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Effect of relative humidity on carvacrol release and permeation properties of chitosan based films and coatings

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ABSTRACT

The influence of water vapour conditions on mass transport and barrier properties of chitosan based films and coatings were studied in relation to surface and structural properties. Water contact angles, material swelling, polymer degradation temperature, barrier properties (PO_2, PCO_2, WVP) and aroma diffusion coefficients were determined. The solvent nature and the presence of carvacrol influenced the surface and structural properties and then the barrier performance of activated chitosan films. Increasing RH from 0% to 100% led to a significant increase in material swelling. The plasticization effect of water was more pronounced at high humid environment, while at low RH the matrix plasticization was induced by carvacrol. The deposit of a thin chitosan layer on polyethylene decreased PO_2 and PCO_2 both in dry and humid conditions. The carvacrol release from the chitosan matrix was strongly influenced by RH. A temperature increase from 4 to 37 °C also had an impact on carvacrol diffusivity but to a lesser extent than RH.

1. Introduction

Active packaging and more specifically antimicrobial packaging films are innovative concepts in food packaging. They have been developed to meet consumer demand for greater food and microbiological safety. Indeed, these systems provide greater efficiency in food protection because they allow the stability of the antimicrobial agent, and ensure the control of its release to the food over time. For example, a too slow release might cause insufficient microbial inhibition, while a too fast release might be the reason why the inhibition is not sustained (Li, Kennedy, Peng, Yie, & Xie, 2006). The release rate depends on the polymer type, on the film preparation method, on the interactions between polymeric and antimicrobial materials (Cha, Cooksey, Chinnan, & Park, 2003) and environmental conditions (Cagri, Ustunol, & Ryser, 2004). Therefore, developing new antimicrobial delivery technologies and utilising them in product development is crucial for food industries to compete and survive.

Much research in material sciences is focused on the structure-properties relationship to predict and to control the functional film properties. Currently, special attention is given to chitosan, N-acetyl-D-glucosamine, due to its low toxicity, biodegradability, stability and relatively low cost as it is a by-product and a renewable material from some industries. Chitosan is a water sensible material that naturally interacts with water. Yakimets et al. (2007) determined the water content of biopolymer films as a critical variable that leads to water-induced transformations (for example, amorphous-crystalline transition) that have a strong impact on the molecular mobility and functional properties. The crystalline structure of hydrated chitosan is a twofold helix. This structure can be converted to a dehydrated form, very similar to the hydrated one, but with molecular packing and water content quite different (Ogawa, Yui, & Okuyama, 2004). Moisture has a plasticizing or swelling effect on polymers, so it increases gas permeability (Ashley, 1985). Water increases the polymer-free volume, allowing the segments of polymeric chains to be mobile (McHugh, Aujard, & Krochta, 1994). Moreover, in order to satisfy adequate functional properties, the film must be designed according to some surface properties. Contact angle measurements enable investigation of the wetting behaviour of the biopolymer surface and can be a good indicator for the determination of their hydrophilic nature (Peroval, Debeaufort, Despre, & Voilley, 2002). Then it represents a good way for the development of hydrophilic biodegradable and well-characterised delivery systems and for understanding the mechanisms of polymer surface degradation and active compound release, which could be of importance both for food packaging and for pharmaceutical applications. However, poor water resistance

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and mechanical performance are limiting factors for use of biopolymer materials manufactured only from natural polymers. That is why there is growing demand in development and characterisation of bio-based/synthetic polymer systems.

Today, it is very fashionable to use essential oils and their constituents as they show a great potential to be used as antimicrobial compounds both in direct food contact and via vapour. Carvacrol is a phenolic compound extracted from oregano and thyme oil. Its inhibitory effect on the growth of various microorganisms is well documented and described extensively (Ben Arfa, Combes, Preziosi-Belloy, Gontard, & Chalier, 2006; Burt, 2004; Nostro & Papalia, 2012).Carvacrol might be incorporated within biopolymer material that can be used as a self standing film or it can be coated onto the synthetic packaging materials. The efficiency of this system is determined by the controlled diffusion and release and is maintained in concentrations high enough for antimicrobial impact where necessary. The use of volatile antimicrobial agents has many advantages. This system can be used effectively for fresh products such as meat, cheese, fruits, vegetables, or dry products, highly porous food etc. Because spices and extracts provide the majority of volatile antimicrobial agents and are commonly GRAS classified (Generally Recognised As Safe), this system is linked to the food and pharmaceutical research and development area and is easily accepted by consumers and regulatory bodies.

