-carrageenan films were prepared according to the protocol detailed in a previous paper [9]. Basically, they were obtained by casting a hot iota-carrageenan film-forming solution onto a polymethylmethacrylate (PMMA or Plexiglas) plate, cooling below the sol-gel transition temperature of the polymer, and lastly, evaporating the solvent (water) from the gel. Five types of films were used:

- “Carra – gly” = iota-carrageenan.
- “Carra + gly” = iota-carrageenan containing 30 wt% (dry basis) plasticizer (glycerol).
- “GBS 30%” = “Carra + gly” containing 30 wt% (dry basis) emulsified fat (blend of GBS fat and GMS emulsifier in a ratio 90:10, w/w).
- “GBS 60%” = “Carra + gly” containing 60 wt% (dry basis) emulsified fat (blend of GBS fat and GMS emulsifier in a ratio 90:10, w/w).
- “GBS 60% – gms” = “Carra + gly” containing 60 wt% (dry basis) emulsified fat (GBS fat alone without GMS emulsifier).

All measurements were performed on both sides of the films. The surface in contact with PMMA support during drying will be referred to as the “support side” in this study and the other surface in contact with air during drying will be referred to as the “air side”.

2.3. Environmental scanning electron microscopy observations

Transversal section and surfaces of films were observed by environmental scanning electron microscopy (ESEM, Philips XL 30 ESEM, Japan). A $5\text{ mm} \times 10\text{ mm}$ film was fixed on the support using double side adhesive tape to allow these observations.

2.4. Fourier transform infra-red (FTIR) spectroscopic analyses

FTIR spectra were recorded at room temperature ($294 \pm 1\text{ K}$) on a BRUKER IFS Vector 22 infra-red spectrometer over the wavenumber range $4000\text{--}700\text{ cm}^{-1}$. The ATR (attenuated total reflectance) method was used with a ZnSe crystal (surface: 6.2 cm^2) set at an angle of incidence of 45° (Fig. 1). Spectra were averaged with 10 scans recorded at a resolution of 2 cm^{-1} and corrected from the background. For surface characterization, the background corresponds to the spectrum of the empty cell collected in the same conditions without sample.

For diffusion experiments, the film surface was tightly maintained in contact with the crystal, where the infrared radiation penetrates the surface of the film, in order to achieve good resolution (Fig. 1). Time zero is defined as the time when liquid water (2 mL) was added on the opposite side of the film. The spectrum of the film surface before contact with water was used as the background for diffusion measurements. Then, a characteristic absorption band of the water molecule (between 2900 and 3800 cm^{-1}) is detected on the film surface in contact with the crys-

Download English Version:

<https://daneshyari.com/en/article/635788>

Download Persian Version:

<https://daneshyari.com/article/635788>

[Daneshyari.com](https://daneshyari.com)