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Improvement of the physicochemical properties of composite materials based on cassava starch and polycaprolactone reinforced with sodium montmorillonite

Mejora de las propiedades fisicoquímicas de materiales compuestos a base de almidón de yuca y policaprolactona reforzados con montmorillonita de sodio

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Abstract

The present work aims to analyse the incorporation of montmorillonite clays (MM), and polycaprolactone (PCL) to a matrix of thermoplastic cassava starch (TPS) plasticized with glycerol. The blends were made by extrusion and the films by compression moulding. The material obtained was characterized in its physicochemical, mechanical, optical and barrier properties. The controls used were pure TPS and the TPS-PCL composite. The addition of polycaprolactone and montmorillonite reduced the water solubility of the films by up to 24.2% and improved the water vapour transmission rate by up to 57.1%, compared to TPS. The oxygen transmission rate of the formulations is lower than some conventional polymers and comparable to ethylene vinyl alcohol (EVOH). The addition of montmorillonite produced films up to 81.2% stiffer and up to 30% stronger than TPS, and up to 73.3% less deformable than TPS-PCL. The plasticizing effect of the PCL overlapping the reinforcing effect of the clay. The materials had low brightness and low internal transmittance at 650 nm. The composites obtained are friendly to the environment and have functional properties suitable for packaging foods with low humidity, such as bakery products or flours.

Keywords: Clays, filler, physicochemical properties, extrusion process

Resumen

El presente trabajo tiene como objetivo analizar la incorporación de arcillas de montmorillonita (MM) y policaprolactona (PCL) a una matriz de almidón de yuca termoplástico (TPS) plastificado con glicerol. Las mezclas se obtuvieron por extrusión y las películas por moldeo por compresión. El material obtenido se caracterizó en sus propiedades fisicoquímicas, mecánicas, ópticas y de barrera. Los controles usados fueron TPS puro y el composite de TPS-PCL. La adición de policaprolactona y montmorillonita redujo la solubilidad en agua de las películas en un 24,2% y mejoró la tasa de transmisión del vapor de agua en un 57,1%, comparado con TPS. La tasa de transmisión de oxígeno de las formulaciones es menor que la de algunos polímeros convencionales y comparable con el etileno-vinil-alcohol (EVOH). La adición de montmorillonita produjo películas 81,2% más rígidas y 30% más fuertes que TPS y 73,3% menos deformables que TPS-PCL. El efecto plastificante del PCL se sobrepuso al efecto de refuerzo de la arcilla. Los materiales tuvieron bajo brillo y baja transmitancia interna a 650 nm. Los materiales obtenidos son amigables con el medio ambiente y poseen propiedades funcionales aptas para el envasado de alimentos con baja humedad, como productos de panadería o harinas.

Palabras clave: Arcillas, material de relleno, propiedades fisicoquímicas, proceso de extrusión.

1 Introduction

There is currently a need to reduce conventional polymers, generating a way to use and develop new materials from renewable sources and biodegradable nature. Starch is one of the natural polymers most used to develop biodegradable films (Ortega Toro *et al*., 2014). It is the most abundant polymer in nature and can form a continuous matrix; it is also a highly available, biodegradable, inexpensive raw material and comes from various renewable sources (Oleyaei *et al*., 2016).

