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EFFECT OF POLYVINYL ALCOHOL ON THE PHYSICO-CHEMICAL PROPERTIES OF BIODEGRADABLE STARCH FILMS

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Starch-based biodegradable films typically have suboptimal mechanical properties, which restrict their use as food packaging material. However, combining two or more polymers can create new materials with improved functional properties. In this study, blends with varying proportions (0-60%) of polyvinyl alcohol (PVA) were examined to determine the effects on water adsorption, mechanical properties (including the percentage of relative elongation at break and ultimate tensile strength), and thermal properties (Tg). Both polymers were compatible during processing and in the final material for all formulations. Adding PVA significantly enhanced the functional and mechanical properties of the potato starch films. The S4P6 formulation, containing 60% PVA, displayed the best water vapor barrier, lower density and solubility, and superior mechanical properties. The PVA composite produced potato starch films with promising characteristics for potential use in food packaging and as a biodegradable substitute for synthetic packaging materials.

Keywords: polyvinyl alcohol, starch, biodegradable films, strength, transparency.

1. Introduction

Biodegradable materials that can be efficiently and sustainably integrated into the environment are attracting attention because of the pollution problems associated with the use of synthetic plastics. Products derived from agricultural resources such as proteins, starch, cellulose, etc. are suitable alternatives for the development of biodegradable materials [1]. Starch is a biopolymer usually found in the form of granules in seeds, roots or tubers from various sources including maize, wheat, potato and rice. In nature, starch represents the main energy reserve of plants and it has been widely studied because of its abundance, low cost, edible and biodegradable properties [2,3]. Starch consists of a mixture of amylose, a predominantly linear glucan, and amylopectin, a high molecular weight and highly branched glucan [4]. Among all starches, potato starch gives the most viscous suspensions and has the lowest gelatinisation temperature. This behaviour has been ascribed to endogenous phosphate groups in the amylopectin chains, which is unique to potato starch. The phosphate groups are located in the amorphous shells of the starch granules and generate charged groups on the amylopectin chains, which makes starch susceptible to electrolytes when dissolved in water [5]. Starch is a sustainable alternative for the production of biodegradable materials for food packaging; however, starch-based films have poor mechanical properties and high stiffness, which limits their application in materials science [3]. To compensate for the poor mechanical properties of starch-based films, blending with other biopolymers such as chitosan [6], gelatin [7,8] and polyvinyl alcohol [9-13] has been studied. The combination of two or more polymers results in new materials with better mechanical properties and gas

barrier properties, which could be a viable alternative to replace existing synthetic
food packaging materials. Polyvinyl alcohol (PVA) is a biodegradable synthetic polymer produced in the largest volumes worldwide due to its excellent physical properties, chemical resistance and complete biodegradability [14]. PVA is a water-soluble, non-toxic and non-carcinogenic polymer with a linear structure. It has good compatibility with other materials, excellent film- forming ability and high emulsification and adhesion properties, which has led to a wide industrial application [10]. It is approved by the US Food and Drug Administration (FDA) and the European Medicines Agency (EMA) for human use and can be used in food packaging [15-17]. PVA films have a semi- crystalline structure resulting in lower water adsorption capacity, high tensile strength and flexibility, and good oxygen and aromatic barrier properties [10,17,18]. The introduction of PVA has been shown to improve the mechanical properties and water resistance of biodegradable packaging based on several hydrocolloids, including isolated whey protein [19] and corn starch [9,10]. Combining these biopolymers with PVA yields materials with superior mechanical properties at a lower cost than using PVA alone. Some starch-PVA blends have been developed and evaluated for biodegradable packaging applications, demonstrating excellent functional properties suitable for use as food packaging [10,20-22]. Starch and PVA are compounds with highly polar hydroxyl groups (-OH) that form intermolecular and intramolecular hydrogen bonds [9,17], which can improve the integrity of mixed films and alter their functional properties. This study was conducted to evaluate the effect of different proportions of biodegradable polymers (synthetic PVA and native potato starch) on the functional properties of their biodegradable films. Furthermore, as both polymers are hydrophilic, it is important to evaluate the ability to adsorb water as an important property when used as food packaging material. The main objective is to obtain a fully biodegradable packaging material while maintaining its physical integrity as much as possible, even in high humidity conditions. Films made from a combination of potato starch and PVA could have
better mechanical properties, parameters that are desirable for packaging material.

