Polímeros
ISSN 1678-5169 (Online)

https://doi.org/10.1590/0104-1428.20240103

ORIGINAL ARTICLES

Physico-mechanical and structural characterization of polyethylene films and thermoplastic pinto bean starch

Tomás Jesús Madera-Santana[1], Anabell Espinoza Verdugo[2], Víctor Rejón-Moo[3] and Judith Fortiz Hernández[1]*

[1]Coordinación de Alimentos de Origen Vegetal, Centro de Investigación en Alimentación y Desarrollo A.C., Hermosillo, Sonora, México

[2]División Académica, Universidad Tecnológica de Etchojoa, Etchojoa, Sonora, México

[3]Laboratorio Nacional de Nano y Biomateriales, Centro de Investigación y de Estudios Avanzados del IPN, Mérida, Yucatán, México

**jfortiz@ciad.mx*

Abstract

Starch is a biopolymer that is abundant in nature, low-cost, biodegradable, and can be transformed into a thermoplastic material. This work evaluates the films' physicochemical, thermal, and mechanical properties based on low-density polyethylene (LDPE) and thermoplastic starch (TPS) from beans. Films of four formulations of LDPE with TPS (0, 5, 10, and 15%) were formulated by the extrusion process. The films were evaluated for thickness, color, mechanical properties (tensile strength, Young's modulus, elongation at break), barrier, and morphological properties. The barrier properties (WVTR and WVP) significantly increased when TPS was incorporated into the films. While the tensile strength and Young's modulus did not present changes with the addition of TPS, the elongation at break increased from 204.14 to 343.81% with the addition of TPS. Adding TPS to an LDPE matrix modifies its physico-mechanical properties favorably so that it can be applied as a material for flexible packaging.

Keywords: *thermoplastic starch, LDPE, blown-extrusion, films, physicochemical properties.*

How to cite: Madera-Santana, T. J., Verdugo, A. E., Rejón-Moo, V., & Hernández, J. F. (2025). Physico-mechanical and structural characterization of polyethylene films and thermoplastic pinto bean starch. *Polímeros: Ciência e Tecnologia*, *35*(2), e20250018. https://doi.org/10.1590/0104-1428.20240103

1. Introduction

Petroleum-based packaging materials are non-degradable and affect the environment. Biopolymers are considered the solution for replacing synthetic plastics, although they have similar characteristics; they possess a short biodegradation time, good biocompatibility with other materials, and high availability[1,2]. Starch is a natural, inexpensive, and abundantly obtained polymer with a good cost-benefit ratio and film-forming properties[3]. Starch is composed of amylose units (~25%) and amylopectin (~75%). The shape and size of the starch granule, and the amylose/amylopectin content and ratio vary according to botanical origin and species. Starch contents have been reported for sorghum (61 to 71%), sweet potato (45 to 67%), common bean (22 to 45%), and maize (70 to 75%)[4]. However, the use of native starch in film formation has some disadvantages, such as low hydrophobicity and mechanical and barrier properties, with limited applications[5]. Developing and producing thermoplastic starch (TPS) could be an alternative for developing new materials of biodegradable products. Developing biodegradable thermoplastic starch (TPS) is considered important in reducing the total amount of synthetic plastic waste in the world. TPS has several attributes; in addition to its biodegradability, it is a renewable and flexible material and can be conditioned to different thermoplasticization processes using standard equipment in the manufacture, such as injection molding, blow extrusion, and 3D-printing[6]. TPS research in the development of biodegradable bioplastics is focused on the origin of starch, characteristics, and uses of starches, the plasticization process and properties, and mixtures for developing of new materials. TPS is a material obtained from structural modification (disruption) that occurs in starch granules processed with low water content and when thermal and mechanical forces are applied in the presence of plasticizers[2,6]. The possibility of transforming native starch into thermoplastic starch (TPS) has shown considerable interest[7]. The properties of starch-based bioplastics are directly a result of the amylose–amylopectin ratio within the total starch content of a starch material. Thus, one of the most viable strategies for improving starch-based bioplastics' properties is altering the molecular structure, ratio, and interactions of amylose and amylopectin within the polymeric matrix. Thermoplastic extrusion is a high-temperature, high-pressure, and high-shear process[5]. However, it is a material with hydrophilic characteristics, and its mechanical properties vary as a function of moisture. The inherent hydrophilicity and high

starch density (1400 kg/m^3) lead to quite hygroscopic and brittle materials, thus limiting their application range[8]. TPS has good oxygen barrier properties but is susceptible to humidity, exhibiting rapid biodegradation and sticky behavior during blown film extrusion[9]. One strategy to improve TPS's properties is using plasticizers and making blends with other polymers[10]. Plasticizers are generally small molecules of polyols (sorbitol and glycerol) that are cross-linked and inserted between polymer chains[11]. They are added to the polymers to improve the flexibility and extensibility of the film. Glycerol is one of the most effective plasticizers because it has certain advantages, such as being low-cost and a compound recognized as safe for health (GRAS). TPS has several attributes besides being a biodegradable, renewable, and flexible material that can be thermoplasticized using standard equipment for synthetic polymer processing[6]. Prachayawarakorn et al.[7] reported the fabrication of composite films of mung bean starch, cotton fiber, and low-density polyethylene; they observed an increase in maximum stress, Young's modulus, and water absorption. García-Guzmán et al.[2] reported that the incorporation of glycerol improves the flexibility of the edible coating and reduces film puncture resistance, elasticity, and water vapor barrier properties in films made with wheat gluten. Hydrophobic functional groups in modified starch increase compatibility between TPS and low-density polyethylene (LDPE), leading to a more homogeneous starch in the LDPE matrix[9]. Starch from various sources has been studied as TPS, including corn, potato, wheat, and rice[7]. The films cast from cereal and root starches have been broadly developed and studied for their properties. Nonetheless, the studies on films produced from legume starches are uncommonly limited. Thermoplastic starch prepared from pinto bean starch has not yet been reported. This study aimed to investigate the optical, mechanical, barrier, and thermal properties of films made from bean starch. TPS formulations (0, 5, 10, and 15% by weight) and polyethylene (LDPE) were processed by blown film extrusion. To evaluate if adding TPS in an LDPE matrix modifies its physico-mechanical properties favorably to provide a feasible application as a material for flexible packaging.