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Nowadays, these biodegradable materials have been used to extend the shelf life of foods, but single component-based films have often been viewed as not having enough functional properties for industrial applications, such as food packaging. These deficiencies could be overcome by using additives or formulations that include materials like hydrocolloids, plasticizers, emulsifiers, or surfactants, resulting in a better-structured polymer with improved matrix characteristics (Buso-Ríos, O. *et al*.,2020). Thermoplastic starch (TPS) is formed by breaking the native structure of starch in the presence of a plasticizer. This transformation requires a process such as melt blending or extrusion. The substances most used to plasticize starch are low molecular weight hydrophilic polyols (i.e., glycerol, xylitol, sorbitol and polyethene glycols). The most used is glycerol; this substance is non-toxic and suitable for containers in contact with food (Basiak *et al*., 2018). Starch-based films have low permeability to gases and poor water vapour barrier properties due to the inherent hydrophilic characteristic of starch. Besides, mechanical properties, such as brittleness and strength, require substantial improvement if they are to be used as biodegradable packaging materials (Rodríguez-Marín *et al*., 2013). These plasticizers are generally used in a liquid state and with a higher viscosity than water, which gives the blend improvements in terms of the material's flexibility by reducing the intermolecular force (Medrano de Jara, *et al*., 2019). The blend with other biopolymers such as hydroxypropyl methylcellulose or essential oils has also been shown to change the physicochemical properties of starch-based films and improve the films' flexibility (Villabona-Ortiz, *et al*., 2020). The presence of plasticizers in the matrix generates plasticizer-plasticizer and plasticizer-polymer interactions, which increases the intermolecular space and generates continuity in the matrix; these are necessary to maintain the film's integrity, avoiding the formation of pores that lead to the brittleness of the material (Thakur *et al*., 2019).

TPS is a biodegradable polymer with a low production cost, with great applicability in the food industry. This biopolymer has an excellent barrier to oxygen, carbon dioxide and lipids. However, it has some drawbacks due to its strong hydrophilic character and poor mechanical properties compared to conventional polymers. It has been studied to blend different biodegradable polymers such as polycaprolactone (PCL), polylactic acid (PLA), polyvinyl alcohol (PVA) in low proportions to improve the properties of TPS. The addition of polycaprolactone to a starch matrix significantly reduces the material's strong hydrophilic character, thus improving its water vapour barrier (Ortega-Toro *et al*., 2016a). The addition of compounds such as nanoparticles, nanofibrils and clays is also a widely studied methodology to improve materials' properties (Averous, 2004). The incorporation of montmorillonite (MMT) is a practical resource to strengthen the properties of TPS, especially the rigidity, being a layered silicate characterized by a moderate negative surface charge (Romero-Bastida *et al*., 2018). MMT is an inexpensive clay with a high specific area, polymer-clay interactions increase with increasing surface area (Vaezi *et al*., 2019), and the addition of MMT decreases the viscosities of the TPS compounds (Adamus *et al*., 2018). The mechanical properties are negatively affected by the addition of MMT in large proportions since it generates brittleness in the starch matrix (Chivrac *et al*., 2010). The barrier properties could be improved with the addition of MMT since an increase in the tortuosity factor of the film is generated by decreasing the mass transfer through the film. This improvement gives applicability to the material in the food packaging. Interactions between MMT and the film matrix could be obtained due to the formation of new hydrogen bonds. Likewise, MMT has a high interfacial area that modifies the molecular mobility of film components with the consequent change in the mechanical and barrier properties (Rodríguez-Marín *et al*., 2016). This work aims to study the influence of MMT on the physicochemical, mechanical, optical and barrier properties of starch films obtained by extrusion and compression moulding with low PCL content to formulate new environmentally friendly products.

2 Materials and Methods

2.1 Materials

The starch was obtained from cassava variety Venezuelan MCol 2215 (San Juan de Nepomuceno, Bolivar, Colombia). The starch was about 18% amylose. Sigma Aldrich provided polycaprolactone (Mn 80000). Panreac supply sodium montmorillonite and glycerol.

Table 1. Mass fraction (Xi, g compound/g dry formulation) of the different components (Starch, PCL, glycerol, and montmorillonite: MMT) in wet formulation before melt blending.

