

Starch-Pectin Films Obtained By Extrusion And Compression Molding

Gamboni, Jimena Elizabeth; Slavutsky, Aníbal Marcelo; Bertuzzi, María Alejandra
Instituto de Investigaciones para la Industria Química-INIQUI- CONICET
Salta, Argentina
jimenagamboni@gmail.com

Slavutsky, Aníbal Marcelo; Bertuzzi, María Alejandra
Facultad de Ingeniería – Universidad Nacional de Salta
Salta, Argentina

Abstract— Starch and pectin are biopolymers that can achieve thermoplastic properties and can be processed through extrusion and thermos-compression to obtain edible films. The aim of this work was to evaluate the effect of starch-pectin blending on the extrusion processability and the performance of the resulting films. Starch-pectin films, plasticized with glycerol, were obtained by extrusion followed by compression molding. Different extrusion temperature profiles were assayed, whereas feeding speed and screw speed remained constant. Blending starch and pectin allowed a reduction of around 30% in torque and pressure values during extrusion, compared with extruding conditions of starch. Physical and functional characterizations of the film samples were performed. The obtained composed films were homogenous and had intermediate mechanical properties between the starch and pectin films. No relevant differences were found in water barrier properties of films based on pure polysaccharides and blends. Thus, starch-pectin blends can be extruded and molded into films under milder operational conditions than starch alone, without resigning their functional properties. This could lead to reduced operating costs in the manufacturing process.

Keywords— biodegradable, edible films, thermoplastic material, biopolymer

I. INTRODUCTION

In recent decades, scientific and commercial interest in the development of bio-polymeric materials has grown. Applications of biopolymers are gaining ground in areas in which synthetic polymers used to be the chosen materials [1], [2]. Packaging is one of the most widespread uses of plastics. Environmental concern on the impact caused by conventional plastics on the environment has led to an increasing interest in the use of biodegradable polymers. Biodegradable film properties can be tailored according to the specifications of the final applications. In this sense, this versatility turns these films into materials with a wide range of applications [3].

Biodegradable polymers, polysaccharides and proteins, proceed from renewable sources. Over the last years, starch has been the raw material of choice in several kinds of research works on edible films, due to its processing characteristics and fundamentally, its abundance and low cost [4] [5].

Starch is a polysaccharide consisting of anhydroglucose units joined by glucosidic bonds. Starch is a homopolysaccharide composed of two components, amylose (essentially linear) and

amylopectin (branched). Amylose is a linear polymer of α -(1-4)-linked glucose units and it can be attributed to this structure a behavior similar to that of synthetic polymers. On the other hand, amylopectin consists of α -(1-4)-linked glucose units and α -(1-6)-linked branched points and this molecule is responsible for the lower mobility of the polymer chains [6].

Starch edible films have been studied for several years. Casting technique is the most commonly used for preparation of starch films at laboratory scale and there are industrial processes implementing this wet method by casting the film forming solution onto belt conveyors (belt casting). However, casting methodology presents some disadvantages like film irregularities related to geometric and drying conditions and long drying times [7]. Extrusion is an alternative technology that displays versatility and low cost [8][5][9].

Extrusion is one of the most employed methods to process conventional thermoplastic synthetic materials. Blends of corn starch, traditional plastic, and other biopolymers have been successfully extruded [10] [11] [12] [13]. The parameters of extrusion process of the starch to obtain films have been widely studied. It is worth noting that starch presents a more complex processing behavior than other traditional synthetic polymers, displaying different phase transitions, such as gelatinization, melting, decomposition, and recrystallization. Thus, detailed assessments on barrel temperature, moisture content, screw speed, and feed rate, must be done to determine their influence in the processability of starch [13][14][6][15].

In order to obtain a starch film, before processing and molding, starch must turn into thermoplastic starch. In this sense, the starch semi-crystalline granules must be transformed into a homogeneous amorphous material [15].

In contrast to what happens in the starch gelatinization conducted in aqueous suspensions, during the extrusion process, granular disruption is achieved by applying thermal and mechanical energy, in the presence of appropriate plasticizers. Extrusion is a continuous process, faster and more energy-efficient than casting method. Thus, extrusion can result in a more profitable process to obtain starch films. Blending polymers is a very common strategy to produce materials with different physical properties. By varying the blend composition and processing conditions, the morphology and hence, the functional and structural properties can be regulated effectively [16][4][17]. In

this sense, the formulation of blends allows obtaining materials with adequate properties regarding their final applications. Furthermore, blending can lead to improving processability and costs reduction.

Pectins are soluble polysaccharides composed by linear chains of α -(1-4)-d-galacturonic acid linked, partially esterified with methanol. Pectins can be classified according to the degree of methoxylation (DM) into high methoxyl pectins (DM > 50) and low methoxyl pectins (DM < 50).

Pectin has mainly been used as a setting agent in food, to thicken, stabilize and provide gel structure to different products like jams, jellies, yoghurts, desserts, and ice creams [18]. In medicine and pharmaceutical industry it is been extensively used in drug delivery systems for controlled release [17][19].

Recently, mixtures of starch and pectin crosslinked by sodium trimetaphosphate were assessed for food applications and showed superior mechanical properties in comparison to the isolated polymers [20][21].

Even when extrusion appears to be an advantageous technique for the elaboration of edible films, no further investigation has been made in order to employ this process on pectin film elaboration.

Fishman and Coffin [22] oriented their work to add value to pectin as an agricultural product with new uses and profitable processes to use it. However, since pectin itself is expensive, they studied blending as a way of reduce costs. They obtained edible films from pectin and high amylose starch [23]; pectin, orange albedo, and starch [12]; and pectin, high amylose starch, and poly-vinyl alcohol [8], using the casting technique and extrusion-calendering process. In their works, pectin was the mayor component and the responsible of the film-forming properties of the mixture. They obtained films which have a wide range of good mechanical properties and excellent oxygen barrier properties.

