

Research Article

Improving Functional Properties of Cassava Starch-Based Films by Incorporating Xanthan, Gellan, or Pullulan Gums

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The effect of the partial substitution of cassava starch in edible films for 10 and 20 wt% of gellan, xanthan, or pullulan gums was analysed in films obtained by casting. The tensile properties, barrier capacity to water vapour, and oxygen and water sorption isotherms of the samples were analysed. The blend of starch with gellan gum was effective to reduce the moisture sorption capacity of starch films while reducing water vapour permeability, enhancing the film strength and resistance to break and preserving films against starch retrogradation throughout the storage time. Xanthan gum improved the tensile behaviour of the starch films, but did not reduce their water sorption capacity and water vapour permeability. Pullulan did not notably improve the functional properties of the starch films. Gellan gum at 10 and 20 wt% in the blend could be used to obtain starch films with more adequate properties for food packaging purposes.

1. Introduction

The growth in environmental concerns over nonbiodegradable petrochemical-based plastics has been the driving force behind studies seeking to solve the problems associated with the plastic waste by developing biobased/biodegradable polymers as more environmentally friendly materials, which can be produced from a variety of agricultural commodities and/or of food waste products [1, 2].

Due to its availability, biodegradability, renewability, film-forming ability, and low cost [3], starch from different botanical sources (cassava, corn, wheat, rice, potato, pea, and others) is one of the most promising natural polymers for packaging applications [4, 5]. Starch-based films are transparent [6], odorless, tasteless, and highly impermeable to oxygen [7]. However, they have some limitations such as their highly hydrophilic nature (water sensitivity), which negatively affects tensile and barrier properties as compared with conventional synthetic polymers [8]. Therefore, various approaches, such as blending with additives and/or other biopolymers [9–15] or the starch chemical modification, have been studied to improve these characteristics [16].

Polysaccharides produced by microorganisms, such as pullulan, gellan, or xanthan, have found a wide range of applications in the food, pharmaceutical, and other industries due to their particular functional properties. Some of these applications include their use as emulsifiers, stabilizers, gelling agents, film formers, or thickening agents [17]. Gellan gum is a microbial polysaccharide secreted by the bacterium *Sphingomonas elodea*. Gellan polymer consists of a linear tetrasaccharide repeat unit composed of two molecules of D-glucose, one of D-glucuronic acid and one of L-rhamnose [18, 19]. Kim et al. [13] reported that gellan gum was effective at improving the storage stability and mechanical properties of the starch films.

Xanthan gum is a high molecular weight extracellular polysaccharide produced by the bacterium *Xanthomonas campestris* and is one of the most important commercial microbial hydrocolloids used in the food industry as thickening agent and stabilizer [17]. It is composed by a linear β -1,4-linked D-glucose chain substituted on every second glucose unit by a charged trisaccharide side chain with glucuronic acid residue between two mannose units. The inner mannose residue is normally acetylated at C(6), which is

located at the external part of the helical conformation of the polysaccharide. About half of the terminal mannoses are linked to pyruvyl residues. Deprotonation of acetyl and pyruvyl residues at $\text{pH} > 4.5$ increases the negative charge density of the xanthan chain. It has been reported that xanthan influenced the mechanical parameters and moisture adsorption isotherm of cassava starch films [9, 15]. The xanthan gum enhanced film traction resistance but generated a less deformable matrix, which was associated to the gum and starch chain interaction through hydrogen bonds developing a more resistant network but with lower deformability due to the impossibility of polymeric chains to slide for maintaining the ductile behaviour observed in the absence of gum [9]. In accordance with Veiga-Santos et al. [15], the interaction between the xanthan gum and the starch might avoid the occurrence of amylose:amylose interaction, inhibiting the starch retrogradation. The prevention of the amylose:amylose interaction provoked by this gum could also give rise to a more unfolded network with weaker interaction forces, resulting in films with lower elongation at break [15]. Likewise, the development of gum-starch hydrogen bonds might interfere with amylose packing, inhibiting the formation of polymer-water hydrogen bonds in the amorphous areas, thus limiting the water sorption capacity of the blend films [9].

On the other hand, pullulan is a neutral, linear, and water-soluble polysaccharide [20, 21], composed of maltotriose units linked by α -1,6-glycosidic bonds [11]. It is produced by *Aureobasidium pullulans* in starch and sugar cultures. Pure pullulan films are transparent, water-sensitive, and mechanically weak [22]. The hydrophilic nature of pullulan, however, often makes its films sticky when exposed to high relative humidity conditions [13]. Kim et al. [12] found that tapioca starch-pullulan blend films exhibited greater mechanical strength and stability during storage under humid conditions and at the same time the composite films were less water-soluble.

The blending of starch with small amounts of the above polysaccharides could represent a simple method that has the potential of improving the starch film properties while keeping the competitive cost of the material. Although there are several studies which analyse the effect of the partial substitution of starch by different gums on blend films, in terms of the improvement of the starch-based film functionality, few comparative analyses have been reported by using the same film obtaining process [13], in order to select the most appropriate blend to effectively reduce the water sensitivity of the starch-based materials. It is well known that differences in the polymer characteristics, as well as different processing techniques to obtain films, can affect the final properties of the material [23, 24]. Therefore, for an adequate comparison, standardization of the raw materials and methods must be carried out. Likewise, no studies were found into the effect of the gums on the starch retrogradation phenomena, responsible for changes in the film mechanical properties throughout the storage time.

In this sense, the objective of this study was to analyse the effect of the partial starch substitution by three different microbial gums (xanthan, gellan, and pullulan) on the relevant physical properties of the cassava starch-based films

(tensile, barrier, and water adsorption capacity), as well as the ageing behaviour of the films through the changes in the film tensile properties during storage, when equilibrated at different relative humidities.