Formulations	Starch	PCL	Glycerol	MMT
F1	0.769	0.000	0.231	0.000
F2	0.714	0.071	0.214	0.000
F3	0.709	0.071	0.213	0.008
F4	0.698	0.070	0.209	0.023
F5	0.687	0.069	0.206	0.038

2.2 Preparation of composites

The native cassava starch, previously dried overnight in an oven at 60 °C under vacuum (humidity close to 3%), was mixed with glycerol, water, and starch in proportions of 0.3: 0.5: 1 w /w, respectively. This mixture was extruded to obtain thermoplastic starch pellets (TPS). After that, TPS and other components (PCL and MMT) were extruded to obtain the composites. The PCL was added at 10% concerning the TPS, and sodium montmorillonite was added at 1%, 3% and 5% considering both polymers (TPS and PCL). Table 1 shows the mass fraction of each formulation. The extrusion process allows more efficient mixing of materials than processes such as melt blending using a double roll mill. In addition, it allows continuous processing (Ortega-Toro, 2015).

The processing conditions were carried out according to previous studies (Ortega-Toro *et al*., 2016b). Each formulation was premixed and then extruded using a co-rotating twin-screw extruder, with L / D = 40, screw diameter (D) 18 mm equipped with five heating zones. The temperature profile (from the feeder to the die) and the screw speed were: 90/110/120/130/110 ºC and 40 rpm for both extrusion processes. After extrusion, films were obtained by compression moulding at 130 °C and 10 bars for 5 min. The films were conditioned at 25 C and 53% relative humidity (R.H.) for one week, and then the films were characterized.

2.3 Characterization of films

2.3.1 Thickness

A digital micrometre was used to measure the film thickness at six random locations around the film.

2.3.2 Moisture content

The Films that had been previously conditioned at 53% RH and 25 ºC were dried for 1 day at 60 ºC and stored in a phosphorous pentoxide desiccator at 0% RH and 25 ºC for 2 weeks. The procedure was carried out in triplicate for each formulation.

2.3.3 Solubility in water

The film's solubility was determined by keeping the sample in water with a film: water ratio of 1:10 for 2 days. Three replicates were made for each formulation. Subsequently, the film samples were transferred to a convection oven for 1 day at 60 ºC to remove free water and then transferred to a desiccator with phosphorous pentoxide at 25 ºC for 2 weeks. The water solubility of the film was estimated from its initial and final weights according to Equation 1 (Shabbir Ahammed *et al*., 2021).

$$\text{Water solubility}(\%) = W_0 - W_1 \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

2.3.4 Tensile properties

A universal testing machine was used to determine the tensile strength (TS), young modulus (YM) and elongation (E) of the films, according to the standard method ASTM D882 (ASTM, 2001). TS, YM and E were determined from the stress-strain curves, estimated from the force-distance data obtained for the different films (2.5 cm wide and 5 cm long). The balanced samples were stretched at 50 mm min^{-1} until they broke. At least ten replicates were obtained from each sample.

2.3.5 Water vapour permeability (WVP)

According to the Standard Method ASTM E96-95 (ASTM, 2002), water vapour permeability was determined gravimetrically, with some modifications. The mixtures were sealed in a permeation cell containing distilled water (100% RH). The cells were placed in desiccators with a saturated solution of magnesium nitrate (53% RH) and weighed at intervals of 1 h for 24h at 25°C. The WVP (g mm kPa^{-1} h^{-1} m^{-1}) was calculated using Equation 2, according to the methodology reported by (Ortega-Toro *et al*., 2014a,b).

$$WVP = \frac{W * L}{A * T * \Delta P} \quad (2)$$

where W is the weight increase of the permeation cell (g); L is the thickness of the film (mm); A is the exposed area of the film (m^2); t is the time of weight gain (h); ΔP is the difference in vapour pressure across the film (kPa).

2.3.6 *Oxygen permeability*

The films' oxygen transmission rate was measured at a relative humidity of 53% and 25 ºC using an OX-TRAN 2/12 OTR Analyzer. The samples were conditioned at a relative humidity of 53% using saturated solutions of $Mg(NO_3)_2$. Measurements were made in triplicate, and transmission values were collected every 30 min until equilibrium was reached. The studied area of films was 0.005 m^2 for each sample. The thickness of the film was considered to obtain oxygen permeability values. This parameter was determined according to standard test method D 3985 (ASTM, 2010).