The aim of the present work was to evaluate the effect of blending starch and pectin on extrusion processability, to achieve moderate processing conditions, in comparison with those required to process each of the pure polymers. In addition, starch-pectin blends obtained by extrusion were compression molded into films, and their physicochemical and mechanical properties are reported.

II. EXPERIMENTAL PROCEDURES

A. Materials

Edible films were prepared from native corn starch (Unilever, Argentina, 75% amylopectin, 25% amylose, moisture content 10%) and low methoxyl pectin (LM-104-AS CP Kelpo, Denmark; amide substitution 20%, methyl substitution 27%, moisture content 12%). Glycerol (Biopack, Argentina) was used as plasticizer.

B. Extrusion process

Edible films were prepared from native corn starch and different starch-pectin ratios, as shown in Table I. Every sample powder was first mixed at 2800 rpm with 30% w/w of glycerol with a basic analytical mill (IKA A11, USA), to enhance plasticizer incorporation and achieve a homogeneous mixture.

TABLE I. POLYMER BLEND COMPOSITION

Sample	Starch	Pectin	Glycerol (%w/w _{of biopolymer})
S0	0	100	30
S25	25	75	30
S50	50	50	30
S75	75	25	30
S100	100	0	30

The mixtures were processed in a co-rotating twin screw extruder (Thermo Fisher Scientific, USA) using a 40 L/D barrel with eight heating zones. The actual barrel and die temperatures used in the experiments are given in Table II. Starch-glycerol samples were extruded using four different temperature profiles (TP) in order to analyze temperature effects on starch plasticization. However, Profile 1 was selected for processing starch-pectin blends because pectin is sensitive to high temperatures. After a series of screening assays, the screw speed was set at 100 rpm. Lower velocities excessively increased torque exceeding its limit, while higher velocities reduced residence time in the extruder.

Pictures of the obtained filaments were taken with a digital microscope (Barska, USA) using a 40x magnification.

After processing, the filaments obtained from the extruder were allowed to cool to room temperature (25 °C) before being pelletized. The pellets were kept at 30% relative humidity during two weeks before molding.

C. Film formation

Approximately 4 g of pelletized material was placed between two aluminum foils and was compression molded into flat sheets using a thermostated hydraulic press. In order to select the appropriate process conditions, a series of screening assays were made. The samples were processed at three molding temperatures (100, 120 and 150 °C) and three compressing times (1, 3 and 5 minutes). Finally, the starch samples were molded at 120 °C and 20 kgf cm⁻² during 3 minutes, while starch-pectin samples were molded for 1 minute.

D. Materials Characterization

The pellets obtained as well as the compression molded films were characterized.

E. Differential Scanning Calorimetry (DSC)

Samples of starch-glycerol pellets were studied by DSC. Powder of pelletized material was kept at 70% relative humidity during two weeks before the assay. The thermograms of the samples were obtained in a

TABLE II. EXTRUSION CONDITIONS: TEMPERATURE OF BARREL ZONES AND SCREW SPEED

Temperature profiles	Temperature of Barrel Zones (°C)								Screw Speed (rpm)
	I	II	III	IV	V	VI	VII	Die	
TP0	120	120	120	120	120	120	120	120	100
TP1	120	130	140	140	140	140	140	140	100
TP2	120	130	140	145	150	150	145	140	100
TP3	120	130	140	150	160	160	150	140	100

DSC 2000 TA instruments (USA). The samples were heated from -50 °C to 200 °C at a rate of 10 °C/min. To avoid dehydration of the samples, hermetic pans were used. Humidity content of the samples, before processing, was determined by measuring the weight loss of the samples, upon drying in an oven at 105 °C until constant weight.

F. Scanning electron microscopy (SEM)

Cross-section and surface of the samples (films and filaments) were examined by SEM using a JEOL JSM 6480 LV scanning microscope (Japan). Samples were previously stored in a relative humidity controlled ambient during a week (53% RH). Samples were cryofractured by immersion in liquid nitrogen and stored at 25 °C over silica gel. Then, samples were mounted on aluminium stubs and coated with gold plasma. Samples were observed using an accelerating voltage of 15 kV.

G. Solubility in water

Pellets and film solubility in water was measured as a percentage of dry matter of the sample solubilized in water. Samples were kept in desiccators containing silica gel during a week, in order to obtain the initial dry weight (m_i). Film samples of 100 mg were immersed in 30 mL of distilled water at 30 °C, sealed and periodically agitated. Not solubilized film matter was separated by centrifugation (Gelec 142, Argentina) and dried to determine the final dry weight (m_f). Tests were performed in quintupled and the solubility was calculated as follows:

$$S = \frac{m_i - m_f}{m_i} 100\% \quad (1)$$

H. Sorption capacity (Water uptake)

A static gravimetric method was used to determine the sorption capacity of pellets and films. Samples were conditioned in a desiccator with silica gel for 2 weeks. Pellets of 0.1 g approximately and film samples, cut into square pieces with a side length of 2 cm, were weighted. Then, samples were placed in quintupled inside desiccators with different oversaturated salt solutions of known equilibrium relative humidity at 25 °C. Constant relative humidity environments were established with the following salts used: $Mg(NO_3)_2$, NaBr, NaCl, KCl, $BaCl_2$ recommended by COST-90 project [24], to cover a water activity (a_w) range from 0.50 to 0.90. All salts used were analytical grade. The desiccators were kept at 25 °C until equilibrium was attained.

Equilibrium was judged to have been attained when the difference between two consecutive samples weightings was less than 1 mg/g dry solid.

I. Thickness

Film thickness (e) was determined using an analogical thickness gauge (Digimes, Buenos Aires, Argentina). Ten measurements were randomly taken at different locations for each specimen and the mean value was reported.

