

Influence of film forming solutions on properties of chitosan/glycerol films

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INTRODUCTION

Edible and biodegradable films have been successfully explored at experimental level, attracting interest in the food preservation and packaging technology fields. Chitosan is considered as being biocompatible, biodegradable and possesses antimicrobial activity and filmogenic properties. However, film technology still presents several challenges for researchers. Namely, there is a lack of systematic information on the relationship between the composition and properties of film forming solutions and the properties of the obtained films. Polymer/plasticizer concentrations in solutions may be crucial in film forming solutions viscosity, and as a result in films mechanical properties, water retention capacity and water affinity. The primary role of plasticizers is to improve the flexibility and processability of polymers. Also, these additives reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, at the same time as increasing its chain flexibility, resistance and dielectric constant. All these effects, contribute to changes on the polymer free volume and thus on the molecular mobility of the polymeric matrix. The relationship between molecular mobility and films physical properties are still largely unknown and it is of utmost importance to determine the effect of films composition on the matrix free volume. Glycerol is the most used plasticizer due to its good plasticization efficiency, large availability and low exudation. The aim of this study is to investigate the relationship between film forming solution and corresponding film. Also, assemble systematic information, on the effect of polymer/plasticizer concentrations of film forming solution viscosity and the outcome on the mechanical behaviour and water retention and solubility of the films.

MATERIALS & METHODS

Film forming solutions were prepared by dissolving different chitosan concentrations in a 1% lactic acid with 3 different levels of plasticizing agent, glycerol. Water activity of film forming solutions and films was determined. Rheology of film forming solutions was studied by flow curves. Moisture content (MC) and solubility (SOL) of films were determined. Films mechanical properties were determined in extension with an Instron Universal Testing Machine following the guidelines of ASTM D 882-91 (1991). Results were analysed by analysis of variance (one-way ANOVA) and post hoc multiple comparison tests (Tukey's test).

RESULTS & DISCUSSION

Characterization of film forming solutions (FFS)

For all the tested FFS, results show a shear thinning behaviour, which is commonly used for describing the polymer melt behaviour. Glycerol addition showed no significant effect on FFS rheological behaviour, assessed by n and K estimates. As for chitosan concentration, it affects significantly FFS rheological behaviour, ranging from close to Newtonian to a pseudoplastic behaviour. K significantly increased with chitosan addition. These results can be related with the lower amounts of water present in the solutions with higher polymer/plasticizer concentration.

Regarding water activity, addition of plasticizer will have a different effect depending on chitosan concentration: for lower chitosan concentration (1%), the addition of glycerol will not affect water activity. With increasing chitosan concentration, glycerol addition will lower the solutions water activity. This effect was even more evident for higher chitosan concentrations.

Characterization of chitosan films

Experimental results obtained for the characterization of chitosan films are presented in Table 1. Both chitosan and glycerol caused significant differences in elongation at break (EB) and tensile strength (TS). The amount of glycerol added show a conventional action of plasticizers, increasing elongation at break and decreasing the tensile strength.

This effect is believed to be due to chitosan chains interference, decreasing intermolecular attraction and increasing polymer mobility which facilitate film elongation [1, 2]. However, solutions with 50% of glycerol and higher percentages of chitosan concentrations show higher values of EB than solutions with 90%. This decrease may occur due to the relationship between polymer/plasticizer concentrations, corresponding to an antiplasticization phenomenon: A stronger interaction might be occurring between the polymer and the plasticizer, producing a “cross-linker” effect, which decreases the free volume and the molecular mobility of the polymer [1, 3].

Table 1. Experimental results obtained for the characterization of film forming solutions and films

Sample			Viscosity Parameters		Mechanical Parameters		MC (%)	SOL (%)
% of Chit	% of Gly	% of Water	K (Pa.s ⁻¹)	n	EB (%)	TS (MPa)		
1	90	97.91	0.219±0.069	0.813±0.04	67.93±6.738	1.822±0.337	51.179±1.237	67.521±2.985
	50	98.40	0.254±0.087	0.802±0.05	62.173±5.191	4.498±0.629	36.635±3.498	54.091±1.862
	10	98.89	0.197±0.09	0.810±0.07	46.097±2.189	8.245±0.700	28.867±2.414	48.911±0.863
2	90	95.90	1.587±0.38	0.683±0.03	32.670±1.556	0.281±0.019	51.924±1.846	61.399±1.722
	50	96.84	1.449±0.43	0.682±0.04	34.553±1.034	0.952±0.091	38.324±1.905	51.021±1.545
	10	97.80	2.113±0.90	0.654±0.06	19.995±2.580	12.147±1.162	17.834±0.523	36.055±0.388
3	90	93.98	3.034±0.50	0.635±0.02	19.659±1.467	0.475±0.026	55.057±0.338	63.453±0.265
	50	95.34	3.220±0.34	0.623±0.01	25.579±0.754	1.471±0.074	38.874±0.554	49.774±0.364
	10	96.73	3.370±0.83	0.619±0.03	9.500±2.177	6.031±0.565	16.355±0.359	29.726±0.433

Regarding samples water solubility (SOL), higher glycerol concentrations led to higher film solubility in water, which gives an indication on the film’s water affinity. This fact may occur due to the three hydrophilic hydroxyl groups present in glycerol, that are responsible for its solubility in water and its hygroscopic nature [4]. It was observed that high chitosan/glycerol concentration solutions led to films with significantly higher water content (MC). This can be related with higher molecular entanglement and viscosity (evaluated by K) in FFS, leading to higher retention of water molecules during drying of the films. For every tested chitosan concentration, plasticizer addition lead to a significant increase of water content of the film – despite the fact that FFS had less water in its composition. This shows that, besides decreasing intermolecular attraction and increasing polymer mobility which facilitate film elongation, glycerol addition may promote water retention in the polymer matrix during the drying process.

CONCLUSIONS

Chitosan and glycerol concentrations of the film forming solutions straightly affected films properties. Higher chitosan concentrations led to higher K values of the solutions and to films higher tensile strength and lower elongation at break. Glycerol concentrations also affected mechanical properties of films as well as moisture content and water solubility. Particularly, in mechanical properties it is possible to observe a combined effected between chitosan and glycerol concentrations. Since glycerol has a highly hygroscopic character, greater glycerol concentrations led to films more soluble in water with higher moisture content. This research shows that there are still important water and polymer/plasticizing effects to be studied in food materials science.

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