2. Materials and Methods

2.1 Materials

Native pinto bean (*Phaseolus vulgaris*) starch (moisture content 8%, fat 0.112%, protein 0.84%, and ash 0.26%) was obtained by an aqueous extraction process. Glycerol and acetic acid (98%) were obtained at Laboratory Reasol (Mexico City, Mexico). Low-density polyethylene (LDPE) Certene grade 4 resin was used (Houston, TX, USA).

2.2 Methods

2.2.1 Starch characterization

Proximal analysis of pinto bean starch included moisture, ash, protein, ethereal extract, and nitrogen-free extract. The proximate composition was performed using the methods of the AOAC International[12]. The starch characterization was measured in three samples prepared at the same conditions.

Apparent amylose. The apparent amylose content of starch was determined by McGrance et al. methodology[13] in combination with the technique of Barraza-Jauregui et al. [14], with slight modifications. The absorbance of the blue color produced in amylose solutions of the tri-iodide ion was measured as an indicator of the linear fraction present in the solution. 25 mg of the starch sample was dissolved in 10 mL of 6 M urea (JT Baker, Mexico), 2 mL of 90% dimethyl sulfoxide (DMSO) (Sigma-Aldrich, USA) was added, and the mixture was stirred for 20 min. The absorbance was read at 635 nm in a Varian UV-visible spectrophotometer model Cary 50Bio (New London, USA). Quantification was measured with an amylose curve (Sigma-Aldrich, USA). Amylose content was expressed as a percentage.

Water absorption capacity (WAC). The WAC of bean starch was determined using the methodology of Sindhu et al.[15]. Suspensions of 5% starch in 40 mL of distilled water were prepared, left to stand for 40 min with shaking every 10 min, and centrifuged (Thermo Scientific™ ST) for 25 min at 3250 rpm. The supernatant was discarded, and the sediment was weighted to determine the WAC using Equation 1. The test was performed in triplicate:

$$\mathbf{WAC}(\%) = \frac{\mathbf{sediment\ weight\ (g) - initial\ sample\ weight\ (g)}}{\mathbf{initial\ sample\ weight\ (g)}} \mathbf{x}100 \quad (1)$$

Solubility index and swelling power. The starch solubility index (SI) and swelling power (SP) were determined using the method of Martinez et al.[16] with some modifications. Specifically, 1% starch suspensions were prepared in 40 mL of distilled water and heated in a water bath (Ecoline Staredit. LAUDA® E100) at 60 °C, 70 °C, and 80 °C for 30 min. Then, it was cooled to 25 °C and centrifuged (Thermo Scientific™ Sorvall ST 8) at 4000 rpm for 50 min. The supernatant was discarded, while the gel formed was recovered and dried at 60 °C for 20 h to determine the SI (Equation 2) and SP (Equation 3):

$$\%\mathbf{SI} = \frac{\mathbf{dry\ gel\ weight\ (g)}}{\mathbf{initial\ sample\ weight\ (g)}} \mathbf{x}100 \quad (2)$$

$$\mathbf{SP}\left(\frac{\mathbf{g\ water}}{\mathbf{g\ dry\ sample}}\right) = \frac{\mathbf{wet\ gel\ weight\ (g)}}{\mathbf{weight\ initial\ sample\ (g) - dry\ gel\ weight\ (g)}} \quad (3)$$

The whiteness index (IB*) of starch was calculated according to Sindhu et al.[15], and was calculated using Equation 4:

$$[\mathrm{IB}] = \sqrt{[100 - (100 - L)^2 + a^2 + b^2]} \quad (4)$$

2.2.2 Preparation of thermoplastic starch

The preparation of thermoplastic starch (TPS) was produced by the addition of bean starch (70%) and glycerol (30%); it was also produced by extrusion. The TPS filament was processed in a Beutelespacher (Mexico City, Mexico) 25:1 l/d single-screw extruder, which was subsequently cut in a Beutelespacher Pelletizer (Mexico City, Mexico). To produce the TPS the extrusion conditions of the equipment were zone 1: 80 °C, zone 2: 100 °C, die zone 120 °C, screw speed 50 rpm, and torque of 5 Nm.

2.2.3 Processing of LDPE-TPS films

The blown film extrusion was used to produce the LDPE-TPS; for this purpose, several TPS formulations were made with 0% TPS (TPS0 or LDPE), 5% (TPS5), 10% (TPS10), and 15% (TPS15) by weight and mixed with LDPE resin. The extrusion conditions were temperature zone 1: 100 °C, zone 2: 120 °C, zone 3: 140 °C, die zone 150 °C, screw speed 50 rpm, and torque of 4 Nm.

2.2.4 Characterization of the films

The thickness, optical, barrier, mechanical, thermal, and properties of the films were measured to evaluate the effect of the addition of TPS on the properties of LDPE films.