J. Density

Film samples cut into square pieces with a side length of 2 cm were kept in desiccators containing silica gel during a week, in order to obtain the dry weight (m_i). The density (ρ) was then calculated as the ratio between the weight (m_i) and volume (V), where the volume is equal to the thickness (e) by area (A) of each sample according to the equation (2). The density experiments were undertaken in quintupled and the data reported as the mean values.

$$\rho = \frac{w}{V} \quad (2)$$

K. Water vapor permeability

Water vapor permeability determination of the different films was carried out according to the methodology described in the ASTM E 96 [25] with some modifications. Films were conditioned for 72 hours at 25 °C and 53% relative humidity (saturated solution of $Mg(NO_3)_2$) prior to the analysis. Test cups were placed in a desiccator cabinet maintained at constant temperature provided with a fan to maintain uniform conditions at all test locations over the specimen. The cabinet contained silica gel ($a_w=0$) and the tests cups contained distilled water ($a_w=1$), so as to achieve a driven force $\Delta a_w=1$. Periodical weightings monitored the weight changes. Weight loss was plotted over time. Thickness value was the mean value of five measurements and it was used for water vapor permeability calculations. The water vapor transmission rate (WVTR) was calculated from the slope (G) of a linear regression of weight loss versus time (equation 3), thus, permeability was calculated according to equation 4.

$$WVTR = \frac{G}{A} \quad (3)$$

$$P = \frac{a(WVTR \times e)}{(p_{w1} - p_{w2})} \quad (4)$$

Where e is the thickness of the film, A is the exposed area; p_{w1} and p_{w2} are the partial pressure of the water vapor outside and inside the cup, respectively. Finally, a is a unit conversion constant.

L. Mechanical properties

The tensile properties were measured using a texturometer Brookfield (USA) following the ASTM D882 [26] norm with some modifications. The films were cut into strips 10 mm wide and 80 mm long using a sharp scalpel. The ends of the strips were mounted between cardboard grips using double-sided adhesive tape. The final film area exposed was 10 mm long and 50 mm wide. The texturometer was set to tensile mode. Initial grip separation was 50 mm. Force and elongation were recorded during extension at 20 mm/min up to break. All film strips were equilibrated during a week in a cabinet conditioned at 25 °C and 53% relative humidity (saturated solution of $Mg(NO_3)_2$) previously to tension assay. Tensile strength (TS), percentage of elongation at break (%E) and Young's module of films were evaluated after storage. The test was carried out in quintupled for each film.

M. Statistical analysis

Analyses of variance (ANOVA) using GraphPad Prism (Version 5.01, California, USA) software were employed to analyze the data, and the results were shown as mean values \pm SD. Differences between the mean values of the measured properties were compared using a multiple-range Tukey's test. A significance level of 0.05 was used.

III. RESULTS AND DISCUSSIONS

A. Extrusion process

In order to determine the most suitable operating conditions, such as temperature profiles and screw speed, a series of screening assays were performed. Special care had been taken when these parameters were settled. Complete starch plasticization must be achieved without polymers degradation.

Extrusion processability can be determined by torque and die pressure. Li et al. [6] stated that sample premixing enhances processing, leading to more stable conditions, as regards, torque and die pressure.

Samples used in this study were premixed as indicated previously.

Premixing promotes plasticizer diffusion into the starch granules deriving on a more homogenous distribution and improving gelatinization, melting, and disruption of the starch granules during extrusion. Premixing can also enhance the swelling and moisture diffusion through the starch granules.

The processing temperature has a very important role in the starch extrusion; it has to guarantee the complete gelatinization of starch and to decrease the viscosity of the molten starch. For starch-glycerol samples processed at the four different temperature profiles, the mean values of torque and die pressure obtained were 8.64 Nm and 2.2×10^3 KPa, respectively. No significant differences were observed among the processing temperatures. On the other hand, starch-pectin samples, for every compositions ratio, showed lower torque and die pressure mean values (6 Nm, 1.4×10^3 KPa). These results indicate that blending improves samples processability. This can be explained in terms of the different structures of the polymers. While the long linear pectin chains can easily be enchainned, folded and reoriented, the highly branched amylopectin chains are quite inflexible. Thus, pectin chains reduce viscosity lowering the torque. On the other hand, the proportion of branched chains in the sample is reduced by the amount of pectin in the blend, contributing to the lowering of viscosity. Another important processing parameter is screw speed. In order to accomplish a complete disruption and blend of the biopolymers, a higher screw speed is required to increase shear stress in the extruder. However, high screw speeds decrease the residence time of the material in the extruder, which, in the case of starch, could lead to underprocessing. A screw speed of 100 rpm was selected for starch-glycerol samples. The use of lower speeds derived in a light brown material which smelt slightly burnt. On the other hand, higher speeds caused a sharp increase in torque and pressure.

Figure 1 shows the extruded starch-glycerol filaments obtained with the different temperature profiles, along with a cross-section photomicrograph of each filament. Filaments obtained under TP0 conditions were white and flexible, whereas the others were translucent and rigid.

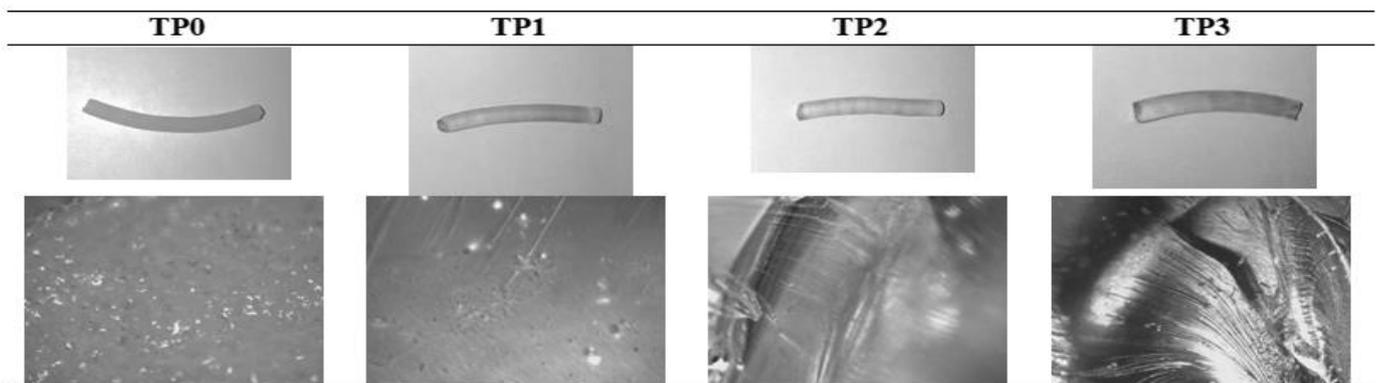


Fig. 1. Extruded starch-glycerol filaments at different temperature profiles and cross section photomicrograph.

