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Development of biodegradable plastic films from cassava starch

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Abstract
Plastic has become part of daily life because it is used in all industrial applications. Although it is beneficial and practical, it is the material that generates the most pollution in ecosystems. Therefore, the main objective of this research is to produce plastic films capable of degrading the environment in a shorter time (bioplastics). For this purpose, different samples were made with cassava starch (pulp or commercial), using amounts in the solution of 4% w/v and 30% w/w of cassava starch and glycerol, respectively, considering variations between the percentages of chitosan. The results showed that it is possible to obtain bioplastic by the casting method with the mixture of cassava starch (pulp or commercial), glycerol, and chitosan. Likewise, thanks to the laboratory tests carried out, was possible to determine that the use of commercial starch to produce biodegradable plastic films significantly favors moisture adsorption, solubility, and biodegradability, compared to starch extracted from cassava by hand, with good statistics validity of the analyzed data.

Keywords: bioplastic; biodegradability; plastic; chitosan.

Desarrollo de películas plásticas biodegradables a partir de almidón de yuca

Resumen
El plástico se ha convertido parte del diario vivir debido a que se utilizada en todas las aplicaciones industriales, aunque es muy útil y práctico, es el material que genera más contaminación en los ecosistemas. Por lo tanto, el objetivo principal de esta investigación es la producción de películas plásticas capaces de degradarse con el medio ambiente en un menor tiempo (bioplásticos). Para este propósito, se realizaron diferentes muestras con almidón de yuca (pulpa o comercial), utilizando cantidades en la solución de 4% p/v y 30% p/p de almidón de yuca y glicerol, respectivamente, considerando variaciones entre los porcentajes de quitosano. Los resultados demostraron que con la mezcla de almidón de yuca (pulpa o comercial), glicerol y quitosano, fue posible la elaboración de bioplástico por el método casting. Asimismo, gracias a las pruebas de laboratorio realizadas se determinó que la utilización de almidón comercial para la elaboración de películas plásticas biodegradables favorece a una mayor adsorción de humedad, solubilidad y biodegradabilidad, comparado con el almidón extraído de la yuca artesanalmente, con buena validez estadística de los datos analizados.

Palabras clave: bioplástico; biodegradabilidad; plástico; quitosano.

1 Introduction

Plastic is one of the primary ecosystem pollutants due to its more than 3,000 chemical substances that make it up [1]. In the long term, plastic devastates maritime life, birds, and humans because they are not exempt from this massive pollution [2]. Most plastics are produced from petrochemical compounds (high molecular weight molecules), which can remain in the environment, producing pollution that is not biodegradable because, as is known, the decomposition process delays hundreds or thousands of years [3]. Plastics derived from petroleum are mostly used in sectors of the world economy, such as livestock, services, industrial, and agricultural because they have properties that benefit their applications and marketing. Considering the above, the demand for these materials has progressively increased, and

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consequently, their participation in solid waste production is also due to their low degradation rate [4]. For this reason, the use of synthetic polymers in agriculture is a technology that has been growing because it has managed to convert unproductive lands into agricultural production, generating a controlled environment and improving the quality of fruits and vegetables. This practice is called plasticulture, which uses plastic in agriculture to make productive land [5].

1.1 Literature review

According to the literary review of scientific articles and works related to the development of biodegradable films that use polymers derived from renewable natural resources, it was possible to highlight:

Briones Muñoz and Riera, 2020, evaluated waste such as cassava peel and beeswax as potential materials to produce bioplastics; the starch from the cassava peel was extracted by wet and dry grinding, while beeswax was obtained by applying heat to the mixture of water with pieces of honeycomb. To determine the proximal composition of the extracted starch, humidity, crude protein, crude fat, ash, and the amount of amylase and amylopectin were determined, while the physicochemical characterization of the beeswax was evaluated: density, saponification index, acidity index, ash, and pH. The results demonstrate that the materials evaluated suitably function as a matrix in bioplastic preparation film-forming solutions. Likewise, using these materials as raw materials to produce thermoplastic starches is suggested [6].

Minh and Rangrong, 2016, evaluated the morphological characteristics and water vapor and oxygen barrier properties of blown starch-chitosan thermoplastic edible film, hydrophilicity of TPS and TPS/CTS films, scanning electron microscopy (SEM), focal laser scanning microscopy (CLSM) and X-ray photoelectron spectroscopy (XPS). Confirming that the existence of chitosan on the surface generates an improved barrier to water vapor and oxygen, reducing the surface hydrophilicity of the film. It is also concluded that biodegradable TPS/CTS films could be edible for food and pharmaceutical products [7]. Minh and Rangrong, 2015, developed thermoplastic starch-blown films incorporating plasticized chitosan, evaluating the effects of chitosan on extrusion processability and TPS melt flow capacity, as well as appearance, optical properties, thermal properties were investigated, viscoelastic properties and tensile properties of the films. Furthermore, FTIR and X-ray diffraction (XRD) techniques evaluated possible interactions between chitosan and starch molecules. The results demonstrated that chitosan and starch molecules interact through hydrogen bonds. Although the incorporation of this caused a decrease in the extensibility and flow capacity of the melt, as well as an increased opacity, the films had better extrusion processability, higher tensile strength, stiffness, temperature stability, and UV absorption, achieving a reduction in water absorption and surface adhesion [8].

Valarezo Ulloa, 2012, developed biopolymers from cassava bark starch (Manihot esculenta), using water and glycerin as plasticizers and acetic acid to modify the hydrophilic character. The starch was obtained by wet grinding and sedimentation, considering that the concentrations of the different components were modified to obtain a biopolymer with the best characteristics. The results showed that the biopolymer presented an average yield of 64% of starch obtained from the bark. In comparison, the biopolymer with the best characteristics was the mixture of 19.36% starch, 6.31% glycerin, 74.08% water, and 0.25% acetic acid; the samples made of this material have a humidity between 9.97% and 11.58%; observing that lower than this humidity the biopolymer becomes fragile and brittle, likewise the density of 6.44 gr/cm^3, 25.3% increase in weight due to absorption of water [9].

