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"Physical and microstructural properties of biodegradable films based on pea starch and PVA"

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ABSTRACT

The effect of storage time on the physical properties of pea starch (PS) and polyvinyl alcohol (PVA) films and their blend was studied to develop biodegradable packaging materials for food applications. To this end, an analysis was performed of the microstructural and physical properties (solubility, moisture content, barrier, mechanical and optical properties) of PS, PVA and PS:PVA films stored for five weeks (25ºC-53%RH). Whereas SEM micrographs showed a homogenous appearance for PS films, PVA presented irregularities typical of semi-crystalline structures. Blend films showed a structure which was more similar to PVA films. After 5 weeks, the physical properties of PVA films did not change; in the case of PS, however, the elastic modulus and tensile strength increased markedly but the stretchability and gloss significantly decreased, which was associated with water loss in the starch matrix. All the physical properties of blend films remained unchanged throughout time, except the elastic modulus and the tensile strength, which slightly increased. Therefore, the incorporation of PVA into pea starch films improved their physical properties and inhibited the changes that occurred in the starch matrix caused by ageing.

Keywords: barrier, SEM, mechanical, pea starch, gloss, storage time.

1. **Introduction**

In the last few years, an important effort has been made by the scientific community to search for bioplastics, which represent an environmentally-friendly and sustainable alternative, whose production has greatly increased over the last few years (Avérous & Pollet, 2012).

Starch is the one of the most important polysaccharides used to develop biodegradable films due to its potential to form a continuous matrix at low cost (Gupta et al., 2014). It is well known that starch has a granular structure and is composed of two macromolecules: amylose and amylopectin. Both polymers are responsible for the starch crystallization which leads to changes in the mechanical response (increased stiffness) of starch products (Talja et al., 2007). The amylose:amylopectin ratio depends on the source of starch, ranging from 15:85 to 35:65. Several studies have reported the use of starches from various sources to prepare biodegradable films and coatings with different properties (Chen et al., 2008; Bonilla, et al., 2013; Gupta et al., 2014; Jiménez, et al., 2012; Luo et al., 2012 and Ortega-Toro, et al., 2014). Of the different kinds of starches, pea starch has a high-amylose content, which normally leads to an improvement in both the mechanical strength and the gas barrier properties of starch-based films (Han et al., 2006). Films based on starch are odorless, colorless, transparent and with very low oxygen permeability. Nevertheless, starch films present some drawbacks, such as poor water vapor barrier properties and high rigidity, which increase throughout the storage time due to the progress of crystallization in high relative humidity conditions and chain aggregation due to the progressive formation of hydrogen bonds (Cano et al. 2014; Forssell et al., 1999; Myllärinen et al., 2002; and Rindlav-Westling et al., 1998).

Different attempts have been made to overcome these problems when designing starch-based biodegradable films, the most common being to obtain blends with other biopolymers or bioplastics (Bonilla et al., 2013; Gupta et al., 2014 and Ortega-Toro et al., 2014) which are obtained from renewable sources or synthesis and which are biodegradable or compostable.

Of the bioplastics, polyvinyl alcohol (PVA), aliphatic polyesters, such as poly B-hydroxyalkanoates (PHA) and polylactic acid (PLA) or poly ε-caprolactone (PCL), represent interesting alternatives because of their good mechanical properties and, in some cases, hydrophobic nature, which can contribute to modulate starch properties. Of the different bioplastics, PVA presents the greater compatibility with starch molecules at lower cost (Lu et al., 2009), which is important to ensure the competitive cost of the blend.

Polyvinyl-alcohol is a synthetic bioplastic, which is fully degradable and water soluble. Recently, PVA has received attention because of its biocompatibility and its good physical properties, which are due to the presence of OH groups and the hydrogen bond formation (Bonilla et al., 2014). PVA also has good film forming capability, giving rise to odourless, non-toxic films with high tensile strength and flexibility, good oxygen and aroma barrier properties, good transparency and chemical resistance.

Different studies into starch-PVA blends can be found in the literature, thus showing the increasing interest produced by these systems. Some of them mainly focus on biodegradability studies (Gupta et al., 2014; Lu et al., 2009 and Siddaramajah et al, 2004). Other authors have analyzed the effect of the incorporation of different additives to the starch: PVA blends, such as citric acid, glutaraldehyde or urea (Gupta et al 2014; Luo et al, 2012; Ramaraj et al., 2006 and Shi et al, 2008), calcium chloride (Jiang et al, 2012), or nanoparticles (Yoon e t al., 2012) for different purposes (compatibility enhancement or biomedical and packaging applications). Few of them studied the effect of different starch:PVA ratios on film properties (Chen et al, 2008; Siddaramianh et al., 2003 and Srrekumar et al., 2012).