2. Materials and Methods

2.1. Materials. Cassava starch (S) was supplied by Quimirodroga S.A. (Barcelona, Spain). The amylose content (w/w , %) of cassava starch was 10%, with an amylose:amylopectin ratio of 1:9.9 (determined by using an Amylose/Amylopectin Assay Procedure enzymatic kit, Megazyme International Ireland, Bray Business Park, Bray, Co. Wicklow, Ireland). Xanthan gum (X) (high molecular weight, $\sim 10^6$ Da) was supplied by EPSA (Valencia, Spain). Negatively charged, low acyl gellan gum (G) KELCOGEL F (M_w $3 - 5 \times 10^5$ Da) was purchased from Premium Ingredients (Murcia, Spain), and pullulan (P) (M_w 2×10^5 Da) was provided by Nagase GmbH (Dusseldorf, Germany). Glycerol, used as plasticizer, and P_2O_5 , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, CuCl_2 , NaCl , and KCl salts were provided by PanReac Química S.A. (Castellar del Vallés, Barcelona, Spain).

2.2. Preparation of Films. Films were obtained by casting after the preparation of the film-forming solutions (FFSs). Starch (2% w/w) was dispersed in distilled water at 95°C for 30 min, while hand-stirring, as described by other authors [23, 25, 26], to induce complete starch gelatinization and cooled down to reach room temperature. This low starch concentration was selected in order to make the blending with the gum solutions easier due to their high viscosity. Glycerol was added to the aqueous gelatinized starch at 0.25 g/g of starch, on the basis of previous studies using glycerol plasticized starch-based films [27, 28]. The starch-glycerol aqueous system was homogenized using a rotor-stator homogenizer (Ultra Turrax D125, Janke and Kunkel, Germany) at 13,500 rpm for 3 min. Aqueous solutions of pullulan (2% w/w), xanthan (1% w/w), and gellan (2% w/w) gums were prepared in distilled water. Gum concentration was selected on the basis of the high viscosity of the respective solutions, especially for xanthan and gellan gums. Pullulan was dissolved in water under magnetic stirring (400 rpm) at room temperature. Xanthan and gellan gums were heated while magnetically stirred (400 rpm) at 90°C for 60 min until the complete dissolution. Glycerol was also added to the gum solutions (0.25 g/g polymer). The solution heating was carried out to accelerate the dissolution kinetics. For the starch-gum blends, the polymer solutions were mixed in the adequate proportion to obtain starch:gum ratios of 90:10 and 80:20. The FFSs were stirred for at least 60 min and degassed at room temperature by using a vacuum pump (MZ 2C NT, Vacuubrand GMBH + CO KG, Wertheim, Germany). Additionally, the apparent viscosity of the newly prepared FFSs at steady shear rate of 100 s^{-1} was characterised in triplicate at 25°C using a rotational rheometer (HAAKE RheoStress 1, Thermo Electric Corporation, Karlsruhe, Germany) with a sensor system of coaxial cylinders, type Z34DIN Ti. Table 1 shows the apparent viscosity values, where the effect of each gum on the

TABLE 1: Mean values and standard deviation of the apparent viscosity ($\eta_{100} \text{ s}^{-1} \text{ Pa s}$) of the film-forming solutions with pure polymers and the different starch : gum ratios.

Sample	Starch : gum ratio		
	90 : 10		80 : 20
S	$0.0118 \pm 0.0003^{\text{ab}}$	—	—
X	$0.0838 \pm 0.0006^{\text{c}}$	$0.0331 \pm 0.0001^{\text{c}}$	$0.0619 \pm 0.0005^{\text{d}}$
G	$1.62 \pm 0.03^{\text{f}}$	$0.0220 \pm 0.0001^{\text{bc}}$	$0.0301 \pm 0.0002^{\text{c}}$
P	$0.00321 \pm 0.00003^{\text{a}}$	$0.00780 \pm 0.00002^{\text{ab}}$	$0.0083 \pm 0.0001^{\text{ab}}$

Different superscript letters (a-f) indicate significant differences among formulations ($p < 0.05$).

starch solution viscosity can be observed. Likewise, it shows the much higher viscosity of gellan gum due to its tendency to gelation at the used concentration.

To obtain the films, a mass of the FFSs containing 1.5 g of total solids was poured onto polytetrafluorethylene (PTFE) plates (15 cm diameter) and allowed to dry under natural convection for approximately 48 h at 25°C and 45% relative humidity (RH). Films with 100% starch, gellan gum, and pullulan were also analysed for comparison purposes, whereas it was not possible to obtain pure xanthan gum films, since a homogeneous film could not be obtained.

2.3. Film Conditioning and Storage. Before characterising the films, samples were equilibrated for one week at two different relative humidities (53 and 75%) at 25°C by using oversaturated solutions of $\text{Mg}(\text{NO}_3)_2$ and NaCl, respectively. Net pullulan films showed deformations during conditioning at high RH, which complicated their handling. One part of the samples was stored under the same conditions for five weeks in order to perform the second series of analyses. Film thickness was measured using a Palmer digital micrometer (Comecta, Barcelona, Spain) to the nearest 0.001 mm. Six random positions in each film sample were considered.