Bourtoom, 2008, evaluated the plasticizing effect on the biodegradable mixture film of rice starch and chitosan, where three plasticizers were studied: sorbitol, glycerol, and polyethylene glycol in a concentration range of 20 to 60%. Increasing the concentration of these plasticizers resulted in a decrease in tensile strength and increased water vapor permeability, film solubility, and elongation at break. The results of the films plasticized with sorbitol were more brittle, higher tensile strength, and low water vapor permeability compared to the other two plasticizers with a flexible structure, low tensile strength, and high water vapor permeability [10].

Pelissari et al. (2009) studied the effect of adding chitosan to starch-based polymeric systems. Research reports the improvement of the properties of TPS films due to the decrease in the hydrophilic character of these systems since adding chitosan results in a decrease in the interaction of starch with humidity. An essential disadvantage of chitosan is its high cost; however, improvements in mechanical properties have been demonstrated using small concentrations [11]. Lili Rena, et al. 2017 investigated the influence of chitosan concentration on the mechanical and barrier properties of films prepared with the starch solution mixture. In the research, the effects of chitosan were characterized and analyzed, evaluating the physicochemical properties of the material (density, volume, solubility in water mixture (WS) and color), water vapor permeability (WVP), crystallinity, characterization of microstructures. The results showed that incorporating chitosan increased film solubility, color differences, tensile strength, elongation at break, and decreased WVP. The elongation at the break of the films increased as a function of the chitosan concentration and reached a maximum of 41%, making these films suitable for use as active packaging films in food and pharmaceutical applications [12].

Finally, Godbillot, et al., 2005, studied the water-binding properties of the wheat starch film by determining the water vapor adsorption isotherms at 20°C, determining that the unplasticized starch film absorbs less water than native starch granules. Absorption by plasticized films depends on the equilibrium relative humidity (ERH) value and the glycerol content. When the ERH is equal to 44%, the plasticized film is less hygroscopic than starch, and above this value, the water absorbed increases with the glycerol content. Therefore, it is estimated that a maximum of 20% glycerol should be used to act as a plasticizer since, above this percentage, phase separation occurs and the amount of adsorbed water increases as it binds to the starch film, as well as to the "free" glycerol.

In conclusion, water vapor absorption is proportional to the number of hydrophilic sites (hydroxyl groups) in the plasticizer; the higher the hydrophobicity of the substituent, the lower the amount of water adsorbed [13].

1.2 Aim of this work

Due to the need to develop new sustainable materials, this research focuses on developing biodegradable plastic films made from renewable materials that generally contain a high percentage of starch. Thanks to their production process, these plastics are biodegraded by microorganisms and introduced into the environment as an organic fertilizer beneficial for the soil [14]. Then, highlights for the development of biodegradable plastic films from cassava starch: 1) The utilization of cassava starch as a raw material for biodegradable plastic films offers an eco-friendly alternative to traditional plastics. These films can help reduce the environmental impact of plastic waste by degrading naturally and minimizing pollution. 2) Cassava is a renewable and abundant resource in many regions, making it an attractive source for biodegradable plastic production. This can contribute to sustainable agricultural practices and reduce dependence on non-renewable resources used in conventional plastics. 3) Biodegradable plastic films derived from cassava starch are designed to break down into environmentally benign components over time. This property is particularly valuable in applications where single-use plastics are common, such as packaging and agricultural films, and 5) Biodegradable films can find applications in various industries, including food packaging, agriculture, and more. Their versatility and environmentally friendly nature make them viable for industrial applications.

2 Materials and methods

2.1 Localization

The Municipality of Aguachica is located in the South of the Department of Cesar, which has a latitude of 8.317 and a longitude of -73.617, between the Eastern Cordillera and the valley of the Magdalena River, with a territorial extension of 876.26 km^2, which occupies 3.8% of apartment area [15]. The municipality has two types of climates which are: Warm Thermal Floor, with temperatures greater than 24°C and heights between 50 and 1,000 masl. Temperate Thermal Floor, with temperature variations between 18–24°C and heights between 1,000 and 2,000±200 masl. The average annual temperature is 28°C, in July, the temperature reaches the highest values of up to 40°C, and in October, the lowest temperature occurs, reaching 22°C [16]. Thanks to the climate of the municipality of Aguachica, the economy revolves around the agricultural sector and agroindustry [17], where extractive energies, agriculture, livestock, and fishing have a GDP of 7.6% for the year 2018, being the Crops Cassava is the second most important crop (56,000) with a 12.7% share, after oil palm cultivation. On the other hand, it is highlighted that in the department of Cesar for 2018, 916,616.20 hectares were planted, with a production of 8,064,401.78 tons of cassava. On the other hand, for 2019, the municipality of Aguachica had a planted area of 120 hectares with a yield of 9 tons/hectare [18].

2.2 The cassava

Cassava (Manihot esculenta) is characterized by developing laticiferous vessels composed of secretory cells or galactocytes that produce a milky secretion. The yucca plant grows in the warm, humid lowland tropics, in the subtropics with cold winters and summer rains, and in the mid-altitude tropics; its main advantage is the ability to grow with sporadic rainfall or long periods of drought and in acidic soils. Note that this plant does not tolerate saline soil conditions and waterlogging [19].

Cassava is divided into sweet and bitter cassava groups; this depends on the hydrocyanic acid content of the roots. Generally, the roots contain a glucose-cyanogen known as linamarin, which releases hydrocyanic acid when activated by the enzyme linamarin. The pulp contains a smaller amount of hydrocyanic acid than the peel. It is important to mention that the level of hydrocyanic acid is found in greater quantities in bitter cassavas and small quantities in sweet cassavas, and its presence varies according to the plant's physiological state and the humidity and fertility conditions of the soil [9]. As shown in Fig. 1, cassava is a perennial, woody, semi-shrub plant of variable size that reaches 1 to 4 meters in height, consisting of aerial and underground parts. The aerial part is made up of the stem (maximum height of 100 cm), leaves (length between approximately 14 and 17 cm), flowers, and fruits; while the underground part is composed of roots and radicals, although the roots are made up of an external part (bark or shell) corresponding to 12-20% of the root and the internal or central part (pulp) [16].

