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Development of pectin films with pomegranate juice and citric acid

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ABSTRACT

The influence of pomegranate juice (PJ, replacing water as solvent) and citric acid (CA) on properties of pectin films was studied. PJ provided the films with a bright red color, and acted as a plasticizer. Increasing PJ/water ratio from 0/100 to 100/0 resulted in enhanced elongation (from 2% to 20%), decreased strength (from 10 to <2 MPa) and modulus (from 93 to <10 MPa), increased water vapor permeability (WVP, from 3 to 9 g.mm.kPa^{-1}.h^{-1}.m^{-2}), and decreased insoluble matter (IM, from 35% to 24%). Although a crosslinking effect by CA was not confirmed, it has been suggested to occur from its effects on films. CA noticeably increased IM (from <10% to almost 40%); moreover, when measured on a dry film basis, the CA effects presented a noticeable tendency to increases strength and modulus, and to decrease WVP. The red color density was decreased by CA, suggesting a destabilization of anthocyanins.

1. Introduction

The development of edible films and coatings has been extensively studied in the last few decades. Those structures are supposed to act as a barrier between the food and the surrounding environment, helping the external packaging in its protective role. Moreover, some of them are supposed to have sensory or nutritional characteristics of their own. The use of fruit purees in edible films has been explored previously (Azeredo, Miranda, Rosa, Nascimento, & De Moura, 2012; Azeredo et al., 2009; Otoni et al., 2014; Rojas-Graü et al., 2006), conferring peculiar flavors and colors which could be exploited for applications such as sushi wraps, fruit strips, or colored coatings for specific foods.

Pomegranate (*Punica granatum* L.), a fruit native to the Middle East, has gained widespread popularity for its alleged health benefits (Johanningsmeier & Harris, 2011). One of the most remarkable sensory characteristics of pomegranates is the intense red color of their arils, caused by anthocyanins (Boroch-Neori et al., 2011). Anthocyanins naturally occur as glycosides of flavylium (2-phenylbenzopyrylium) salts. They are highly sensitive to degradation reactions affecting their stability and color. The color displayed by anthocyanins depends on the pH-dependent equilibrium between five chemical species (Fernandes, Faria, Calhau, Freitas, & Mateus, 2014). Pectins have been reported to improve anthocyanin stability (Buchweitz, Speth, Kammerer, & Carle, 2013a,b; Holzwarth, Korhummel, Siekmann, Carle, & Kammerer, 2013; Melgarejo, Martínez, Hernández, Martínez, & Legua, 2011), explaining the higher anthocyanin stability in jams than in spreads (Holzwarth et al., 2013), and suggesting that pectin may be an interesting matrix for anthocyanin-containing films. The anthocyanin – pectin interaction is ascribed to hydrogen bonding between oxygen atoms of carboxylic groups of pectins and hydrogen atoms of phenolic hydroxyl groups of anthocyanins (Fernandes, Brás, Mateus, & Freitas, 2014). The effects of citric acid (CA) on anthocyanins have been disputed. Some studies have reported citric acid as beneficial to anthocyanin stability (Durge, Sarkar, & Singhai, 2013; Mei et al., 2014), which could be attributed to its lowering pH effect. On the other hand, other studies reported citric acid as destabilizing anthocyanins (Buchweitz et al., 2013a; Hubbermann, Heins, Stöckmann, & Schwartz, 2006).

Citric acid has been reported as a crosslinking agent for polysaccharide films (Olsson, Hedenqvist, Johansson, & Järnström, 2013; Olsson, Menzel et al., 2013), with the advantage that any unreacted CA is nutritionally acceptable and may also act as a plasticizer (Chabrat, Abdillahi, Rouilly, & Rigal, 2012; Shi et al., 2008). The crosslinking mechanism is attributed to covalent intermolecular di-ester linkages between hydroxyl groups of the polysaccharide and two carboxyl groups of the crosslinker (Olsson, Hedenqvist et al., 2013). Sodium hypophosphite (SHP) is a catalyst for the reaction (Reddy & Yang, 2010; Salam, Pawlak, Venditti, & El-tahlawy,

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2011) by weakening the hydrogen bonding between the carboxylic acid groups (Xiaohong & Yang, 2000).

This study was developed to evaluate the influence of pomegranate juice (as a flavor and color providing component) and citric acid on some physical properties of pectin films for applications in which a bright red color may be desirable, such as sushi wraps or fruit strips.

2. Materials and methods

2.1. Materials

Pomegranates were purchased at a local supermarket (Norwich, UK), and the juice (pH 3.51, 16.2% total solid content) was extracted from the arils by using a Philips HR1861 juicer (Philips Co., Beijing, China). The other film components were: pectin from apples (Sigma-Aldrich, 70–75% methyl esterification), citric acid (Sigma-Aldrich, ACS reagent, ⩾99.5%), and sodium hypophosphite monohydrate (Sigma-Aldrich, ⩾99%).