Ruiz Avilés [27] had reported that cassava starch-glycerol samples extruded at 120 °C were white due to an incomplete disruption of starch granules. Thus, the operating conditions provided by TP0 were not enough to obtain a thermoplastic starch. Micrographs corroborated this observation, considering the heterogeneity presented by the sample of TP0, caused by the incomplete disruption of starch granules.

Starch-pectin blends were extruded at TP1 conditions. Higher temperature profiles resulted in burnt filaments. The screw speed was set at 100 rpm to maintain comparable operational conditions, although higher screw speed could be employed without increasing pressure or torque for starch-pectin blends.

B. Differential Scanning calorimetry (DSC)

DSC results are shown in Table 3. Glass transition temperatures were not observed in the temperature range studied and under the used experimental conditions. The pellet samples processed showed two endothermic peaks.

The first transition appeared at a mean temperature of 147°C and was related to the evaporation of bound water. According to several authors [28][29], the state of water in a polymer matrix depends on the kind of water-polymer interaction, varying from strongly bound water to completely free one. Strongly bound water constitutes the water and polymer molecules bound through hydrogen bonds. Temperatures associated with these transitions had been reported to be among 120°C and 160°C [28]. Furthermore, [4] reported an inflection of temperature at 120 °C for thermoplastic starch containing 20% glycerol. The higher temperature reported for the samples analyzed in this work can be attributed to the higher glycerol content. The hydrophilic nature of the plasticizer may retard the loss of water.

The second inflection of temperature could be associated with the evaporation of plasticizer. Galicia-Garcia et al. [4] and Wu et al. [30] reported the initial evaporation of plasticizer at 160°C. Moreover, Tunjano et al. [31] found two endothermic peaks on the DSC

TGA analyzes for evaporation of the plasticizer. The second peak, between 210.5 ° C and 212 ° C, was associated with the fusion of crystalline zones of the starch. The notorious increase in enthalpy ΔH , from conditions TP0 to TP1, shows that only after TP1 an adequate processing of the material is achieved.

C. Film formation

The pelletized materials were compression molded into flat films using a hydraulic press. A series of screening assays were made in order to define the working range.

Starch-glycerol extruded materials were processed at 3 molding temperatures (100, 120, and 150°C) and 3 compressing times (1, 3, and 5 minutes). It was not possible to obtain homogeneous films from pellets extruded at TP0 at any of the conditions assayed. Figures 2 a), b), and c) show samples obtained after 3 minutes molding at 100°C, 120°C, and 150°C, respectively. In each case, the pellets remained partially melted on the film matrix.

On the other hand, pellets extruded at the remaining temperature profiles showed better processability properties. When pellets were compressed at 100 °C samples did not achieve a totally homogeneous appearance (Figure 2 d)), while at 150°C the films were burnt (Figure 2, f)). Thus, 120°C was selected as the optimal molding temperature with 3 minutes of compression, as shown in Figure 2 e).

Similarly, the compression molding of starch-pectin extruded blends was performed at 3 different temperatures and 3 compressing times. It was not possible to achieve homogeneous pectin films molded at 100°C (Figure 3 g) and at 150°C films were burnt and it was difficult to release the film from the molding surface (Figure 3 i).

Finally, the films were obtained by molding at 120°C but the compression time was reduced to 1 minute, otherwise, the films would get slightly burnt. The obtained films S0, S25, S50, and S75 are shown in Figure 3, h), j), k), and l) respectively.

As a final remark, it is important to mention that pellets were kept at 30% relative humidity. The extra water content in the samples would lead to steam production in the material that generates bubbles, which are not desirable in the film matrix.

D. Scanning electron microscopy (SEM)

The study of sample morphology is very important to understand the properties of the polymer blends. Scanning electron micrographs of fracture surfaces of filaments extruded at TP1 and films of starch (S100), starch-pectin (S50) and pectin (S0) are shown in Figure 4. No residual granular structure was observed in the surfaces analyzed. It should be noted that the extrusion conditions resulted in the complete gelatinization of the starch. No morphological characteristics similar to starch granules were observed. This is important to determine the extrusion conditions that achieve the total gelatinization of the starch [6].

Sample	T_1 (°C)	T_2 (°C)	ΔH (J/g)
PS100 TP0	149.33	177.13	82.34
PS100 TP1	149.61	174.70	304.2
PS100 TP3	142.63	164.24	314.2

performed on thermoplastic starches.