Because starch is needed as a raw material, it was decided to obtain starch from cassava (Manihot esculenta), planted in the municipality of Aguachica Cesar, taking advantage of this tuber characterized by its high starch content. In turn, it is highly perishable; it begins to deteriorate two or three days after harvesting if no treatment is developed. Consequently, chemical processes cause a color change inside the root, followed by microbial growth that accelerates damage. Cassava is made up of protein, fat, carbohydrates, fiber, and ash. Table 1 exposes the tuber-represented percentages in highly humid percentages with up to 72%.

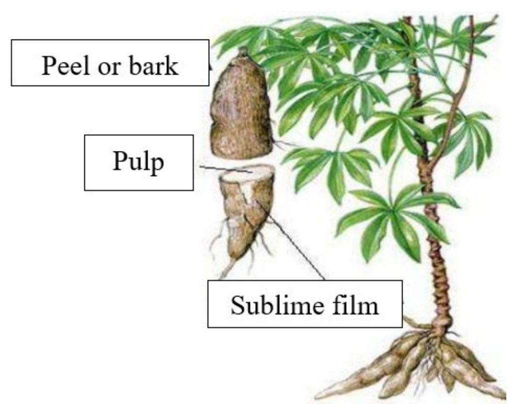

Figure 1. Parts of the cassava root.
Source: Obtained from [20].

Table 1.
Cassava composition.

Fractions	Whole root		Cortex		Central cylinder	
	Wet	Dry	Wet	Dry	Wet	Dry
Humidity	61.0	-	72.0	-	59.0	-
Protein	1.2	3.1	1.5	5.4	1.0	2.4
Fat	0.4	1.1	0.6	2.1	0.4	1.0
Carbohydrates	34.9	89.4	21.7	77.2	37.3	91.0
Fiber	1.2	3.3	2.1	8.9	1.1	2.7
ashes	1.3	3.3	1.7	6.1	1.2	2.9

Source: [21].

2.2.1 Cassava starch obtention:

Starch is a polymer from natural sources, also known as starch, which is made up of granules that have a macromolecular configuration organized in layers whose particularity to its composition, its portion, and its appearance, which largely depend on the source of the starch that proceeds. The most abundant carbohydrate in nature is starch, and in plants, it is one of the main energy reserves and is found in sources as diverse as cereal seeds such as wheat, corn, and rice, in plant seeds, legumes of lentils, and beans, in the stem the sago palm, in leaves such as tobacco, in fruits such as apples, in tubers such as potatoes and bananas, and finally in roots such as sweet potatoes and cassava [16].

2.2.2 Starch structural properties:

Starch is made up of two different polymeric structures: amylopectin and amylose, made up of glucose units, respectively. So, amylopectin is a branched polymer, while amylose is a linear polymer. The bond between amylopectin and amylose is an essential factor in the manufacture of films and dominates the physical and mechanical properties of the materials [22]. The property of interest in natural starch lies in its semi-crystallinity. For this reason, amylopectin is the element that contributes to the crystallization of most starches. The commercially significant properties of starch, which refer to its mechanical resistance and flexibility, those governed in nature by the strength and the crystalline zone, and the link between amylose and amylopectin, are also contemplated, molecular weight fraction, the structuring procedure of the components types in the polymer, the branching level and the plant type [23].

2.2.3 Starch extraction:

Starch extraction can be carried out at an artisanal or technical level. Different methods exist to obtain starch from corn, cassava, potatoes, or bananas. The main methods are dry grinding and wet grinding. Although the usual process for extracting cassava starch is through wet milling, which consists mainly of fracturing the cell walls in order to release the starch granules through a grating, followed by the addition of water and filtration, which allows the separation of the starch particles suspended in the liquid medium of those that are relatively larger, such as fiber elements, then the water is removed, and the settled material is washed to remove the last different fractions of the starch to subject the purified starch to a drying finally; It should be noted that this method is considered a high-performance and economical process. On the other hand, obtaining starch by dry milling is proposed as an alternative to reduce water use, considering that washing and hulling, grating, pre-dehydration, pre-ground, dehydration, grinding, and sieving must be carried out [24].

2.2.4 Bioplastic production process from starch:

Bioplastics are manufactured from renewable resources of natural origin, such as starch; they require chemical structures that allow the degradation of the material by microorganisms, such as fungi and bacteria [25]. Bioplastic is defined as "a plastic of biological origin produced by a living organism and with a biodegradable appearance, synthesized from renewable energy sources, such as starch (corn, cassava, and potato), so it hardly produces pollution" [26]. On the other hand, according to the American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO), degradable plastics are polymers that can present changes in their chemical structure under specific environmental circumstances, causing a notable loss in their mechanical and physical properties. Considering the above, bioplastics could decompose with enzymes produced by microorganisms such as bacteria, fungi, and algae [27].

Fig. 2 shows the process of obtaining cassava starch, where initially, the root was washed, weighed, and peeled. When peeling, the rind and pulp were separated. Following this, it was grated, ground, or crushed with 350 mL of distilled water per kilogram of pulp to release the starch granules contained in the cells. Once the size was reduced, the mixture obtained was filtered through a filter, separating the fibers and impurities. Subsequently, a liter of water was added to the fiber obtained and filtered again; this step was carried out twice. The liquid obtained was left to stand in beakers for 4 h in sedimentation, where granules of various sizes settled to the bottom. Finally, the starch obtained was dried at 45°C for 24 h and then ground and sieved [28]. Note that, according to the FAO Agricultural Services Bulletin, the cassava starch extraction method which includes the following stages: collection, washing, shearing, grating and roots, extraction, sedimentation, drying, and adaptation; the latter includes the crushing, sieving, and packaging processes [16].