2.4. Characterisation of Films

2.4.1. Water Vapour Permeability. Water vapour permeability (WVP) was determined gravimetrically at 25°C and RH gradients of 53-100% and 75-100%, following the ASTM E96-95 gravimetric method [29], applying the correction proposed by Gennadios et al. [30]. Payne permeability cups, 3.5 cm in diameter (Elcometer Sprl, Hermelle/s Argenteau, Belgium), were filled with 5 mL of distilled water (100% RH). Four circular samples of each formulation (3.5 cm in diameter) were secured in the cups and placed in preequilibrated cabinets containing oversaturated solutions of magnesium nitrate or sodium chloride to generate 53% or 75% RH inside the cabinet, with a fan on top of the cup in order to reduce the resistance to water vapour transport. The cups were weighed every 1.5 h for 24 h by using an analytical balance (ME36S, Sartorius, Germany, 0.0001 g). The slope of the weight loss vs. time curve at stationary state was used to determine the water vapour transmission rate (WVTR) and the water vapour permeability [31].

2.4.2. Oxygen Permeability (OP). The oxygen permeation rate of the films was determined by following the ASTM standard method D3985-05 [32]. Measurements were taken at 53% RH and 25°C in films previously equilibrated in the same

conditions, using an OX-TRAN 1/50 system (MOCON, Minneapolis, USA). The transmission values were determined every 20 min until equilibrium was reached. The exposure area of each sample during the tests was 50 cm². To obtain the oxygen permeability, the film thickness was considered in every case. At least two replicates per formulation were taken into account.

2.4.3. Tensile Properties. A texture analyser (Stable Micro Systems, TA.XTplus, Haslemere, England) was used to measure the mechanical properties of the films equilibrated at 53 and 75% RH and 25°C, following the ASTM standard method D882 [33]. Film strips (25 mm × 100 mm) were mounted in tensile grips (A/TG model), exposing a length of 5 cm for stretching at 50 mm min⁻¹, until breaking. The elastic modulus (EM), tensile strength at break (TS), and percentage of elongation at break (%E) were determined from the stress–Hencky strain curves, obtained from force–deformation data.

2.4.4. Isothermal Water Sorption Capacity. Triplicate film samples (15-20 mg), accurately weighed, were placed in desiccators at 25°C and equilibrated at different RH (or water activities: $a_w = \text{RH}/100$) by using oversaturated solutions of MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, CuCl_2 , NaCl, and KCl (% RH: 32.8, 43.2, 52.9, 67.5, 75.3, and 84.3, respectively). Samples were weighed periodically (0.00001 g precision) for 3 weeks, when equilibrium was reached. Finally, the equilibrium moisture content was determined by drying in a vacuum oven (Vacuoterm-T, JP Selecta S.A., Barcelona, Spain) at 60°C for 24 h and placed in desiccators containing P_2O_5 until reaching constant weight.

2.5. Statistical Analysis. A statistical analysis of data was performed through analysis of variance (ANOVA) using Statgraphics Centurion XVI.II (StatPoint Technologies Inc., Warrenton, VA, USA). Fisher's least significant difference (LSD) was used at the 95% confidence level.

3. Results and Discussion

3.1. Barrier Properties. The water vapour permeability (WVP) of polymeric films depends on many factors, including the solubility coefficient, integrity of the film matrix, hydrophobicity, diffusion rate, thickness, polymeric chain mobility, and interactions between the functional groups of polymers and the permeant. Packaging has to be able to prevent moisture and gas exchange between the environment and the product. Then, the water vapour and oxygen barrier capacity of the films is key to determining the efficiency of the

material as packaging. The values of the WVP of the studied films stored for 1 week under controlled conditions (53 or 75% RH) are shown in Table 2. As expected, the WVP of the films greatly increased for the 100-75% RH gradient, due to the greater degree of plasticization of the material and the consequent rise in molecular mobility, promoting the mass transfer rate. In both RH conditions, starch-gellan blend films exhibited the lowest WVP values. This suggests that interactions between the negatively charged gellan chains and the linear amylose chains, through hydrogen bonds, are enough effective to reduce the possibilities of water molecules to interact with the mixed matrix, which, in turn, would reduce their solubility and permeation capacity. At 53-100% RH, pure pullulan films had the highest WVP of all the formulations, as also reported by Kanmani and Lim [11]. On the other hand, except for the starch-gellan blends, there were no notable differences between formulations at 75-100% RH. Probably, the high plasticization level of the polymers at these high RH conditions makes differences in the polymer packing less relevant to determine the barrier capacity of the films.

The oxygen permeability (OP) values of films conditioned for 1 week at 53% RH are shown in Table 2. The OP values of net gellan and starch-pullulan blend films were significantly higher than those of the other films. The incorporation of xanthan and gellan gums contributed to a decrease in the oxygen permeability of the films, although all the films had notably low OP values, as previously reported for starch-based films [34]. The reduction in the OP values provoked by the incorporation of both negatively charged chains, gellan, and xanthan could be attributed to the promotion of the hydrogen bond interactions between the gum and amylose, as previously reported by other authors [9, 15], creating a more compact network where the permeation of the gas molecules would be more hindered.

3.2. Tensile Properties. The elastic modulus (EM), related to the stiffness of the material, the tensile strength (TS), and the deformation percentage (%E) at break, of the films equilibrated at different relative humidities were determined for samples conditioned for 1 and 5 weeks in order to analyse the changes associated with the film hydration and ageing. These mechanical parameters, useful for describing the film tensile behaviour, are closely related to its microstructure [35] and therefore reflect the microstructural changes that occurred during storage. Table 3 shows the values of the mechanical parameters obtained for the pure polymer films at the initial and final times for both conditioning conditions (53 and 75% RH). Films obtained from pure pullulan, equilibrated at 75% RH, exhibited deformations along with the moisture gain which did not permit the adequate measurement of their tensile properties. In contrast, pure gellan films were the stiffest (the highest EM) and most resistant to fracture (the highest TS), regardless of the storage conditions. This mechanical behaviour of the gellan films can be attributed to the high packing capacity of the linear polymer chains, also responsible for its high gelling capacity, where interactions and hydrogen bonds can occur throughout a great extent in the chains. The increase in the moisture

TABLE 2: Mean values and standard deviation of water vapour (WVP) and oxygen permeability (OP) of the films conditioned at 25°C and 53 and 75% RH.

