Physical characterization of biopolymers with starch from potato and cassava organic wastes polymerized in water

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Abstract. During the last decades, the use of plastic has become indispensable for the daily life of people; the global production of these materials reaches approximately more than 200 million tons per year. For this reason, research has been carried out to manufacture substitute materials that have similar physical properties, such as starch-based biopolymers; in this research we initially characterized the physical properties of a biopolymer based on starch polymerized in water, without plasticizers, and also to find an optimal proportion between starch and water; in this way an experimental design is generated where the proportion of these two varies, in which starch extracted from potato and cassava wastes was used. These biopolymers were characterized for linear shrinkage, density, and hardness properties. The results of the characterizations showed that the proportions lower than 1:5 starch-water present difficulty to process and deficiency in the homogeneity of the mixture, while the proportions higher than 1:5 presented a linear shrinkage higher than 82.69% and a loss in weight higher than 74.45%; on the other hand, the hardness analysis showed an average of 79 points on the shore A scale and density with an average of 1.055 g/cm³, the results determined that the most adequate proportion is 1:6.5 starch-water.

1. Introduction

Plastics of fossil origin are synthetic materials derived from the petroleum refining process; the term "plastic" comes from the Greek "plastikos" and means "that can be molded by heat" [1]; these petroleum-derived polymers have a wide variety of applications in everyday products and in industries, thanks to the characteristics of their physical properties [2]; however, they are materials that are resistant to degradation and their increasing accumulation in natural environments is threatening the environment; this is due to the fact that their production reaches more than 200 million tons per year with an accumulation rate of 25 million tons per year [3].

In order to attack this problem, several researches have been carried out in search of alternative materials that are biodegradable; in this way, bio-based biopolymers have become a widely researched alternative in the world, being classified in 3 study groups according to their origin; biodegradable biopolymers based on bioderived monomers (vegetable oils and lactic acid), biopolymers synthesized by microorganisms (polyhydroxyalkanoates (PHA)) and biopolymers based on renewable resources (starch and cellulose) [4].

This last group of biopolymers consists of materials based on renewable resources because they are obtained directly from nature; starch is a source of energy in plants and animals and is found in granular...
form; it is a polysaccharide or also called "glucose polymer" that is formed by polymeric chains of amylose and amylopectin [5]; the glucose polymer manufactured as bioplastic presents physical properties similar to petroleum-derived plastics [4].

This research seeks to analyze the physical characteristics of biopolymers based on starches extracted from potato and cassava organic wastes; in this way, a quantitative and qualitative factorial experimental design is carried out in three phases; in this work only the first phase is presented, which consists of synthesizing biopolymers based on starch and water, without adding plasticizers; in this way, an experimental design is established for the first phase of 2 factors with 2 and 8 levels respectively, in addition, 3 replicates are performed in each test. Once synthesized, a characterization of the physical properties of the biopolymers is carried out by means of the analysis of linear contraction, hardness, and density; finally, a comparison is made with the physical properties of petroleum-derived plastics.

2. Materials and methods
The research is divided into 4 processes: starting with the extraction of the raw material, where the potato and cassava residues are collected, cleaned, crushed and starch extracted; then the polymerization of the raw material was carried out by means of a heating plate, controlling the parameters of time, temperature, and pH; then the different samples were molded, poured into acetate molds, and dried in an oven; and finally, the biopolymers were characterized.

The method of this study is of mixed factorial experimental type, with quantitative and qualitative analysis; likewise, 16 different biopolymers were obtained from the experimental design, each one with 3 repetitions for a total of 48 samples. Each sample was subjected to hardness and density tests; in addition to calculating its linear shrinkage during the polymerization process.

2.1. Extraction
Solid waste was collected from different restaurants in the municipality of Sogamoso, Colombia; this waste was cleaned and disinfected with a solution of water and hypochlorite [6]. Then, following the starch extraction method of Dania Fonseca, Lily Monroy, and Carlos Rodríguez [7], the residues were ground in a humid medium with the help of a disk mill, obtaining a lumpy and humid mass as a result; this mass was diluted in water and agitated with the help of a flocculator for one hour, in order to separate the starch granules from the rest of the unwanted material, such as cellulose fibers and dirt.