2.3.7 *Gloss*

The gloss was determined on the film's surface, at an angle of incidence of 60 °, using a flat surface gloss meter Lovibond TG268, according to the standard method D523 (ASTM, 1956). Measurements were made in triplicate. Results were reported as gloss units (GU), relative to a black glass standard with a value close to 100 GU.

2.3.8 *Internal transmittance*

The films' internal transmittance was determined throughout the UV-VIS range in film samples (1 cm x 3 cm) equilibrated at 25 ºC and 53% R.H., using a UV-VIS spectrophotometer, within a length range of wave between 200 nm and 1000 nm. A wavelength of 650 nm was used for analysis.

2.3.9 *Statistical analysis*

The statistical analysis of data was carried out using Statgraphics Plus for Windows (Manugistics Corp., Rockville, MD). An analysis of variance (ANOVA) and Fisher's Least Significant Difference (LSD) was used at the confidence level of 95 %.

3 Results and discussion

3.1 *Thickness, moisture content, solubility in water*

The measurement of thickness, moisture content and solubility of the films obtained by the compression moulding method are presented in Table 2. In the different characterizations, there are significant differences ($p < 0.05$) between the formulations studied. The films' thickness changes can be explained by the phase separation of the TPS-PCL mixture and the disruption generated by the MMT particles when they are added to the polymer matrix. In general, the interfacial separation between the polymers is undesirable because it generates discontinuities in the matrix and some micro-ruptures. This phenomenon could lead to poor barrier and mechanical properties. However, with the amount of PCL added to the TPS, it is expected that the interfacial separation will be minimal, as reported in previous works (Ortega-Toro *et al*., 2016a).

The presence of PCL increased the thickness of the film with respect to the thickness of the blank. This phenomenon is related to the decrease in the fluidity of the mixture when PCL is present in the mixture (Ortega-Toro *et al*., 2014b; Ortega-Toro *et al*., 2016a; Talon *et al*., 2019).

Table 2. Mean values and standard deviation of thickness, moisture content (g water/g dried film) and solubility in water (g solubilized film/g initial dried film) of the studied films conditioned at 53% RH and 25 ºC for 1 week.

Formulation	**Thickness (μm)**	X_w	**Solubility in water**
1	244 ± 4^a	0.067 ± 0.005^a	0.182 ± 0.006^a
2	409 ± 4^d	0.058 ± 0.003^b	0.151 ± 0.004^b
3	360 ± 10^c	0.051 ± 0.005^{bc}	0.148 ± 0.003^b
4	340 ± 8^b	0.048 ± 0.006^c	0.141 ± 0.005^{bc}
5	380 ± 8^c	0.041 ± 0.007^c	0.138 ± 0.005^c

Different superscript letters within the same column indicate significant differences between formulations ($p < 0.05$).

The same effect is observed with the addition of MMT due to the chemical interaction that the clays present with the polymeric matrix. Different authors have observed this behaviour (Orsuwan *et al*., 2017; Llanos & Tadini, 2018; Vaezi *et al*., 2019). The moisture content of the formulations decreased significantly as the loading of the MMT particles increased because of the hydrogen bonds formed between the ceramic and the starch molecules. These bonds contribute to generating resistance to water diffusion during drying, leading to the lower availability of hydroxyl groups to interact with water molecules resulting in lower water content in the films. According to the literature, Orsuwan *et al*. 2017 state that this fact was mainly due to the platelet structure of MMT obstructing water diffusion through the film. This behaviour was also observed for a blend of cationic starch with 5% by weight of MMT where the moisture content decreased by 10%, and for a blend of carboxymethyl starch with 5% of MMT, where the moisture content decreased by 18% (Wilpiszewska *et al*., 2015; Vaezi *et al*., 2019) different authors have reported the effect of moisture content reduction by the addition of MMT (Llanos & Tadini, 2018; Kumar *et al*., 2018; Mathew *et al*., 2018). On the other hand, the addition of PCL causes a significant decrease in the moisture content. This behaviour is attributed to the fact that a small fraction of this material is miscibilized by the starch matrix, which generates an interaction between the hydroxyl and ester groups, leaving fewer free hydroxyl groups that can interact with water molecules. The immiscible PCL has a nonpolar character. Therefore, it does not easily interact with water molecules. Similar results has been reported in literature (Ortega-Toro 2015; Tampau *et al*., 2017; Tampau *et al*., 2020, Piñeros-Guerrero *et al*., 2020; Gutiérrez *et al*., 2021).

