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Development and characterisation of composite films made of kefiran and starch

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ABSTRACT

In this study, new edible composite films were prepared by blending kefiran with corn starch. Film-forming solutions of different ratios of kefiran to corn starch (100/0, 70/30, 50/50, 30/70) were cast at room temperature. The effects of starch addition on the resulting films' physical, mechanical and water–vapor permeability (WVP) properties were investigated. Increasing starch content from 0% to 50% (v/v) decreased the WVP of films; however, with further starch addition the WVP increased. Also, this increase in starch content increased the tensile strength and extensibility of the composite films. However, these mechanical properties decreased at higher starch contents. Dynamic mechanical thermal analysis (DMTA) curves showed that addition of starch at all levels increased the glass transition temperature of films. The electron scanning micrograph for the composite film was homogeneous, without signs of phase separation between the components. Thus, it was observed that these two film-forming components were compatible, and that an interaction existed between them.

1. Introduction

Chemically synthesized polymeric films have long been used in the food packaging industry due to their desirable features such as lightness, softness and transparency. However, their negative environmental impact caused by their total non-biodegradability is a serious disadvantage to the use of these materials. In recent years, researchers and industry have paid increasing attention to biopolymer-based packaging as a potential alternative to synthetic polymer-based food-packaging materials. Biopolymers, such as starches, cellulose derivatives, gums, proteins (animal or plant-based) and lipids are usually used for this purpose. These materials offer the possibility of creating thin edible films and coatings for covering fresh or processed foods to extend shelf life (Siracusa, Rocculi, Romani, & Rosa, 2008). These edible and/or biodegradable polymer films can be used to cover food surfaces, form a barrier against oxygen, aroma, oil and moisture, prevent quality deterioration of food products, separate incompatible zones and ingredients or perform as pouches or wraps. Among other important features, they can be used as carriers of functional agents, as antimicrobials or antioxidants and to improve appearance and handling (Kester & Fennema, 1986). Some proposed applications of such films include pouches or sachets to package dry ingredients (e.g., beverage mixes), individual packaging of small portions of food, particularly products that currently are not individually packaged for practical reasons such as pears, nuts, beans and strawberries (Bourtoom, 2008).

Starch is a renewable and abundant resource with the capability to form a continuous matrix. Beside its relatively low cost compared to other biopolymers, starch can form films that exhibit physical characteristics similar to synthetic polymers: transparent, tasteless, odorless, semi-permeable to CO_2 and resistant to O_2 passage (Nisperos-Carriedo, 1994). These properties make starch the most important polysaccharide polymer that is used to develop biodegradable films. When converted to thermoplastic material, starch is an interesting alternative for synthetic polymers in applications where long-term durability is not needed and rapid degradation is an advantage (Flieger, Kantorová, Prell, Rezanka, & Votruba, 2003). However, starch exhibits several disadvantages, such as poor mechanical properties and a strong hydrophilic character (water sensitivity) compared to conventional synthetic polymers and other biopolymers which make it unsatisfactory for some packaging applications (Averous & Boquillon, 2004). Blending of biopolymers is a promising strategy to improve the properties of edible films and coatings. Biocomposite films are prepared by various methods, and are usually composed of two or three biopolymers (Gerschenson & Goyanes, 2009).

Kefiran is a microbial exopolysaccharide obtained from the flora of kefir grains. It contains glucose and galactose, is water-soluble and improves the viscosity and viscoelastic properties of acid milk gels (Piermaria, Pinotti, Garcia, & Abraham, 2009). It can also form gels with interesting viscoelastic properties at low temperatures (Piermaria, De la Canal, & Abraham, 2008). Furthermore, compared

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to other polysaccharides, kefiran has several important advantages, such as immunomodulation, antibacterial, antifungal and antitumour properties (Maeda, Zhu, Omura, Suzuki, & Kitamura, 2004). Recent studies have reported that high yields of these exopolysaccharides can easily be isolated from the grains in deproteinized whey (Rimada & Abraham, 2001). According to the literature, as well as data and preliminary studies in our laboratory, kefiran can produce films with satisfactory mechanical properties and good appearance: it appears to have excellent potential as a film-forming agent (Ghasemlou, Khodaiyan, Oromiehie, & Yarmand, 2011).

Polysaccharide-based films are relatively stiff. To improve film flexibility, it is necessary to add plasticizer agents. Because of its stability and compatibility with hydrophilic bio-polymeric packaging chains, glycerol is one of the most popular plasticizers used in film-making. Normally, plasticizers are added to the film-forming solution before casting and drying (Fernández-Cervera et al., 2004).

