Effect of polyamines on low methoxyl pectin-based films

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Abstract

Low methoxyl pectin (LMPEC) contains a high amount of free carboxylic acid groups able to interact withCa^{2+}originating a gel network. LMPEC gelation primarily involves electrostatic forces between the cation and the negative charged cavity formed by the polymer chains where $Ca^{2+}$are inserted. These structures, called*egg-boxes*, are stabilized by both Van der Waals interactions and hydrogen bonds. They are of great importance both in the area of fruit and vegetable processing as well as for the use of LMPEC in various food products. Polyamines (PAs) are low mol.wt organic cations known to mimic the action of divalent cations both *in vitro* and *in vivo*. The different length of PA aliphatic chains, thus, stimulated us to investigate their effect on the mechanical and barrier properties of LMPEC-based edible films. In fact, LMPEC represents also a suitable polymeric matrix for the preparation of coating films potentially useful for food active packaging for its biodegradability and biocompatibility. One of the main additives of the bio-based edible films is the plasticizer, generally a small molecule of low volatility, like glycerol or sorbitol, able toimprove film extensibility and flexibilityby increasing both free volume and polymer chain mobility. Therefore, our research focused on the specific comparison among calcium, and the two PAs putrescine (PT) and spermidine (SPD) as possible agents influencing the functionality of LMPEC-based films prepared in the presence or absence of glycerol. Zeta potential and particle size were determined on LMPEC aqueous solutions as a function of pH and the effect of calcium ions, PT and SPD on LMPEC-based films were studied. Ca^{2+} and PAs were found to differently influence thickness, as well as mechanical and barrier properties, of 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 to break only in the presence of glycerol and did not affect film thickness and permeability to both water vapor and CO_2. Conversely, increasing PA concentrations progressively reduced film tensile strength and markedly enhanced film thickness, elongation to break and permeability to water vapor and CO_2, both in the presence and absence of glycerol. Our findings suggest that PAs give rise to a LMPEC structural organization different from that determined by calcium ions, previously described as "*egg box*" model, and that PAs can be used as effective plasticizers to obtain more flexible and less brittle hydrocolloidal films.