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Hydrophilicity and physicochemical properties of chemically modified cassava starch films

J. Colivet[a,b], R.A. Carvalho[a,*]

[a] College of Animal Science and Food Engineering, University of São Paulo, Avenida Duque de Caxias Norte, 225, Pirassununga, SP, CEP 13635-900, Brazil
[b] College of Animal Science and Food Technology, Universidad de Oriente, Campus Los Guaritos, CEP 6201, Maturín, Monagas, Venezuela

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ABSTRACT

The surface properties and microstructure of films composed of chemically modified cassava starches (cross-linked, acetylated and doubly modified) were evaluated in this study. The films were produced using a casting technique with fixed concentrations of starch and sorbitol (4.0 and 1.2 g/100 g in the filmogenic solution, respectively). The hydrophilicity and surface characteristics of the films were analyzed by determining the optical contact angle (θ). The films were also evaluated for surface properties (polarity and nonpolar and polar components), water solubility, and water vapor permeability. It was determined that films produced from cross-linked and acetylated cassava starch showed greater hydrophobicity and better mechanical properties than those prepared with native cassava starch. The films prepared with doubly modified and acetylated cassava starch had a lower surface energy than the film prepared with untreated and cross-linked starch. The results from scanning electron microscopy, infrared spectroscopy and X-ray diffraction demonstrated marked differences between the films, which were dependent on the type of starch. According to the results obtained in this study, the physicochemical properties of films are related to the chemical structure, microstructure and surface properties.

1. Introduction

Cassava starch is an ingredient with excellent functional characteristics, exploited in formulation of foods and biodegradable materials. It is characterized as containing amylose and amylopectin with high molecular weight and low levels of impurities (fat, protein and ash) (Breuninger et al., 2009). It is commonly used as a thickener and stabilizer in food processing and also as an additive in the textile and papermaking industries (Anggraini et al., 2009).

According to Zain et al. (2016), starches are a viable alternative in the preparation of plastic materials as it is a cheap, renewable, and biodegradable polymer. Films made with starches are odorless, tasteless, colorless, non-toxic, and are semi-permeable to carbon dioxide, moisture, and oxygen (Shah et al., 2016). However, its semicrystalline nature is an undesirable characteristic during the preparation of films, due to its hydrophilicity, increased solubility, poor mechanical properties, and low stability compared to other synthetic materials (Shah et al., 2016). These characteristics can be modified using various chemical and physical treatments in order to enhance the applicability of starches.

According to Chen et al. (2015), crosslinking is one of the most important changes for the treatment of starches because it improves the thermomechanical properties and stability under acidic conditions. Cross-linked starches are produced by their treatment with polyfunctional reagents, such as sodium tripolyphosphate, sodium metaphosphate, phosphorus oxychloride, and epichlorohydrin. However, other agents such as glutaraldehyde, boric acid (Shah et al., 2016), ascorbic acid (Yoon, 2014), citric acid (Reddy and Yang, 2010), and physical treatments such as ultraviolet irradiation and plasma (BeMiller and Huber, 2015) are also used in the crosslinking of starches. The cross-linking of starches adds intra- and intermolecular bonds in random positions in the starch granules, resulting in the stabilization of the molecule (Qiu et al., 2013).

The characteristics of modified cross-linked starches are exploited in the preparation of films as they provide better mechanical properties than native starch. Gutiérrez et al. (2015b) reported that the modification of cassava starch and cush–cush yam by cross-linking reinforces the structure of the starch, resulting in films with a higher tensile strength and higher elasticity compared to films prepared with native starches.

* Corresponding author.
E-mail address: rosecarvalho@usp.br (R.A. Carvalho).

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Moreover, He et al. (2013) found that films produced from potato starches which had been modified by cross-linking had increased surface hydrophobicity compared to films produced with native starches. However, Woggum et al. (2014) reported low flexibility and poor transparency of films made with cross-linked rice starches.

Acetylation is a chemical modification that adds mono acetyl esters groups to starch by its reaction with acetic anhydride or vinyl acetate (Mason, 2009). The introduction of these functional groups modifies the physical and chemical properties of starches, reducing the gelatinization temperature, improving the clarity of the pastes, increasing its resistance to retrogradation, and providing stability during freezing and thawing cycles (Sun et al., 2016). According to Chandra and Rustgi (1998), acetylated starches provide numerous advantages in the production of films compared to native starches, such as increasing the hydrophobicity and tensile strength.

Fringant et al. (1996) studied the acetylation of pea starch and found that acetylation was a more efficient modification in the production of thermoplastic materials with high thermal stability and hydrophobicity, due to the strong intramolecular interactions produced during the acetylation process. Moreover, Chen et al. (2002) reported that acetylation of potato starches improved considerably the tension, elongation, and hydrophobicity of films produced by casting and extrusion, in comparison with films developed with native starches.