2. Methodology

2.1 Materials

Potato starch with crystallinity degree χ = 26.5±3.2% produced by Allegro- Species LLC, (Russia). Polyvinyl alcohol (PVA, Mw=124000-186000 g/mol ≈ 1, hydrolysis 88-92%) was obtained from SINOCHEN NANJING CORPORATION (China). Reagent glycerin CJSC "Vekton" (Russia) was used as plasticizer.

2.2 Preparation of the films

Film-forming solutions were prepared using 4% (by weight) polyvinyl alcohol and 5% (by weight) potato starch. Glycerol (25% by weight of polymers) was added as a plasticizer. PVA solution was prepared by dissolving 4 g PVA in 100 ml distilled water (w/v), the solution was heated at 70°C under stirring for 2 h. The film-forming solutions were prepared in a 500 ml flat-bottomed flask by adding distilled water, polymers and plasticizer in the amount required to prepare 100 g of each formulation, according to the data in Table 1 8 formulations were prepared.

Table 1. Composition of composite material.

Film composition based on mixtures of potato starch and PVA, plasticised with glycerine in an amount of 25% (by weight of polymers). Appropriate amount for the preparation of 100 g film-forming solution

Composite composition	*Starch to PVA ratio by mass fraction (%)*	*Potato starch (g)*	*PVA (g)*	*Glycerine (g)*
S_1P_0	100:0	5	0	1,25
S_9P_1	90:10	4,5	0,4	1,225
S_8P_2	80:20	4	0,8	1,2
S_7P_3	70:30	3,5	1,2	1,175
S_6P_4	60:40	3	1,6	1,15
S_5P_5	50:50	2,5	2	1,125
S_4P_6	40:60	2	2,4	1,1
S_0P_1	0:100	0	4	1,00

For PVA starch-based films, a potato starch solution was prepared in a flat- bottomed flask, glycerol was added to distilled water and stirred for 5 min, then the starch was added and incubated while stirring as the temperature increased. When the starch solution reached 50 °C, the appropriate amount of PVA solution was added, stirred for 10 min and the temperature was increased to 85 °C and incubated for 10 min to promote complete gelatinization of the starch granules. A vacuum pump (Primelab PL-PL1, Russia) was then used to remove the air bubbles formed in the film-forming solution. 80 g of film-forming solution was poured into 15 × 15 cm acrylic moulds and dried in an oven at 65 °C for 5 h at an air flow rate of 1 m s≈1. The biodegradable films were then cooled, cleaned and cut into suitable shapes and sizes for each characterization test. The films were incubated at 56% relative humidity for 48 h before analysis. The films were labelled SxPy where x and y represent the mass ratio of potato starch (S) to PVA (P).

3. Characteristics of the films

3.1 Thickness

The thickness of PVA starch-based biodegradable films was measured using a micrometer (Electronic Digital Outside Micrometer ST 200-521 (China), 0.001 mm accuracy). Measurements were made at ten random points on each sample. The results were expressed as mean value and standard deviation for at least 10 film samples.

3.2 Density

Films with dimensions of 2 cm × 1 cm were dried at room temperature (~25°C) for seven days on silica gel (~0% relative humidity). The density was calculated by dividing the dry weight of the film sample by the volume, which was calculated by multiplying the area and thickness. The mean value and standard deviation for 5 samples were obtained.

3.3 Microstructural analysis

The microstructure of the films was observed with a scanning electron microscope (SEM) (SEM EVO MA 10 (Carl Zeiss)) in films pre-incubated at 25°C and 53% relative humidity for 1 week (initial storage time). SEM observations were made on the surface of the films and in their cross-section. For sample preparation, the films were frozen in liquid N2 for cross-sectional observations. Two copies of each composition were fixed on gold-coated copper plugs and observed using an accelerating voltage of 2 kV at the surface (×750) and 5 kV at the cross sections (×1,500).