TABLE III. DSC OF STARCH PELLETS

P: pellets, S: starch. Numbers indicate starch content. TP: temperature profile. T1: first temperature inflection, T2 second temperature inflection. ΔH : Enthalpy change

The first one, between 183.72 °C and 185.3 °C, coincided with the temperature range reported in the

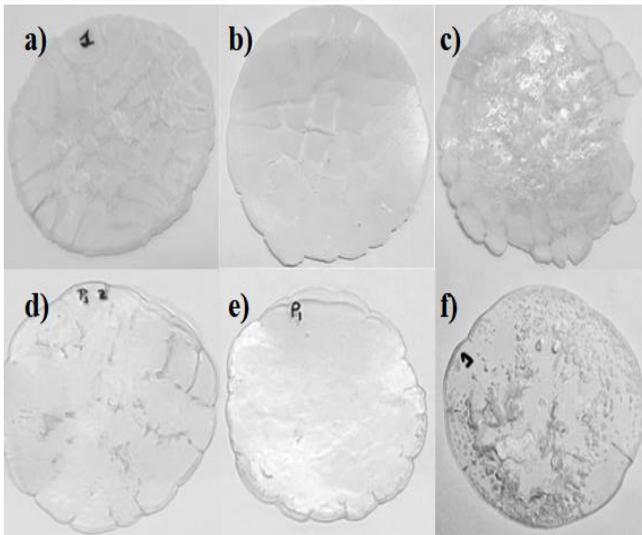


Fig.2. Starch films obtained during screening assays: a) S100 TP0 TC=100°C t=3min, b) S100 TP0 TC=120°C t=3min, c) S100 TP0 TC=150°C t=3min, d) S100 TP1 TC=100°C t=3min, e) S100 TP1 TC=120°C t=3min, f) S100 TP1 TC=150°C t=3min,

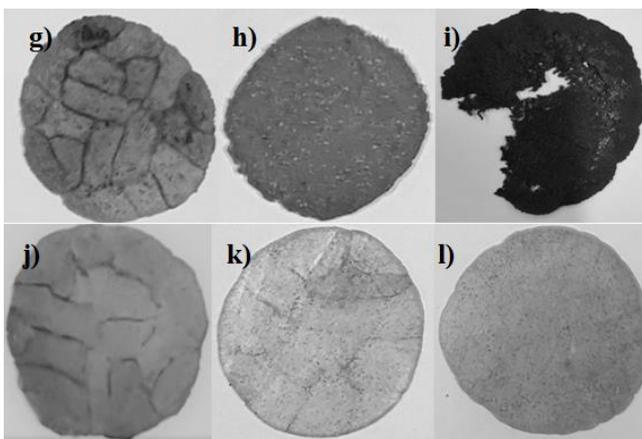


Fig.3. Starch-pectin films obtained during screening assays g) S0 TP1 TC=100°C t=1min, h) S0 TP1 TC=120°C t=1min, i) S0 TP1 TC=120°C t=3min, j) S25 TP1 TC=120°C t=1min, k) S50 TP1 TC=120°C t=1min, l) S75 TP1 TC=120°C t=1min

The components of the S50 matrix were indistinguishable from each other in all the images. Starch filament and film presented smooth surfaces. The pectin film surface presented heterogeneities; this can be attributed to a slight burning of the material during thermocompression molding. The results indicated that composite samples developed a matrix with a homogenous structure. The absence of phase separation indicated that a good interaction of both materials was achieved.

E. Material characterization

Pellet and film samples were characterized. Water uptake ability of pellets and films was evaluated (Table 4). The sorption capacity of starch samples (pellets and films) was assayed for each extrusion temperature

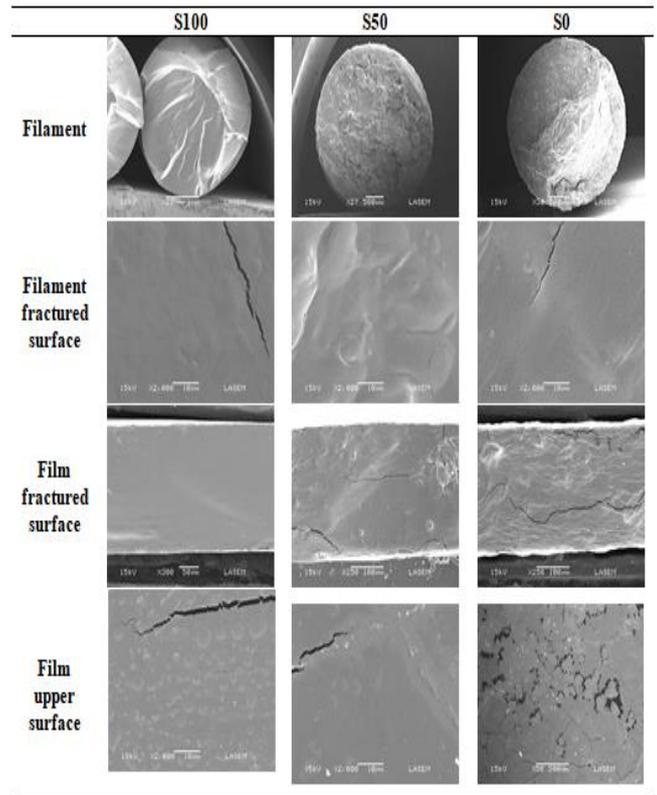


Fig.4. SEM micrographs of S100, S50 and S0

profile. The sorption capacity of films was similar to those reported for pellets, which indicates that during the molding process there were no additional modifications into the material. These results were similar than those reported by [5] [14]. In addition, extrusion temperature profiles had no significant effect on sorption capacity.

Films exhibited greater sorption capacity than pellets for the films and the pellets made of pectin and starch-pectin. This can be attributed to the area-volume ratio; the area exposed in films is higher than in pellets, thus, the sorption process can be enhanced.

Sorption capacity values of pectin-starch films are higher than the corresponding values of starch samples. The S75 blend showed the lowest value.

The film solubility presented a similar behavior. For all the samples, the solubility of the films was higher than the solubility of the pellets. The solubility of the pectin-starch films increased with the pectin content in the formulation. This behavior in the solubility of the composed films can be attributed to the influence of pectin, since it is highly hydrophilic and completely soluble under the conditions tested.

As shown in Table 5, the density of starch films slightly diminished when extrusion temperature increased, while in the starch-pectin films, no significant differences were observed. The mean density of films was 1.38 g cm^{-3} , which is in accordance with the value reported by [32].

The results from permeability measurements showed that water vapor permeability of the starch samples increases as the temperature of the extrusion profile increases. The starch-pectin films were more

TABLE IV. SORPTION CAPACITY AND SOLUBILITY OF PELLETS AND FILMS.