The water solubility of materials is an essential factor when choosing a film for specific applications. Being an important characteristic directly influences other properties such as mechanical and barrier (Bohórquez-Ayala *et al*., 2020). The water solubility can provide insight into the behaviour and resistance of the films in aqueous environments when the MMT was added significantly decreases the percentage of soluble matter because the interactions between the molecules and the polymer matrix's cohesion, different authors have reported this same effect (Orsuwan *et al*., 2017; Llanos *et al*., 2018; Kumar *et al*., 2018; Vaezi *et al*., 2019). According to Vaezi *et al*. (2019) and Wilpiszewska *et al*. (2015), the percentage of the soluble matter of MMT was reduced by 9% for the cationic starch mixture with 5% by weight. The percentage of MMT solubility decreased by 23% for the carboxymethyl starch blend. The addition of PCL significantly reduced the solubility of the studied mixtures. This event is attributed to the effects previously mentioned where the amount of hydroxyl groups is decreased by the interaction with the ester groups of the PCL, making interaction with water molecules difficult. has been observed in previous works (Ortega-Toro 2015; Piñeros-Guerrero *et al*., 2020).

3.2 Mechanical properties

Figure 1 shows the graphs of tensile stress (a), tensile strain (b), and Young's modulus (c) for the formulations studied.

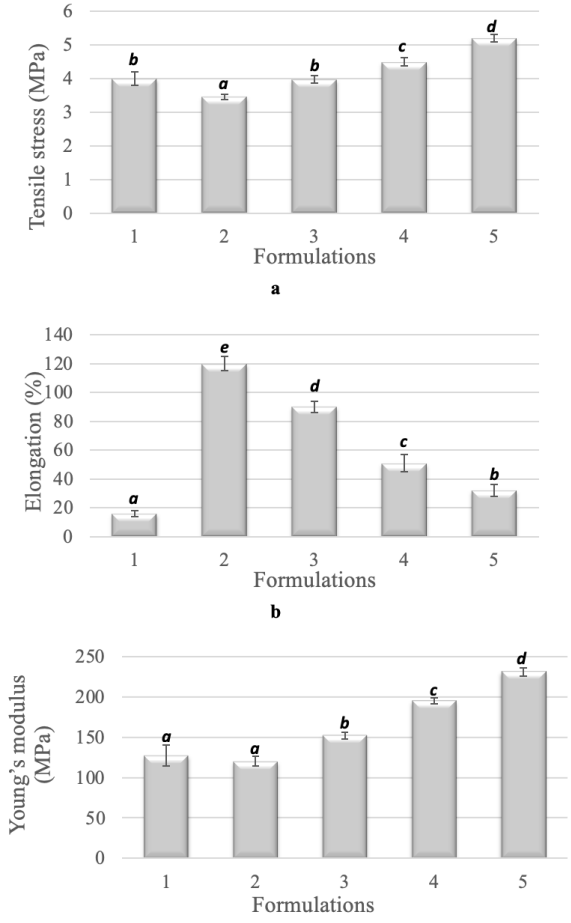

Fig. 1. Mechanical properties of studied formulations conditioned at 53% RH and 25 ºC for 1 week: a.) Tensile stress; b.) Elongation; c.) Young's modulus. Italics letters over the bars indicate significant differences ($p < 0.05$).

