



Polyamines as new cationic plasticizers for pectin-based edible films



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ABSTRACT

Zeta potential and particle size were determined on pectin aqueous solutions as a function of pH and the effects of calcium ions, putrescine and spermidine on pectin film forming solutions and derived films were studied. Ca^{2+} and polyamines were found to differently influence pectin zeta potential as well as thickness and mechanical and barrier properties of pectin films prepared at pH 7.5 either in the presence or absence of the plasticizer glycerol. In particular, Ca^{2+} was found to increase film tensile strength and elongation at break only in the presence of glycerol and did not affect film thickness and permeability to both water vapor and CO_2 . Conversely, increasing polyamine concentrations progressively reduced film tensile strength and markedly enhanced film thickness, elongation at break and permeability to water vapor and CO_2 , both in the presence and absence of glycerol. Our findings indicate that polyamines give rise to a structural organization of the heteropolysaccharide different from that determined by calcium ions, previously described as "egg box" model, and suggest their possible application as plasticizers to produce pectin-based "bioplastics" with different features.

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1. Introduction

The heteropolysaccharide pectin (PEC), one of the most complex biomacromolecules occurring in nature, is the main component of the cell wall of all higher plants and contributes to the integrity and rigidity of their tissues by influencing both mechanical strength and cell–cell adhesion (Jolie, Duvetter, Van Loey, & Hendrickx, 2010). The main domain of PEC is constituted by a linear chain of α -(1,4)-linked galacturonic acid residues, partially amidated and/or esterified with methanol, and the percentage of methoxylated residues defines either low (LMPEC) or high (HMPEC) methoxylated PEC (Sila et al., 2009). However, PEC chemical composition is extremely variable among different plant species, their developmental stages and tissues, as well as within a single cell wall. Thus, PEC hetero polymer organization is still subject of debate and its precise macromolecular architecture has not been totally clarified (Coenen, Bakx, Verhoef, Schols, & Voragen, 2007; Vincken et al., 2003).

LMPEC contains higher amount of free carboxylic acid groups able to interact with calcium ions resulting in the formation of a continuous network (gelation) due to different intermolecular interactions (Thibault & Ralet, 2003). In fact, the gelation of LMPEC primarily involves electrostatic forces between the cations and the negative charged cavities formed by the polymer chains where Ca^{2+} are inserted and previously described as "egg box" structure (Fu et al., 2011; Grant, Morris, Rees, Smith, & Thom, 1973). Then, the egg-boxes formed between two neighboring chains are stabilized by both Van der Waals interactions and hydrogen bonds (Fraeye, Duvetter, Doungla, Van Loey, & Hendrickx, 2010). PEC is an ingredient widely used in food industry (Laurent & Boulenguer, 2003; Rolin, 2002; Thakur, Singh, & Handa, 1997), being recognized as safe (GRAS) by the FDA (Espitia, Du, Avena-Bustillos, Soares, & McHugh, 2014), and PEC– Ca^{2+} interactions are of great importance in the area of fruit and vegetable processing

Polyamines (PAs) are low molecular weight organic cations often capable to mimic the action of divalent cations both *in vitro* and *in vivo* (Tabor & Tabor, 1984). The effects of the different PAs, compared to calcium ions, were recently studied by using layers of phosphatidic acids as biological systems to understand the stabilization mechanisms of cell membranes (Rudolphi-Skorska, Zembala, & Filek, 2014). The very low toxicity of PAs, attested by an acute oral toxicity of 2000 and 600 mg/kg in rats, for putrescine

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(PT) and spermidine (SPD) respectively (Til, Falke, Prinsen, & Willems, 1997), and by LD50 values higher than 2000 mg/kg in mice (www.oryza.co.jp/html/english/pdf/polyamine_vol.2.pdf), indicate their possible addition to film forming solutions (FFSs) in obtaining safe food coatings. Therefore, the different length of the aliphatic chains of these positively charged compounds stimulated us to investigate the effect of PT and SPD on the mechanical and barrier properties of PEC-based edible films. PEC represents also a suitable polymeric matrix for the preparation of coatings potentially useful for food active food packaging, for its versatile both chemical and physical properties as well as for its biodegradability and biocompatibility (Espitia et al., 2014; Giosafatto et al., 2014a, 2014b; Porta, Mariniello, Di Pierro, Sorrentino, & Giosafatto, 2011; Rossi Marquez, Di Pierro, Esposito, Mariniello, & Porta, 2014). One of the main additives of the bio-based edible films is the plasticizer, generally a small molecule, like glycerol or sorbitol, able to modify the polymer three-dimensional organization by decreasing attractive intermolecular forces and increasing both free volume and chain mobility and, consequently, improving film extensibility and flexibility (Kokoszka, Debeaufort, Hambleton, Lenart, & Voilley, 2010). Therefore, this work focuses on the effects of Ca^{2+} , PT and SPD as cationic agents on the functionality of PEC-based films compared to glycerol.