Sample	Sorption capacity (g H ₂ O/100g dry sample)					Solubility (%)
	a _w =0.516	a _w =0.638	a _w =0.743	a _w =0.821	a _w =0.916	
PS100 TP0	5.16±0.33 ^a	6.03±0.25 ^a	11.61±0.55 ^a	16.58±0.70 ^a	21.78±0.22 ^a	29.0±1.15 ^a
PS100 TP1	4.92±0.09 ^{a,b}	5.48±0.19 ^a	12.06±0.01 ^a	17.48±0.57 ^a	21.57±0.15 ^a	25.84±0.4 ^{a,b}
PS100 TP2	4.40±0.32 ^b	5.71±0.28 ^a	11.61±0.41 ^a	17.16±0.56 ^a	21.99±0.35 ^a	23.19±1.44 ^b
PS100 TP3	4.17±0.12 ^b	5.8±0.19 ^a	11.33±0.50 ^a	16.28±0.51 ^a	21.85±0.18 ^a	23.94±0.08 ^b
FS100 TP1	5.31±0.19 ^a	5.60±0.42 ^a	11.29±0.71 ^a	15.88±0.85 ^a	20.95±0.74 ^a	35.21±3.00 ^c
FS100 TP2	5.46±0.53 ^a	5.86±0.22 ^a	9.89±1.23 ^a	16.78±0.17 ^a	21.69±0.88 ^a	32.07±7.83 ^c
FS100 TP3	5.22±0.42 ^a	6.85±0.30 ^b	10.27±1.43 ^a	16.02±1.02 ^a	21.89±0.67 ^a	37.82±1.63 ^c
PS0	6.49±0.15 ^c	9.24±0.18 ^c	16.47±0.17 ^b	26.25±1.00 ^b	33.26±1.14 ^b	82.66±9.29 ^d
PS25	6.92±0.03 ^c	8.78±0.15 ^{c,d}	16.03±0.43 ^b	22.34±0.32 ^b	31.69±1.28 ^{b,c}	68.10±4.31 ^e
PS50	6.26±0.34 ^c	8.02±0.11 ^{d,e}	14.24±0.13 ^c	20.66±1.41 ^b	29.72±0.39 ^c	55.29±1.61 ^f
PS75	5.60±0.17 ^d	7.45±0.19 ^e	14.01±0.19 ^c	21.09±0.47 ^b	26.80±0.57 ^d	38.49±3.36 ^g
FS0	9.1±0.35 ^e	11.98±0.48 ^f	16.55±0.49 ^d	23.37±1.25 ^c	30.51±0.58 ^e	87.10±5.93 ^h
FS25	9.84±0.47 ^e	12.00±0.07 ^f	16.98±0.37 ^d	21.21±1.19 ^c	28.56±0.65 ^e	71.43±7.19 ⁱ
FS50	9.98±0.46 ^e	10.38±0.32 ^g	16.49±1.24 ^d	17.29±1.15 ^d	24.82±1.76 ^f	59.70±10.37 ^j
FS75	8.17±0.14 ^f	9.66±0.11 ^g	14.68±0.44	16.87±1.6 ^d	23.27±0.66 ^f	45.41±2.89 ^k

Equal letters in the same column indicate that not statistical difference is observed with $p < 0.05$. P: pellets, F: films, S: starch. Numbers indicate starch content. TP: temperature profile.

permeable than starch films, but no significant differences were observed among them. These results are consistent with the obtained values for solubility and the water uptake (Table 5).

The functional properties of films, such as barrier and mechanical properties are strongly influenced by the hydrophilicity of both polymers and the high pectin solubility. The high hygroscopicity of pectin promotes water adsorption into the film matrix, increasing polymer chain mobility and, thus enhancing water diffusion through the films.

Mechanical properties resulted from the tensile tests are shown in Table 5. It was observed that the tensile strength of starch films, obtained at the different extrusion temperature profiles, were not significantly different.

Among the samples studied, starch films presented the highest elongation and exhibited viscoelastic behavior. Several authors reported elongation values around 120% for the starch film [32][33][31].

Liu et al. [34] assessed the ability to form films using extrusion technologies of different biopolymers. They reported values of tensile strength of 3.64 MPa and modulus of 0.28 MPa, for pectin films. Furthermore, the reported values for starch films were 2.6 MPa and 0.34 MPa for tensile strength and modulus, respectively.

The tensile strength of the starch-pectin films decreased slightly when the pectin content increases.

The starch-pectin films presented a lower modulus than each of the pure polysaccharide films. The elongation at break of the blend films was lower than the elongation of the starch films, but higher than the elongation of the pectin films. This behavior was attributed to the low flexibility of the pectin films in relation to the starch films with the same plasticization.

IV. CONCLUSION

The results of this study showed that starch-pectin-glycerol blends can be successfully extruded and molded into films. It was possible to obtain different blend compositions at the same processing conditions. The blending enhanced processability of pectin and starch separately. On the one hand, working with the blend of pectin and starch allowed to increase the screw speed without increasing the torque and the pressure, while working only with starch required more severe processing conditions. On the other hand, the presence of starch made it possible to work at higher extrusion temperatures compared to the processing of pectin alone, which tended to burn.

The physical and functional properties of the pellets and films were evaluated and reported. Comparing solubility in water of pellets and films and the water sorption capacity, compression molding did not modify the structure or the behavior of the material when it is in contact with water.

It was observed that the starch-pectin films have intermediate mechanical properties between those

TABLE V. THICKNESS, DENSITY, PERMEABILITY AND MECHANICAL PROPERTIES OF FILMS.