Siddaramaiah, et al., (2003) studied the influence of crystal imperfections caused by starch on the mechanical and optical properties of films. Their results support the formation of hydrogen bonds between the hydroxyl groups of PVA and starch in the polymer network. Chen et al., (2008) studied the effect of pea starch nanocrystals (PSN) and native pea starch (NPS) on the structure and physicochemical properties of the PVA films. They concluded that

PSN are smaller in size and more homogeneously dispersed in the PVA matrix than the NPS, resulting in stronger interactions with PVA and better mechanical behavior.

Sreekumar et al., (2012) studied the structure and physical properties of different blends of corn starch and PVA, by analyzing X-ray diffraction and thermal and mechanical response. They concluded that the blends presented a partial compatibility, thanks to the addition of glycerol. Likewise, polymer compatibility and PVA crystallinity greatly decreased when the starch content rose, which affected the mechanical response of the films.

To the best of our knowledge, no studies have been found into the effect of PVA on the ageing behavior of starch films, which is one of the main drawbacks for the practical use of starch films as packaging material, as previously commented on.

The objective of this work was to analyze how PVA affects the development of the starch film properties throughout the storage. To this end, optical, mechanical and barrier properties of PS:PVA (1:1) blend films stored for five weeks were analyzed and compared to pure PS and PVA films.

2. **Materials and Methods**

2.1. Materials

Pea starch was purchased from Roquette (Roquette Laisa España, Benifaió, Spain) and Poly (vinyl alcohol) (M_w: 89.000-98.000, degree of hydrolysis > 99%, and viscosity: 11.6-15.4cP) was supplied by Sigma (Sigma Aldrich Química S.L., Madrid, Spain). Glycerol, as starch plasticizer, was provided by Panreac Química S.A., (Castellar de Vallès Barcelona, Spain)

2.2. Preparation and characterization of films

Films were prepared by casting. For the preparation of pure pea starch films (PS), 2% (w/w) starch aqueous dispersions were heated in a water bath at 95 ºC for 30 min to induce starch gelatinization and homogenized for 1 min at 13,500rpm and for 3 min at 20,500 rpm using a rotor –stator-homogenizer (Ultraturrax D125, Janke and Kunkel, Germany). Finally, glycerol was incorporated in a ratio of 1:0.25 (Starch:Glycerol) and mixed. For pure PVA films, 1 % (w/w) PVA dispersion was dissolved in distilled water by stirring for 30 minutes at 90 ºC. In PS:PVA composite films, PVA was added to the starch dispersion at 90 ºC in a ratio of 1:0.5 (PS:PVA) and stirred until dissolved (30 min). 1.5 g of total solids of different film forming dispersions (FFD) were gently spread over a Teflon plate (15 cm diameter) resting on a level surface, which would provide a density of solid of 84.7 g/m^2. Films were formed by drying at 25 ºC and 45 %RH for approximately 48 hours. The RH was monitored by means of a portable Alarm-Hygrometer testo 608-H2 (Lenzkirch, Germany) placed in the same drying room.

2.3. Film conditioning

After the drying process, films were conditioned in desiccators at 25 ºC and 53 %RH by using magnesium nitrate-6-hydrate oversaturated solution (Sigma Aldrich Química S.L., Madrid, Spain) for one week (considered as initial storage time, t_0) when the first series of analysis were carried out. One part of the samples was stored under the same conditions for five weeks (final storage time, t_F) in order to perform the second series of analysis of stored films. After this storage period, the physical properties of pea starch films have been shown to remain almost unaffected by time due to its low amylopectin content (Cano et al., 2014).

The film thickness of every sample was measured after these two times at six random positions with a Palmer digital micrometer to the nearest 0.0025 mm.

2.4. Characterization of films

2.4.1. Microstructural analysis

The microstructure of films was observed by Field emission scanning electron (SEM) (JEOL®, model JSM-5410, Japan) in films previously equilibrated (conditioned) at 25 ºC and 53 %RH for 1 week (initial storage time).