During the storage and the use of packaging material, the properties of chitosan films may be changed after the incorporation of active compound. The loss of active volatile compounds from bio-based matrix at specified temperature and relative humidity (RH) (that will simulate the timeline in the 'real food product' shelf life), requires the knowledge of the polymer water sensitivity, the diffusion coefficient of active compounds, release rates and migration amounts according to moisture levels. Mass transfers through food packaging films exist whatever the type of material used, even if several of them are associated. The transfer mechanism of molecules like water vapour and gases through the film are different according to the film structure that might be changed during processing and storage. Increased storage temperature and humidity can accelerate the migration of the active agents in the film. Thus, the protective action of antimicrobial films will be minimized, due to the high diffusion rates in the polymer and in the food.

The aim of this study was to investigate the influence of RH on the surface and thermal properties of bio-based polymer self standing films and coatings applied onto polyethylene films. For this purpose we used chitosan and carvacrol as models of biopolymer matrices and active compounds with an antimicrobial potential. The effect of incorporated carvacrol on the structure changes was studied. Water vapour, oxygen and carbon dioxide permeability has also been studied in order to monitor the film behaviour according to the temperature and RH. Furthermore, to better understand the influence of both temperature and RH on the carvacrol release, kinetics were studied at 4, 20 and 37 °C and 0%, 75% and >96% RH during more than 2 months. Chosen temperatures represent the storage conditions of most fresh food products, of ambient conditions or conditions of use, and those for optimal microbial growth.

2. Materials and methods

2.1. Materials and reagents

Commercial grade chitosan (CS) (France Chitine, Marseille, France, powder 652, having a molecular mass of 165 kDa, low viscosity, food grade, degree of deacetylation of >85%) was used as the film-forming matrix. A commercial, low density polyethylene film (LDPE) (Wipak, Lille, LD-PE45 UFP; thickness of 45 μm) was used as a polyolefin material. Carvacrol (CVC) (purity >97%, Fluka) was used as the aroma compound in order to improve the functional film properties. Acetic acid (glacial 100%, Merck, Darmstadt, Germany) and pure ethanol (absolute, Sigma–Aldrich) were used as solvents in the preparation of the film forming solutions (FFS). Silica gel, magnesium chloride ($MgCl_2$, Sigma), sodium chloride (NaCl, Sigma) were used to prepare saturated salt solutions to fix the RH at <2%, 33% and 75% and for water vapour permeability measurements, aroma release measurements and for sample conditioning prior to thermal analysis. Deionised water was used for surface analysis, aroma release determination and to fix RH at >96% for permeability measurements. No further purification of chemicals has been done and freshly prepared solutions were always used.

2.2. Film preparation

2.2.1. Self standing chitosan films

A chitosan solution was prepared by dissolving the chitosan powder in a 1% (v/v) aqueous acetic acid, to obtain 2% (w/v) film forming solutions (FFS). To achieve a complete dispersion of the chitosan, the solution was stirred for 2 h at room temperature. To prepare the aqueous hydroalcoholic acid media, ethanol was mixed in a ratio ethanol:aqueous acetic acid of 30:70. Carvacrol (0.5%, w/v) was homogenised either in aqueous acid CS solution or hydroalcoholic acid CS solution at 24000 rpm for 10 min with an Ultra Turrax (T25 IKA) to obtain film forming solutions with an incorporated aroma compound. In order to obtain films, solvents were removed by drying in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) at 20 °C and 30% RH. After drying, the films were peeled off and stored in the same ventilated climatic chamber at 25 °C and 30% RH before measurements. The films prepared in the acetic acid solution were coded as CSA, those in hydroalcoholic acid solution as CSE and those containing carvacrol as CVC.

2.2.2. Chitosan coated polyethylene films

The hydroalcoholic acid chitosan solution with/or without carvacrol was prepared as described in Section 2.2.1. The coating was carried out according to Sollogoub et al. (2009), at room temperature, using a Nordson slot die (ChameleonTM), appropriate to fluids of viscosity ranging between 0.5 and 2 Pa/s. The die is fed continuously by a gear pump, the flow rate of which is adjustable from 5 to 500 mL/min. A roll winding device creates the movement of the support material at a speed ranging between 0.2 and 4 m/min. The deposit width is set to 100 mm and the die opening to 150 m. Films were dried in a flow of a dry air at 50 °C and RH <10%. After drying, the films were stored in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) before measurements at 25 °C and 30% RH.

2.3. Film characterisation

2.3.1. Film thickness

The film thickness was measured with an electronic gauge (PosiTector 6000, DeFelsko Corporation, USA). The average value of five thickness measurements per type of film was used in all calculations.

2.3.2. Contact angle and wettability

The contact angle, surface hydrophobicity and wettability of films were measured by the sessile drop method, in which a droplet of the tested liquid was placed on a horizontal film surface using a DGD-DX goniometer (GBX, Romans-sur-Isere, France), equipped with the DIGIDROP image analysis software (GBX, Romans-sur-Isere, France) according to Karbowiak, Debeaufort, and Voilley (2006). Water droplets (1.5 μL approx.) were deposited