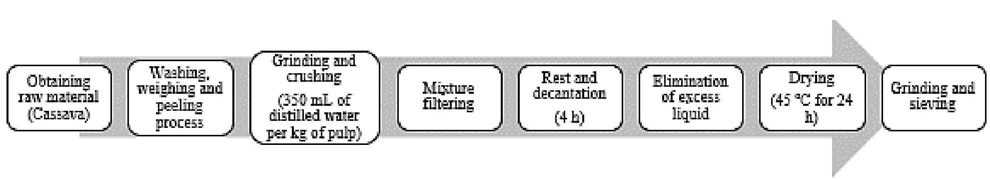

Figure 2. Starch diagram of the process.
Source: The authors.

The bioplastics process from starch has three stages: gelatinization (plasticizer and mechanical work), de-structuring of the granule, and film formation. First, there is gelatinization or initiation, defined as the loss of semi-crystallinity of starch granules in the presence of heat and high amounts of water. For this reason, it must be known that starch granules are insoluble in cold water because their structure is highly organized and presents great stability due to the multiple interactions that exist between the polysaccharides that constitute them. However, when they are heated, a slow process of water absorption begins in the amorphous intermecellar zones, which are the least structured and the most accessible; this is thanks to the fact that the hydrogen bonds are not as solid or numerous as in the crystalline areas. As the temperature increases, more water is contained, and the granule begins to bulge and increase in volume [27].

Gelatinization is generated in a tight range of temperatures that is altered depending on the source of the starch. Therefore, cassava starch gelatinizes in water at a temperature between 55 and 65 °C, which consists of swelling of the starch molecules because water penetrates its molecular structure. The unwinding of the molecules and their thermal mobility produced by swelling results in a decrease in crystallinity, breaking the structure. The behavior of the mixture is subject to the level of water absorption by the starch and the concentration. When gelatinization occurs, swollen starch granules occupy the empty spaces. The viscosity increases with temperature until the granules fragment, which disintegrates, and dissolves generates a decrease in viscosity. Secondly, there is destructuring, the transformation of the semi-crystalline starch grains into a homogeneous matrix of amorphous polymer, and the partial depolymerization of the molecules, on the one hand, and breaking the hydrogen bonds between the starch molecules. , of the other. The one that initially depolymerizes is amylopectin, then amylose, using greater energy. The increase in temperature increases the solubility of starch in water, leading to significant depolymerization around 150ºC. However, only above 190ºC can the increase in solubility be confirmed [25]. Finally, there is film formation, where the molding and drying of the sample are considered.

2.2.5 Starch films production:

For the preparation of biodegradable films of cassava starch (pulp or commercial), the Solvent casting method was used, highlighting that the concentration of starch in the solution was 4% w/v and glycerol was 30% w/w, as shown in Fig. 3. Glycerin was pre-homogenized with distilled water at room temperature for 10 min with the help of a magnetic stirrer at 200 RPM. Note that the disadvantages of starches lie in their low tensile strength, deformation at the break, and, therefore, the functionality of the film as a function of time. The high intermolecular interaction can be reduced between the polymer chains of starch and plasticizers such as water, urea, glycerol, and sorbitol, among others, must be used to reduce its fragility. Also, these are hydrophilic, which increases the polymeric material's interaction. The above requires finding an alternative mixture, making it necessary to use a less hydrophilic biopolymer such as chitosan, whose function will reduce the hydrophilic character (water vapor) permeability of the biodegradable film obtained. However, its use is limited due to the high cost, so polyethylene-based films are still used in underdeveloped countries like Colombia.

After starch granule destructed was obtained, chitosan was added in concentrations of 0, 1, and 2% w/w concerning the mass of starch, previously diluted in 1% acetic acid. It was subsequently stirred at temperatures of 25°C for 45 min. Finally, the solutions obtained were added to Petri dishes for drying in a forced convection oven at 55°C for 24 h.

2.2.6 Determination and analysis process of the physicochemical properties, hydrophilicity, and biodegradability of the bioplastics obtained:

The moisture absorption test was carried out to determine the moisture gain the films can obtain, which was reflected through the weight. For this reason, the films measuring 5x5 cm were cut into square shapes and dried in an oven at 100 °C for 24 h. Following this, they were exposed to the environment, and weight gain was monitored as a function of time using an analytical balance [29]. The percentage of moisture gain was determined by applying Eq. 1. Note that the thickness of the films was measured with a conventional vernier caliper.

a) Weighing the starch on the analytical balance. **b)** Addition of glycerin to the solution. **c)** Prehomogenization of glycerin. **d)** Solution temperature at 90 °C. **e)** Addition of starch.

Figure 3. Process of making starch films.
Source: The authors.

$$\% \text{ Weight gain} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \times 100 \quad (1)$$

The density of the films was measured considering biopolymer samples measuring 2x2 cm and weighed on the analytical balance. Then, a 10 mL test tube was used, and 5 mL of distilled water was added. The biopolymer sample was carefully introduced until it was submerged entirely. It was recorded how much the water level rose; this is the plastic volume (cm^3), and the density was calculated with Eq. 2.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \quad (2)$$

On the other hand, the percentage of solubility of the films was determined according to the methodology proposed by Trujillo Rivera, 2014. First, the films were cut with dimensions of 2x3 cm and stored in a desiccator for 7 days at a relative humidity close to 0%. After this, the samples were weighed and placed in a 100 mL beaker with 80 mL of distilled water. The samples were kept under constant stirring for one hour at room temperature (25°C). After the stirring time had elapsed, the film pieces were dried at 60°C for 2 h, considering the percentage of soluble matter (% solubility) calculated according to Eq. 3.

$$\% \text{ Solubility} = \frac{\text{initial dry weight} - \text{final dry weight}}{\text{initial weight}} \times 100 \quad (3)$$

For the biodegradability analysis, the films measuring 5x5 cm were cut into a square shape and placed under environmental conditions, exposed explicitly to soil microorganisms, sunlight, and humidity for an exposure time of 15 days, as shown in Fig. 4, where weight loss was evaluated every 5 days using Eq. 4.

$$\% \text{ Weight loss} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \times 100 \quad (4)$$

Figure 4. Biodegradation of plastic films.
Source: The authors.