SEM observations were carried out on the film surface and at their cross section. To prepare the samples, films were frozen in liquid N_2 and cryofractured to observe the cross section. Two replicates per formulation were fixed on copper stubs, gold coated, and observed using an accelerating voltage of 2kV to surface (x750) and 5kV to cross sections (x1.500).

2.4.2. Solubility

The solubility of films was determined by means of a gravimetric method previously described by Ortega-Toro et al., 2014. For this purpose, the samples were kept in distilled water in a film:water ratio of 1:10 for 48 h, and later on, they were transferred to a convection oven (J.P. Selecta, S.A., Barcelona, Spain) for 24 h at 60ºC to remove the free water, and afterwards, they were completely dried in a desiccator with P_2O_5 ºC until constant weight. Three replicates were analyzed for each formulation, and results were expressed in g of dissolved film / g dry film.

2.4.3. Moisture content

The films moisture content (MC) was analysed using a gravimetric method. Five replicates per formulation were dried at 60 ºC for 24 h in a vacuum oven, and then they were equilibrated with P_2O_5 until constant weight.

2.4.4. Mechanical properties

Mechanical properties were measured by means of a Universal Machine (TA.XT plus, Stable Micro Systems, Haslemere, England). Equilibrated specimens were mounted in the film-extension grips of the testing machine and stretched at 50 mm min^{-1} until breaking, following the ASTM standard method D882 (ASTM, 2001). Force-distance curves were obtained and transformed into stress-strain curves. The mechanical behavior was analyzed in terms of: elastic modulus (EM), tensile strength (TS) and percentage of elongation at break (%ε). A minimum of eight replicates (2.5 cm wide and 10 cm long) were assayed per formulation.

2.4.5. Optical properties

The films' optical properties were described by means of the gloss and internal transparency as a measure of film opacity. The transparency of films was calculated by applying the Kubelka-Munk theory of multiple dispersion of reflection spectrum (Judd and Wyszacki, 1975 and Hutchings, 1999). This theory was based on the fact that the light passes through the film and is partially absorbed and scattered, which is quantified by the absorption (K) and the scattering (S) coefficients. The internal transmittance (Ti) of the films was quantified using eq. (1). In this equation, R0 is the reflectance of the film on an ideal black background. Parameters a and b were calculated by using eqs. (2) and (3), where R is the reflectance of the sample layer backed by a known reflectance, Rg. The reflection spectrum on the white and black background was determined from 400 to 700 nm with a MINOLTA spectrocolorimeter CM.36000d (Minolta Co. Tokyo, Japan). Measurements were taken on the side of film which was in contact with air during the drying and each formulation was made in triplicate.

$$Ti = \sqrt{((a - R_0)^2 - b^2} \quad (1)$$

$$a = \frac{1}{2}(R + \frac{R_0 - R + R_g}{R_0 R_g} \quad ...(2)$$

$$b = (a^2 - 1) \quad ...(3)$$

The gloss measurements were taken using a flat surface gloss meter (Multi-Gloss 268, MINOLTA) at an incidence angle of 60° on the black background, following the standard method ASTM D523 (1999). Three replicates of each formulation were carried out.

2.4.6. Barrier properties

Water vapour and oxygen permeability were determined as a measurement of the film barrier properties. The water vapour permeability (WVP) was evaluated following the gravimetric method, ASTM E96-95, using Payne permeability cups (Payne, elcometer SPRL, Hermelle/sd Argenteau, Belgium) of 3.5 cm in diameter. The relative humidity gradient was 53-100 %, which was achieved using pure water in cups and magnesium nitrate-6-hydrate saturated solution in desiccators, respectively. Cups were placed into desiccators and these, in turn, into a temperature-controlled camera at 25 ºC. The permeability study was performed by means of the weight control of cups using an analytical balance (±0,00001 g).

The oxygen permeation rate of the films was determined at 53 %RH and 25 ºC by an OX-TRAN (Model 2/21 ML Mocon Lippke,Neuwied, Germany) following the standard method (ASTM D3985-05, 2005). The samples were placed into the equipment to perform the permeation assay: an oxygen sensor read the permeation through the film and the rate of oxygen transmission was calculated taking into account the amount of oxygen and the sample area (50 cm^2). Oxygen permeability (PO) was calculated by dividing the oxygen transmission by the difference in oxygen partial pressure between the two sides of the film, and multiplying it by the average film thickness. Measurements were taken in triplicate.