Films thickness. The thickness of the films was measured using a micrometer (Mitutoyo MDC-1 SB, Japan) at five different points, and their average value was calculated.

Optical properties of films. The color determination of the films was determined using a colorimeter, the Chroma Meter (Minolta CR300, Japan), calibrated to a standard (Y: 94.1, X: 0.3155, y: 0.3319). From the parameters L^*, a^*, and b^*, the parameters of hue angle (°Hue), chromaticity (C^*), and color difference (ΔE^*) were evaluated. Measurements were recorded at three specific points on the film, and an average of the measurements was reported for each formulation. The equation for calculating hue angle (°*Hue*) was Equation 5:

$$°Hue = \arctan\left(\frac{b^*}{a^*}\right) \tag{5}$$

Equation 6 was used to determine the chromaticity (C^*):

$$C^* = \left(a^{*2} + b^{*2}\right)^{1/2} \tag{6}$$

The color difference (ΔE) of each film was compared between the TPS0 formulation and other formulations (5-15%) and calculated using Equation 7:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \tag{7}$$

where $\Delta L = L\text{-}L_0$, $\Delta a = a\text{-}a_0$, $\Delta b = b\text{-}b_0$. The L^*, a^*, and b^* parameters are the chromatic values of the simple, and L_0, a_0, and b_0 represent the control chromatic values (TPS0).

Transparency. The transparency measurement was performed according to the methodology established by Escárcega-Galaz et al.[17]. Rectangular samples (3x1 cm) were made and placed inside a spectrophotometric cell. The absorbance readings were determined at 600 nm in a UV-Vis spectrophotometer Varian Cary 50 Bio. Transparency was calculated using the following Equation 8:

$$Transparency = \frac{A_{600}}{T} \tag{8}$$

where A_{600} is the recorded absorbance value at 600 nm, and T represents the average thickness of the film in mm. The transparency of the films was analyzed, and the average value of two replicates was reported for each formulation.

Barrier properties. Water vapor transmission rate (WVTR) was performed according to the ASTM E96 method[18] with slight modifications. For this purpose, a plastic container with deionized water (30 mL) was sealed with a lid containing the sample firmly fixed on its top. The container was stored at 25 °C and 30% RH in a desiccator with dry silica. The assay was performed in triplicate for each sample, and the container weight was recorded periodically for 30 h. WVTR was calculated from the slope of the straight line, where time (h) vs. weight difference (g) was plotted using Equation 9.

$$WVTR = \frac{w}{t.\ A} \tag{9}$$

where w is the weight loss of the container in g, t is the time in h, and A corresponds to the permeation area in m^2.

Water Vapor Permeability (WVP). The determination of WVP was calculated from the WVTR and using Equation 10.

$$WVP = \frac{WVTR * l}{P} \tag{10}$$

where l is the average thickness of the film in m and ΔP corresponds to the difference in water vapor pressure on the internal and external sides of the container where the film sample is located.

Mechanical properties. The mechanical properties of the films were measured using the texture analyzer TA-XT plus texture (Surrey, UK) according to the ASTM D882-02 procedure[19]. Rectangular samples (10x60 mm) were obtained, and the thickness of each film was measured in triplicate. The separation distance of 30 mm was set, and a 10 mm/min crosshead speed was programmed. The tensile strength (σ), elongation at break, and Young's modulus (E) were calculated. The tensile parameters were reported on an average of six replicates per film.

Structural properties. The films were characterized by infrared (IR) spectroscopy using a spectrometer Thermo Scientific™ Nicolet iS-50 FT-IR (Madison, WI, USA.) coupled to a universal crystal diamond of attenuated total reflectance (ATR) attachment. Spectra were recorded from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}, a scan rate of 0.475 cm^{-1}/s, and 100 scans.

Thermal properties. Thermogravimetric analysis (TGA) of the films was performed using Perkin Elmer's TGA-8000 equipment (Boston, MA, USA). The temperature range was from room temperature (25 °C) to 700 °C, at a heating rate of 10 °C/min under a nitrogen atmosphere.

Morphological analysis. A Field Emission Scanning Electron Microscope (FE-SEM) JEOL JSM-7600F (Peabody, MA, USA) was used to examine the films' surface morphology. The samples were previously fixed in aluminum tubular cells using double-sided carbon adhesive tape. A thin Au/Pd composite layer was applied to them using a Quorum model QI5OR-EN sputtering device (Sussex, UK). The surface section micrographs were taken at 200 μm scales and 150X magnification.

2.2.5 Experimental design and data analysis

Data were analyzed by one-way analysis of variance (ANOVA). When there was significance, Tukey's multiple range test compared means with a significance level of $p \leq 0.05$. All data were processed in NCSS-9 Statistical Software 2017 (Kaysville, UT, USA).

3. Results and Discussions

3.1 Characterization of bean starch

The characterization of native bean starch was carried out to determine the characteristics of the raw material. This starch presented 7.92% moisture, 0.11% fat, 0.84% protein, 0.26% ash, and 23.87% apparent amylose (Table 1). It has been reported that the type of starch (wheat, corn, potato, etc.) influences the physical and chemical properties of the processed films. In addition, their amylose/amylopectin ratio can influence their thickness, color, moisture, thermal, and mechanical properties[4]. Starches with higher amylose content have lower wettability properties and better mechanical strength, which is highly dependent on water content due to the hydrophilic nature of starch films. The linear structure of amylose promotes the formation of hydrogen bridges between the chains of the structure compared to the branched structure of amylopectin. In this work, the amylose content of bean starch was 23.87%, which indicates a normal value (20-35%) according to its amylose content (waxy (<15%), normal (20-35%) and high (>40%) reported by Goncalves et al.[8]. Similar values have been reported by Basiak et al.[5] have reported the 27, 25, and 20% amylose values for corn, wheat, and potato starch, respectively. However, this value was lower than that reported by Hoover et al.[20] for mung bean starch with an apparent amylose content of 39.8%.

