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IRRADIATED GELATIN-POTATO STARCH BLENDS: EVALUATION OF PHYSICOCHEMICAL PROPERTIES

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ABSTRACT

Macromolecular polysaccharides of large chains as starch can interlace with gelatin modifying their mechanical resistance. In this work, biodegradable bovine gelatin-potato starch blends films were developed using glycerol as plasticizer. Three formulations of gelatin/starch proportions (w/w) were used (1:0; 3:1; 1:1) and casting was the chosen method. The dried samples were then submitted to ionizing radiation coming from an electron beam (EB) accelerator with doses of 20 and 40 kGy, at room temperature, in the presence of air. Mechanical properties such as puncture strength and elongation at break were measured. Color measurements, water absorption, moisture, and film solubility were assessed. The results showed that starch addition to films based on gelatin as well as irradiation affected physical and structural properties of the films. Although the increase of starch content in the mixture led to decrease of the puncture force even in samples irradiated with the higher dose, there was a decrease of water absorption of films with the increase of the dose, and also by the higher starch content. Samples irradiated at 20 kGy presented higher moisture and film solubility. The methodology developed in this paper can be applied to other composite systems to establish the best protein:starch ratio, and the contribution of the radiation crosslinking in each specific case.

Key words: gelatin, potato starch, ionizing radiation

1. INTRODUCTION

Gelatin is a biopolymer derived from collagen, the most abundant protein in animal bodies [1], and is widely used in food, cosmetic, pharmaceutical, and photographic industries. Unlike other hydrocolloids, gelatin is thermoreversible, and can exist as a solution or gel depending on temperature, which provides its main advantage over other gelling agents such as carrageenan, alginates, and pectin. Gelatin presents excellent film forming properties [2]. Meanwhile, the polar groups present in its structure cause a gelatin film to have high moisture absorption. Due to this disadvantage, pure gelatin films are not suitable for many applications.

As additives for food processing, food starches are typically used as thickeners and stabilizers. Potatoes' starch granules are roughly twice as big as other starch granules (tapioca or grain starches) resulting in much higher water absorption capacity and better texture. Potato starch contains approximately 800 ppm phosphate bound to the starch; this increases the viscosity and gives the solution a slightly anionic character, a low gelatinization temperature (approximately 60 °C) and high swelling power. These typical properties are used in food and technical applications.

The functional properties of starch edible films are influenced by starch properties, including chain conformation, molecular bonding, crystallinity, types, and concentration of plasticizer types [3]. Starch films generally show poor mechanical properties, and provide a minimal barrier to moisture. The presence of plasticizer leads to overcome the brittleness of these films, and contents between 15-40 g glycerol/ 100 g starch are commonly used for improve these properties [4,5].

Edible film technology employs proteins as biomaterial because they have specific structure, which confers a wide range of functional and film-forming properties as a function of various extrinsic or intrinsic conditions, such as plasticizer type and concentration [6]. Amino acids as well as proteins proved to modify functional behavior of starch, and that action was attributable to its binding to the starch chain [7,8]. Gelatin and polysaccharide polymers are able to form structural networks by interactions between anionic groups of polysaccharides, and cationic groups of gelatin that can result in improved physical, and mechanical properties of the blend [8,9].

There are descriptions in the literature about the use of crosslinking agents to affect mechanical properties of gelatin, and starch [10-14], UV radiation [15] or ionizing radiation coming from gamma sources or electron beam (EB) [16,17]. In this work, the effects of increasing addition of potato starch to gelatin films as well as the action of the EB radiation-induced crosslinking were evaluated.

2. MATERIAL AND METHODS

2.1. Material

Bovine gelatin type B, 240 Bloom/10 mesh (Gelita do Brasil Ltda), potato starch obtained at local market, glycerol PA ACS from Casa Americana de Art. Lab. Ltda (CAAL).

2.2. Preparation of Gelatin-Potato Starch Films

Aqueous solution of gelatin (10% w/w), potato starch (10% w/w) with glycerin (5% w/w) was prepared by heating up to 70 ºC under constant stirring for total dissolution. Three formulations of gelatin/starch proportions (w/w) were used: 1:0; 3:1; 1:1 named as GEL100; GEL75 and GEL50 respectively. The homogeneous solutions were cast on flat glass plate for film formation, and then dried for 24 h in an air-circulating oven at 25.0±0.1 ºC and 50±5% RH.

2.3. Irradiation

The dried gelatin/starch films were irradiated with 20 and 40 kGy, using an EB accelerator (Dynamitron II, Radiation Dynamics Inc.), at room temperature, in the presence of air, dose rate 22.4 kGy s^{-1}, energy 1.407 MeV, beam current 3.29 mA, tray speed of 6.72 m min^{-1}. Dosimetry was carried out with cellulose triacetate film dosimeters “CTA-FTR-125” (Fuji Photo Film Co. Ltd).