2.5. Statistical analysis

Statistical analyses of data were performed through analysis of variance (ANOVA) using Statgraphics Plus 5.1. Program (Manugistics Corp., Rockville, MD). Fisher′s least significant difference (LSD) procedure was used at the 95% confidence level.

3. **Results and Discussion**

3.1. Microstructure of films

The SEM images of the surface and cross section of the PS, PVA and blend PS:PVA films are shown in Figure 1. This analysis provides information about the surface morphology and internal microstructure of the films. Starch films exhibited a homogeneous, smooth appearance and the presence of starch granules was not detected. These results coincide with those obtained by several authors working on pea starch films obtained by means of casting (Chen et al., 2009 and Wu et al., 2010). On the contrary, the cross section images presented a heterogeneously-fractured layer near the film surface, which points to the progress of crystallization in this region, probably associated to the greater water molecular mobility near the film surface (Cano et al., 2014).

PVA films also presented a homogenous, smooth surface, in agreement with that found by other authors (Bonilla et al., 2014; Chen et al., 2008 and Fortunati et al., 2013). The cross section of these films showed some irregularities typical of semi-crystalline structures, associated with the ordered arrangement of some segments of the polymer chains. In fact, PVA has been reported to present a high degree of crystallinity (around 54%) (Arvanitoyannis, 1999).

The surface of blend films was rougher in appearance, usually due to a certain degree of immiscibility between polymers and the co-existence of two phases: the PVA-rich phase and the PS-rich phase. These observations coincide with those found by Chen et al., (2008) who explained that aggregations of starch and micro-phase separation between pea starch and PVA occurred during film formation, due to the lack of total miscibility. Chaléat et al (2012) also confirmed the phase separation of both polymers when working with extruded plasticized starch/polyvinyl alcohol blends, but also suggested a small degree of inter-mixing.

Cross section micrographs of blend films also showed the co-existence of two phases: a crystalline and an amorphous phase, as observed for PVA films.

The thickness values of the films were 0.087±0.017mm, 0.107±0.019mm and 0.123±0.013mm, for pure PS, PVA and blend films, respectively. Blend films presented the greater values, as may be seen in the SEM observations. This result suggests that the chains in the blend matrix were less tightly packaged, giving rise to a more open network, probably due to steric hindrances caused by the different polymers.

3.2. Solubility and moisture content

Table 1 shows the solubility and moisture content mean values and the standard deviation of the films. The water solubility values of films are relatively high, concordant with the hydrophilic nature of the polymers. Nevertheless, blend films exhibited significantly lower solubility ($p<0.05$) than pure polymers. This fact suggested that a decrease in the hydrophilic nature of the matrix occurred in the blend, probably due to the establishment of polymer interactions, leading to decreased water affinity. In this sense, hydrogen bonds between hydroxyl groups of PVA and starch have been reported by Valencia et al (2013) and Chaléat et al (2012). The formation of hydrogen bonds between PVA hydroxyls and those of amylose or amylopectin would imply the re-orientation of the hydrophobic side of the PVA chain, generating hydrophobic regions in the matrix, which would reduce the water affinity of the blend films.

Table 1 also shows the moisture content (MC) of PS, PVA and blend films equilibrated at 53 % RH at the beginning (t_0) and the end (t_F) of the storage time. At the beginning of the storage (t_0), significant differences ($p<0.05$) were found between the water content of the three matrices. PS and PVA films exhibited a higher moisture content than blend films. This decrease is coherent with the loss of water solubility and has been attributed to the formation of hydrogen bonds between the two polymers, which reduced their water sorption capacity (Chaléat et al., 2012 and Chen et al., 2008).

At the end of the storage time (t_F), the moisture content tended to decrease, but becoming significantly different only for PS films. This could be attributed to progressive chain aggregations through hydrogen bonds, limiting the water sorption capacity of the films. The water loss could provoke a greater chain aggregation in the amorphous region, which will imply an increase in the film compactness that will affect the mechanical, optical and barrier properties (Cano et al., 2014).

3.3. Mechanical properties

Figure 2 shows the typical stress-strain curves obtained for all the films after one and five storage weeks under controlled conditions (53% RH and 25ºC), where the different mechanical behaviour of the matrices and the effect of ageing can be observed. Starch films exhibited the typical mechanical behaviour of a brittle material, without plastic deformation and with very low extensibility at break. On the other hand, the great resistance to break of PVA is highlighted.