Starch color. Starch color is an important parameter in determining the application of food starches because it can give brightness or opacity to the final product. Starch color had an average brightness (L^*) of 46.73 (Table 2). Barraza-Jauregui et al.[14] reported higher luminosity values with values of 90 in potato starches. The °Hue value was 76.37, and the *Chroma* value was 29.57 since it presented a slightly yellow tone. While the whiteness index had a value of 71.30, higher values were reported by Sindhu et al.[15] in wheat starch (buckwheat), with a value of 97.8. Whiteness index values greater than 90 have been reported in potato starch[12].

Solubility index and swelling power. The solubility index and swelling power of bean starch were shown to be directly related to the increasing temperature of gel preparation, as reported by Martinez et al.[16] in 9 potato starch varieties. Table 3 shows the highest solubility index at 80 °C and the highest swelling power. Solubility increased its values from 13.34 to 16.80 (g water/g starch) when the heating temperature increased from 60 °C to 80 °C. The same behavior was observed in the swelling power of starch, where an increase from 1.35 to 5.60 (g water/g starch), respectively, was presented when it was from 60 °C to 80 °C. Barraza-Jauregui et al.[14] mentioned that the higher starch solubility can be attributed to a higher solubilization of starch granules with weaker rigidity when heated at high temperatures.

On the other hand, water absorption capacity is a property that indicates the starch's ability to interact with water and form pastes and gels, which is an important use in the food industry. It has been reported that starches that have high water absorption capacity are used as thickening agents. A water absorption capacity of 102.38% (1.0238 g/g) was presented for bean starch (Table 3). Montoya-Anaya et al.[21] reported similar values for potato starch (101.63%). In this sense, this property is influenced by starch type and granule size (small granules require more water than large granules). Martinez et al.[16] reported that the water absorption capacity is due to the presence of hydrophilic groups that retain water.

Table 1. Physicochemical characteristics of native beans starch.

Parameters	Value (% wt. d.b.)
Moisture	7.92 ± 0.3
Ash	0.26 ± 0.04
Ether extract	0.11 ± 0.02
Protein	0.84 ± 0.17

d.b. = dry basis. Average ± standard deviation, n = 3.

Table 2. Color parameters (L^*, °Hue, and *Chroma*) of native beans starch.

Parameters	Value
L^*	46.73 ± 2.17
°Hue	76.37 ± 0.90
Chroma	29.57 ± 2.54
Whiteness index	71.30 ± 3.50

Average ± standard deviation, n = 3.

Table 3. Solubility index (SI), swelling power (SP), and water absorption capacity (WAC) of native beans starch.

Temperature (°C)	SI (g water/g starch)	SP (g water/g starch)
60	13.34 ± 1.82[a]	1.35 ± 0.09[a]
70	12.54 ± 1.32[a]	1.40 ± 0.29[a]
80	16.80 ± 0.44[b]	5.60 ± 0.18[b]
WAC (%)	102.38 ± 4.08	

Mean values ± standard deviation are reported for each treatment. Different letters in the same column indicate a signific ant difference ($p<0.05$).

3.2 Characterization of the films

An increase in the thickness of the films was observed as the TPS0 to TPS15 content increased, with values ranging from 1.62 to 3.76 mils (Table 4); this behavior was also reported for LDPE and TPS from potato starch films[21]. Basiak et al.[5] mentioned that the type of starch influences the optical properties and thickness of the films, i.e., potato starch films are more transparent than corn and wheat starch films; they are opalescent. Also, the color parameter values are dependent on the film thickness. The greater the thickness, the opaquer the films appear. They mentioned that the films were more opalescent and had a higher thickness. In contrast, the films were more transparent and thinner with lower starch content. They also reported 2.18, 2.91, and 4.41 mils thickness for potato, wheat, and corn starch films. The color of the formulated films presented similar values in luminosity (L^*), as shown in Table 4. Likewise, they presented differences in the values of a^* and b^* concerning the control film (TPS0) or LDPE. An increase in the color difference (ΔE^*) from 1.31 to 4.83 was also observed when increasing the content of TPS (5 to 15%) with respect to the TPS0 film. Another optical property is transparency (Table 4). The TPS0 y TPS5 films were more transparent than the films that were added to the TPS. Meanwhile, the films

Table 4. Color parameters (L^*, °Hue, and ΔE) and transparency of LDPE-TPS films.

Formulation	Thickness (mils)	L^*	°Hue	ΔE	*Transparency*
TPS0	1.62 ± 0.02[a]	91.53 ± 0.54[a]	138.7 ± 2.01[c]	0	0.894 ± 0.02
TPS5	2.86 ± 0.06[b]	90.62 ± 0.44[a]	33.11 ± 1.75[b]	1.31 ± 0.72[a]	0.712 ± 0.02
TPS10	3.03 ± 0.03[b]	90.49 ± 1.35[a]	31.53 ± 1.48[b]	2.62 ± 0.82[b]	0.651 ± 0.01
TPS15	3.76 ± 0.13[b]	88.88 ± 0.87[b]	12.61 ± 1.65[a]	4.83 ± 0.97[c]	0.627 ± 0.04

Different letters in the same column indicate a significant difference (p<0.05).

with thermoplastic starch were less transparent and slightly yellow. It coincides with what Basiak et al. reported[5], who mentioned that the films' color depends on their thickness; the thinner the films, the more transparent, and the thicker films are more opaque.