There are several studies on starch-based films and a few on kefiran films (Averous & Boquillon, 2004; Ghasemlou et al., 2011; Piermaria et al., 2009; Salleh & Muhamad, 2007; Xu, Kim, Hanna, & Nag, 2005), but to the best of our knowledge, there is no specific study on the effect of blending kefiran and corn starch to produce biocomposite films. Kefiran's good mechanical properties can overcome the weaknesses of starch mechanical properties. In recent years, the search for new microbial biopolymers with different compositions and properties has become a topic of great interest, and several candidate polymers have been under investigation. The objective of this study was to develop new biocomposite edible films by blending corn starch with kefrian, using glycerol as a plasticizer, and to characterise their physical, mechanical and water–vapor permeability properties.

2. Materials and methods

2.1. Materials

Corn starch with 12% moisture and with an average molecular weight of 328.2×10^6 Daltons (practical grade) was used. It was provided by Glucosan Industry (Ghazvin, Iran). Kefir grains, used as a starter culture in this study, were obtained from a household in Tehran, Iran. Glycerol, magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$) and calcium chloride (analytical grade) were purchased from Merck (Darmstadt, Germany).

2.2. Starter culture

Kefir grains were kept in skimmed milk at room temperature for short periods and the medium was exchanged daily with new culture medium to maintain grain viability. After the culture process was continued for 7 days, the grains were considered active.

2.3. Isolation and purification of kefiran

Kefiran exopolysaccharides were extracted from kefir grains by the method of Piermaria et al. (2009). In brief, a weighed amount of kefir grains was added to boiling water (1:10) and stirred for 1 h discontinuously. After reaching uniformity, the mixture was centrifuged (Sigma 3–16 k Frankfurt, Germany) at 10,000g for 15 min at 20 °C. To precipitate the polysaccharides secreted in the supernatant of the centrifuged samples, an equal volume of chilled ethanol was added. Then the mixture was kept at −20 °C overnight. Then, the pellets were collected by centrifuging at 10,000g for 20 min at 4 °C. The precipitates were re-dissolved in hot distilled water and the precipitation method was repeated twice. The resulting solution was concentrated, yielding a crude polysaccharide. The samples were tested for the absence of other proteins and sugars by high-performance liquid chromatography and the phenol–sulphuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956), respectively. Kefiran was obtained at high purity (99%) without mono- or disaccharides. The molecular weight was higher than 5.2×10^6 Da.

2.4. Preparation of films

A starch solution (2%; w/v) was prepared by dispersing 2 g of corn starch in 100 mL of distilled water and heating the mixture with stirring until the starch gelatinized (85 °C for 5 min). The solution was then cooled to 27 ± 2 °C. Kefiran solution (2%; w/v) was prepared by weighing the amount of film-forming solution under constant magnetic stirring for 15 min. Preliminary experiments had shown that filmogenic solutions containing 2% kefiran were easily removed from the plate. On the other hand, films formulated with 1% kefiran had low thickness values and were difficult to handle (Ghasemlou et al., 2011). Kefiran/starch composite films were prepared by mixing various levels of 2% kefiran solutions with various levels of 2% starch solutions (100/0, 70/30, 50/50, 30/70). The films prepared without plasticizer were brittle and cracked on the casting plates during drying. Thus, plasticizer was incorporated into the film-forming solution to achieve more-flexible films. To do this, glycerol (Merck, Darmstadt, Germany) was added (30% of the total solid weight). Following the addition of plasticizer, stirring was continued for a further 15 min. The film solutions were transferred into a vacuum oven for about 30 min at 30 °C to remove most of the air bubbles incorporated during stirring. The mixtures were cast onto flat, leveled, non-stick Teflon plates and were held at room temperature and room relative humidity for 18 h to set. Once set, they were peeled from the casting surface and stored in plastic bags in desiccators at 25 ± 1 °C for further testing. All treatments were made in triplicate.

2.5. Film conditioning

According to the standard method D618-61 (ASTM, 1993), all films were conditioned prior to subjecting them to permeability and mechanical tests. Films used for testing water–vapor permeability (WVP), tensile strength (TS) and elongation-at-break (E) were conditioned at 51% RH and 25 ± 2 °C by placing them in desiccators over a saturated solution of magnesium nitrate for 48 h or more. For other tests, film samples were transferred to plastic bags after peeling and placed in desiccators.

2.6. Determination of physical properties of films

2.6.1. Film thickness

Film thickness was measured (to an exactness of 0.001 mm) using a manual digital micrometre (Mitutoyo No. 293–766, Tokyo, Japan) at 10 different points of the film, and an average value was calculated. The average value was used in calculations for tensile properties and WVP tests.

2.6.2. Moisture content

Film moisture content (approximately 1×3 cm^2) was determined by measuring the weight loss of films before and after drying in a laboratory oven (Blue M Electric Co., Blue Island, IL) at 103 ± 2 °C until constant weight was reached (dry sample weight). Three replications of each film treatment were used for calculating the moisture content.

2.6.3. Film solubility in water

Solubility in water was defined as the percentage of the total soluble matter (%TSM) of film that is solubilised after immersion