In Figure 1a, the effect of the addition of MMT and PCL is shows. The addition of MMT increases the maximum value of tensile stress (TS) and decreases the percentage of deformation (%E), generating more rigid and less deformable films with a higher young modulus (YM) compared to blank, attributed to the strong interfacial interaction created between starch and MMT. The improved mechanical property has been attributed to various reasons, such as the resistance to deformation force exerted by the clay with its high surface area and the hydrogen bonds that formed between the hydroxyl groups of the starch and the MMT (Rohini *et al*., 2020; Vaezi *et al*., 2019; Llanos *et al*., 2018). The addition of PCL to the starch matrix provoked a twofold effect on the mechanical response of the film: matrix plasticization effect (Tg decrease of starch) caused by the small PCL miscible fraction and matrix discontinuity due to the non-compatible PCL fraction (Averous *et al*., 2000; Matzinos *et al*., 2002). Both effects caused the weakening of the starch phase's cohesion forces, which decreased the elastic modulus and the tensile strength, although the plasticizing effect enhanced the film stretchability. PCL is a ductile polymer with high deformability, whose deformation at break is almost 5 times the original size. These effects have been evidenced in previous works (Ortega-Toro 2015; Piñeros-Guerrero *et al*., 2020). The effect of the ductile nature of the PCL can be evidenced when comparing formulations 1 and 2, where a similar value of tensile stress is observed, but there is a significant difference in the percentage of elongation of more than 100%, this behaviour also is reported by different authors (Collazo-Bigliardi *et al*., 2019; Gutiérrez *et al*., 2021; Khorramnezhad *et al*., 2021).

As reported in the literature, the blend of carboxymethyl starch with MMT had the same effect of increasing the maximum tensile stress as the concentration of MMT increases, for a formulation with 5% MMT, tensile stress increase of 1.1 MPa and, in the case of a cationic starch mixture, increase of 5 MPa was obtained (Vaezi *et al*., 2019; Wilpiszewska *et al*., 2015). The addition of PCL caused a decrease of this parameter by 0.5 MPa. In Figure 1b, the increase in the concentration of MMT drastically decreases the percentage of maximum deformation that the films undergo before breaking; this effect is linked to the fact that the films become more rigid with the addition of clays because of chemical interaction reduce de molecular motion (Rohini *et al*., 2020). For the formulation with MMT at 5 %w/w, the maximum deformation was approximately 30%. Vaezi *et al*. (2019) and Wilpiszewska *et al*. (2015) reported at concentrations of 5% of MMT deformations of 70% in films based on cationic starch and 35% in films based on carboxymethyl starch.

Figure 1c shows how the addition of MMT progressively increases Young's modulus. At higher clay loading, the clay-clay and clay-polymer interactions increased the surface area by forming agglomerated networks and hence considerably reducing the polymer chain entanglements (Perumal *et al*., 2018). There is a strong trend of increasing toughness with increasing MMT content, as noted for all the composites until reaching 230 MPa with 5% MMT. Wilpiszewska *et al*. (2015) reported Young's modulus of 50 MPa for films based on carboxymethyl starch and MMT at 5%. The addition of PCL generated a significant reduction in the elastic modulus of the studied materials, generated by the plasticizing effect mentioned above. This behaviour was evidenced in previous works (Ortega-Toro 2015; Piñeros-Guerrero *et al*., 2020; Gutiérrez *et al*., 2021).

3.3 Water vapour permeability and Oxygen permeability

Figure 2 shows the map of barrier properties exhibited by the studied formulations, some conventional plastics commonly used in food packaging, and barrier requirements for some food groups' packaging. Data were taken and adapted from the authors Schmid *et al*., 2012 and Ortega-Toro, 2015.