Sample	WVP $\times 10^{10}$ (g/Pa s m)		OP $\times 10^{13}$ (cm ³ /m s Pa)
	53% RH	75% RH	53% RH
S	7.1 \pm 0.2 ^c	14.0 \pm 1.0 ^{cd}	3.6 \pm 0.2 ^c
S ₉₀ :X ₁₀	7.1 \pm 0.3 ^c	13.0 \pm 1.0 ^{bc}	2.6 \pm 0.1 ^b
S ₈₀ :X ₂₀	6.2 \pm 0.4 ^{ab}	13.0 \pm 1.0 ^b	2.7 \pm 0.1 ^b
G	9.0 \pm 0.1 ^d	14.5 \pm 0.5 ^d	4.0 \pm 0.1 ^d
S ₉₀ :G ₁₀	5.9 \pm 0.2 ^a	11.2 \pm 0.3 ^a	2.7 \pm 0.1 ^b
S ₈₀ :G ₂₀	6.6 \pm 0.3 ^b	10.7 \pm 0.3 ^a	2.3 \pm 0.1 ^a
P	11.8 \pm 0.3 ^f	—	2.7 \pm 0.1 ^b
S ₉₀ :P ₁₀	10.3 \pm 0.5 ^e	13.9 \pm 0.2 ^{bcd}	4.1 \pm 0.1 ^d
S ₈₀ :P ₂₀	10.5 \pm 0.2 ^e	14.0 \pm 1.0 ^{bcd}	4.8 \pm 0.1 ^e

Different superscript letters (a-f) within the same column indicate significant differences among formulations ($p < 0.05$).

content of the films when equilibrated with the highest RH reduced the film strength in all cases due to the enhanced plasticising effect of the water molecules, which promoted molecular mobility and reduced the cohesion force between chains. This effect was more intense for starch (EM was reduced by 4.5) than for gellan films (EM reduction by 1.5), but could not be quantified for pullulan films due to their deformation at the highest RH. Film moisturising also promoted the stretchability, which increased more markedly in starch films.

The film ageing behaviour could also be analysed through the changes in the tensile properties over 5 storage weeks. No significant differences in the initial and final values of the tensile parameters were observed for gellan films, whereas the starch samples became stronger and less extensible under both RH conditions. This change in the mechanical behaviour of starch films could be attributed to the retrogradation phenomenon or partial migration of the plasticizer. Different authors [26, 36–38] reported that the starch retrogradation process in starch films after gelatinization is mainly due to the amylose recrystallization in a relatively short time period, depending on the final water content, whereas amylopectin recrystallization is a long-time process. Apart from crystallization, a progressive aggregation of polymer chains throughout time has been observed for starch films [25] which provokes an increase in the matrix compactness and the consequent changes in the tensile response. In contrast, pullulan films become softer, exhibiting a notable decrease in the EM. This could be attributed to a progressive water gain in the films during storage, which progressively plasticize the polymer matrix to a greater extent, giving rise to a greater chain mobility and more extensible films [13].

Figure 1 shows the elastic modulus (EM), tensile strength (TS), and elongation at break (E) for the different starch-gum blend films. In films conditioned for 1 week, adding gums to the starch matrix provoked a strengthening effect reflected in the higher values of the EM compared to the net starch film, except for starch-pullulan blends conditioned at the highest RH. Likewise, although the film's resistance to break (TS) was considerably increased for xanthan and gellan blends, it

TABLE 3: Mean values and standard deviation of tensile properties (EM: elastic modulus; TS: tensile strength; %E: percentage of elongation) of the pure polymer films conditioned at 25°C and 53 or 75% RH for 1 (initial) or 5 (final) weeks.

			S	Sample G	P
RH – 53%	Initial	EM (MPa)	160 ± 50 ^{a,1}	1300 ± 150 ^{c,1}	500 ± 60 ^{b,2}
		TS (MPa)	10 ± 2 ^{a,2}	80 ± 30 ^{b,1}	9 ± 1 ^{a,2}
		E (%)	12 ± 1 ^{ab,2}	10 ± 6 ^{a,1}	30 ± 10 ^{b,1}
	Final	EM (MPa)	340 ± 50 ^{b,2}	1140 ± 120 ^{c,1}	52 ± 8 ^{a,1}
		TS (MPa)	6 ± 2 ^{a,1}	34 ± 25 ^{b,1}	2 ± 1 ^{a,1}
		E (%)	6 ± 2 ^{a,1}	3 ± 2 ^{a,1}	50 ± 20 ^{b,1}
RH – 75%	Initial	EM (MPa)	36 ± 5 ^{a,1}	840 ± 50 ^{b,1}	—
		TS (MPa)	4 ± 1 ^{a,1}	80 ± 13 ^{b,1}	—
		E (%)	34 ± 2 ^{b,2}	16 ± 5 ^{a,1}	—
	Final	EM (MPa)	55 ± 7 ^{a,2}	1000 ± 150 ^{b,1}	—
		TS (MPa)	4 ± 1 ^{a,1}	81 ± 4 ^{b,1}	—
		E (%)	15 ± 3 ^{a,1}	15 ± 2 ^{a,1}	—

Different superscript letters (a-c) in the same row indicate significant differences among formulations ($p < 0.05$) for each parameter. Different superscript numbers (1, 2) in the same column for each parameter and film sample indicate significant differences between the two storage times ($p < 0.05$).