2. Materials and methods

2.1. Materials

Citrus peel low-methylated (7%) PEC (Aglupectin USP) was from Silva Extracts srl (Gorle, BG, Italy), glycerol (about 87%) was purchased from the Merck Chemical Company (Darmstadt, Germany) and the PAs PT and SPD were acquired from Sigma Chemical Company (St. Louis, MO). All other chemicals and solvents used in this study were analytical grade commercial products.

2.2. Zeta potential and particle size measurements

PEC zeta potential and the size of the dispersed polymer nanoparticles were measured using the Zetasizer Nano-ZS (Malvern®, Worcestershire, UK). Three independent zeta potential measurements at various pH values were carried out on each sample of 0.1% (w/v) PEC aqueous solution. 1.0 mL of PEC solution was introduced in the measurement vessel. Temperature was set at 25 °C, applied voltage was 200 mV and duration of each analysis was approximately 10 min. The mean hydrodynamic diameter of particles was also determined as a function of pH with the Zetasizer Nano-ZS by using dynamic light scattering. The device uses a helium-neon laser of 4 mW output power operating at the fixed wavelength of 633 nm (wavelength of laser red emission). All the results were reported as mean \pm standard deviation. PEC zeta potential was also measured in the presence of increasing concentrations of either calcium ions or polyamines both without and with glycerol (30%, w/w PEC) addition.

2.3. PEC film preparation

PEC (1.0 g) was dissolved in 100 mL of distilled water. The solution was stirred until PEC was completely solubilized. Three different kinds of 10 mg/mL PEC-based film forming solutions (FFSs) at pH 7.5, containing either CaCl_2 , PT or SPD at different concentrations (4, 8 and 20 mM) were prepared both in the absence and presence of 30% glycerol (w/w PEC). Prior to film casting, all the film forming solutions (FFSs) were de-aerated under vacuum to prevent pinhole formation and then poured onto 8 cm diameter polystyrene Petri dishes (10 mg/cm² PEC). All the samples were allowed to dry in an environmental chamber at 25 °C and 45% RH for 48 h. Dried

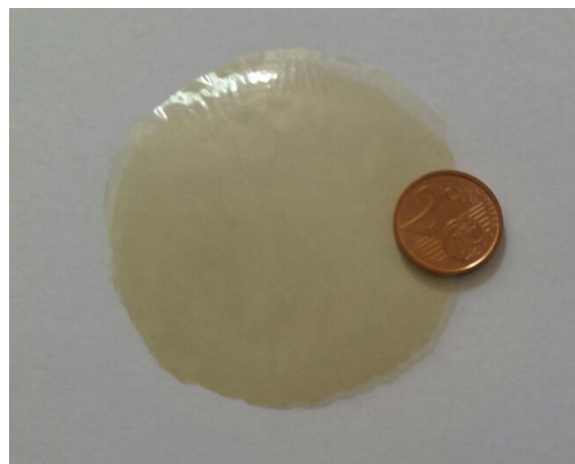


Fig. 1. Typical glycerol containing PEC film obtained in the presence of 20 mM SPD. Experimental details are given in the text.

films were peeled intact from the casting surface and always conditioned at 25 °C and 53% RH for 2 h, by placing them in a desiccator over a saturated solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, before being tested. Film thickness was measured with an electronic digital micrometer (DC-516, sensitivity 0.001 mm) at different positions for each film sample. At least five measurements were taken on each film sample and the thickness mean values were considered in the different tests. No macroscopic differences among the films obtained in the absence or presence of Ca^{2+} (4 and 8 mM) or PT and SPD (4, 8 and 20 mM), containing or not glycerol, were observed. The image of a typical glycerol containing PEC film obtained in the presence of 20 mM SPD is shown in Fig. 1.

2.4. Film mechanical and barrier properties

Film tensile strength and elongation at break were determined by using an universal testing instrument model no. 5543A (Instron, Norwood, MA, USA). Film samples strips (10–11 mm wide and 50 mm long), obtained by using a sharp razor blade, were conditioned in an environmental chamber as reported above and, finally, ten samples of each film type were tested. The mechanical properties were measured according to the ASTM D882-97 (1997) using Test Method A, the static weighing, constant rate-of-grip separation test. The initial grip separation was 40 mm, and the crosshead speed was 10 mm/min in tension mode.

The permeability to CO_2 of duplicate samples of each film was determined, after conditioning as mentioned above, by using a modified ASTM D3985-81 (1981) with a MultiPerm apparatus (ExtraSolution s.r.l., Pisa, Italy). Aluminum masks were used to reduce the film test area to 5 cm², whereas the testing was performed at 25 °C under 50% RH. Water vapor permeability (WVP) was evaluated by a gravimetric test according to ASTM E96-93 (1993) as previously reported (Porta et al., 2015).

2.5. Statistical analysis

JMP software 5.0 (SAS Institute, Cary, NC, USA) was used for all statistical analyses. The data were subjected to analysis of variance, and the means were compared using the Tukey-Kramer HSD test. Differences were considered to be significant at $p < 0.05$.

3. Results

Several ionic bonds between PA amino groups and monomers of polysaccharide chains endowed with negative charges can be

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