The mixture is filtered, and the resulting liquid is allowed to settle to obtain the starch and other impurities or fine dirt particles in the form of sediment; to remove the impurities and dirt from the starch mass, it is washed 3 times with distilled water. Finally, drying of the wet starch mass is done in an electric oven at 50 °C for 24 h; this dried starch should be ground and stored in an airtight container to avoid moisture absorption [8].

2.2. Polymerization
The polymerization method is generated by the addition of water in larger quantities to the starch, so in the presence of heat it causes the swelling of the starch granules, to generate the polymer the water penetrates the amorphous regions causing the granular structure to fragment, this is originated by exposing the mixture of water and starch to the gelatinization temperature (60 °C to 71 °C), where the formation of a gel begins to be observed [9]; During the polymerization process, water is also lost by evaporation, leaving a mixture with less humidity than at the beginning of the process, at the end of the process when the biopolymer reaches room temperature, the total conformation of the gel is perceived.

2.3. Molding
The process to generate the bioplastic parts is done with the gravity molding method, where the acetate mold is prepared with release agent, then the biopolymer in a liquid state with high viscosity at an average temperature of 50 °C is poured by moving the material on the surface of the mold; Finally, the biopolymer sheet is demolded and cut to extract the shape of the specimens, which will then be subjected to a linear shrinkage analysis, physical hardness and density tests.
2.4. Experimental design
A mixed factorial experimental design is generated with two factors (type of starch and % water), each one with 2 and 8 levels respectively, in addition, qualitative and quantitative result analyses are performed; this in order to find the best relation between the amount of water and starches, to generate the mixture that will later polymerize, for this reason the water ratio is varied in 8 levels of starch: water, for 2 starch factors (potato, cassava) as can be seen in Table 1, in order to generate better statistics, 3 runs will be made for each test.

| Table 1. | Experimental design with 4 starch factors and three proportion levels. |
| --- | --- |
| Starches | 1:2 | 1:3.5 | 1:4.5 | 1:5 | 1:6.5 | 1:7.5 | 1:8.5 | 1:10 |
| Potato | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 |
| Cassava | P9 | P10 | P11 | P12 | P13 | P14 | P15 | P16 |

2.5. Physical tests
The physical analysis of the tests carried out is qualitative and quantitative; in the qualitative analysis, we observed the ease of the molding process, where the different percentages of raw material affected the viscosity and fluidity of the material; in addition, the homogeneity of the mixture (water and starch) was analyzed, since the samples already polymerized with low water content generated lumps of unpolymerized material.

For the quantitative analysis, a study of the linear shrinkage, hardness and density of the manufactured sheets was carried out. Linear shrinkage is caused when the biopolymer generates tensile stress when drying, this volumetric shrinkage occurs in the curing process; the method for measuring linear shrinkage consists of measuring two points as far apart as possible, before and after curing of the polymer [10], this taking into account the measurement of the film thickness; to determine the shrinkage percentage is done by means of Equation (1), where %CL is linear shrinkage in percentage, LP initial polymer length (cm), and LC length after curing (cm) [11].

\[
%CL = 100 \frac{LP - LC}{LP}. \tag{1}
\]

The hardness analysis method is performed by means of a Type A PC-511/A digital hardness tester, with an indenter at its end in shore A scale for plastics or soft rubbers; the measurements are performed on the surface of the biopolymer sheets [12].

The density is analyzed with the water displacement method; initially a test tube with water is placed on a balance, then the balance must be placed on zero to subsequently submerge the sample in the water contained by the test tube, the sample must be completely submerged; finally the respective values of volume and weight are taken [13], the density will be calculated with the Equation (2), where \( \rho \) is density (g/cm\(^3\)), \( m \) is the mass of the sample (g), and \( v \) is the volume of the sample (cm\(^3\)) [14].

\[
\rho = \frac{m}{v}. \tag{2}
\]

3. Results and discussions
The characterization made it possible to identify the effects and/or contributions of the raw materials in their different proportions to the properties of the materials under study; in addition, key behaviors were identified for future applications during the process, such as homogeneity of the biopolymer, ease of molding, deformations, and contractions of the material during drying, surface cracks and internal bubbles.
As a result of the analysis and with the help of Minitab software, it was possible to establish an optimal combination of raw materials that, when polymerized, allows obtaining a more homogeneous polymeric matrix with better physical characteristics in terms of hardness and density.