Sample	Thickness ($\times 10^{-4}$ m)	Density (g/cm^3)	Permeability $\times 10^{-9}$ ($\text{g}/\text{m}\cdot\text{Pa}\cdot\text{s}$)	Mechanical Properties		
				Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)
FS100 TP1	4.88 \pm 0.30 ^a	1.40 \pm 0.01 ^a	1.38 \pm 0.02 ^a	2.47 \pm 0.22 ^a	0.32 \pm 0.04 ^a	82.02 \pm 7.38 ^a
FS100 TP2	5.20 \pm 0.57 ^a	1.35 \pm 0.02 ^b	1.51 \pm 0.01 ^{a,b}	1.92 \pm 0.35 ^{a,b}	0.18 \pm 0.02 ^{b,c}	94.82 \pm 4.67 ^{a,b}
FS100 TP3	5.45 \pm 0.13 ^a	1.19 \pm 0.03 ^c	1.63 \pm 0.06 ^b	2.06 \pm 0.13 ^a	0.16 \pm 0.02 ^{b,c}	102.90 \pm 8.88 ^b
FS0	3.59 \pm 0.22 ^b	1.41 \pm 0.03 ^a	2.35 \pm 0.17 ^c	1.31 \pm 0.27 ^c	0.23 \pm 0.01 ^b	33.54 \pm 2.92 ^e
FS25	4.44 \pm 0.67 ^a	1.48 \pm 0.02 ^a	2.57 \pm 0.35 ^c	1.24 \pm 0.31 ^c	0.14 \pm 0.02 ^{d,c}	61.08 \pm 2.71 ^c
FS50	4.60 \pm 0.50 ^a	1.44 \pm 0.03 ^a	2.31 \pm 0.24 ^c	1.72 \pm 0.20 ^b	0.14 \pm 0.01 ^{d,c}	50.40 \pm 5.59 ^{c,d}
FS75	4.49 \pm 0.50 ^a	1.41 \pm 0.04 ^a	2.42 \pm 0.33 ^c	2.02 \pm 0.03 ^a	0.17 \pm 0.02 ^{d,c}	40.23 \pm 5.15 ^d

Equal letters in the same column indicate that not statistical difference is observed with $p < 0.05$. P: pellets, F: films, S: starch. Numbers indicate starch content. TP stands for temperature profile.

presented by the starch films and those of pectin films. The composite films presented a lower percentage of elongation than starch films and were more flexible than pectin films. The properties related to the interaction with water are strongly influenced by the hydrophilicity of the polymers and the solubility of the pectin. Nevertheless, no relevant differences were found in water barrier properties of pure polysaccharides and blend films.

In conclusion, starch-pectin films were successfully obtained by extrusion. Blending starch and pectin allowed extruding the samples under moderate conditions, which led to a more stable operation, in terms of operating conditions such as torque and pressure. In addition, the application of more moderate operating conditions could derive in a reduction in the operating costs involved in the process.

ACKNOWLEDGMENTS

The financial support provided by Consejo de Investigación de la Universidad Nacional de Salta (CIUNSa-Proyecto No 2260) and CONICET (PIP 2015 N° 11220150100348) is gratefully acknowledged. The authors acknowledge I.D. Adrián Oviedo and Dr. Juan José Ortiz from Fundación Argentina de Nanotecnología (FAN) for equipment and technical assistance during extrusion; Engr. Hugo Destéfanis for assistance with compression molding and DSC assays, and technical assistance of Engr. Silvia Blanco from LASEM (Laboratorio de Microscopía Electrónica de Barrido, ANPCyT, CONICET, UNSA).

REFERENCES

- [1] Q. Yan, H. Hou, P. Guo, and H. Dong, "Effects of extrusion and glycerol content on properties of oxidized and acetylated corn starch-based films," *Carbohydr. Polym.*, vol. 87, no. 1, pp. 707–712, 2012.
- [2] R. Zullo and S. Iannace, "The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure," *Carbohydr. Polym.*, vol. 77, no. 2, pp. 376–383, 2009.
- [3] T. Janjarasskul and J. M. Krochta, "Edible Packaging Materials," *Annu. Rev. Food Sci. Technol.*, vol. 1, no. 1, pp. 415–448, 2010.
- [4] T. Galicia-García et al., "Thermal and microstructural characterization of biodegradable films prepared by extrusion-calendering process," *Carbohydr. Polym.*, vol. 83, no. 2, pp. 354–361, 2011.
- [5] O. V. López, N. E. Zaritzky, M. V. E. Grossmann, and M. A. García, "Acetylated and native corn starch blend films produced by blown extrusion," *J. Food Eng.*, vol. 116, no. 2, pp. 286–297, 2013.
- [6] M. Li et al., "Extrusion processing and characterization of edible starch films with different amylose contents," *J. Food Eng.*, vol. 106, no. 1, pp. 95–101, 2011.
- [7] M. A. Bertuzzi and A. M. Slavutsky, "Standard and New Processing Techniques Used in the Preparation of Films and Coatings at the Lab Level and Scale-Up," in *Edible Films and Coatings. Fundamentals and Applications*, M. Montero Garcia, M. Gómez-Guillén, M. López-Caballero, and G. Barbosa-Cánovas, Eds. CRC Press, 2016, pp. 21–42.