2.2. Preparation of films

For each film forming dispersion, pectin (2.75 g), citric acid, and sodium hypophosphite (SHP) were solubilized in 120 mL of solvent (water and/or pomegranate juice) containing 0.75 g glycerol. Eleven films were formulated, according to a central composite design (CCD) based on response surface methodology, carried out on eleven (Table 1, on randomized runs) with two independent variables: pomegranate juice/water volume ratio (from 0/100 to 100/0) and citric acid (from 0 to 30 g/100 g pectin). SHP was added at 0.5 g/g citric acid. The film forming dispersions were homogenized at 11,000 rpm for 45 min (Ystral X10/25 homogenizer, Ballrechtar-Dottingen, Germany) at 24 °C. Air bubbles were removed under vacuum, and the films were cast on petri dishes to a final dried thickness of 0.10 mm, left to dry at 40 °C for 24 h using a fan oven (Memmert, Schwabach, Germany).

The dried films were detached from the petri dishes and conditioned under controlled relative humidity (50% RH) and temperature (24 °C) in an environmental chamber (Weiss Gallenkamp, Loughborough, UK) for 40 h before the analyses.

2.3. Characterization of films

The water vapor permeability (WVP) determination was modified from the method E96-05 (ASTM, 2005) for five circular samples (30 mm in diameter). The thicknesses were measured using a micrometer screw gauge (Moore & Wright, Sheffield, UK) to the nearest 0.01 mm at 6 random locations, and the average value was calculated. The test films were sealed as patches onto acrylic permeation cells (2.4 cm in diameter and 1 cm in height) containing 2 mL of distilled water. The cells were placed in a desiccator connected to a tube providing a steady flow of dried air (less than 1% RH) from a Balston 75-60 air drier at 24 °C, and were weighed 7 to 8 times over a 24 h period. For each sample, measurements were taken in 4 replicates.

The water solubility determination was carried out on 2 cm × 2 cm film pieces in quadruplicate, based on the method proposed by Ojagh, Rezaei, Razavi, and Hosseini (2010), with some modifications. Previously dried and weighed samples were immersed in 50 mL of distilled water for 6 h at 25 °C, under stirring (150 rpm). The dry weight of the remaining film pieces was obtained after filtration on previously dried and weighed filter paper, and was used to calculate the insoluble matter as a percentage of the initial dry weight (g/100 g). All the dry weights (of the initial and final film pieces and the filter paper) were determined after drying at 103 °C for 24 h using a fan oven (Memmert, Schwabach, Germany).

Tensile tests were conducted according to the method D882-09 (ASTM., 2009), on a Texture Analyzer TA.XT Plus (Stable Micro Systems, Godalming, UK), using A/TG Tensile Grips and a 5 kg load cell, on 50 mm × 8 mm strip film samples. The thicknesses of the specimens were determined by using a micrometer screw gauge (Moore & Wright, Sheffield, UK) to the nearest 0.01 mm at 6 random locations. The initial grip separation and crosshead speed were set to 40 mm and 1 mm/s, respectively. Force (N) and deformation (mm) were recorded during extension. Tensile strength was calculated by dividing the required force for film rupture by the cross-sectional area, and elongation at break was calculated as the percentage increase in sample length. The elastic modulus was calculated from the slope of the stress–strain curve in the elastic deformation region. The reported values are the averages of five measurements.

In order to assess the intensity/stability of the red color, images from film samples previously exposed to indirect sunlight for 7 days were captured at 0.75× magnification on a Leica M165C stereomicroscope. The mean red intensity was calculated using ImagePro-Plus v7.0 (Media Cybernetics Inc., Rockville, MD, USA). A background value (corresponding to a film without pomegranate juice) was subtracted from the test values, and the data were inverted to provide data on optical density rather than intensity (since the original intensity values were inversely related to the red color density of the samples). The inverted intensities were normalized to the sample thickness and expressed as the inverse intensity/μm.

Table 1
Experimental conditions and responses.

Run	Citric acid (g/100 g pectin)		PJ/W		TS (MPa)	EB (%)	EM (MPa)	WVP ($g.mm.kPa^{-1}.h^{-1}.m^{-2}$)	IM (g/100 g)	RCI (inverse intensity/μm)
	Coded	Uncoded	Coded	Uncoded						
1	−1	4.39	−1	14.64/85.36	7.77	8.38	45.67	3.40	25.30	17.99
2	1	25.61	−1	14.64/85.36	6.69	9.87	37.44	4.11	34.89	7.06
3	−1	4.39	1	85.36/14.64	3.05	17.99	10.01	10.91	15.76	28.94
4	1	25.61	1	85.36/14.64	2.46	20.15	8.65	9.62	30.47	25.57
5	−1.41	0.00	0	50/50	5.15	13.69	38.05	6.78	9.36	24.65
6	1.41	30.00	0	50/50	3.37	17.38	20.17	7.18	36.97	18.93
7	0	15.00	−1.41	0/100	10.64	2.00	92.70	3.12	35.00	0.00
8	0	15.00	1.41	100/0	1.82	19.38	7.58	9.49	24.28	31.23
9	0	15.00	0	50/50	4.26	15.63	31.25	6.83	28.65	20.43
10	0	15.00	0	50/50	4.12	13.01	30.27	7.50	30.02	21.02
11	0	15.00	0	50/50	4.40	14.88	31.62	7.31	35.53	20.20

Coded values of the variables are based on a central composite design; uncoded values are the real experimental values of the variables. PJ/W: pomegranate juice/water volume ratio. TS: tensile strength; EB: elongation at break; EM: elastic modulus; WVP: water vapor permeability; IM: insoluble matter; RCI: red color intensity.