# Mechanical and barrier properties of thermoplastic starch based composites by the incorporation of montmorillonite clays

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**ABSTRACT:** In the present work, the effect of the incorporation of clays of montmorillonite and polycaprolactone to a matrix of thermoplastic starch of cassava plasticized with glycerol was studied, the blends were obtained by the extrusion process and the films by compression moulding. The mechanical and barrier properties were characterized. The addition of polycaprolactone and montmorillonite improved the oxygen barrier and the water vapour transmission rate. The addition of montmorillonite produced more rigid and less deformable films.

**RESUMEN:** En el presente trabajo, se estudió el efecto de la incorporación de arcillas de montmorillonita y policaprolactona a una matriz de almidón termoplástico de yuca plastificada con glicerol, las mezclas se obtuvieron mediante el proceso de extrusión y las películas mediante moldeo por compresión. Se caracterizaron las propiedades mecánicas y de barrera. La adición de policaprolactona y montmorillonita mejoró la barrera de oxígeno y la tasa de transmisión al vapor de agua. La adición de montmorillonita produjo películas más rígidas y menos deformables.

**Palabras clave: Proceso de extrusión, arcillas de montmorillonita, almidón termoplástico.**

**Área:** Development of new products

## INTRODUCTION

Starch is the biopolymer most commonly used to develop biodegradable films since it can form a continuous matrix, it is also a highly available, biodegradable, economical raw material and comes from diverse renewable sources (Oleyaei *et al.,* 2016). The plasticization of the native starch forms the thermoplastic starch (TPS) through the application of a thermo-mechanical process. Different substances are used to plasticize starch, in general, hydrophilic low molecular weight polyols like (glycerol, xylitol, sorbitol, polyethene glycols, etc.), the most used polyol is glycerol, since it is considered non-toxic and therefore, it is suitable for use in the food industry (Basiak *et al.*, 2018). The plasticizers generate the plasticizer-plasticizer or plasticizer-polymer interactions in the system which increases the intermolecular volume, these are necessary to maintain the integrity of the film avoiding the formation of pores that lead to film fragility (Thakur *et al.*, 2019). TPS is a biodegradable polymer of low production cost, with high applicability in the food industry, it is used as an edible coating since it is not composed of any toxic compound.

This work aimed to analyze the influence of MMT on the mechanical, and barrier properties of compression moulded starch films containing a low proportion of PCL to obtain low-cost starch films with improved properties for being applied in the food industry. The addition of a hydrophobic copolymer and clays significantly reduced the water solubility of the films, improved the oxygen barrier and the water vapour transmission barrier also produced more rigid and less deformable films, with low brightness and low light transmission. The properties of the materials were improved to satisfy some requirements of the food packaging industry.

# MATERIALS AND METHODS

## Preparation of composites

Native corn starch, previously dried overnight in an oven at 60 °C under vacuum, was hand-blended with glycerol and water in a starch: glycerol: water weight ratio of 1:0.3:0.5 w/w. This blend was extruded to obtain thermoplastic starch pellets (TPS). After that, TPS and other components were extruded to obtain the composites. The PCL was added at 10% respect to TPS and sodium montmorillonite was added at 1%, 3% and 5% respect to polymers (TPS and PCL). Table I shows the mass fraction of each formulation.

**Table I**. 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** |

Each formulation was pre-mixed manually 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 feeder to die) and screw speed were: 90/110/120/130/110 °C and 40 rpm for both extrusion process. 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 relative humidity (R.H.) of 53 % for one week and then films were characterised.

## Characterization of films

### Mechanical properties

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

### Water vapor permeability

Water vapour permeability (WVP) was measured in films equilibrated for 1 week in sealed desiccators at 25 °C and relative humidity of 53 %, using a gradient of relative humidity of 53 % - 100 % and 25 °C, by using the standard method E96-95 (ASTM, 2002), according to the modifications reported by (Ortega-Toro *et al.,* 2014).