Table 2.
Treatment's definition.

		B Factor - CC (%)		
		0	**1**	**2**
A Factor -	**Commercial**	ACMG-Q0	ACMG-Q01	ACMG-Q02
(Type of starch)	**Pulp**	APG-Q0	APG-Q01	APG-Q02

Source: The authors.

2.3 Experimental design

T the effect of the type of starch used and the effect of chitosan on the properties of the films was evaluated using a factorial design proposed with two factors for each of these and three levels per factor. For data analysis, ANOVA was applied, where the first factor corresponded to the type of starch used and the levels (starch) obtained with pulp and commercial starch. The second factor corresponds to the concentration of chitosan; the levels are 0, 1, and 2% w/w of the starch mass if there are significant differences for at least two means of the four treatments of each test, using the Tukey test [30].

For the evaluation of bioplastics according to the different response variables that will determine the hydrophilic and biodegradable characteristics, four replicas of the different treatments were developed to guarantee the statistical validity of the results [31]. The quantities of components to be used in general for the formulations without considering the type of starch was 4.2%, glycerol 1.8%, chitosan (0.042 and 0.084%), and the remaining water to complete 100%. Table 2 defines the 2 factors: starch type and chitosan concentration (CC).

3 Results and Discussions

3.1 Humidity absorption

The humidity gain of the biodegradable films of the two types of commercial starch was carried out considering the weight monitoring of gain as a function of time. Based on the data, some general observations are raised in Fig. 5. As the concentration of chitosan increases (from 0 to 2%), there is a general trend of increasing weight in most cases (treatments 1, 2, 3, and 4). This behavior suggests that a higher chitosan concentration leads to higher weights. Then, within each chitosan concentration level, weight variations exist across different treatments. For example, for a chitosan concentration level 0%, the weights range from around 0.298 to 1.293, depending on the treatment [32].

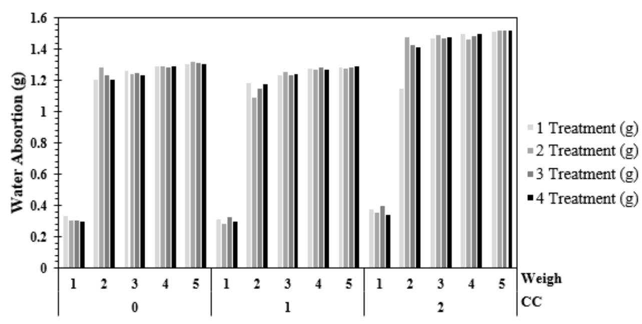

Figure 5. Humidity absorption for different treatments for commercial starch.
Source: The authors.

3.2 ANOVA for the humidity absorption

After having evaluated the moisture adsorption expressed in percentage of weight gain, according to the statistical analysis carried out, it was evident that there were no significant differences (that is, P values>0.05) as shown in Table 3 for the differences between weighing. Therefore, it is deduced that for the three different concentrations of chitosan in the first 5 days, there was no effect on the moisture adsorption of the films, as evidenced by good statistical results [8].

The humidity gain of the biodegradable films of the two types of starch pulp and the following results were obtained according to the monitoring of the weight gain as a time function. The different percentages of weight gain of the biodegradable films with starch pulp with the three types of chitosan concentration are seen in Fig. 6. Note that the weighing values vary depending on the chitosan concentration and the treatment. In general, there is a decreasing trend in weighing as the concentration of chitosan increases; this suggests that, at higher concentrations of chitosan, weighing tends to decrease. Each treatment (1, 2, 3, and 4) shows differences in weighing, which may result from the interaction between the chitosan concentration and the specific treatment. Each weighing group (1, 2, 3, 4, and 5) seems to have slightly different behavior. Some groups show more constant weighing across different treatments and chitosan concentrations, while other groups show more marked variation [33].

According to the statistical analysis in Table 4, no significant differences (P≥0.05) existed between the second and third weighing of the four treatments of the biodegradable films with starch pulp. Therefore, it is deduced that the three different concentrations of chitosan in the first 10 days did not affect the moisture adsorption of the films. According to the statistical analysis, there were significant differences (P<0.05) between the pulp in the third and fourth weights of the four biodegradable films with commercial starch treatments. Likewise, it is deduced that for the three different concentrations of chitosan in the first 15 days, there were differences between at least two of them in the moisture adsorption test of the films [10].

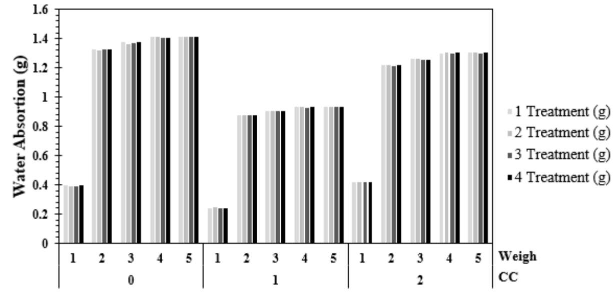

Figure 6. Humidity absorption for the different treatments for starch pulp.
Source: The authors.

Once the Tukey test was carried out, it was possible to verify the differences in humidity adsorption of the biodegradable films with starch pulp between the first and second weighing of the four treatments. Chitosan concentrations were obtained from 0-1%, 0-2%, and 1-2%. According to the statistical analysis, there were significant differences (P≤0.05) between the third and fourth weighing of the four biodegradable films with commercial starch treatments [34]. Therefore, it is deduced that the three different chitosan in the first 20 days differed in at least two in the moisture adsorption test of the concentration films. The Tukey test was carried out to determine in which of the three concentrations there was a difference, where if the difference in the means is more significant than the value found in the Tukey test (Tα= 0.37, Tα= 0.62, Tα= 1.03 and Tα= 5.59).