The mechanical behaviour of films was analysed in terms of elastic modulus (EM), tensile strength at break (TS) and percentage of elongation at break (%ε). EM represents the stiffness of the material, TS the resistance to elongation at break and ε is a measure of the films' capacity for stretching. In Table 2, the mean values of the mechanical parameters and the standard deviation of the studied films throughout the storage time are shown. The values obtained are similar to those reported by other authors for pea starch films (Cano et al., 2014 and Da Matta et al., 2011) and PVA films (Chen et al., 2008 and Fortunati et al., 2013).

Significant differences ($p<0.05$) were found between the mechanical parameters of the different films. At the beginning of the storage time (t_0), PS films exhibited the poorest mechanical properties because of their lower resistance and stretchability (lower TS and % ε). This may be explained by the strong interchain interactions of starch polymers through hydrogen bonds, which increases the cohesion forces of the matrix but makes it difficult for the chains to shift during the tensile test. On the contrary, although PVA films were very resistant and stretchable, they were not as stiff as PS films. Blend films exhibited better mechanical properties than pure starch films; these being stiffer, more resistant and stretchable. Thus, PVA can be used to enhance the poor mechanical features of starch-based films.

After the storage period (t_F), PS films significantly ($p<0.05$) increased in rigidity, becoming more resistant and brittle; this was due to the greater compactness of the matrix associated with water loss (Table 1), coinciding with what was found by other authors (Cano et al., 2014 and Jiménez et al., 2012). On the contrary, the mechanical behavior of PVA films did not change throughout the ageing process ($p>0.05$).

The rigidity and resistance (high EM and TS) of blend films significantly increased ($p<0.05$) through storage, following the same, but less pronounced, pathway as PS films. However, film stretchability was not significantly affected by the storage time in blend films, these maintaining their high extensibility. The greater stability PVA provided to blend films could be attributed to the inhibition of the re-arrangement of the starch polymer chains throughout time due to interactions between the chains of both polymers.

These satisfactory results indicate that the blend of both polymers improved the mechanical response of pure starch films. These blend films behaved similarly to some commercial plastics very flexible and resistant, such as the typical black low density polyethylene bag used for trash, whose values obtained using the same experimental conditions and equipment were: thickness = 0.02 mm, EM = 370±74 MPa, TS = 27±7 MPa and %ε = 39.7±0.2 %.

3.4. Optical properties

According to Hutchings (1999), the gloss and internal transmittance (Ti) parameters are the best optical properties with which to evaluate the appearance of the films. Ti is related to the transparency of films and their structural homogeneity: high values of Ti are associated with structural homogeneity and high transparency. The main Ti differences among the films occurred at 450 nm; so, at 450 nm, Ti is taken to evaluate differences in the films' transparency. These values are shown in Table 3. At the initial storage time (t_0), the Ti values of PVA and blend films were slightly higher than those of PS films, but these small differences disappeared the longer they were stored. The different transparency level is linked to the internal structure developed in each film.

Table 3 also shows the mean gloss values of studied films at an incidence angle of 60º. The gloss of the films is related with the surface morphology achieved during film drying. In general, the smoother the surface, the glossier the film (Ward and Nussinovitch, 1996). In this sense, the decrease in the gloss values of the blend films may be explained by an increase in the surface roughness of these films associated with the co-existence of two interpenetrated phases in the matrix which alternatively emerge on the surface. After the storage period (t_F), the gloss values of pure starch films decreased ($p<0.05$) while those of pure PVA and blend films did not change. Changes in the gloss of starch films have been observed by different authors (Jimenez et al., 2012) and related with the progress of surface level crystallization, as observed in SEM micrographs.

3.5. Barrier properties

Table 1 shows the WVP values of films analyzed at 25ºC and a RH gradient of 53-100 %. PVA films exhibited slightly lower WVP values than starch films, in accordance with their less marked hydrophilic nature and, coherently with this, blend films had an intermediate WVP value. The values obtained for PS and PVA films agree with those found by other authors (Cano et al., 2014; Mehyar & Han, 2004). In no case were the WVP values significantly affected by the storage time.

The mean oxygen permeability (OP) values of the films are also shown in Table 1. In the case of PS films, similar values have been reported by Mehyar and Han (2004). The OP values were significantly lower for blend films, which can be due to a decrease in the oxygen solubility of the matrix. The OP values were greatly ($p<0.05$) reduced in PS films after the storage period (t_F), coinciding with the increased matrix compactness as a result of water content reduction. The incorporation of PVA into the starch matrix seems to inhibit these changes in the starch phase, thus also inhibiting changes in the barrier properties.