was reduced in pullulan mixtures, mainly in the films conditioned at the highest RH. However, the film extensibility was generally reduced in all blend films with respect to net starch samples. For the negatively charged polymers (gellan and xanthan) the strengthening effect could be associated with the gum and starch chains interaction through hydrogen bonds, developing a more resistant network but with lower deformability. The restrictions associated to bonded polymeric chains to slide during the stretching compromised the ductile behaviour observed for the gum-free starch films. Pullulan also exerts a reinforcing effect on the starch matrix, but this disappears when films were conditioned at high RH, which could be attributed to the high water sensitivity of pullulan, which becomes highly deformable at high RH [12]. Likewise, the preferential adsorption of water molecules of this gum could limit its interactions with the starch chains at high RH conditions, thus limiting its strengthening effect, as previously observed by other authors [12].

In terms of ageing, all the blend films exhibited a decrease in EM and TS values after five weeks, in contrast with the increase observed in the net starch matrix. This indicates that blending it with these gums inhibited starch retrogradation. The observed decrease in the film strength could be attributed to the rearrangement of the polymer chains during film storage, obtaining a more open matrix with greater molecular mobility, which could be due, in part, to a progressive film hydration till the true equilibrium moisture content was reached. In the films conditioned/stored at the highest RH, the values of EM and TS also decreased during storage for xanthan and pullulan blends, but increased or did not change significantly for gellan blends. At the highest RH, starch retrogradation kinetics become faster due to the highest molecular mobility associated to the water plasticization [36]. In this sense, this phenomenon seems to occur to a certain extent in gellan blends whereas it was limited in the other blend films, where a decrease in the film strength was observed. The hydration kinetics of the films till equilibrium

would be affected by the gradient of water activity (a_w) between the initial dried film and the external RH; the lower the driving force (at the lowest RH), the slower the hydration rate, and by the compactness of the film structure which affects the diffusion rate of water molecules. Gellan blends, in particular, did not exhibit EM or TS reduction during storage when conditioned at the highest RH, which could indicate that no changes in the film moisture content and the consequent plasticization level occurred during storage, whereas the starch retrogradation effect was prevalent in these conditions with high molecular mobility.

As concerns extensibility, gum blending provoked a reduction with respect to the net starch films, although this was less noticeable when conditioned at 53% RH. As commented on in the next section, the gums probably limit the water sorption capacity of the films, thus reducing the water plasticising effect. This would be more noticeable at the highest RH (75%), when water plasticization was highly intense in net starch films, as previously commented on. Likewise, the water partition between the polymers, according to their relative water affinity, could also affect the plasticization level of the starch matrix, this affecting its mechanical behaviour.

3.3. Isothermal Water Sorption Capacity of the Films. Table 4 shows the equilibrium moisture content (g/100 g solids) obtained for pure and blend films conditioned under different RH (between 32.8 and 84.3%) at 25°C, in order to compare the water binding capacity of the different blends and pure polymer films. At low RH, pure gellan films exhibited similar water sorption capacity to the starch films, whereas pure pullulan films are slightly less hygroscopic. However, from intermediate RH, the water binding capacity of pure gellan overcame that of starch, whereas pullulan exhibits similar or lower values than does starch. The different water interactions with polar groups of the polymer chains determine the water binding capacity of the matrices depending on the equilibrium relative humidity. As concerns the blend