Table 3.
ANOVA for the data of the weight gain percentage of the biodegradable films with commercial starch for the treatments.

Variation origin	R^2 sum	DOF	R^2	F	Probability	F-Value
---			Between 1 and 2			
Between groups	947.56	2	473.78	2.9	0.10	4.26
Within the groups	1455.12	9	161.68	--	--	--
Total	2402.68	11	--	--	--	--
---			**Between 2 and 3**			
Between groups	0.4	2	0.2	0.4	0.68	4.26
Within the groups	4.46	9	0.5	--	--	--
Total	4.85	11	--	--	--	--
---			**Between 3 and 4**			
Between groups	5.08	2	2.54	6.1	0.02	4.26
Within the groups	3.76	9	0.42	--	--	--
Total	8.84	11	--	--	--	--
---			**Between 4 and 5**			
Between groups	0.661	2	0.331	6.1	0.02	4.26
Within the groups	0.491	9	0.055	--	--	--
Total	1.152	11	--	--	--	--

Note: Where DOF are degrees of freedom and R^2 quadrate.
Source: The authors.

Table 4.
ANOVA for the data of the weight gain percentage of the biodegradable films with pulp starch for the treatments.

Variation origin	R^2 sum	DOF	R^2	F	Probability	F-Value
---			**Between 1 and 2**			
Between groups	9775.58	2	4887.79	400.4	1.61E-09	4.26
Within the groups	109.86	9	12.21	--	--	--
Total	9885.44	11	--	--	--	--
---			**Between 2 and 3**			
Between groups	0.3	2	0.15	1.33	0.312	4.26
Within the groups	1.017	9	0.113	--	--	--
Total	1.317	11	--	--	--	--
---			**Between 3 and 4**			
Between groups	1.35	2	0.68	4.53	0.04	4.26
Within the groups	1.34	9	0.15	--	--	--
Total	2.69	11	--	--	--	--
--			**Between 4 and 5**			
Between groups	0.192	2	0.096	3.21	0.089	4.256
Within the groups	0.27	9	0.03	--	--	--
Total	0.462	11	--	--	--	--

Source: The authors.

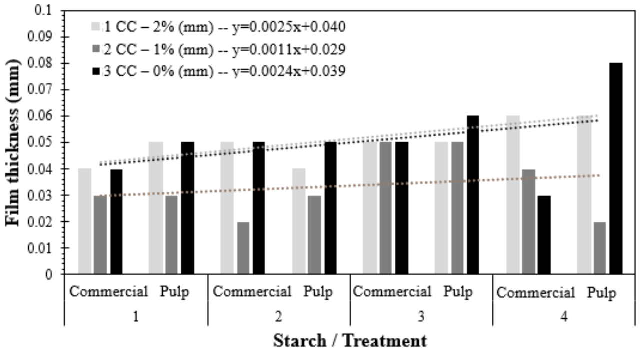

Figure 7. Thicknesses of biodegradable films corresponding to commercial starch and pulp.
Source: The authors.

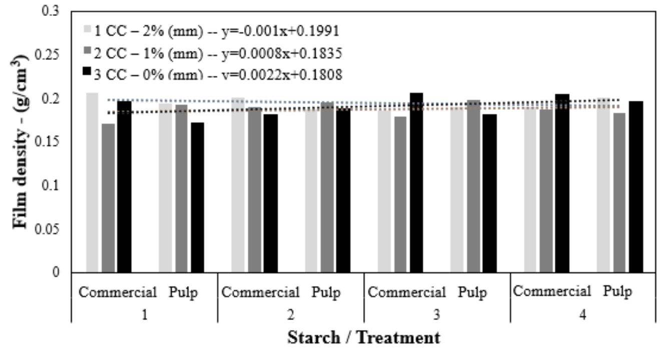

Figure 8. Densities of biodegradable films corresponding to commercial starch and pulp.
Source: The authors

3.3 Film thickness behavior

According to the measurements made on the biodegradable films of the types of starch used in the research, the thicknesses shown in Fig. 8 were obtained, where the data on starch, treatments, and the concentration of chitosan at three levels can be observed, different (0, 1, 2%) with their respective millimeters (mm) measurements. Some notable trends and patterns were evident, and the data is divided into two types of starch: "Commercial" and "Pulp" in terms of treatment, four treatments (1, 2, 3, 4) are presented for each type of starch. For "Commercial" starch, as the concentration of chitosan increases (from 0 to 2%), the film thickness measurement tends to increase generally in all treatments based on the data; some general observations are raised from Fig. 7. This behavior suggests that, in this starch type, the addition of chitosan is associated with a significant increase. For "Pulp" starch, the relationship between chitosan concentration and measurement is more varied as observed. In some treatments, the increase in chitosan concentration is associated with an increase in film thickness; in other treatments, a decrease occurs. The variability indicates that the effect of chitosan on "Pulp" starch may be more complex and depends on the specific treatment [11].

Some treatments may be more sensitive to chitosan concentration than others, suggesting the importance of the interaction between treatment and chitosan concentration. In summary, the data indicate that chitosan concentration influences starch measurements, but the nature of this relationship varies depending on the type of starch and treatment. It is important to understand these relationships to determine how adding chitosan should be optimized based on improving starch properties or characteristics in particular applications. Likewise, a trend equation was established for each one that governs the behavior of each starch concerning the experimental conditions with the addition of chitosan.