3.4 Solubility in water

Biodegradable potato starch-PVA films were cut into samples at 20°C and dried at room temperature (~25°C) for 7 days over silica gel to remove as much water as possible and then weighed. Film samples were placed individually in 50 mL plastic tubes with a lid and 30 mL distilled water was added. The tubes were closed and shaken periodically for 20 h at room temperature. The tube contents were filtered on dry filter paper and dried at 135 °C for 4 h to determine the dry weight. The percentage of water soluble matter was calculated using Formula 1. Five replicates were made.

Formula 1. Determining the solubility of the sample

Solubility (%) = initial dry weight − final dry weight ∗ 100
initial dry weight

3.5 Physical and mechanical properties

The physical and mechanical tests were carried out on a ZWISK tensile testing machine. To evaluate the tensile strength and modulus of elasticity of the obtained polymer mixtures we prepared samples according to STATE STANDARD 11262-80 and STATE STANDARD 9550-81. The ultimate tensile strength (TS) and percentage of relative elongation at break (% ε) of 10×90 mm specimens were calculated. Ten repetitions were measured and the values of the specimens broken in the centre of the film were taken. The mean value and standard deviation were indicated.

3.6 Thermogravimetric analysis

Samples of 5-10 mg potato starch-PVA films were used for the analysis. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a TGA DSC STA PT 1600 derivatograph (Linseis, Germany) at a heating rate of 10ºC/min. The initial, mean and final transition temperatures Tg were calculated using the tangents drawn on the displacement curve. The midpoint was regarded as the Tg of the films.

4.Results and discussion

4.1Appearance of films

The appearance of the biodegradable films made from mixtures of potato starch and PVA was homogeneous, without visible phase separation or bubbles, translucent and easily removable. In all formulations combining both polymers, good compatibility was observed during processing as well as in the resulting material. In previous studies, several authors [10,23-25] mentioned that starch and PVA are incompatible and therefore compatibilisers such as formaldehyde should be added to avoid phase separation [10, 23-25], especially when the proportion of starch exceeds 40%. However, in this study it was possible to mix potato starch with PVA according to the described procedure without visible phase separation; this result may be due to the presence of phosphate groups in the amylopectin chains of potato starch. Starches from other sources do not contain phosphate groups, so several authors have reported the use of some additives to produce a stable solution of starch and PVA [10,22,24].

Tang and Alavi [17] reported that the addition of PVA to mixtures of corn starch and glycerol prevented the formation of cracks on the surface of the films, indicating good compatibility between starch and PVA. Similarly, the use of substances that prevent the formation of air bubbles in the solution has been reported to produce homogeneous films [24]. In this study, a vacuum pump was used to extract the air bubbles generated by stirring the film-forming solutions. Vacuuming was carried out immediately before the mixed film-forming solution was poured into the mould, resulting in homogeneous biodegradable films without bubbles or cracks.

4.2 Thickness, density of the composite material.

The pure potato starch film (S1P0) showed higher thickness values than pure PVA films (S0P1), which were 182.70 × 8.31 and 109.43 × 8.69 μm respectively. Films obtained from potato starch - PVA mixtures had higher thickness values compared to those obtained with pure PVA (S0P1), which ranged from 133 to 177 μm (Table 2), intermediate values compared to those represented by starch films (S1P0).

It has been reported that film thicknesses are influenced by the composition of the composition [26]. Thickness values are lower in films whose polymer chains are more linear and higher in films with branched polymers. Considering that the starch used contains only 30 % amylose, which is linear starch chains; the rest of the starch, i.e. 70 % amylopectin, has branched chains. PVA is a linear-chain polymer, so when the film is formed, the polymer chains can be arranged in a more orderly way, reducing the thickness of the material. When mixed with starch, it increases the number of linear chains in the formulation and the thickness varies considerably in each formulation; however, the variation does not present a linear relationship to the PVA concentration. The density of films made from mixtures of potato starch: PVA was higher than both polymers alone; however, there was no significant difference with increasing proportion of PVA (Table 2), suggesting that the chains are more compactly arranged in the mixed films, which would lead to a reduction in the inter-nodal space of the polymer matrix [27].

Table 2. Mechanical properties of starch-containing film composites.
Thickness, solubility and density of the composition potato starch: PVA.