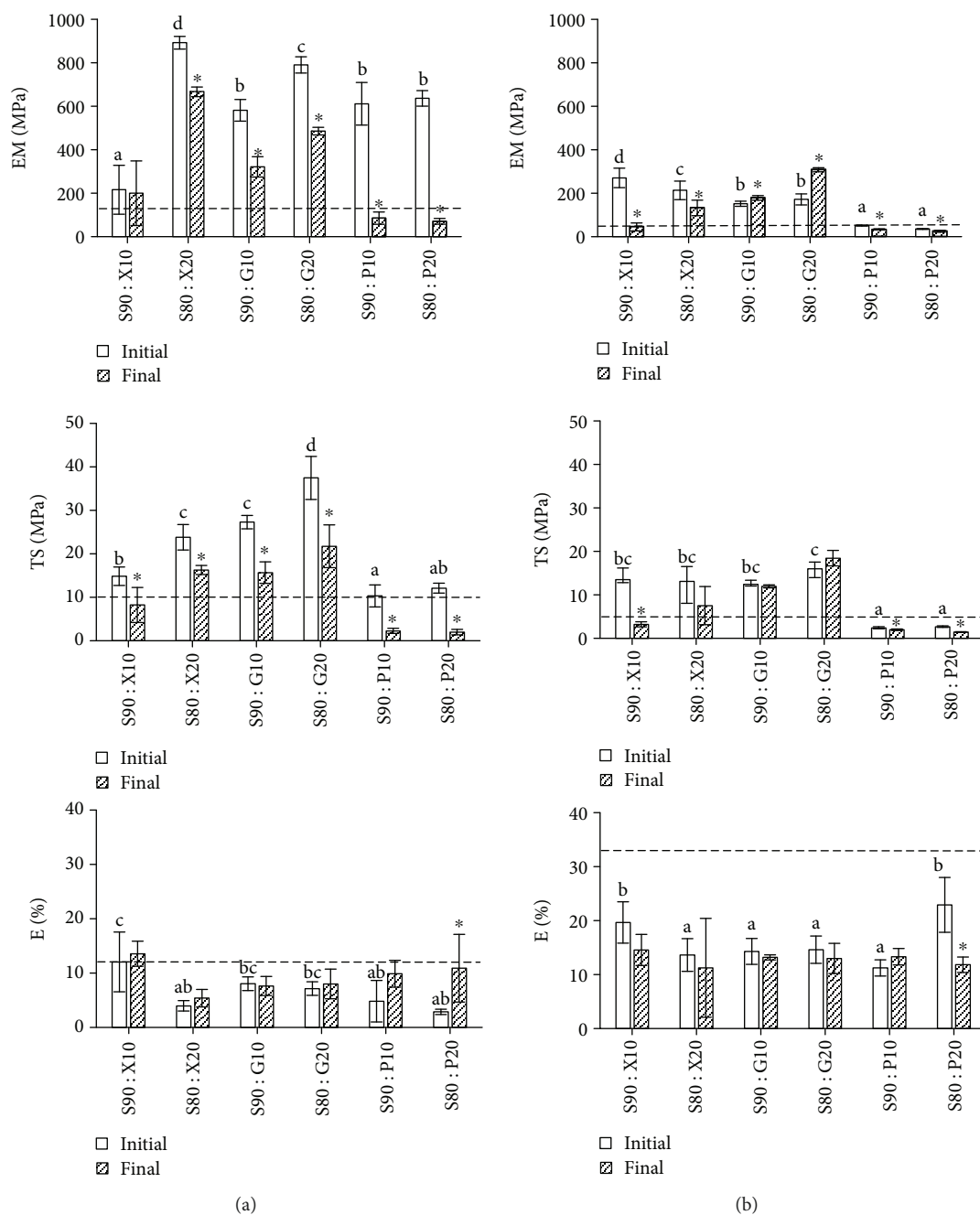


FIGURE 1: EM: elastic modulus; TS: tensile strength; %E: percentage of elongation. LSD intervals (95% confidence level) of starch-gum blend films conditioned at (a) 53% RH or (b) 75% RH, for 1 (initial) or 5 weeks (final). Different superscript letters (a-d) indicate significant differences among formulations ($p < 0.05$) for each parameter after 1 week of storage. Significant differences among formulations ($p < 0.05$) after 5 weeks of storage are indicated (*). The horizontal dashed line indicates the respective value of net starch films (conditioned for 1 week).

films, the interactions between gums and starch polymers led to different effects on water sorption capacity of the blend films. Contrary to what occurs with xanthan blend films, the gellan or pullulan blends with starch exhibited lower water sorption capacity than did the corresponding films with pure polymers. This could be attributed to the establishment of more efficient hydrogen bonds between the chains of the different polymers, which could reduce the number of active points for water sorption. Then, the incorporation of

gellan and pullulan gums led to a decrease in the water sorption capacity of the starch films, which, in turn, will reduce their water sensitivity, making them more suitable for food packaging purposes.

4. Conclusions

Blending starch with gellan gum was effective at reducing the moisture sorption capacity of starch films and also reduced

TABLE 4: Equilibrium moisture content (g water/100 g solids) for the different film formulations conditioned at different relative humidities (RH) or a_w (RH/100).

Sample	RH (%)					
	32.8	43.2	52.9	67.5	75.3	84.3
S	8.2 ± 0.1 ^c	11.3 ± 0.5 ^{cd}	12.5 ± 1.3 ^c	21.4 ± 1.0 ^{de}	26.2 ± 0.3 ^c	39.8 ± 1.5 ^d
S ₉₀ :X ₁₀	11.2 ± 1.0 ^e	12.3 ± 0.6 ^d	14.9 ± 1.0 ^d	22.2 ± 0.7 ^e	26.4 ± 0.4 ^{cd}	37.1 ± 3.6 ^{cd}
S ₈₀ :X ₂₀	10.0 ± 0.3 ^d	11.3 ± 0.9 ^{cd}	14.8 ± 0.7 ^d	18.2 ± 1.3 ^{bc}	26.4 ± 0.4 ^{cd}	35.6 ± 1.4 ^{bc}
G	8.8 ± 0.4 ^c	10.5 ± 0.1 ^c	11.3 ± 1.5 ^{bc}	26.3 ± 1.6 ^f	29.9 ± 0.3 ^e	47.2 ± 101 ^e
S ₉₀ :G ₁₀	7.2 ± 0.2 ^b	7.7 ± 0.8 ^{ab}	9.0 ± 0.5 ^a	17.9 ± 1.0 ^b	26.1 ± 0.5 ^c	33.4 ± 1.2 ^b
S ₈₀ :G ₂₀	6.3 ± 0.4 ^a	7.9 ± 1.5 ^{ab}	8.7 ± 1.0 ^a	17.3 ± 1.5 ^{ab}	27.7 ± 1.6 ^d	35.3 ± 1.8 ^{bc}
P	6.5 ± 0.3 ^{ab}	8.5 ± 0.3 ^b	9.7 ± 0.2 ^{ab}	19.8 ± 0.2 ^{cd}	22.2 ± 1.0 ^b	39.4 ± 1.2 ^d
S ₉₀ :P ₁₀	6.1 ± 0.1 ^a	7.2 ± 0.1 ^a	8.2 ± 0.4 ^a	16.9 ± 0.7 ^{ab}	19.1 ± 0.7 ^a	29.9 ± 0.4 ^a
S ₈₀ :P ₂₀	5.9 ± 0.1 ^a	6.7 ± 0.4 ^a	9.0 ± 1.2 ^a	15.6 ± 0.4 ^a	19.2 ± 0.5 ^a	28.5 ± 1.1 ^a

Different superscript letters (a-f) within the same column indicate significant differences among formulations ($p < 0.05$).