3.4 Density behavior

The density results are summarized in Fig. 8, exposing data on starch, treatments, and chitosan concentration at three different levels (0, 1, 2%) with their respective measurements in g/cm³. The data is divided into two types of starch: "Commercial" and "Pulp". In terms of treatment, four treatments (1, 2, 3, 4) are presented for each type of starch. For "Commercial" starch, as the concentration of chitosan increases (from 0 to 2%), the density (measured in g/cm³) tends to vary in all treatments. For "Pulp" starch, the relationship between chitosan concentration and density is more varied. In some treatments, the density increases with chitosan concentration, while in others, it decreases. This behavior suggests that the effect of chitosan on "pulp" starch may be more complex and depends on the specific treatment. Within each type of starch, different treatments show variations in density. Some treatments may be more sensitive to chitosan concentration than others, highlighting the importance of the interaction between treatment and chitosan concentration. Likewise, a trend equation was established for each one that governs the behavior of each starch concerning the experimental conditions with the addition of chitosan, evidencing a high correlation coefficient R^2 between the measured variables and the treatments, considering the value of the equation slope [33].

3.5 Percent solubility determination

The results obtained from the percentage determination of solubility of the plastic films are shown in Table 5. Solubility of biodegradable films corresponding to commercial starch and pulp. The difference in dry weight between the initial and final state could be observed. The difference represents a change in dry weight during treatment. Overall, “Commercial Starch” appears to experience a greater dry weight difference than “Pulp Starch.” This suggests that the type of starch influences how it reacts to the treatment. As the concentration of chitosan increases (from 0 to 2%), the difference in dry weight generally tends to increase in both types of starch. This indicates that chitosan has a positive effect on dry weight change. The different treatments (1, 2, 3, 4) show variations in the difference in dry weight. Some treatments show significantly greater differences than others, suggesting that the specific treatment also has an impact. In some cases, the difference in dry weight is relatively small, while in other cases, it is more significant; this behavior could be related to specific factors of the treatments and the reaction of the starches to those conditions [8].

Table 5.
Weighing of biodegradable films corresponding to commercial starch.

Treatments	Initial dry weight (g)	Final dry weight (g)	Difference	Initial dry weight (g)	Final dry weight (g)	Difference
	Commercial starch			Starch pulp		
---	CC - 0%					
1	0.2875	0.1615	0.1260	0.3807	0.3166	0.0641
2	0.2357	0.1477	0.0880	0.5074	0.4817	0.0257
3	0.4015	0.2511	0.1504	0.3938	0.3362	0.0576
4	0.4174	0.2717	0.1457	0.4693	0.4371	0.0322
---	CC - 1%					
1	0.2974	0.2123	0.0851	0.3092	0.2800	0.0292
2	0.3825	0.2805	0.1020	0.2118	0.1315	0.0803
3	0.291	0.1942	0.0968	0.3601	0.3518	0.0083
4	0.2607	0.1703	0.0904	0.2484	0.2023	0.0461
---	CC - 2%					
1	0.3726	0.2288	0.1438	0.427	0.3325	0.0945
2	0.3829	0.2421	0.1408	0.4159	0.3298	0.0861
3	0.3806	0.2334	0.1472	0.3862	0.3294	0.0568
4	0.3536	0.2149	0.1387	0.4492	0.3545	0.0947

Source: The authors.

In Table 6, an analysis of the percentage of solubility of the films for commercial starch and pulp was carried out to determine the main changes between treatments and chitosan concentration. Likewise, chitosan concentration data (%) and 1-T (%), 2-T (%), 3-T (%), and 4-T (%) values are presented for two types of starch ("Commercial starch " and "Starch pulp") at three levels of chitosan concentration (0, 1, 2%). In commercial starch, as the concentration of chitosan increases, the 1-T, 2-T, 3-T, and 4-T values generally increase. This performance suggests that the chitosan concentration positively affects the values for this type of starch. For the other case (pulp starch), the relationship between chitosan concentration and values is more varied. In some cases, such as 1-T, the values increase with chitosan concentration, while in other cases, such as 3-T, they decrease. This behavior indicates that the effect of chitosan on pulp starch is more complex and depends on the specific treatment. On the other hand, the different treatments for both types of starch (1, 2, 3,

Table 6.
Solubility percentage of biodegradable films corresponding to commercial starch and pulp.

CC (%)	1-T (%)	2-T (%)	3-T (%)	4-T (%)
---	Commercial starch			
0	43.82	37.33	37.46	34.90
1	28.61	26.67	32.26	34.67
2	38.59	36.77	38.44	39.22
---	Starch pulp			
0	16.84	5.06	14.63	6.86
1	9.44	37.91	2.30	18.56
2	22.13	20.53	14.70	21.08

Note: Where T is treatment.
Source: The authors.

4) show variations in values. Some treatments may be more sensitive to chitosan concentration than others, highlighting the importance of the interaction between treatment and chitosan concentration.

3.6 Biodegradability analysis

The results of the biodegradability determination of the commercial starch and plowing results were obtained according to the monitoring of weight loss as a function of time, as shown in Table 7. The data reveals that, in general, commercial starch exhibits higher CC percentages compared to starch pulp across all treatment levels and weighing conditions. Commercial starch consistently has values above 1.5, whereas starch pulp values are generally below 1.4; this value suggests that commercial starch contains more chitosan than starch pulp.

3.7 Properties comparison of bioplastics made of starch type and chitosan concentration

For humidity adsorption, the differences obtained between commercial starch and pulp films for the 0% chitosan concentration were 37.6% in the first 5 days, 0.26% for the first 10 days. of 0.2% for the first 15 days and 0.3% for the

Table 7.
Weight loss of biodegradable films with commercial starch in the first weighing of the four treatments.