The effect of PCL and MMT in the studied formulations is observed in the barrier properties map. Formulation 1 (pure TPS) presents the highest barrier against oxygen transmission and the lowest barrier against water vapour transmission compared to the other formulations studied and the other materials present in figure 2, thus validating what has been reported by current literature (Chivrac *et al*., 2010; Tran *et al*., 2017; Ghanbari *et al*., 2018). TPS's high oxygen barrier is due, in addition to its chemical nature, to the compact and homogeneous microstructure presented by the material, which generates a more tortuous path and makes it difficult for oxygen molecules to pass through it. The low water vapour barrier is explained by the material's strong hydrophilic nature, allowing water molecules to move more quickly through the material (Ortega-Toro *et al*., 2014b, 2016a, b).

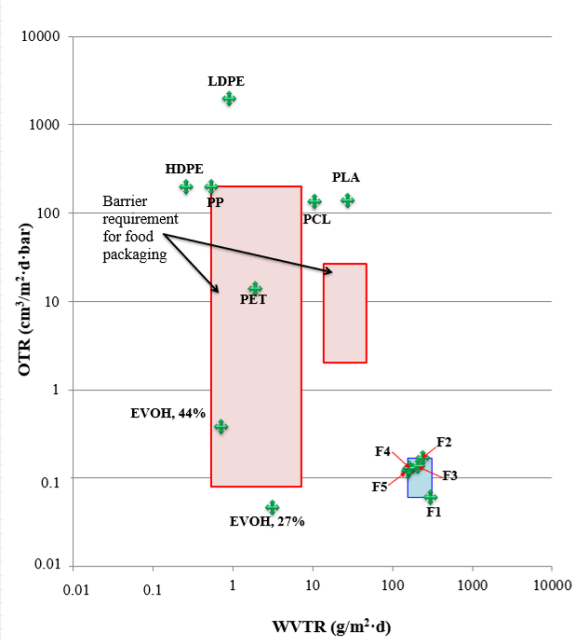

Fig. 2. Map of barrier properties showing the studied formulations (blue square), some commonly used plastics in food packaging and barrier requirement ranges for some foods (pink squares).

Adding a low proportion of PCL to the TPS matrix improves the barrier against water vapour due to this polymer's hydrophobic nature, but at the same time affects the barrier against oxygen because PCL also has a high affinity for molecules of oxygen. The addition of MMT particles to the TPS-PCL matrix slightly improved the oxygen and water vapour barrier compared to the effect of the addition of PCL; this is because the MMT particles increase the tortuosity of the material to the passage of both oxygen and water molecules (Tran *et al*., 2017). Compared to conventional polymers, the studied blends have a better barrier to oxygen and a worse water vapour barrier, analyzing Figure 2 and the results of oxygen and water permeability, the studied materials do not meet the requirements for postulated food packaging, which is why some improvement strategies are presented below. Different strategies can be applied to improve the water vapour permeability of the developed materials. One of these strategies is to increase the proportion of PCL, but this would generate a high cost of the material, making it challenging to apply it to the food packaging. However, this high cost could be mitigated if PCL is partially or replaced by other cheaper polymers such as polylactic acid (PLA). Different authors have advanced in developing materials based on TPS and PLA, reaching high compatibility and barrier against water vapour (Przybytek *et al*., 2018; Akrami *et al*., 2016; Heidemann *et al*., 2019; Palai *et al*., 2019). Another alternative to generate an improvement in the hydrophobicity of the material is the chemical modification of the starch, replacing the hydroxyl groups present in the material's structure with other more apolar ones such as the alkyl or aryl groups. (Wang *et al*., 2020), the chemical modifications of starch most applied for this purpose are acetylation and esterification. Different authors have found significant improvements in the hydrophobic behaviour of materials with high degrees of substitution of hydroxyl groups (Zhou *et al*., 2009; Wang *et al*., 2021; Cuenca *et al*., 2021). Finally, a striking strategy is the inclusion of additives that reduce the affinity to polar compounds, as is the case with nanoparticles isolated from proteins, among many other additives. (Yang *et al*., 2021; Liu *et al*., 2021).

3.4 Gloss and Internal transmittance

Figure 3 shows the average values and the standard deviation of gloss and internal transmittance at a wavelength of 650 nm of the studied formulations.