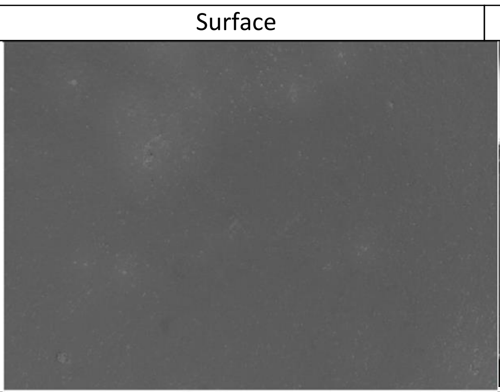
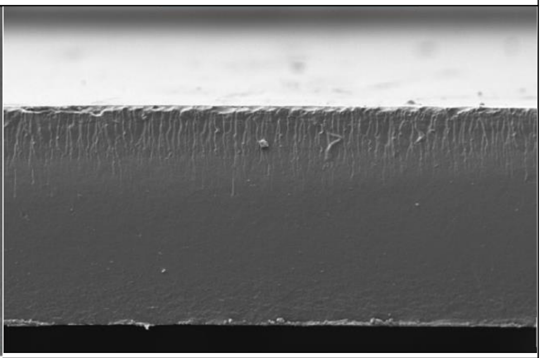
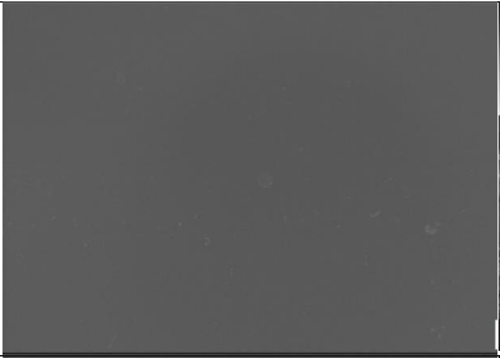
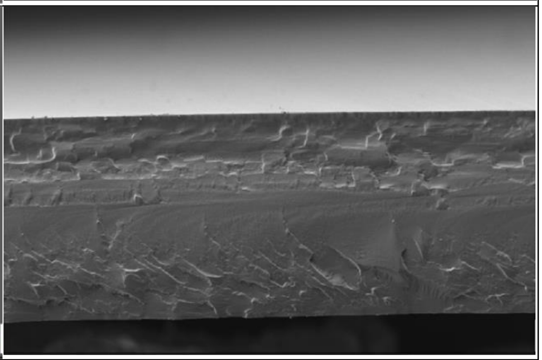
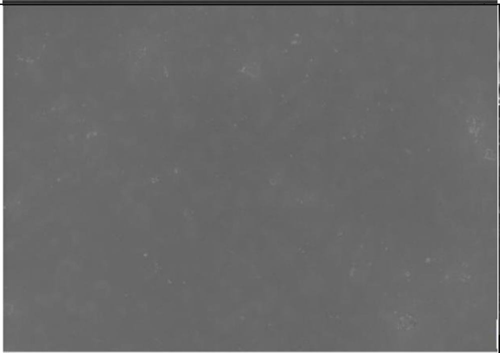
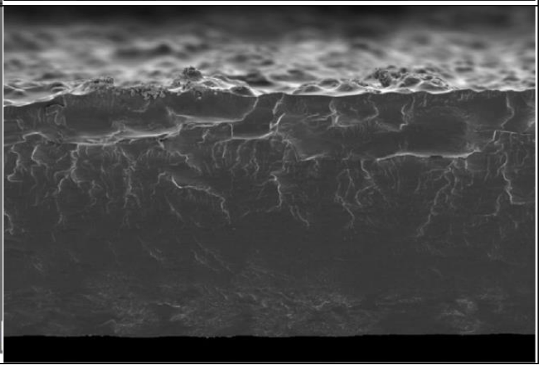
Composite composition	Thickness (m)	Density (g/cm)^3	Solubility (%)
S_1P_0	182,70±8,31	1,13±0,06	28,05±1,68
S_9P_1	162,46±8,99	1,30±0,02	32,90±0,14
S_8P_2	176,30±1,23	1,28±0,03	35,18±0,87
S_7P_3	162,77±6,70	1,24±0,04	24,88±0,62
S_6P_4	176,87±7,16	1,26±0,03	31,68±0,81
S_5P_5	166,65±8,37	1,28±0,02	29,23±2,55
S_4P_6	133,77±8,78	1,24±0,02	28,15±0,99
S_0P_1	109,43±8,69	1,12±0,01	25,24±0,49

Mean values ± standard deviation (n=3).