4. **Conclusion**

The incorporation of PVA into starch-based films appears to be a successful alternative means of improving the mechanical and barrier properties of these films, while providing enough stability to the matrix to inhibit physical changes provoked by ageing. This effect can be attributed to the establishment of interactions between both polymers, which were not completely compatible, but partially miscible. These blends led to films which were less water soluble and not as sensitive to water sorption, more stretchable and resistant than starch films while maintaining the low oxygen barrier property of starch films. These promising films could be used to prevent oxidative reactions in food packaging, although more studies submitting the films under different conditions and environments are needed to validate them.

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Table 1: Solubility (S), moisture content (MC), water vapour permeability (WVP) and oxygen permeability (OP) of pea starch (PS), PVA and composite (PS:PVA) films at the beginning (t_0) and the end (t_F) of the storage time. Mean values and (standard deviation).

	S ($g_{dissolved}$ / $g_{dry\ film}$)	MC (%d.b.)		WVP (gmm/hm^{2}KPa)		OP (cm^{3}mm/m^{2}hKPa)	
		t_0	t_F	t_0	t_F	t_0	t_F
PS	0.208(0.019) ^{a}	11.4(0.4)^{a1}	8.7(0.4)^{a2}	6.0(0.3)^{a1}	6.7(0.7)^{a1}	1.39(0.09)^{a1}	1.01(0.06)^{a2}
PVA	0.19(0.05)^{b}	12.8(1.2)^{b1}	11.9(1.3)^{b1}	4.74(1.05)^{b1}	4.8(0.8)^{b1}	0.623(0.009)^{b1}	0.71(0.06)^{b1}
PS:PVA	0.1157(0.0008)^{c}	8.03(0.54)^{c1}	7.06(1.69)^{a1}	5.09(1.17)^{ab1}	5.1(0.4)^{b1}	0.53(0.02)^{b1}	0.609(0.018)^{c2}

a, b, c. Different superscripts within a column indicate significant differences among formulations. ($p<0.05$).

1,2. Different superscripts within the same file indicate significant differences among storage times for the same formulation. ($p<0.05$).

Table 2: Elastic modulus (EM), tensile strength at break (TS) and percentage of elongation at break (%ε) of pea starch (PS), PVA and composite (PS:PVA) films at the beginning (t_0) and the end (t_F) of the storage time. Mean values and (standard deviation).

	t_0			t_F		
	EM (MPa)	TS (MPa)	%ε	EM (MPa)	TS (MPa)	%ε
PS	417(41)^{a1}	14.2(1.3)^{a1}	10(2)^{a1}	964(88)^{a2}	24(2)^{a2}	4.7(0.9)^{a2}
PVA	95(22)^{b1}	27(2)^{b1}	69.13(0.43)^{b1}	103(20)^{b1}	27.2(0.9)^{b1}	69.296(0.013)^{b1}
PS:PVA	506(62)^{c1}	26.9(1.4)^{b1}	40(4)^{c1}	689(44)^{c2}	32.3(1.6)^{c2}	41(3)^{c1}

a, b, c. Different superscripts within a column indicate significant differences among formulations. ($p<0.05$).

1,2. Different superscripts within the same file indicate significant differences among storage times for the same formulation. ($p<0.05$).

Table 3: Gloss values at 60º and internal transmittance (Ti) of pea starch (PS), PVA and composite (PS:PVA) films at the beginning (t_0) and the end (t_F) of the storage time. Mean values and (standard deviation).

	Gloss 60º		Ti (450nm)	
	t_0	t_F	t_0	t_F
PS	47(17)^{a1}	33(8)a^{2}	85.4(1.6)^{a1}	87.09(0.12)^{a1}
PVA	53(23)^{a1}	32(11)^{a1}	88.2(0.2)^{b1}	85.7(0.9)^{a1}
PS:PVA	13.2(1.6)^{b1}	12.9(1.2)^{b1}	86.2(0.5)^{b1}	85.2(0.9)^{a1}

a, b, c. Different superscripts within a column indicate significant differences among formulations. ($p<0.05$).

1,2. Different superscripts within the same file indicate significant differences among storage times for the same formulation. ($p<0.05$).