Gloss is a property related to roughness. The addition of MMT generated a significant reduction in the gloss of the studied formulations. This effect is attributed to incorporating clays in the free spaces of the materials, increasing their roughness. This phenomenon is because a higher formation of agglomerates is promoted on the surface of the film. This effect has been evidenced by different authors who have used MMT as reinforcing materials (Valencia *et al*., 2018; Vaezi *et al*., 2019; Pulla-Huillca *et al*., 2021). The addition of PCL in the same way as MMT generated a significant reduction in the brightness of the materials. This effect is attributed to the low miscibility of PCL in the starch matrix, generating changes in the surface roughness of the materials. (Ortega-Toro., 2015; Collazo-Bigliardi *et al*., 2019). The internal transmittance is an indicator of the transparency of the film to VIS radiation, the addition of MMT generated a significant reduction can be attributed to the obstruction of the light path generated by the concentration of clays in the starch matrix, different authors have evidenced this effect (Mathew *et al*., 2018; Vaezi *et al*., 2019).

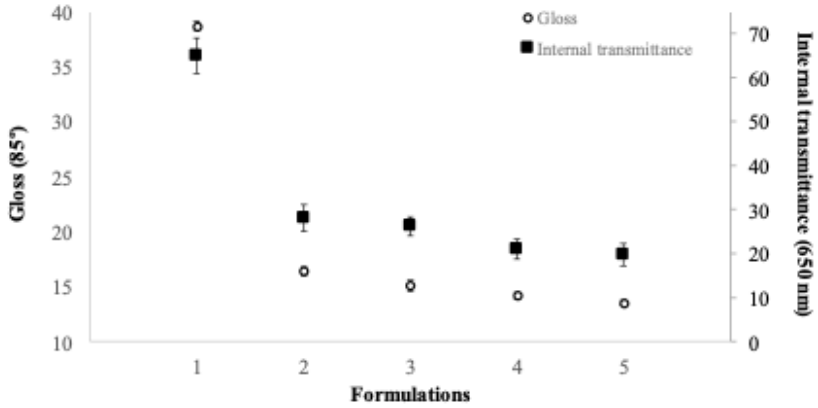

Fig. 3. Mean values and standard deviation of gloss (85°) and Internal transmittance (650nm) of studied formulations conditioned at 53% RH and 25 ºC for 1 week.

The addition of PCL generated an effect similar to MMT, significantly reducing internal transmittance values due to the higher number of scattered PCL domains with the consequent increase in discontinuities in the refractive index through the film and irregularities at the surface level. (Ortega-Toro., 2015; Collazo-Bigliardi *et al*., 2019). Both gloss and transparency are essential properties in polymeric materials used in the food packaging industry because they are crucial factors to avoid distorting the optical properties of food and make these attractive to consumers.

Conclusions

The effect of adding montmorillonite and polycaprolactone to a thermoplastic starch matrix was successfully analyzed. The addition of these two components significantly modified the properties of the studied materials. The hydrophilic nature of these starch-based materials was significantly reduced (solubility in water was reduced up to 24.2%, and water content was reduced to 38.8%), improving their applicability in food packaging. Besides, MMT promotes films more rigid (81.2%), less deformable (73.3%) and stronger (30%). Regarding the barrier properties, MMT and PCL's addition improved the water vapour barrier properties (up to 33.2%), and the oxygen barrier properties worsened (up to 239%). However, the oxygen barrier is still higher than those of other polymers, comparable to EVOH and satisfactory for food packaging. The materials have a low brightness and low transmittance at a wavelength of 650 nm, thus providing reasonable protection to photosensitive foods. The materials have functional properties suitable for packaging food with low humidity, such as bakery products or flours. The originality of the work lies in obtaining suitable materials for food packaging, using autochthonous raw materials from the Caribbean region (Venezuelan variety MCol 2215), grown in the San Juan de Nepomuceno town (Bolivar-Colombia). With these results, agricultural production is encouraged, and other marketing options are given to primary products.

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