the water vapour and oxygen permeability and increased the film strength and resistance to break, without markedly limiting the film stretchability. Likewise, gellan-starch blends preserve films against the phenomenon of retrogradation. Xanthan gum was effective at increasing the tensile strength of the starch films but did not reduce their water sorption capacity and water vapour permeability. Pullulan was not so effective at enhancing the barrier capacity of starch films or increasing tensile strength. From the obtained results, starch substitution in the films by gellan gum at both 10 and 20 wt% is the one that most improved the barrier and tensile properties of the films and can be used to obtain films that are more useful for food packaging purposes. Particularly, foods such as nuts or snacks with low oxygen pressure requirements to avoid oxidations, and without free water to avoid film moisturising, may be successfully packaged, allowing to extend their self-life.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

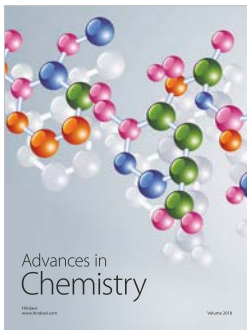
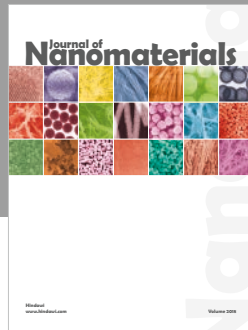
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References

- [1] B. Ghanbarzadeh, H. Almasi, and A. A. Entezami, "Improving the barrier and mechanical properties of corn starch-based edible films: effect of citric acid and carboxymethyl cellulose," *Industrial Crops and Products*, vol. 33, no. 1, pp. 229–235, 2011.
- [2] B. Hassan, S. A. S. Chatha, A. I. Hussain, K. M. Zia, and N. Akhtar, "Recent advances on polysaccharides, lipids and protein based edible films and coatings: a review," *International Journal of Biological Macromolecules*, vol. 109, pp. 1095–1107, 2018.
- [3] C. H. Chen and L. S. Lai, "Mechanical and water vapor barrier properties of tapioca starch/decolorized hsian-tsoo leaf gum films in the presence of plasticizer," *Food Hydrocolloids*, vol. 22, no. 8, pp. 1584–1595, 2008.
- [4] O. V. López, L. A. Castillo, M. A. García, M. A. Villar, and S. E. Barbosa, "Food packaging bags based on thermoplastic corn starch reinforced with talc nanoparticles," *Food Hydrocolloids*, vol. 43, pp. 18–24, 2015.
- [5] C. L. Luchese, J. C. Spada, and I. C. Tessaro, "Starch content affects physicochemical properties of corn and cassava starch-based films," *Industrial Crops and Products*, vol. 109, no. 5, pp. 619–626, 2017.
- [6] S. Mali, M. V. E. Grossmann, M. A. García, M. N. Martino, and N. E. Zaritzky, "Barrier, mechanical and optical properties of plasticized yam starch films," *Carbohydrate Polymers*, vol. 56, no. 2, pp. 129–135, 2004.
- [7] R. Ortega-Toro, S. Collazo-Bigliardi, P. Talens, and A. Chiralt, "Influence of citric acid on the properties and stability of starch-polycaprolactone based films," *Journal of Applied Polymer Science*, vol. 133, no. 2, pp. 1–16, 2016.
- [8] A. Jiménez, M. J. Fabra, P. Talens, and A. Chiralt, "Edible and biodegradable starch films: a review," *Food and Bioprocess Technology*, vol. 5, no. 6, pp. 2058–2076, 2012.
- [9] C. Arismendi, S. Chillo, A. Conte, M. A. del Nobile, S. Flores, and L. N. Gerschenson, "Optimization of physical properties of xanthan gum/tapioca starch edible matrices containing potassium sorbate and evaluation of its antimicrobial effectiveness," *LWT - Food Science and Technology*, vol. 53, no. 1, pp. 290–296, 2013.
- [10] S. K. Flores, D. Costa, F. Yamashita, L. N. Gerschenson, and M. V. Grossmann, "Mixture design for evaluation of potassium sorbate and xanthan gum effect on properties of tapioca starch films obtained by extrusion," *Materials Science and Engineering*, vol. 30, no. 1, pp. 196–202, 2010.
- [11] P. Kanmani and S. T. Lim, "Development and characterization of novel probiotic-residing pullulan/starch edible films," *Food Chemistry*, vol. 141, no. 2, pp. 1041–1049, 2013.