2.4. Mechanical Properties of Gelatin-Potato Starch Films

Puncture force and elongation at break were measured using a Texture Analyzer of Stable Micro Systems, TA-XTPlus, with a load cell of 50 kg. A film support rig (HDP/FSR) and a stainless steel spherical probe (P/0.5S) were used to perform the assays at 0.5 mm s^{-1}, and distance of 15 mm.

2.5. Color Measurements

Color values of films were measured with a Chroma meter (CR-400, Minolta Camera Co., Osaka, Japan). Film specimens (n=10) were placed on the surface of a white standard plate (calibration plate CR-A43), and Hunter L* (lightness), a* (redness), and b* (yellowness) color values were measured. The color coordinates ranges were: L* (0 black to 100 white), a* (-greenness to +redness), and b* (–blueness to +yellowness). All the tests were performed in triplicate. The parameters C* (Chroma), and h (Hue angle) were obtained by equations (1) and (2) as follow:

$$\boldsymbol{h} = \mathbf{arctan}\left(\frac{\boldsymbol{b}^*}{\boldsymbol{a}^*}\right) \tag{1}$$

$$\boldsymbol{C}^* = \sqrt{(\boldsymbol{a})^2 + (\boldsymbol{b})^2} \tag{2}$$

2.6. Water Uptake

To evaluate the water uptake resistance of the gelatin/starch films, specimens (10x10 mm) of dry samples were weighed (Mi) and placed in distilled water, and storage at room temperature for 24 h. After 24 h, the swollen gels were removed from water, blotted dry, and weighed (Mf). The tests were performed in triplicate. The water uptake (WU) of the films was obtained by the following equation (3):

$$\mathbf{WU\ (\%) = ((Mf - Mi)/Mi))\ x\ 100} \tag{3}$$

2.7. Moisture Content

Moisture contents of gelatin/starch films were determined by measuring the weight loss of specimens (10x10 mm), upon drying under air-circulating oven at 105 ± 1 °C until constant weight. The tests were performed in triplicate.

2.8. Film Solubility

Gelatin/starch films specimens (10x10 mm) were weighed, and dried under air-circulating oven at 105 ± 1 °C for 24 h. Then, the samples were placed in beakers with 50 mL of distilled water, and stored at room temperature for 24 h with occasional gentle stirring. After

24 h, the undissolved film were dried under air-circulating oven at 105 ºC for 24 h, and weighed. Film solubility was calculated by the equation (4):

$$\mathbf{FS\ (\%) = ((Wi – Wf)/Wi)\ x100} \tag{4}$$

where Wi was the initial weight of the film expressed as dry matter and Wf was the weight of the undissolved dried film residue. The tests were performed in triplicate.

3. RESULTS AND DISCUSSION

Biscarat et al. [18] described the preparation of dense gelatin membranes by combining temperature-induced gelation and dry-casting. In the present work, blends of gelatin and potato starch were prepared also by gelation and dry-casting and then EB irradiated. Some selected physical properties of the blend films were investigated. The increase of potato starch proportion led to the decrease of the puncture strength even with the increase of radiation dose (Tab. 1).

Table 1: Rupture force and elongation at break of gelatin-potato starch blends before and after irradiation

Parameters	Samples	Dose (kGy)		
		0	20	40
Puncture Force (N)	GEL100	39.1 ± 1.4^{Aa}	34.1 ± 0.9^{Ba}	27.7 ± 0.5^{Ca}
	GEL75	29.9 ± 0.6^{Ab}	26.8 ± 0.8^{Cb}	26.8 ± 1.3^{BCab}
	GEL50	21.3 ± 0.8^{Bc}	21.3 ± 0.6^{BAc}	17.4 ± 0.1^{Cc}
Elongation at Break (%)	GEL100	48 ± 3^{Bc}	52 ± 1^{Ac}	48 ± 2^{BCc}
	GEL75	59 ± 1^{Ab}	60 ± 4^{Aa}	57 ± 4^{Aa}
	GEL50	62 ± 3^{Aab}	57 ± 4^{ABba}	55 ± 3^{CBba}

Means in the same row with different capital letters and column with different lower case letters differ significantly ($p \leq 0.05$).

In reference to color measurements presented in Tab. 2, there was a slight decrease of lightness (L*) with increase of EB irradiation dose, and starch proportion; for yellowness (+b*) and greenness (-a*) the values increased with the increase of the dose. The chroma (C*) presented similar behavior of b*.

