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Development of model for barrier and optical properties of tapioca starch based edible films

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ABSTRACT

The film forming solutions composed of tapioca (cassava) starch (1–3 g), glycerol (0.5–1.0 ml), agar (0.5–1.0 g) and span 80 (0.1–0.5 ml) were prepared according to a three-level, four-factor Box-Behnken response surface experimental design. The films were obtained by casting method and they are homogenous and transparent. The influence of film composition (tapioca starch, glycerol, agar and span80) on the barrier and optical properties of the tapioca starch based edible films was evaluated. The results showed that, hydrophilic nature and plasticizing effect of glycerol increases the water vapor permeability, oxygen permeability, moisture content, solubility and swelling capacity of the films. But surfactant (span80) incorporation reduces the mobility of the polysaccharide matrix and decreases the barrier properties of the films. Transparency of the films was influenced by plasticizer and surfactant concentration due to the dilution effect of glycerol and span80. The results were analyzed by Pareto analysis of variance (ANOVA) and second-order polynomial models were developed using multiple regression analysis. The models developed from the experimental design were predictive and good fit with the experimental data with high coefficient of determination (R^2) values (more than 0.95). The optimized conditions were obtained were tapioca starch of 1.95 g, glycerol of 0.8 ml, agar of 0.7 g and span 80 of 0.3 ml, respectively.

1. Introduction

Recent environmental regulations, societal concerns and growing environmental awareness throughout the world have triggered the efforts in plastic industry to develop new products and processes that cause less or no harm to the environment. Development and characterization of environmentally friendly polymeric materials have attracted extensive interest due to the concerns on environmental impact (Siracusa, Rocculi, Romani, & Rossa, 2008; Weber, Haugaard, Festersen, & Bertelsen, 2002). A significant proportion of research on biodegradable films has been made using biopolymers derived from renewable sources. Biopolymers are usually derived from annually renewable natural resources including carbohydrates and proteins of plant or animal origin (Boredes, Pollet, & Avérous, 2009). Starch has been considered one of the most promising natural renewable resources because of its lower cost, biodegradability, thermoplastic behavior (Mali, Grossmann, García, Martino, & Zaritzky, 2005a) and availability in abundance than other natural resources. The use of starch material for preparation of edible or biodegradable films has been widely recognized (Krochta & De Mulder-Johnston, 1997). Films developed from tapioca starch are described as isotropic, odorless, tasteless, colorless, non-toxic and biologically degradable (Flores, Famá, Rojas, Goyanes, & Gerschenson, 2007). From the literature, it is found that most of the researchers studied the development of biodegradable films using pure tapioca starch that are very brittle in nature as a result of the strong cohesive bond between the polymer molecules (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007; Chang, Abd Karim, & Seow, 2006; Flores et al., 2007; Lu, Xiao, & Xu, 2009; Zhang & Han, 2006).

The addition of an appropriate plasticizing agent to starch based edible films reduces their brittleness and improves the flexibility and extensibility by acting as spacers between polymer chains and decreasing the intermolecular forces between adjacent polymeric chains (García, Martino, & Zaritzky, 2000b; Koskinen, Suortti, Autio, Myllärinen, & Poutanen, 1996; Romero-Bastida et al., 2005). Glycerol is the most widely used plasticizer for improving the mechanical properties and transparency of the edible films (Mali, Sakanaka, Yamashita, & Grossmann, 2005b; Myllarinen, Partanen, Seppala, & Forssell, 2002; Yang & Paulson, 2000). The

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hydroxyl groups present in glycerol are responsible for inter and intramolecular interactions (hydrogen bonds) in polymeric chains, providing films with a more flexible structure (Souza et al., 2012). Surfactants are amphibious substances (possessing hydrophilicity and hydrophobicity simultaneously) that are conventionally added to enhance the stability of the emulsified films (Chen, Kuo, & Lai, 2009). The addition of surfactant into film formulation to reduces the surface tension of the film-forming solution and decreases the water permeability of the film due to the hydrophobic nature (Ziani, Osés, Coma, & Maté, 2008). Rodriguez, Oses, Ziani, and Mate (2006) observed that water vapor permeability (WVP) and wettability of potato starch films were affected by the use of span 80 as the surfactant. Agar is a fibrous carbohydrate extracted from a number of marine algae of the class *Rhodophyceae* (called 'red seaweeds') such as *Gelidium* sp. and *Gracilaria* sp. (Rhim, 2011). Agar has been used to prepare environmental friendly packaging materials such as foams, films and coatings (Freile-Pelegrín et al., 2007; Lee, Lee, & Song, 1997; Phan, Debeaufort, Luu, & Voilley, 2005; Phan, Debaufort, Voilley, & Luu, 2009). Wu, Geng, Chang, Yu, and Ma (2009) reported that the addition of agar to starch improved the barrier properties of the film.