FIGURE CAPTIONS

Figure 1: SEM micrographs of surface (x750) and cross section (x1.500) of pea starch (PS), PVA and composite (PS:PVA) films.

Figure 2: Strain-Stress curves of pea starch (PS), PVA and composite (PS:PVA) films at the beginning (solid lines) and the end (dashed lines) of the storage time.

Figure 1

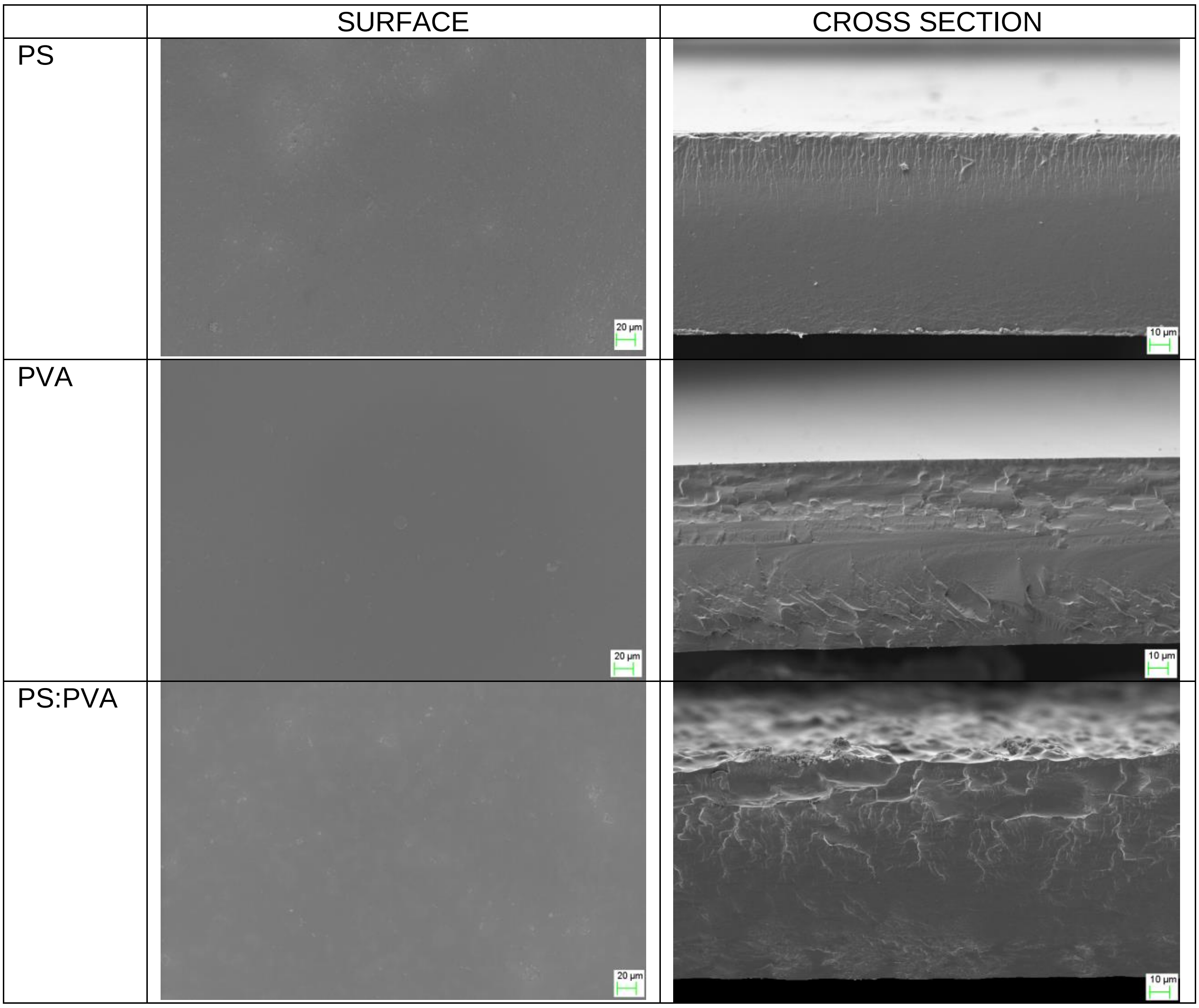
SURFACE
CROSS SECTION
PS
PVA
PS:PVA
20 µm
10 µm
20 µm
10 µm
20 µm
10 µm

Figure 2