- [8] M. L. Fishman, D. R. Coffin, C. I. Onwulata, and J. L. Willett, "Two stage extrusion of plasticized pectin/poly(vinyl alcohol) blends," *Carbohydr. Polym.*, vol. 65, no. 4, pp. 421–429, 2006.
- [9] M. Thunwall, V. Kuthanová, A. Boldizar, and M. Rigdahl, "Film blowing of thermoplastic starch," *Carbohydr. Polym.*, vol. 71, no. 4, pp. 583–590, 2008.
- [10] L. Avérous and C. Fringant, "Association between plasticized starch and polyesters: Processing and performances of injected biodegradable systems," *Polym. Eng. Sci.*, vol. 41, no. 5, pp. 727–734, 2001.
- [11] L. Averous, L. Moro, P. Dole, and C. Fringant, "Properties of thermoplastic blends: Starch-polycaprolactone," *Polymer (Guildf)*, vol. 41, no. 11, pp. 4157–4167, 2000.
- [12] M. L. Fishman, D. R. Coffin, C. I. Onwulata, and R. P. Konstance, "Extrusion of pectin and glycerol with various combinations of orange albedo and starch," *Carbohydr. Polym.*, vol. 57, no. 4, pp. 401–413, 2004.
- [13] M. L. Fishman and D. R. Coffin, "Mechanical , microstructural and solubility properties of pectin / poly (vinyl alcohol) blends '," *Carbohydr. Polym.*, vol. 35, pp. 195–203, 1998.
- [14] P. M. Forssell, J. M. Mikkilä, G. K. Moates, and R. Parker, "Phase and glass transition behaviour of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch," *Carbohydr. Polym.*, vol. 34, no. 4, pp. 275–282, 1997.
- [15] H. Liu, F. Xie, L. Yu, L. Chen, and L. Li, "Thermal processing of starch-based polymers," *Prog. Polym. Sci.*, vol. 34, no. 12, pp. 1348–1368, 2009.
- [16] B. a Ibrahim and K. M. Kadum, "Influence of Polymer Blending on Mechanical and Thermal Properties," *Mod. Appl. Sci.*, vol. 4, no. 9, pp. 157–161, 2010.
- [17] A. Bagliotti Meneguín, B. Stringhetti Ferreira Cury, and R. C. Evangelista, "Films from resistant starch-pectin dispersions intended for colonic drug delivery," *Carbohydr. Polym.*, vol. 99, pp. 140–149, 2014.
- [18] M. A. Laurent and P. Boulenguer, "Stabilization mechanism of acid dairy drinks (ADD) induced by pectin," *Food Hydrocoll.*, vol. 17, no. 4, pp. 445–454, 2003.
- [19] A. B. Meneguín, B. S. Ferreira Cury, A. M. dos Santos, D. F. Franco, H. S. Barud, and E. C. da Silva Filho, "Resistant starch/pectin free-standing films reinforced with nanocellulose intended for colonic methotrexate release," *Carbohydr. Polym.*, vol. 157, pp. 1013–1023, 2017.
- [20] D. Khondkar, R. F. Tester, N. Hudson, J. Karkalas, and J. Morrow, "Rheological behaviour of uncross-linked and cross-linked gelatinised waxy maize starch with pectin gels," *Food Hydrocoll.*, vol. 21, no. 8, pp. 1296–1301, 2007.
- [21] F. G. Prezotti, A. B. Meneguín, R. C. Evangelista, and B. S. Ferreira Cury, "Preparation and characterization of free films of high amylose/pectin mixtures cross-linked with sodium trimetaphosphate," *Drug Dev. Ind. Pharm.*, vol. 38, no. 11, pp. 1354–1359, 2012.
- [22] M. L. Fishman, D. R. Coffin, R. P. Konstance, and C. I. Onwulata, "Extrusion of pectin / starch blends plasticized with glycerol &," vol. 41, pp. 317–325, 2000.
- [23] M. L. Fishman, D. R. Coffin, R. P. Konstance, and C. I. Onwulata, "Extrusion of pectin/starch blends plasticized with glycerol," *Carbohydrate Polymers*, vol. 41, no. 4, pp. 317–325, 2000.
- [24] W. Wolf, W. E. L. Spiess, and G. Jung, "Standarization of isotherm measurements (Cost-Project 90 and 90 Bis)," in *Properties of water in foods in relation to quality and stability*, D. Simatos and J. L. Multon, Eds. Dordrecht: Springer Netherlands, 1985, pp. 661–679.
- [25] ASTM, "E96. Standard test methods for water vapor transmission of materials," *Standards American Society for Testing and Materials*. Philadelphia, 2010.
- [26] ASTM, "D 882. Tensile properties of thin plastic sheeting," *Standars Am. Soc. Test. Mater.*, 2010.
- [27] G. Ruiz Avilés, "Pólimeros Biodegradables a partir de almidón de yuca.," *Eafit*, pp. 15–22, 2005.
- [28] M. Avella, E. Di Pace, B. Immirzi, G. Impallomeni, M. Malinconico, and G. Santagata, "Addition of glycerol plasticizer to seaweeds derived alginates: Influence of microstructure on chemical-physical properties," *Carbohydr. Polym.*, vol. 69, no. 3, pp. 503–511, 2007.
- [29] S. J. Kim, S. G. Yoon, and S. I. Kim, "Synthesis and characteristics of interpenetrating polymer network hydrogels composed of alginate and poly(diallyldimethylammonium chloride)," *J. Appl. Polym. Sci.*, vol. 91, no. 6, pp. 3705–3709, 2004.
- [30] Q. Wu, H. Sakabe, and S. Isobe, "Processing and Properties of Low Cost Corn Gluten Meal/Wood Fiber Composite," *Ind. Eng. Chem. Res.*, vol. 42, no. 26, pp. 6765–6773, 2003.
- [31] E. P. V. Tunjano, F. Salcedo, I.C. Jimenez, J.A. Medina, O.A. Alvarez, "Estudio De Las Propiedades Termicas Y Mecanicas Del Almidon.," *Rev. Latinoam. Metal. y Mater.*, vol. 1, no. 1, pp. 29–36, 2009.
- [32] L. Avérous and P. J. Halley, "Biocomposites based on plasticized starch," *Biofuels, Bioprod. Biorefining*, vol. 3, no. 3, pp. 329–343, 2009.
- [33] R. González-Soto, M. Sotelo-Bautista, and F. Gutiérrez-Méraz, "Películas de Almidón de papa obtenidas por casting y extrusión reforzadas con montmorillonita de sodio modificada," *Investig. y Desarro. en Cienc. y Tecnol. Aliment.*, vol. 1, no. 2, pp. 627–632, 2016.
- [34] Z. Liu and J. H. Han, "Film-forming Characteristics of Starches," *J. Food Sci.*, vol. 70, no. 1, pp. 31–36, 2005.