Although the properties of starch-based films are well known, there are only few studies which have investigated the effects of different types of modifications on the microstructure and surface properties of the developed materials. According to Qiu et al. (2013), the increased knowledge on the effects of specific chemical modifications on the structure of the starch granules, is important for understanding the functional properties of films. The addition of chemical groups to starch can promote or prevent specific interactions, giving rise to the formation of films with different organizational levels and with different characteristics (Pérez-Gallardo et al., 2012). Furthermore, it is important to understand interactions between packaging and food products, as this, in addition to the storage environment, can affect the shelf-life and biodegradability of the material.

According to Karbowiak et al. (2006), determining the surface properties of films provides useful information to characterize the hydrophobicity of the matrix and its susceptibility to high humidity environments. Furthermore, these studies can be used to characterize the surface polarity, surface energy, and wettability of films (Belibel et al., 2016). Understanding these properties could improve the applicability of these materials, in addition to determining associations between the chemical composition and the physical, chemical, and biological properties of the developed films.

Due the broad applicability of the starches in the packaging industry, the aim of this study was to evaluate the effects of chemical changes to these macromolecules on the surface properties and hydrophilicity of films. Chemically modified cassava starch was studied by cross-linking, acetylation, and double modification to determine the effects on the microstructure of the material and other important characteristics of the films (moisture, solubility, microstructure, chemical composition, mechanical properties, and water vapor permeability).

2. Materials and methods

2.1. Materials

Four types of cassava starches were used, including native starches (ASM), and starch which had been modified by acetylation (AC), cross-linking (AR) or double modification (ACR). The ASM and ACR starches (Amilogill 1500 and Amidomax 4500, respectively) were donated by Cargill industry C.A. (São Paulo, Brazil). The AC and AR starches (T13-271 and T13-270, respectively) were donated by Gemacom Tech (São Paulo, Brazil). The plasticizer sorbitol was acquired from Vetec Fine Chemicals Ltd. (São Paulo, Brazil). The cyclohexane and chloroform solvents which were used for determining the surface properties of the films were purchased from Merck (São Paulo, Brazil).

2.2. Production of modified starch-based films

The films were prepared using a casting technique for the four cassava starches (ASM, AR, AC and ACR). The plasticizer (sorbitol) was firstly solubilized in distilled water (30 g/100 g macromolecule), and then, the starch (4 g/100 g solution) was added to this solution. The starch dispersion was stirred for 30 min at room temperature, and then, heated to 90 °C under magnetic stirring (IKA ® C-MAG HS 7; Staufen, Germany) for 10 min to ensure complete starch gelatinization. The solutions were dispersed on an acrylic plate (12 × 12 cm) and then, dried for 24 h in a forced circulation oven at 30 °C (MA 037; Marconi, São Paulo, Brazil). The thickness of the films was kept constant by controlling the mass ratio of the filmogenic solution to the plate area.

2.3. Characterization of films

The analyses of the films were carried out after conditioning in a desiccator containing a saturated salt solution of NaBr (58% relative humidity; RH) at 25 ± 2 °C for 5 days.

2.3.1. Thickness determination

The thickness of the films was determined using a digital micrometer (Mitutoyo, Tokyo, Japan) in 10 random locations of the film.

2.3.2. Scanning electron microscopy

The microstructure of the films was evaluated using scanning electron microscopy, according to the methodology described by Andreuccetti et al. (2009). The films were placed in a desiccator containing silica gel (25 °C) for 7 days. The morphological observations of the film surface were made using a Hitachi scanning electron microscope (TM3030 Tabletop; Hitachi High Technologies Corporation Instruments Co. Ltd., Tokyo, Japan) set to 5 kV.

2.3.3. Contact angle and wettability

The contact angle, hydrophobicity, and surface wettability of the films were evaluated by the static methodology proposed by Karbowiak et al. (2006). One drop (approximately 5 μL) of test liquid was deposited on the surface of the film. The contact angle (θ) was determined as a function of time (t) using an optical tensiometer (Theta Lite; Biolin Scientific AB, Sweden).

The wettability was evaluated over a period of 300 s. Each film was stored in a desiccator containing saturated NaBr solution (58% RH) at 25 ± 2 °C for 5 days prior to the analysis. The effect of evaporation was analyzed according to the method reported by Kurek et al. (2014) using an aluminum laminate, which is considered to be completely impermeable to water vapor and aqueous solutions.

The kinetics of the contact angle was measured using an exponential decay equation including three parameters (Eq. (1)), as proposed by Farris et al. (2011):

$$[\theta(t) = \theta_0 exp(-kt^n)] \quad (1)$$

where the constant "k" is related to the speed variation of θ, the exponent "n" is related to the process kinetics (absorption and spreading), and θ_0 is the initial contact angle.

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