4.3 *Microstructure of the films*

SEM images of the surface and cross-section of S, PVA and S:PVA films are shown in **Figure 1**. Thisanalysis provides information on the surface morphology and internal microstructure of the films.

Figure 1. SEM surface (×750) and cross-section (×1,500) micrographs of potato starch, PVA andcompositefilms (S4P6).

	Surface	Cross-sectional area
Starch		
PVA		
Composition S_4P_6		

The starch films had a uniform, smooth appearance and the presence of starch granules was not detected

These results are in agreement with those obtained by several authors working on pea starch films produced by the casting method [28- 29]. In contrast, cross-sectional images showed a non-uniformly cracked layer near the film surface, indicating crystallisation progress in this area, probably related to the greater molecular mobility of water near the film surface [30]. The PVA films also had a uniformly smooth surface, which is consistent with the results obtained by other authors [31-33]. The cross section of these films showed some irregularities typical of semi- crystalline structures due to the ordered arrangement of some segments of polymer chains. In fact, it has been reported that PVS has a high degree of crystallinity (about 54%) [34]. The surface of the blended films was rougher in appearance, usually due to a certain degree of immiscibility between the polymers and the existence of two phases: the phase with the highest PVA content and the phase with the highest S content. These observations are in agreement with those found [31] which explained that starch aggregation and microphase separation between pea starch and PVA occur during film formation due to a lack of complete miscibility. Chalate C.M., [35] also confirmed the phase separation of both polymers in extruded plasticized starch/polyvinyl alcohol mixtures, but also suggested a small degree of mutual mixing.

Microphotographs of cross sections of mixed films also showed the coexistence of two phases: crystalline and amorphous, as observed for PVA films. The film thickness values were 0.087 ± 0.017 mm, 0.107 ± 0.019 mm and 0.123 ± 0.013 mm for pure S, PVA and composite films respectively. Mixed films showed higher values as can be seen from SEM observations. This result suggests that the chains in the mixture matrix were less tightly packed, resulting in a more open network, probably due to steric hindrance caused by the different polymers.

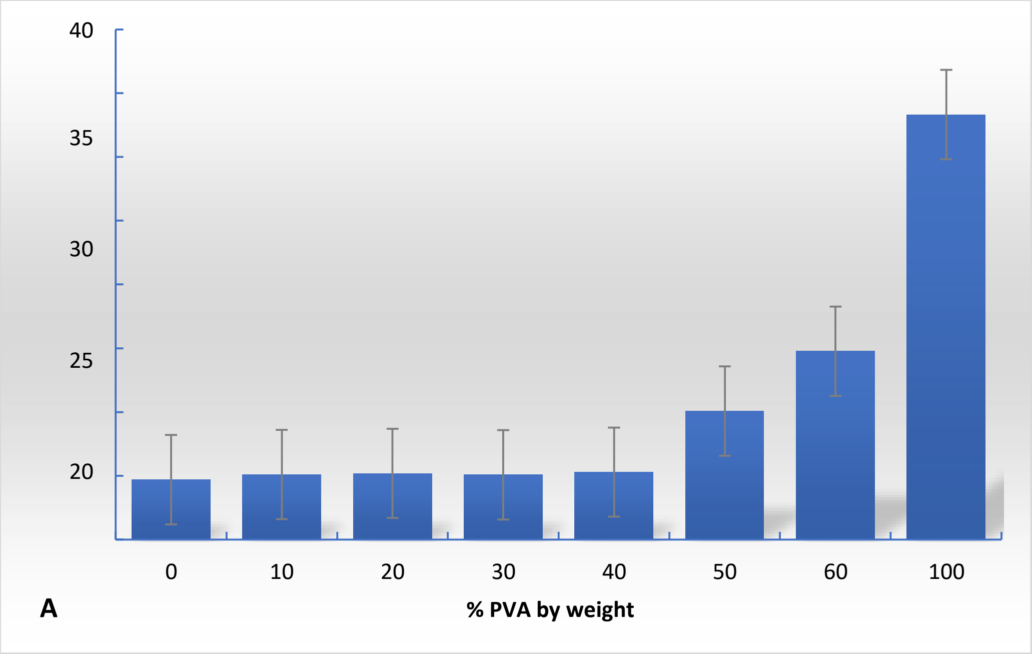
4.4 *Water solubility*

The percentage of water solubility of films made from potato starch-PVA blends was generally higher compared to pure films of each polymer (**Table 2**); thus, combining potato starch with PVA resulted in more hydrophilic films, increasing the water solubility mainly by increasing the OH-groups [9,17,36].