Mechanical properties. The mechanical properties of the formulated films did not show significant changes (p>0.05) with the addition of TPS in the tensile strength and Young's modulus (E) concerning the TPS0 or LDPE film. However, there was an increase in elongation at break, with values ranging from 204 to 343% (Table 5). These values agree with those of other authors, who report values for tensile strength from 3 to 10 MPa, Young's modulus from 5 to 106 MPa, and elongation at break for wheat, corn, and potato starch films[4]. These results indicate that the TPS15 film increased tensile strength, which could indicate a good interaction between the polymeric matrix chains and thermoplastic starch. On the other hand, the TPS15 film showed a significant increase in the average elongation at break value (p<0.05), showing greater flexibility in the film of this formulation. This result is corroborated by the decrease in the average value of Young's modulus presented by this film, although it was not significant (p>0.05). These values indicate that the TPS15 film presented good mechanical properties and could be used as a container and biodegradable agent. The incorporation of 7:3 cotton fiber/LDPE improves the mechanical properties (Young's modulus and tensile strength) of thermoplastic starch from mug beans (TPMBS) [7]. According to Ballesteros-Martínez et al.[11], an increase in the concentration of plasticizers, such as glycerol or sorbitol, provide an increase in water solubility, elongation, and water permeability from tested films. Moreover, starch with high amylose content is responsible for the film forming and produce stiff and strong films[10].

Water vapor transmission rate (WVTR) and water vapor permeability (WVP). The WVTR, permeance, and WVP of the films showed a significant increase (p<0.05) with the addition of TPS from 5 to 15%, with respect to the TPS0 film (Table 6). The WVTR rose from 4.21 to 10.17 g/m²·h, and the permeance rose from 0.273 to 0.517 g/m²·h·mm·Hg. WVP increased from 0.00027 to 0.00099 g/m·d·mm·Hg. Similar WVTR values were reported by Montoya-Anaya et al.[21] in potato starch films with TPS (0 to 20%) and polyethylene formulations, there was an increase in WVTR from 4.21 to 10.64 g/h·m². Basiak et al.[5] reported that potato starch films constitute a high barrier to oxygen and water vapor; however, they have lower mechanical properties than wheat and corn starch films. Panrong et al.[9] reported that the WVP of the films increased with higher TPS content due to the increased hydrophilicity of starch-glycerol components and the non-homogeneous structure of these matrices. The WVP of films is influenced by the diffusivity and solubility of water molecules in the polymer matrix[6]. In films without plasticizers, microcracks or porosities may form that facilitate the release of water vapor, allowing it to equalize or even exceed the WVP values of plasticized films[10].

Table 5. Mechanical properties of LDPE-TPS films.

Formulation	Tensile strength	Elongation at break	Young's modulus
	(MPa)	(%)	(MPa)
TPS0	10.54 ± 3.0[a]	204.14 ± 51.4[a]	117.7 ± 61.8[a]
TPS5	10.82 ± 1.6[a]	304.96 ± 58.9[ab]	128.8 ± 88.3[a]
TPS10	13.16 ± 5.6[a]	297.40 ± 47.3[ab]	122.5 ± 53.5[a]
TPS15	14.32 ± 4.3[a]	343.81 ± 57.4[b]	91.27 ± 38.1[a]

Mean values ± standard deviation are reported for each treatment. Different letters in the same column indicate a significant difference (p<0.05).

Table 6. WVTR, permeance, and WVP of LDPE-TPS films.

Formulation	WVTR	Permeance	WVP
	(g/m²·h)	(g/m²·h·mm·Hg)	(g/m·d·mm·Hg)
TPS0	4.21 ± 0.3 [a]	0.273 ± 0.2 [a]	0.00027 [a]
TPS5	8.42 ± 1.0 [b]	0.556 ± 0.5 [b]	0.00097 [b]
TPS10	8.07 ± 0.6 [b]	0.501 ± 0.5 [b]	0.00092 [b]
TPS15	10.17 ± 2.7 [b]	0.517 ± 0.5 [b]	0.00099 [b]

Mean values ± standard deviation are reported for each treatment. Different letters in the same column indicate a significant difference (p<0.05).

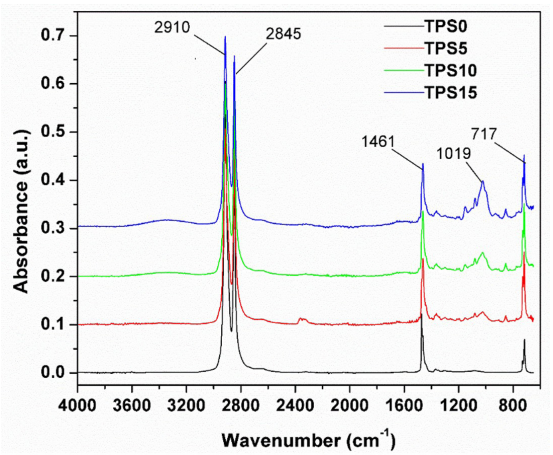

Figure 1. Infrared spectroscopy of LDPE-TPS films.