Table 2: Color measurements of gelatin-potato starch blends

Parameters	Samples	Dose (kGy)		
		0	20	40
L*	GEL100	95.5 ± 0.3^{Aa}	93.0 ± 0.8^{Bc}	92.9 ± 1.0^{CBc}
	GEL75	94.8 ± 0.8^{Ab}	93.4 ± 0.7^{Bcb}	94.0 ± 0.9^{CBa}
	GEL50	94.2 ± 0.8^{Acb}	94.0 ± 0.9^{Aab}	93.7 ± 0.8^{Aca}
a*	GEL100	-0.6 ± 0.1^{Aa}	-1.5 ± 0.2^{Ba}	-2.2 ± 0.3^{Ca}
	GEL75	-1.4 ± 0.1^{Ac}	-2.4 ± 0.2^{Bc}	-2.5 ± 0.2^{Cc}
	GEL50	-1.3 ± 0.1^{Abc}	-2.3 ± 0.2^{Bbc}	-2.3 ± 0.1^{CBab}
b*	GEL100	5.1 ± 0.2^{Ca}	9.6 ± 0.9^{Bb}	13.0 ± 1.7^{Aa}
	GEL75	5.2 ± 0.5^{Ca}	10.6 ± 1.0^{Ba}	11.6 ± 1.1^{Aa}
	GEL50	5.4 ± 0.8^{Ca}	9.0 ± 1.3^{Bbc}	12.0 ± 1.6^{Aa}
C*	GEL100	5.2 ± 0.2^{Ca}	9.7 ± 0.9^{Bb}	13.1 ± 1.7^{Aa}
	GEL75	5.4 ± 0.5^{Ca}	10.8 ± 1.0^{Ba}	11.9 ± 1.1^{Aa}
	GEL50	5.6 ± 0.8^{Ca}	9.3 ± 1.3^{Bbc}	12.2 ± 1.6^{Aa}
h	GEL100	97.2 ± 0.6^{Cc}	98.7 ± 1.0^{Bc}	99.7 ± 1.4^{ABc}
	GEL75	104.9 ± 1.0^{Aa}	102.8 ± 0.9^{Bb}	102.4 ± 1.2^{CBa}
	GEL50	104.1 ± 1.0^{Bba}	104.3 ± 0.9^{BAa}	101.1 ± 1.3^{Cb}

Means in the same row with different capital letters and column with different lower case letters differ significantly ($p \leq 0.05$).

In Tab. 3 are displayed the results of water uptake, moisture, and solubility of gelatin-starch films. The results showed that different gelatin:starch ratios of plasticized composite films affected water uptake, moisture, and solubility of the films.

Table 3: Water uptake, moisture and solubility of gelatin-potato starch blends

Parameters	Samples	Dose (kGy)		
		0	20	40
Water Uptake (%)	GEL100	331 ± 6^{Ab}	274 ± 7^{Ba}	245 ± 12^{Ca}
	GEL75	352 ± 1^{Aa}	225 ± 10^{Bb}	158 ± 4^{Cb}
	GEL50	277 ± 10^{Ac}	177 ± 9^{Bc}	119 ± 4^{Cc}
Moisture (%)	GEL100	21.2 ± 0.2^{Cc}	22.3 ± 0.9^{Ac}	21.7 ± 0.2^{CAc}
	GEL75	24.9 ± 0.4^{Ba}	26.0 ± 0.4^{Ab}	24.3 ± 0.4^{Bb}
	GEL50	24.8 ± 1.8^{Aba}	26.2 ± 0.2^{Aab}	25.5 ± 0.8^{Aa}
Solubility (%)	GEL100	43.9 ± 0.1^{Ca}	63.9 ± 2.3^{Aa}	45.0 ± 0.1^{CBc}
	GEL75	40.6 ± 0.1^{Ca}	51.1 ± 0.2^{Ac}	50.5 ± 0.4^{Bb}
	GEL50	44.1 ± 4.1^{Ca}	58.5 ± 5.4^{Bab}	60.2 ± 0.9^{ABa}

Means in the same row with different capital letters and column with different lower case letters differ significantly ($p \leq 0.05$).

Corradini et al. [19] has described the preparation of starch/zein blends. They found also that the use of the wheat protein, zein, in thermoplastic starch compositions causes a decrease in water sensitive of these materials, and reductions in melt viscosity during processing.

The plasticizer modifies the interactions between the macromolecules [20]. Vanin et al. [21] analyzed the effect of plasticizers (polyols), and their concentrations on the thermal and functional properties of gelatin-based films. They concluded that glycerol, which was employed in the present work, was compatible with gelatin and showed the highest plasticizing effect on the mechanical properties of the film producing a flexible, and easy handling film with no phase separation.

4. CONCLUSION

Gelatin-potato starch irradiated films showed different behavior with the increase of potato starch proportion and radiation dose. Then, the methodology applied in this paper can be employed also to other composite systems. Nevertheless, in each case it is necessary to establish the best protein:starch ratio, and the contribution of the radiation crosslinking that can conduct to better functional applications.

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