Response surface methodology (RSM) is a collection of statistical techniques for designing experiments, building models and evaluating the effect of process parameters. Box-Behnken is a spherical, revolving response surface methodology design that provides efficient solutions compared with a three-level full-factorial design and reducing the number of required experiments which becomes more significant as the number of factors increases (Borkowski, 1995; White, Willis, Keshav, & Dutton, 2001). The present work is focused on the development of model and investigating the individual and interactive effects of process parameters on the barrier and optical properties of tapioca starch-based edible films using Box-Behnken response surface design.

2. Materials and methods

2.1. Raw materials

Tapioca starch was obtained from Local market, Erode, India. Landers, Gbur, and Sharp (1991) method was used for determining the amylose and amylopectin content of tapioca starch. Ash, moisture and starch contents were determined according to the AOAC (1995) techniques. Glycerol (98% purity, Food grade) and span 80 (99% purity, Food grade) were purchased from Merk chemicals, Mumbai, whereas Agar was purchased from Hi-media chemicals, Mumbai.

2.2. Preparation of edible films

Solutions with various proportions of starch, glycerol, agar and span 80 were processed to form films by casting method (Prakash Maran, Sivakumar, Sridhar, & Prince Immanuel, 2013). The homogenous and clear film forming solution was prepared by dispersing starch and additives in distilled water and gradually heating the contents up to 70 ± 5 °C with stirring (100 rpm) and then kept for 30 min at 70 ± 5 °C. By degassing under vacuum, the dissolved air from the solution was removed and then 20 ml of the solution was transferred to 9 cm internal diameter Petri dishes resting on a leveled surface for casting and then the films were dried in a controlled temperature chamber at 25 °C at 60% RH for 48 h. From Petri dishes, the films were carefully separated and equilibrated at 25 °C, 58% relative humidity for 72 h.

2.3. Thickness (THI)

The thicknesses of the dried films were determined using a digital micrometer (Mitutoyo Co., Japan) with an accuracy of ±1 μm. The electronic digital micrometer was calibrated using standards prior to film thickness measurements. Fifty thickness measurements were taken at different random locations of each film and the mean values of each film were calculated and reported in millimeter (mm).

2.4. Water vapor permeability

Water vapor permeability of film was determined according to the methodology described by Mali, Grossmann, García, Martino, and Zaritzky (2004). Anhydrous calcium chloride (0% RH) was taken in a permeation cell and the circular mouth (area = 0.00181 m^2) of the cell was sealed with the film to be tested. The permeation cell was placed in the desiccator that was maintained at 75% RH using saturated sodium chloride solution in order to maintain RH gradient of 75% across the film. The RH inside the cell was always lower than that in the desiccator, and the water vapor transport was determined from the weight gain of the permeation cell after the steady state condition was reached (about 3 h). Weight measurements were made at regular time intervals (about 1 h) and the changes in the weight were plotted as a function of time. The slope was calculated by linear regression method and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (g/s) divided by the transfer area (m^2). After the permeation tests, film thickness was measured and WVP ($g\,m^{-1}\,s^{-1}\,Pa^{-1}$) was calculated using the following equation (Mali et al., 2004):

$$\mathrm{WVP} = \frac{\mathrm{WVTR}}{S(R_1 - R_2)d} \quad (1)$$

where S is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1 is the RH in the desiccator, R_2 is the RH in the permeation cell and d is the film thickness (m). All tests were conducted in triplicates and average values were recorded.

2.5. Gas permeability

Oxygen (O_2) permeability (OP) of the films was evaluated by the accumulation method described by Mali et al. (2004). O_2 concentration was measured in a gas chromatograph (Omega GC, Sc No-303). All the experiments were conducted in triplicates and O_2 was stabilized passing through a NaCl saturated solution. O_2 permeability of films was calculated and expressed in $cm^3/m\,s\,Pa$ at standard temperature (20 °C) and RH (75%).

2.6. Moisture content (MC)

Film moisture content was determined gravimetrically in a hot air oven at 105 °C overnight. Determination of moisture content was performed for five film specimens of each formulation and the average value was recorded. The moisture content was calculated using the following equation (Zhang & Li, 2011):

$$\mathrm{MC}\ (\%) = \left(\frac{M_1 - M_0}{M_1}\right) \times 100 \quad (2)$$

where M_1 is the initial weight of the film and M_0 is the final weight of the film.

2.7. Solubility (SOL)

Solubility of the film was measured according to the method described by Romero-Bastida et al. (2005). Discs of film (2 cm diameter) were cut, weighed, immersed in 50 ml of distilled water. The