## Effect of Spermidine on Physicochemical Properties of Protein Based Films

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Abstract : Protein-based edible films and coatings have attracted an increasing interest in recent years since they might be used to protect pharmaceuticals or improve the shelf life of different food products. Among them, several plant proteins represent an abundant, inexpensive and renewable raw source. These natural biopolymers are used as film forming agents, being able to form intermolecular linkages by various interactions. However, without the addition of a plasticizing agent, many biomaterials are brittle and, consequently, very difficult to be manipulated. Plasticizers are generally small and non-volatile organic additives used to increase film extensibility and reduce its crystallinity, brittleness and water vapor permeability. Plasticizers normally act by decreasing the intermolecular forces along the polymer chains, thus reducing the relative number of polymer-polymer contacts, producing a decrease in cohesion and tensile strength and thereby increasing film flexibility allowing its deformation without rupture. The most commonly studied plasticizers are polyols, like glycerol (GLY) and some mono or oligosaccharides. In particular, GLY not only increases film extensibility but also migrates inside the film network often causing the loss of desirable mechanical properties of the material. Therefore, replacing GLY with a different plasticizer might help to improve film characteristics allowing potential industrial applications. To improve film properties, it seemed of interest to test as plasticizers some cationic small molecules like polyamines (PAs). Putrescine, spermidine (SPD), and spermine are PAs widely distributed in nature and of particular interest for their biological activities that may have some beneficial health effects. Since PAs contains amino instead of hydroxyl functional groups, they are able to trigger ionic interactions with negatively charged proteins. Bitter vetch (Vicia ervilia; BV) is an ancient grain legume crop, originated in the Mediterranean region, which can be found today in many countries around the world. This annual Vicia genus shows several favorable features, being their seeds a cheap and abundant protein source. The main objectives of this study were to investigate the effect of different concentrations of SPD on the mechanical and permeability properties of films prepared with native or heat denatured BV proteins in the presence of different concentrations of SPD and/or GLY. Therefore, a BV seed protein concentrate (BVPC), containing about 77% proteins, was used to prepare film forming solutions (FFSs), whereas GLY and SPD were added as film plasticizers, either singly or in combination, at various concentrations. Since a primary plasticizer is generally defined as a molecule that when added to a material makes it softer, more flexible and easier to be processed, our findings lead to consider SPD as a possible primary plasticizer of protein-based films. In fact, the addition of millimolar concentrations of SPD to BVPC FFS allowed obtaining handleable biomaterials with improved properties. Moreover, SPD can be also considered as a secondary plasticizer, namely an 'extender', because of its ability even to enhance the plasticizing performance of GLY. In conclusion, our studies indicate that innovative edible protein-based films and coatings can be obtained by using PAs as new plasticizers.

Keywords : edible films, glycerol, plasticizers, polyamines, spermidine

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