Infrared spectroscopy (FTIR). FTIR analysis shows bands of glucose rings and their bonds, one of the main components of amylose and amylopectin of starch (Figure 1). There are slight differences in the spectra of the TPS5, TPS10, and

TPS15 films compared to the spectrum of the TPS0 film. TPS5, TPS10, and TPS15 films showed absorption bands between 3000 and 2750 cm^{-1} related to the stretching bonds of methyl groups (C-H). In addition, a signal is observed at 2910 cm^{-1}, corresponding to the asymmetric stretching of methylene groups (-CH_2). The incorporation of thermoplastic starch into the film shows an increase in the intensity of the absorption band at 1019 cm^{-1}. This change in intensity is related to the interactions that develop and the miscibility of the mixture of this biopolymer into the LDPE matrix. The band between 990 and 1082 cm^{-1} could be attributed to C-O stretching and vibration of a functional of C-C and C-O-H. These absorption bands are more similar to those reported by other researchers[7]. Finally, the 760 cm^{-1} bands may be related to the C-O-C stretching of the glucose ring, as reported by Montoya-Anaya et al.[21]. Basiak et al.[5] mentioned that the addition of LDPE in the films with a TPS content between 0 to 20%, reduced the interactions with the O-H groups of the starch matrix.

Thermogravimetric analysis. In the thermogravimetric analysis of TPS films, decomposition occurs in the thermal stages of the samples (Figure 2). The sample presents three significant weight losses. The first stage corresponds to the loss of moisture present in the sample (5.5-10%) occurring at a temperature around 100 °C. The second phase corresponds to the decomposition of carbohydrates, which is when these compounds decompose between 300 °C and 445 °C, corresponding to 80% of the total weight of the sample. Other authors say the thermal degradation of the starch is at 260 °C[7]. Basiak et al.[5] reported for wheat, corn, and potato starch that the second stage ranges from 120 °C to 270 °C, which is related to the depolymerization and evaporation of glycerol (boiling point 180 °C). The volatile products of decomposition in this stage would be mainly water, CO, and CO_2. The third stage ranges from 400 °C to 525 °C, corresponding to the thermal degradation of the starch structure, such as the glycosidic ring. Prachayawarakorn et al.[7] reported four stages of degradation of thermoplastic rice starch (LDPE:starch) and a weight loss of 52%, while for the rice starch-glycerol mixture, they only reported two stages of degradation.

The thermogravimetric analysis establishes possible applications and provides information on the materials' thermal behavior (stability) and composition. Villada et al.[22] mentioned that one problem with using TPS in addition to bioplastics is its brittle nature, which is caused by starch's relatively low glass transition temperature (Tg).

Morphological analysis. Figure 3 shows the micrographs of the surface morphology of LDPE-TPS films obtained by scanning electron microscopy (SEM). The pure LDPE matrix (TPS0) presents a smooth and homogeneous surface (Figure 3a). The micrographs shown in Figures 3b, 3c, and 3d correspond to the surface morphology of the films corresponding to formulations TPS5, TPS10, and TPS15, respectively. It can be observed that as the TPS content of the LDPE matrix increases, an increase in the amount of TPS particles is observed, which are uniformly and homogeneously distributed in films. It is important to note that the LDPE matrix coats the TPS5 and TPS 10 formulations present TPS particles, but these. The micrograph of the TPS15 formulation shows a more significant number of particles on the film's surface, and it can be seen that these only adhere to the matrix.

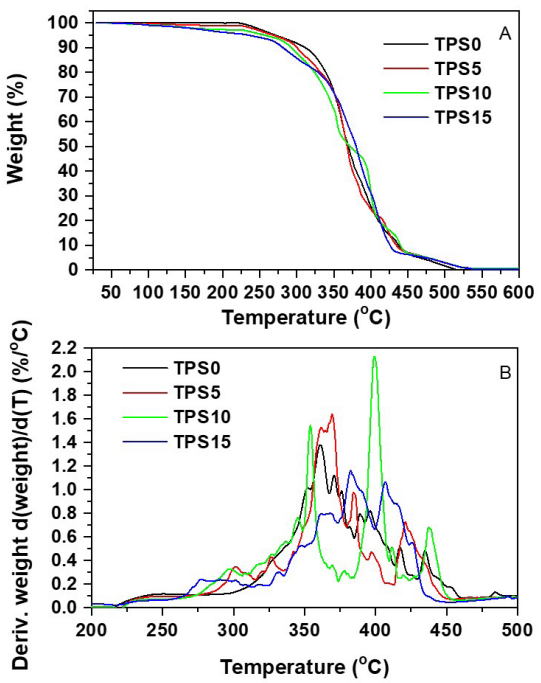

Figure 2. Thermograms of TGA (a) and DTG thermograms (b) of LDPE-TPS films.

4. Conclusions

Adding TPS from pinto beans into LDPE films was possible to formulate and obtain by extrusion-blowing. The solubility and swelling power of bean starch showed an increase with the increasing temperature of gel preparation when the heating temperature increased from 60 °C to 80 °C. The color of TPS films with bean starch was transparent with a slight yellow coloration. The films made with TPS (5, 10, and 15%) presented the highest WTVR, permeance, and WVP values. The mechanical properties of the formulated films did not show significant changes when TPS was added; the tensile strength and Young´s modulus were similar to the control film (TPS0). However, films with TPS showed an increase in elongation at break, indicating that the film became flexible, a characteristic corroborated by the average value of the modulus of elasticity. FTIR analysis shows bands of glucose rings and their bonds, one of the main components of amylose and amylopectin of starch. Several authors have reported the addition of TPS from different resources (potato, wheat, rice, etc.) into the LDPE matrix to produce blow films. The morphological analysis allowed us to observe the uniform and homogeneous distributions of the TPS in the LDPE matrix. The above results suggest that adding TPS from pinto beans into LDPE films could be used as a material for flexible packaging (bioplastic films). In addition, it could be considered that starch extracted from pinto beans could be a source for TPS elaboration.

