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Migration of antimicrobial agents from starch-based films into a food simulant

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ABSTRACT

The migration of antimicrobial (AM) agents carvacrol, thymol and linalool from heat pressed and coated starch-based packaging films into isooctane was investigated and the release of the agents consistently obeyed first-order kinetics. When the test temperature was increased from 15 to 35 °C, the diffusion coefficients increased from 6.3×10^{-13} to 12.9×10^{-13} m^{-2} s^{-1} for carvacrol, from 12.0×10^{-13} to 29.7×10^{-13} m^{-2} s^{-1} for thymol and from 9.5×10^{-13} to 19.0×10^{-13} m^{-2} s^{-1} for linalool from the heat pressed starch-based films. The diffusion coefficients of carvacrol, thymol and linalool from coated starch-based films containing increased from 2.2×10^{-13} to 8.7×10^{-13} m^{-2} s^{-1}, from 2.7×10^{-13} to 6.1×10^{-13} m^{-2} s^{-1} and from 5.1×10^{-13} to 9.4×10^{-13} m^{-2} s^{-1} respectively between 15 and 35 °C. The activation energies for the migration of carvacrol, thymol and linalool from the heat pressed films were 26.2, 33.6 and 25.5 kJ mol^{-1} respectively and those for the migration from the coated systems were 31.3, 3.0 and 22.5 kJ mol^{-1} respectively. The results suggest that the AM agents show a potential for use as AM packaging materials.

1. Introduction

Consumer preference for preservative-free and high-quality food products that are packaged in materials that create a lower environmental impact has inspired research into the application of biopolymeric materials in antimicrobial (AM) packaging systems (López, Sánchez, Batlle, & Nerín, 2007). When a volatile AM agent is incorporated into a package, it is released mainly by permeation and diffusion onto food surfaces to control pathogenic or spoilage microorganisms during the shelf life period (Suppakul, Sonneveld, Bigger, & Miltz, 2011b). Antimicrobial packaging is among the more promising forms of active packaging (AP) systems aimed at protecting food products from microbial contamination. The latter are systems in which the product, the package and the environment interact to extend the shelf life or improve the microbial safety or sensory properties whilst simultaneously maintaining the quality of food products (Miltz, Passy, & Mannheim, 1995). According to Rooney (1995), the additional preservation roles, rendered by AP systems to the packaged food product, differentiates them from traditional packaging systems that offer only protective functions against external influences. Numerous studies (Appendini & Hotchkiss, 2002; Han, 2005; López et al., 2007; Tovar, Salafranca, Sanchez, & Nerin, 2005) have identified migratory and non-migratory as the two main categories of AM packaging systems. In migrating AM packaging systems, AM agents incorporated into the packaging material are released onto food surfaces and/or into the headspace of the packages to suppress microbial growth (Appendini & Hotchkiss, 2002; Han, 2003). The release rate of AM agents from the packaging material has a significant effect on the AM activity and potential applications of AM films in food packaging (LaCoste, Schaich, Zumbrunnen, & Yam, 2005; Rardniyom, 2008, p. 145). An AM agent incorporated into a packaging material is released onto food surfaces mainly by permeation and diffusion to control pathogenic and/or spoilage microorganisms during the storage period (Buonocore, Del Nobile, Panizza, Corbo, & Nicolais, 2003; Limm & Holifield, 1995).

The release rate of the AM agent from the packaging material is primarily influenced by factors that include the film fabrication method, the properties of the AM agent (such as volatility and polarity), the chemical interaction between the AM agent and polymer chains, changes in the packaging film that might be induced by the AM agent incorporated into the film, hydrophobicity and hydrophilicity of the polymer, food composition, water activity (a_w) and pH of the food, as well as environmental factors

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such as storage conditions, primarily temperature and relative humidity (Suppakul, Sonneveld, Miltz, & Bigger, 2003; Weng & Hotchkiss, 1993). In most cases, it is time consuming and expensive to determine the migration of AM agent into the food because most foodstuffs are comprised of a complex mixture of substances such as water, carbohydrates, fats, lipids, proteins, vitamins, fibres and minerals (Cran, Rupika, Sonneveld, Miltz, & Bigger, 2010). Thus, migration studies are usually performed using food simulants (Dopico, Lopez-Vilarino, & Gonzalez-Rodriguesz, 2003). Different food simulants have been identified in the European food-packaging regulations (EC, 1997) for migration testing. The food simulants for various food products include: water (for water-based products); 3% (v/v) acetic acid in water (for acidic products); 50% (v/v) ethanol in water (for dairy products); olive oil; sunflower oil; synthetic fat simulant HB 307; and 95% ethanol in water and isooctane for fatty products (EC, 1997; USFDA, 2007). Very recently, new simulants have been recommended by the European Communities (EC Regulation 10/2011) for different food products. This regulation is aimed to be implemented gradually and will become compulsory from January 1, 2016 (EC, 2011). Furthermore, the compatibility of an AM agent with different types of foods or food simulants is an important factor that must be considered when designing AM packaging systems (Rardniyom, Miltz, Bigger, Cran, & Sonneveld, 2008).