- [12] J. Y. Kim, Y. G. Choi, S. R. Byul Kim, and S. T. Lim, "Humidity stability of tapioca starch-pullulan composite films," *Food Hydrocolloids*, vol. 41, pp. 140–145, 2014.
- [13] S. R. B. Kim, Y. G. Choi, J. Y. Kim, and S. T. Lim, "Improvement of water solubility and humidity stability of tapioca starch film by incorporating various gums," *LWT - Food Science and Technology*, vol. 64, no. 1, pp. 475–482, 2015.
- [14] R. M. D. Soares, A. M. F. Lima, R. V. B. Oliveira, A. T. N. Pires, and V. Soldi, "Thermal degradation of biodegradable edible films based on xanthan and starches from different sources," *Polymer Degradation and Stability*, vol. 90, no. 3, pp. 449–454, 2005.
- [15] P. Veiga-Santos, L. M. Oliveira, M. P. Cereda, A. J. Alves, and A. R. P. Scamparini, "Mechanical properties, hydrophilicity and water activity of starch-gum films: effect of additives and deacetylated xanthan gum," *Food Hydrocolloids*, vol. 19, no. 2, pp. 341–349, 2005.
- [16] H. Samsudin and N. M. Hani, "Chapter 8 - Use of Starch in Food Packaging," in *Starch-Based Materials in Food Packaging*, M. A. Villar, S. E. Barbosa, M. A. García, L. A. Castillo, and O. V. López, Eds., pp. 229–256, Academic Press, 2017.
- [17] J. D. Linton, S. G. Ash, and L. Huybrechtst, "4 Microbial Polysaccharides," in *Biomaterials*, D. Byrom, Ed., pp. 215–261, Palgrave Macmillan, London, UK, 1991.
- [18] R. Chandrasekaran and A. Radha, "Molecular architectures and functional properties of gellan gum and related polysaccharides," *Trends in Food Science and Technology*, vol. 6, no. 5, pp. 143–148, 1995.
- [19] A. M. Fialho, L. M. Moreira, A. T. Granja, A. O. Popescu, K. Hoffmann, and I. Sá-Correia, "Occurrence, production, and applications of gellan: current state and perspectives," *Applied Microbiology and Biotechnology*, vol. 79, no. 6, pp. 889–900, 2008.
- [20] L. Chen, F. Ren, Z. Zhang, Q. Tong, and M. M. A. Rashed, "Effect of pullulan on the short-term and long-term retrogradation of rice starch," *Carbohydrate Polymers*, vol. 115, pp. 415–421, 2015.
- [21] M. Shibata, M. Asahina, N. Teramoto, and R. Yosomiya, "Chemical modification of pullulan by isocyanate compounds," *Polymer*, vol. 42, no. 1, pp. 59–64, 2001.
- [22] F. F. Shih, K. W. Daigle, and E. T. Champagne, "Effect of rice wax on water vapour permeability and sorption properties of edible pullulan films," *Food Chemistry*, vol. 127, no. 1, pp. 118–121, 2011.
- [23] O. Moreno, R. Díaz, L. Atarés, and A. Chiralt, "Influence of the processing method and antimicrobial agents on properties of starch-gelatin biodegradable films," *Polymer International*, vol. 65, no. 8, pp. 905–914, 2016.
- [24] F. M. Fakhouri, D. Costa, F. Yamashita et al., "Comparative study of processing methods for starch/gelatin films," *Carbohydrate Polymers*, vol. 95, no. 2, pp. 681–689, 2013.
- [25] A. Jiménez, M. J. Fabra, P. Talens, and A. Chiralt, "Influence of hydroxypropylmethylcellulose addition and homogenization conditions on properties and ageing of corn starch based films," *Carbohydrate Polymers*, vol. 89, no. 2, pp. 676–686, 2012.
- [26] A. Cano, A. Jiménez, M. Cháfer, C. González, and A. Chiralt, "Effect of amylose:amylopectin ratio and rice bran addition on starch films properties," *Carbohydrate Polymers*, vol. 111, pp. 543–555, 2014.
- [27] A. Cano, E. Fortunati, M. Cháfer, J. M. Kenny, A. Chiralt, and C. González-Martínez, "Properties and ageing behaviour of pea starch films as affected by blend with poly(vinyl alcohol)," *Food Hydrocolloids*, vol. 48, pp. 84–93, 2015.
- [28] A. Jiménez, M. J. Fabra, P. Talens, and A. Chiralt, "Effect of re-crystallization on tensile, optical and water vapour barrier properties of corn starch films containing fatty acids," *Food Hydrocolloids*, vol. 26, no. 1, pp. 302–310, 2012.
- [29] ASTM, "Standard test methods for water vapour transmission of materials. Standard designations: E96-95," in *Annual Book of ASTM Standards*, 1995.
- [30] A. Gennadios, C. L. Weller, and C. H. Gooding, "Measurement errors in water vapor permeability of highly permeable, hydrophilic edible films," *Journal of Food Engineering*, vol. 21, no. 4, pp. 395–409, 1994.
- [31] M. Vargas, A. Albors, A. Chiralt, and C. González-Martínez, "Characterization of chitosan-oleic acid composite films," *Food Hydrocolloids*, vol. 23, no. 2, pp. 536–547, 2009.
- [32] ASTM, "Standard test method for oxygen gas transmission rate through plastic film and sheeting using a colourimetric sensor. Standard designations: 3985-3995," in *Annual Book of ASTM Standards*, 2002.
- [33] ASTM, "Standard test method for tensile properties of thin plastic sheeting. Standard designations: D882," in *Annual Book of ASTM Standards*, 2001.
- [34] P. Forssell, R. Lahtinen, M. Lahelin, and P. Myllärinen, "Oxygen permeability of amylose and amylopectin films," *Carbohydrate Polymers*, vol. 47, no. 2, pp. 125–129, 2002.
- [35] T. H. McHugh and J. M. Krochta, "Sorbitol-vs glycerol-plasticized whey protein edible films: integrated oxygen permeability and tensile property evaluation," *Journal of Agricultural and Food Chemistry*, vol. 42, no. 4, pp. 841–845, 1994.
- [36] P. M. Forssell, S. H. D. Hulleman, A. P. J. Myllärinen, G. K. Moates, and R. Parker, "Ageing of rubbery thermoplastic barley and oat starches," *Carbohydrate Polymers*, vol. 39, no. 1, pp. 43–51, 1999.
- [37] P. Myllärinen, A. Buleon, R. Lahtinen, and P. Forssell, "The crystallinity of amylose and amylopectin films," *Carbohydrate Polymers*, vol. 48, no. 1, pp. 41–48, 2002.
- [38] A. Sa Rindlav-Westling, M. Stading, A.-M. Hermansson, and P. Gatlenholm, "Structure, mechanical and barrier properties of amylose and amylopectin films," *Carbohydrate Polymers*, vol. 36, no. 2-3, pp. 217–224, 1998.



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