### Oxygen permeability

The oxygen transmission rate of the films was measured at a relative humidity of 53 % and 25 °C using an OX-TRAN. The samples were conditioned at a relative humidity of 53 % using $Mg(NO_3)_2$ saturated solutions. Measurements were done in triplicate, and the transmission values were collected every 30 min until equilibrium was reached. The studied area of films was 0.005 m2 for each sample. The film thickness was considered to obtain oxygen permeability values. This parameter was determinate according to the standard test method D 3985 (ASTM, 2010).

### 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 %.

## RESULTS AND DISCUSION

### Mechanical properties

In Figure 1a the effect of the addition of MMT and PCL is evidenced, the addition of MMT increases the maximum tensile stress value (TS); 5 wt. % of MMT increases approximately 1.6 MPa the TS; this significant increase indicates that the films are stronger as the MMT concentration increases due to the high interfacial interaction between the polymeric matrix and the clay caused by the hydrogen bonds that formed between the hydroxyl groups of the starch and the clay. The blend of carboxymethyl starch with MMT had the same effect of increasing the maximum tensile stress as the concentration of MMT increases for the formulation with 5 wt. % (Vaezi *et al.*, 2019; Wilpiszewska *et al.*, 2015). On the other hand, the addition of PCL promotes the decreases in TS by approximately 0.5 MPa in TS.

In Figure 1b it can be seen that the increase in MMT concentration drastically decreases the percentage of maximum deformation suffered by the films before breaking, this effect is linked to the fact that the films become more rigid with the addition of the clays, due to the effect of the chemical interaction. For the formulation with 5 wt. % the maximum deformation was about 30%, for the blend of cationic starch with a concentration of 5 wt.% the maximum deformation was 70% and, for the materials based on carboxymethyl starch with a concentration of 5 wt.% the maximum deformation was 35% (Vaezi *et al.*, 2019; Wilpiszewska *et al.*, 2015). The effect of the addition of PCL to the starch matrix shows a significant change since the maximum deformation increases by almost 100%; this is due to the plasticization that the PCL generates on the TPS.

In Figure 1c the Young modulus is significantly increased by the addition of MMT being 300 MPa for the blends with 5 wt. % of MMT. For blends of carboxymethyl starch, the same tendency of increase of Young's modulus is presented as the concentration of MMT increases, Young's modulus for the blends with 5 wt.% of MMT is 50 MPa (Wilpiszewska *et al.*, 2015). There is no significant effect of the addition of PCL to Young's modulus.