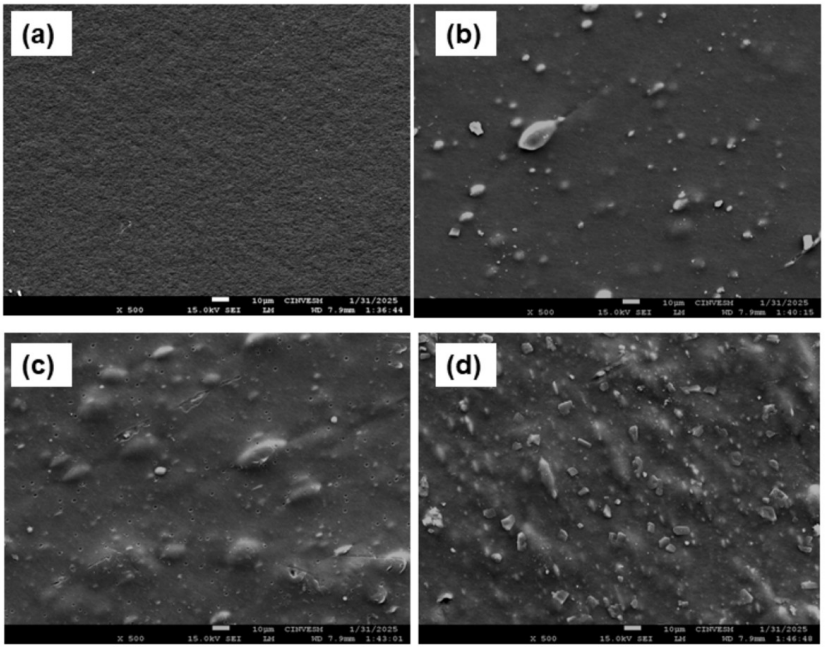

Figure 3. Micrographs of LDPE-TPS films Formulations TPS (a), TPS5 (b), TPS10 (c), and TPS15 (d), at 500X of magnification.

5. Author's Contribution

- **Conceptualization –** Tomás Jesús Madera-Santana.
- **Data curation –** Judith Fortiz Hernández.
- **Formal analysis –** Tomás Jesús Madera-Santana; Judith Fortiz Hernández.
- **Funding acquisition –** Tomás Jesús Madera-Santana.
- **Investigation –** Judith Fortiz Hernández; Anabell Espinoza Verdugo.
- **Methodology –** NA.
- **Project administration –** Tomás Jesús Madera-Santana.
- **Resources –** Tomás Jesús Madera-Santana; Judith Fortiz Hernández.
- **Software –** NA.
- **Supervision –** Tomás Jesús Madera-Santana; Víctor Rejón-Moo.
- **Validation –** NA.
- **Visualization –** Tomás Jesús Madera-Santana.
- **Writing – original draft –** Judith Fortiz Hernández; Tomás Jesús Madera-Santana.
- **Writing – review & editing –** Tomás Jesús Madera-Santana; Víctor Rejón-Moo.

6. Acknowledgements

The authors want to thank the Laboratorio Nacional Nano Biomateriales (LANNBIO). CONAHCYT CINVESTAV del IPN. Unidad Mérida Proy. No. 321119 to provide the facilities to perform this research. We are also grateful for the support provided by Ruth Melisa Felix Poqui in this work.

7. References

1. Samir, A., Ashour, F. H., Abdel Hakim, A. A., & Bassyouni, M. (2022). Recent advances in biodegradable polymers for sustainable applications. *npj Material Degradations*, *6*(1), 68. http://doi.org/10.1038/s41529-022-00277-7.
2. García-Guzmán, L., Cabrera-Barjas, G., Soria-Hernández, C. G., Castaño, J., Guadarrama-Lezama, A. Y., & Llamazares, S. R. (2022). Review progress in starch-based materials for food packaging applications. *Polysaccharides*, *3*(1), 136-177. http://doi.org/10.3390/polysaccharides3010007.
3. Apriyanto, A., Compart, J., & Fettke, J. (2022). A review of starch, a unique biopolymer-structure, metabolism, and in-plant modifications. *Plant Science*, *318*, 111223. http://doi.org/10.1016/j.plantsci.2022.111223. PMid:35351303.
4. Kupervaser, M. G., Traffano-Schiffo, M. V., Dellamea, M. L., Flores, S. K., & Sosa, C. A. (2023). Trends in starch-based edible films and coatings enriched with tropical fruits extracts: a review. *Food Hydrocolloids for Health*, *4*, 100138. http://doi.org/10.1016/j.fhfh.2023.100138.
5. Basiak, E., Lenart, A., & Debeaufort, F. (2017). Effect of starch type on the physico-chemical properties of edible films. *International Journal of Biological Macromolecules*, *98*, 348-356. http://doi.org/10.1016/j.ijbiomac.2017.01.122. PMid:28137462.
6. Rahardiyan, D., Mauren Moko, E., Tan, J. S., & Lee, C. K. (2023). Thermoplastic starch (TPS) bioplastic, the green solution for single-use petroleum plastic food packaging: a review. *Enzyme and Microbial Technology*, *168*, 110260. http://doi.org/10.1016/j.enzmictec.2023.110260. PMid:37224591.
7. Prachayawarakorn, J., Hommanee, L., Phose, D., & Chairapaksatien, P. (2010). Property improvement of thermoplastic mung bean starch using cotton and low-density polyethylene. *Stärke*, *62*(8), 435-443. http://doi.org/10.1002/star.201000002.
8. Gonçalves, I., Lopes, J., Barra, A., Hernández, D., Nunes, C., Kapusniak, K., Kapusniak, J., Evtyugin, D. V., Silva, J. A. L., Ferreira, P., & Coimbra, M. A. (2020). Tailoring the surface