CC (%)	1-T (%)	2-T (%)	3-T (%)	4-T (%)	1-T (%)	2-T (%)	3-T (%)	4-T (%)
---	Commercial starch				Starch pulp			
---	Weigh 1							
0	1.5352	1.5320	1.5292	1.5382	1.7508	1.7543	1.7689	1.7525
1	1.3034	1.3034	1.3034	1.3034	1.3310	1.3343	1.3300	1.3319
2	1.3800	1.3800	1.3800	1.3800	1.3037	1.3040	1.3072	1.3024
---	Weigh 2							
0	1.5147	1.5126	1.5087	1.5174	1.7305	1.7276	1.7325	1.7342
1	1.2852	1.2832	1.2820	1.2871	1.3101	1.3115	1.3095	1.3127
2	1.3639	1.3609	1.3630	1.3659	1.2918	1.2950	1.2898	1.2876
---	Weigh 3							
0	1.4847	1.4790	1.4874	1.4860	1.6943	1.6931	1.6950	1.6939
1	1.2623	1.2598	1.2639	1.2645	1.2855	1.2875	1.2834	1.2840
2	1.3410	1.3403	1.3418	1.3420	1.2678	1.2656	1.2647	1.2688
---	Weigh 4							
0	1.4158	1.4201	1.4138	1.4145	1.6103	1.6094	1.615	1.6125
1	1.2091	1.2096	1.2106	1.2085	1.2303	1.2314	1.2285	1.2330
2	1.2803	1.2790	1.2823	1.2813	1.2146	1.215	1.2167	1.2138

Source: The authors. Note: Where T is treatment.

Table 8.
Averages of the percentages of weight gain between the weighing carried out in the four commercial starch and pulp treatments.

CC (%)	Average weight gain percentage			
---	Commercial starch			
---	1 and 2 weighing	2 and 3 weighing	3 and 4 weighing	4 and 5 weighing
0	274.24	3.96	2.85	0.67
1	294.20	3.88	3.55	0.48
2	276.69	3.54	1.96	1.04
---	Starch pulp			
0	236.46	3.70	2.65	0.37
1	259.45	3.42	2.84	0.23
2	190.78	3.32	3.44	0.06

Source: The authors.

Table 9.
Average values for the response variables in the four commercial starch and pulp treatments.

CC (%)	Commercial	Pulp	Commercial	Pulp	Commercial	Pulp
Average	Thickness		Density		Solubility	
0	0.042±0.002	0.060±0.003	0.20±0.01	0.19±0.01	38.38±0.32	10.85±0.11
1	0.035±0.001	0.033±0.001	0.18±0.01	0.19±0.01	30.55±0.25	17.05±0.12
2	0.050±0.001	0.050±0.001	0.20±0.02	0.18±0.01	38.26±0.27	19.61±0.15

Source: The authors.

first 20 days, for the chitosan concentration 1%, were 34.75% in the first 5 days, 0.46% for the first 10 days, 0.71% for the first 15 days and 0.25% for the first 20 days and the chitosan concentration 2%, were 85.91% in the first 5 days, 0.22% for the first 10 days, 1.48% for the first 15 days and 0.98% for the first 20 days, which proves that commercial starch films have greater moisture adsorption than pulp starch films, thus being the one with 0% chitosan concentration the one with the greatest moisture adsorption, taking into account that chitosan It is used in plastic films to reduce the hydrophilic character [7,8], as was observed in Table 8.

For the thickness determination, the differences obtained between the films of commercial starch and pulp for the 0% chitosan concentration was 0.017 mm; for the 1% chitosan concentration, it was 0.002 mm, and for the 2% chitosan concentration, there was no difference. The data was obtained from the differences between Table 9, shown below. For the density's determination, differences were obtained between the commercial starch films and pulp; for the 0% chitosan concentration was 0.01 g/cm^3, for the 1% chitosan concentration, it was 0.01 g/cm^{3,} and for the 2% chitosan concentration it was 0.02 g/cm^3.

For solubility, the differences obtained between commercial starch films and pulp for the 0% chitosan concentration was 27.53%; for the 1% chitosan concentration, it was 13.5%; and for the 2% chitosan concentration, it was 18.65%, from the above it can be confirmed that the films made with commercial starch have a greater solubility than those of pulp starch, considering the differences obtained from Table 9. For biodegradability, the differences obtained between commercial starch and pulp films, for the 0% chitosan concentration, were 0.13% in the first 5 days, 0.22% for the first 10 days, and 0.25% for the first 15 days. for the 1% chitosan concentration, they were 0.11% in the first 5 days, 0.28% for the first 10 days and 0.02% for the first 15 days and for the 2% chitosan concentration, they were 0.18% in the first 5 days, 0.26% for the first 10 days and 0.43% for the first 15 days, which proves that pulp starch films have greater biodegradability than commercial starch films, with the chitosan concentration being 0%.

4 Conclusions

Using the casting method, the mixture of cassava starch (pulp or commercial) with glycerol and chitosan generates a biofilm with good properties. Within each type of starch used, the different treatments show variations in the density and thickness of the films. Some treatments may be more sensitive to chitosan concentration than others, highlighting the importance of the interaction between treatment and chitosan concentration. Likewise, a trend equation was established for each one that governs the behavior of each starch concerning the experimental conditions with the addition of chitosan, evidencing a high correlation coefficient (R^2) between the measured variables and the treatments, considering the value of the slope of the equation.

It was observed that the plastic films that produced more bubbles at the time of production contained chitosan at a higher percentage. Likewise, the films made with pulp starch have the same colorless tone as the films made with commercial starch; in the end, what caused them to take on an opaque tone was the amount of chitosan in those that contained it.

The different tests carried out in the research determined that using commercial starch to produce biodegradable plastic films favors greater moisture adsorption, solubility, and biodegradability compared to starch extracted from cassava by hand. Regarding the most appropriate concentration of chitosan in the formulation of the films, the potential use of biofilms must be considered, and in this way, the appropriate concentrations and percentages for their industrial application must be established.

Bioplastic films with chitosan offer a potential application in the food industry, considering the environmental sustainability that this type of biomaterials can offer. Bioplastic films incorporating chitosan, especially when combined with cassava starch, present great potential for application in the food industry. These biomaterials stand out for their ability to address environmental and sustainability challenges. Some key benefits they offer include their renewable origin, biodegradability, and the ability to reduce dependence on traditional petroleum-based plastics. The combination of chitosan and cassava starch in bioplastic films can not only improve moisture and fat barrier properties but can also extend the shelf life of food, reducing food waste. These biodegradable films can reduce plastic pollution and relieve pressure on landfills and the environment.

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