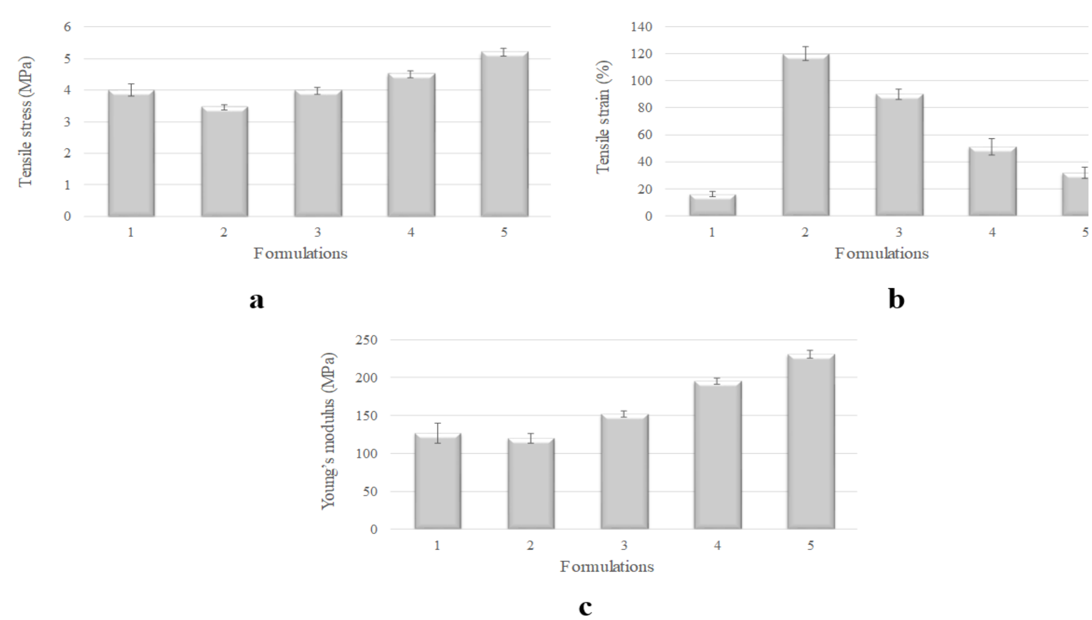


**Figure 1.** Mechanical properties of studied formulations conditioned at 53% RH and 25 ºC for 1 week: a.) Tensile stress; b.) Tensile strain; c.) Young's modulus.

**Water vapor permeability and Oxygen permeability**

Figure 2 shows the barrier properties map that exhibits the formulations studied, some conventional plastics commonly used in food packaging and barrier requirements for the packaging of some foods.

The effect of the addition of PCL and MMT in the studied formulations is observed in the barrier properties map. Formulation one (F1) presents the highest barrier against oxygen transmission and the lowest barrier against water vapour transmission compared to the formulations studied and the other materials present in Figure 2, thus validating what is reported by the current literature (Ghanbari *et al.*, 2018; Tran *et al.*, 2017; Chivrac *et al.*, 2010). The high oxygen barrier of the TPS is due to the compact and homogeneous microstructure presented by the material, which generates a more tortuous path and hinders the passage of oxygen molecules through it. The low water vapour barrier is explained by the strong hydrophilic nature of the material which allows water molecules to move more quickly through the material.

The addition in a low proportion of PCL to the matrix of TPS improves the barrier against water vapour due to the hydrophilic nature of this polymer, but at the same time, it affects the barrier against oxygen because PCL also has a high affinity for oxygen molecules. The addition of MMT particles to the TPS-PCL matrix slightly improved both 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 making the passage of both oxygen and water molecules difficult for them to diffuse through the film (Tran *et al.*, 2017). The mixtures studied compared to conventional polymers have a better barrier to oxygen and a weak barrier to water vapour.

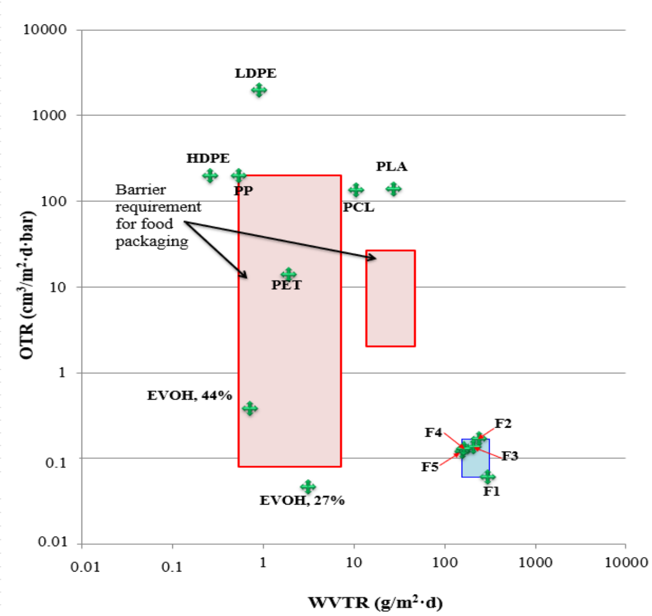


**Figure 2.** Map of barrier properties showing the studied formulations (blue square), some commonly used plastics in food packaging and barrier requirement ranges for some foods (pink squares).

## CONCLUSION

The effect of the addition of clays of montmorillonite and polycaprolactone polymer to a matrix of thermoplastic starch was studied and analysed satisfactorily. The hydrophilic nature of these starch-based materials was significantly reduced, improving their applicability in food packages that are quickly dehydrated and can modify the properties of the material. Also, more rigid materials were obtained, and greater resistance to breaking, but less deformable, the barrier properties were significantly improved but they are not optimal for the materials studied can be applied in the food packaging.

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