properties and flexibility of starch-based films using oil and waxes recovered from potato chips byproducts. *International Journal of Biological Macromolecules*, *163*, 251-259. http://doi.org/10.1016/j.ijbiomac.2020.06.231. PMid:32615230.

9. Panrong, T., Karbowiak, T., & Harnkarnsujarit, N. (2019). Thermoplastic starch and green tea blends with LLDPE films for active packaging of meat and oil-based products. *Food Packaging and Shelf Life*, *21*, 100331. http://doi.org/10.1016/j.fpsl.2019.100331.
10. Bangar, S. P., Whiteside, W. S., Ashogbon, A. O., & Kumar, M. (2021). Recent advances in thermoplastic starches for food packaging: a review. *Food Packaging and Shelf Life*, *30*, 100743. http://doi.org/10.1016/j.fpsl.2021.100743.
11. Ballesteros-Martínez, L., Pérez-Cervera, C., & Andrade-Pizarro, R. (2020). Effect of glycerol and sorbitol concentrations on mechanical, optical, and barrier properties of sweet potato starch film. *NFS Journal*, *20*, 1-9. http://doi.org/10.1016/j.nfs.2020.06.002.
12. Association of Official Agricultural Chemists – AOAC. (2005). *Official methods of analysis of AOAC International*. Rockville: AOAC International.
13. McGrance, S. J., Cornell, H. J., & Rix, C. J. (1998). A simple and rapid colorimetric method for the determination of amylose in starch products. *Stärke*, *50*(4), 158-163. http://doi.org/10.1002/(SICI)1521-379X(199804)50:4<158::AID-STAR158>3.0.CO;2-7.
14. Barraza-Jauregui, G., Soriana-Colchado, J., Obregon, J., Martinez, P., Peña, F., Velezmoro, C., Siche, R., & Miano, A. C. (2020). *Physicochemical, functional and structural properties of starches obtained from five varieties of native potatoes (Solanum tuberosum L.)*. In *Proceedings of the 18th LACCEI International Multi-Conference for Engineering, Education, and Technology: "Engineering, Integration, and Alliances for a Sustainable Development" "Hemispheric Cooperation for Competitiveness and Prosperity on a Knowledge-Based Economy* (pp. 1-10). Boca Raton: LACCEI. http://doi.org/10.18687/LACCEI2020.1.1.623.
15. Sindhu, R., Devi, A., & Khatkar, B. S. (2019). Physicochemical, thermal and structural properties of heat moisture treated common buckwheat starches. *Journal of Food Science and Technology*, *56*(5), 2480-2489. http://doi.org/10.1007/s13197-019-03725-6. PMid:31168130.
16. Martinez, P., Malaga, A., Betalleluz, I., Ibarz, A., & Velezmoro, C. (2015). Caracterización funcional de almidones nativos obtenidos de papas (Solanum phureja) nativas peruanas. *Scientia Agropecuaria*, *6*(4), 291-301. http://doi.org/10.17268/sci.agropecu.2015.04.06.
17. Escárcega-Galaz, A. A., Sánchez-Machado, D. I., López-Cervantes, J., Sanches-Silva, A., Madera-Santana, T. J., & Paseiro-Losada, P. (2018). Mechanical, structural and physical aspects of chitosan-based films as antimicrobial dressings. *International Journal of Biological Macromolecules*, *116*, 472-481. http://doi.org/10.1016/j.ijbiomac.2018.04.149. PMid:29727650.
18. American Society for Testing and Materials – ASTM. (2010). *ASTM E96/E96M-10: standard test methods for water vapor transmission of materials*. West Conshohocken: ASTM.
19. American Society for Testing and Materials – ASTM. (2002). *ASTM D882-02: standard test method for tensile properties of thin plastic sheeting*. West Conshohocken: ASTM.
20. Hoover, R., Li, Y. X., Hynes, G., & Senanayake, N. (1997). Physicochemical characterization of mung bean starch. *Food Hydrocolloids*, *11*(4), 401-408. http://doi.org/10.1016/S0268-005X(97)80037-9.
21. Montoya-Anaya, D. G., Rodriguez-Nuñez, J. R., Aguirre-Mancilla, C. L., Grijalva-Verdugo, C., Quitana-Owen, P., & Madera-Santana, T. (2023). Films made of potato starch from industrial potato straggles and polyethylene: physicochemical, thermal, and mechanical properties. *Iranian Polymer Journal*, *32*(10), 1321-1333. http://doi.org/10.1007/s13726-023-01215-3.
22. Villada, H. S., Acosta, H. A., & Velasco, R. J. (2008). Investigación de almidones termoplástico, precursores de productos biodegradables. *Información Tecnológica*, *19*(2), 3-14. http://doi.org/10.4067/S0718-07642008000200002.

Received: Dec. 08, 2024
Revised: Mar. 13, 2025
Accepted: Mar. 19, 2025