Given the current interest in the use of both starch-based materials and natural AM agents in packaging applications, the objective of this study was to investigate the migration of carvacrol, thymol or linalool incorporated into or coated onto starch-based films. The fatty food simulant isooctane recommended by the US Food and Drug Administration (USFDA, 2007) was used in the experimental work, as it is likely to mimic the packaging environment of a fatty product like Cheddar cheese. The temperature dependency of the AM agents' migration into isooctane was also investigated.

2. Materials and methods

2.1. Materials

The materials used in the present study were a commercial, chemically modified high amylose thermoplastic corn starch (TPS), and a commercial starch-based film comprising a thermoplastic starch blended with an aliphatic polyester (APTPS). The TPS material has been specifically designed for the production of extruded or thermoformed packaging products. The APTPS is a biodegradable material based on a blend of thermoplastic starch, aliphatic polyesters and natural plasticisers. Methylcellulose (MC, 18,804-2); hydroxypropyl methylcellulose (HPMC, 42,321-1) and polyethylene glycol (PEG, 20,236-3) were purchased from Aldrich Chemical Company Inc., Milwaukee, WI, USA. The AM agents were thymol (TO501), linalool (L2602) and carvacrol (W224502) with quoted purities of 99.5%, 97% and 98% respectively. All of the AM agents were purchased from Sigma–Aldrich Pty. Ltd., Sydney, Australia. Analytical reagent grade glycerol was purchased from Merck, Sydney, Australia.

2.2. Preparation of starch-based film by heat pressing under compression

The preparation of the TPS starch-based films was achieved by heat pressing under compression in accordance with the method previously used by Mistry (2006). Master batches were prepared by gradually adding the starch-based material to a plasticiser made of a mixture of water and glycerol. The final composition of the formulation was 61% (w/w) starch-based material, 10% (w/w) water and 25% (w/w) glycerol. Each of the three natural AM agents, thymol, carvacrol and linalool were thoroughly blended with separate samples of the starch-based material at a formulation concentration of 4% (w/w). A sample weighing *ca.* 15 g of the resultant mixture was placed between two Mylar™ films positioned between two aluminium platens and then pressed in a laboratory press (IDM Instruments Pty. Ltd., Australia, model No. L0003). The temperature of the upper and lower platens of the press was maintained at 125 °C for 5 min under a pressure of 30 kPa. The platens were then quench-cooled, removed from the press and the films were peeled away from the Mylar™ film. A starch-based material without any AM agent was similarly prepared and used as the control. The sample film thickness was measured immediately after it was peeled from the moulding film, using a hand-held micrometer with a precision of 0.001 mm (Mitutoyo, Japan). Films thickness was measured at five different positions and an average thickness was calculated from these readings. After measuring the thickness, the films were wrapped in an aluminium foil to prevent loss of the AM agent before being used.

2.3. Coating and drying of starch-based films

The coating solution was prepared from the MC and HPMC materials. Methylcellulose and HPMC were added slowly to absolute ethanol and heated, with stirring, on a magnetic hotplate. The heating was discontinued when the temperature reached 65 °C. With continuous agitation, a mixture of PEG and distilled water, as a plasticiser, was added slowly to the MC–HPMC dispersion whilst the dispersion cooled down. This resulted in the formation of a uniformly clear coating solution or gel (Rardniyom, 2008). The AM agent was then added to the coating solution to form the final coating material with the AM agent at a target level of 3% (w/w). The coating medium was applied to the starch-based material using a hand drawn glass roller and the film was then dried under ambient conditions (temperature 21 °C, RH 38%) for 24 h (Cooksey, 2005). To control the thickness of the coating, the starch-based material was taped onto a 30 × 30 cm glass plate and the edges were framed using 3M™ masking tape. Each of the three solutions containing the natural AM agents: carvacrol, linalool and thymol were coated separately onto the starch-based material. Similarly, a coating solution without AM agent was also prepared and applied to the starch-based substrate as the control. The film thickness was measured in accordance with the method described earlier.

2.4. Quantification of AM agents in starch-based films

The heat pressed starch-based film samples of approximately 5 × 5 cm in dimension were immersed in a sealed vessel of 100 mL isooctane, placed in an incubator shaker (Innova™ 4230, New Brunswick Scientific, USA) and maintained at 37 °C. The concentration of AM agent that was extracted from the film into 100 mL of isooctane as a function of time was analysed by gas chromatography. An auto-sampler (Varian 8200 C_x) attached to a Varian Star 3400-C_x GC system equipped with a fused silica capillary column (DB-5: 30 m × 0.25 mm i.d., film thickness 0.25 μm, J & W Scientific, USA) was used. The conditions applied in the GC were as follows: injected volume 1.0 μL; initial column temperature 80 °C; heating rate 5 °C min^{-1} up to 120 °C, held at this temperature for an additional 10 min; injector temperature 250 °C; FID detector temperature 300 °C; flow rate of splitless nitrogen carrier gas 15 mL min^{-1}. The actual concentration of the AM agents retained in the MC–HPMC coatings after drying was determined on the basis of total dry weight of the film. The experiments were performed in triplicate.