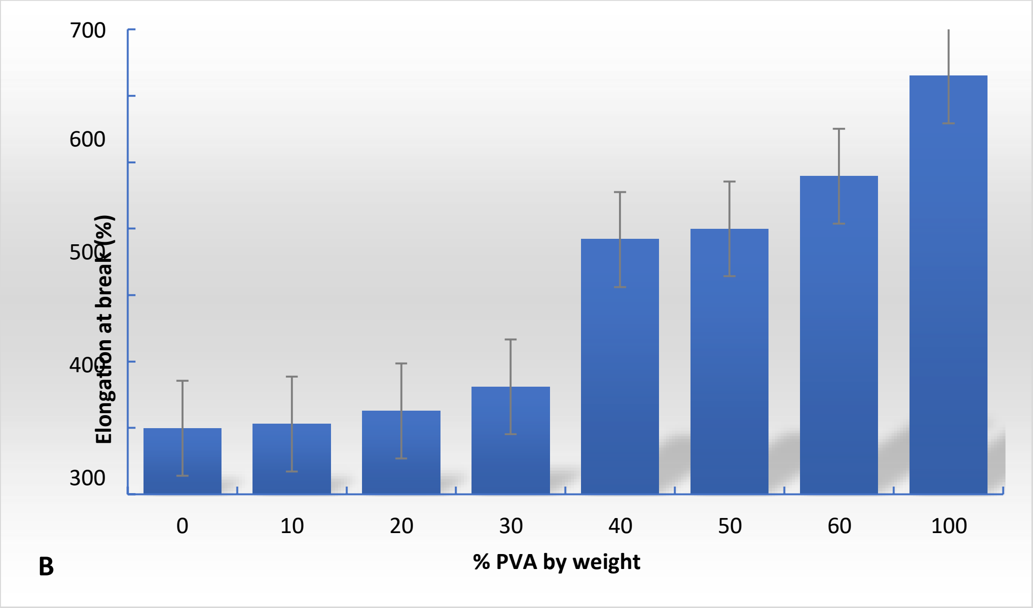
4.5 *Physical and mechanical properties*

The tensile strength (TS) and the percentage elongation at break (% ε) of the potato starch films were significantly altered with increasing proportion of PVA (**Diagram 1**) because PVA acted as a plasticizing agent. A similar effect was reported by other authors [37].

Diagram 1. Tensile strength (A), tensile strength (B).



Mechanical properties of tensile strength (TS) and percentage elongation at break (% ε) of starch films asa functionof PVA content. Mean values ± standard deviation (n=5).



The TS of films based on mixtures of potato starch and PVA significantly increased with an increasing proportion of PVA (**Diagram 1(A)**), especially at percentages above 40%, although much lower than the value observed in pure PVA films (K0P1). The mechanical behaviour is altered due to the formation of intermolecular and intramolecular hydrogen bonds, especially when the PVA fraction is less than 30% [38]. % ε changed in all proportions of PVA (**Diagram 1(B)**), increasing from 93.45 to 484.52% in S1P0 and S4P6 films respectively, although not reaching the % ε value of 630.19% found in pure PVA films (S0P1). The increase in % ε of potato starch films containing PVA may be explained by the disruption of starch crystallinity due to intermolecular hydrogen bond breaking between starch molecules and the formation of hydrogen bonds between -OH from PVA and -OH at C-2 or C-3 and O-5 ring in the glucose ring of starch [36]. Cieśla and Abramowska [39] found that the use of high-molecular-weight PVA leads to improved mechanical properties of corn starch films due to the formation of a dense cross-linked starch-PVA mesh during preparation. The opposite results are observed with low molecular weight PVA. Sufficient amounts of PVA have been reported in the literature to improve the tensile properties of corn starch-PVA-clay nanoparticle- based films [40]; however, adding more PVA to these materials resulted in poorer mechanical properties due to excessive PVA-starch interactions, which could compete with those between PVA, starch and clay surface [40]. The diffusion capacity of water molecules in a polymeric material depends on crystal peaks, which act as a barrier due to the formation of a gel-like structure that can hinder the diffusion of water molecules [41]. Han, Chen [24] reported that the use of formaldehyde to crosslink starch and PVA reduces the water adsorption capacity and gas permeability of the films by promoting inter- and intramolecular -OH group interactions, reducing the number of hydrophilic groups. In this study, it was not necessary to use a crosslinking agent because of potato starch, which naturally has phosphate groups that promote a better interaction with PVA, in addition to being a highly crosslinking starch [5].

4.6 Thermal properties

Tg values for films made from mixtures of potato starch and PVA are given in **Table 3**. Films made from pure starch (S1P0) or PVA (S0P1) showed Tg values of 17.48 or 194.83°C respectively. Thermograms of the compound with a Tg of starch and a second signal between 134.51 and 192.60°C corresponding to the Tg of PVA. Values for both signals were found in the range between Tg of pure starch films and pure PVA. Tg is a parameter related to the molecular mobility of the system and is defined as the physical change of the amorphous atoms in the material causedby heating.

Table 3. Tg films consisting of potato starch:PVA

Composite composition	**Thermal properties**	
	Tg starch (°C)	**Tg PVS (°C)**
S_1P_0	17,48	-
S_9P_1	31,25	137,72
S_8P_2	31,53	137,79
S_7P_3	34,79	134,51
S_6P_4	37,97	143,64
S_5P_5	38,97	178,60
S_4P_6	37,52	192,60
S_0P_1	-	194,83

Mean values ± standard deviation (n=3).

Polymers with Tg above the final temperature of packaged food products have improved barrier properties [42]. The incorporation of PVA into potato starch films significantly improved the thermal properties, suggesting thatthe increase in PVA resulted in a material with a more ordered internal structure, which explains the increase in temperature required to loosen the structural matrix of films made from potato starch:PVA blends. These results are in agreement with those obtained by Sin, Rahman [38] for films made from mixtures of PVA and cassava starch. TheK4P6 film showed a Tg of 192.6 °C, which is very close to the value obtained for pure PVA film, suggesting that the addition of 40% starch does not affect the thermal performance of PVA films. This behaviour is important as it would be possible to produce films that are very similar to pure PVA films, but which significantly reduce the production cost of these packaging materials while retaining their functional properties.

The polythermal behaviour of the composite films of both compositions differs little. According to DTA andTGA data in the temperature range up to 100- 120°C dehydration of the samples is observed. The mass loss in this case is 8-10%, which is consistent with the moisture content of air-dry films (see Table 1). The endothermic melting peak on the DTA curves is realized in the range of 120-150°C. With a further increase in temperature the melting process is superimposed on the thermal decomposition of the sample. When reaching 200°C the mass of the compositedecreases by ~30%. In the interval of 200-400°C the process of thermal degradation continues to develop and when reaching 400°C the mass loss is ~85 wt.%. Complete thermal degradation of the sample is realized in the range of 400- 600°C.

1. Conclusions

The films obtained from different mixtures of potato starch and PVA showed good mechanical properties compared to films made from pure starch. The addition of synthetic polymer PVA significantly improved the mechanical properties. The biodegradable films made from mixtures of potato starch and PVA had a homogeneous appearance without phase separation due to the presence of phosphate groups in the potato starch.

Films containing 60% (wt./wt.) PVA showed the best TS and % ε values, and thermal performance. As PVA is a more expensive polymer than potato starch, 60% (wt.%) was set as the maximum limit for addition in order to obtain a material with improved mechanical properties at low cost; however, regardless of the economic problem, it would be interesting to investigate the behaviour of starch films with higher PVA content. Furthermore, casting was an efficient, simple and economical method to obtain biodegradable films from starch and PVA mixtures, allowing for superior physical properties with potential applications in food packaging.

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