3.1. Material behavior in the polymerization process
In the homogeneity of the mixture in the polymerization process, it was observed that in proportions lower than 1:5 of starch and water, it presents an inability to generate a homogeneous mixture, leaving starch granules without water, when the mixture is exposed to temperature, these granules do not gelatinize and gel formation is not possible; and in proportions higher than 1:5, gelatinization of all the starch granules is possible.

The molding when pouring the different biopolymers, it was observed that the proportions lower than 1:5 presented an inhomogeneous lumpy mass and the material does not mold easily; for the proportions of 1:5 and higher, it presented a viscous and homogeneous mass, in addition, the biopolymer in gel easily took the shape of the mold, for the case of the proportion 1:10 the mass became too liquid, increasing the volume with respect to the other proportions due to the excess of water in its polymeric matrix.

Once the drying process of the biopolymer sheets was completed, the deformation of the sheets was recorded (see Figure 1); a qualitative analysis shows that the higher the water content, the greater the deformation, the fact that the mold does not have a top face containing the film also influences the deformation, cracks and air bubbles contribute to the deformation of the material.

3.2. Linear shrinkage
The behavior before curing of the biopolymer sheets with potato starch, shows that the thickness proportional to the increase of the starch: water ratio, as shown in Table 2, where the minimum thickness was found in the ratio 1:5 with a thickness of 5.95 mm and a maximum in the ratio 1:10 with a thickness of 8.35 mm, the behavior is due to the amount of water integrated in the polymeric matrix; the thickness measurement after drying for the sheets made with potato starch was found with a mean of 0.934 mm ± 0.078 mm, the calculation of the linear shrinkage percentage according to Equation (1) shows a mean of 86.07% ± 2.69%.

In the case of biopolymers with cassava starch, before curing, it shows a behavior similar to that of the potato starch sheets; the sheets show an average thickness of 0.782 mm ± 0.09 mm, for this case the linear shrinkage is 86.82% ± 2.82 %; for the two factors potato and cassava, the linear shrinkage presented has a similar behavior. It is important to consider linear shrinkage as it affects the weight and size of the sheet; shrinkage also affects other widely used materials such as polyethylene terephthalate (PET), high-density polyethylene (HDPE), low-density polyethylene (LDPE) [15]; which regulate considering the shape of the part, the molding system and processing conditions.

Figure 1. Cured biopolymer films; (a) 1:5 cassava; (b) 1:8 potato.
3.3. Hardness

The hardness measurement was carried out in 10 different places on the sheet; the measurements were taken in places that represented the general thickness of the sampled sheet. In Figure 2 of dispersion, we can observe that the hardness has a similar behavior in all the proportions; however, it can be noted that as the amount of water increases with respect to the amount of starch, the hardness increases in parallel, until reaching a limit at the 1:8.5 starch: water ratio, where it is observed that from this point on, the hardness begins to decrease as the water ratio increases. With this we can say that the optimum "starch: water" ratio for hardness is approximately 1:8.5, without considering the other qualitative variables such as ease of molding, drying and flowability.

In Figure 3 of dispersion, we can observe that the hardness has a similar behavior in all proportions of potato vs cassava, however, there is a slight increase in hardness that can be seen in the data corresponding to the tests with 100% potato.

Table 2. Thickness of sheets and percentage of linear shrinkage shown.

| Proportion | Before drying (mm) | After drying (mm) | % of contraction |
|------------|--------------------|-------------------|-----------------|
| 1-Potato 1:5 | 5.95               | 1.03              | 82.69           |
| 2-Potato 1:6.5 | 6.00            | 0.90              | 85.00           |
| 3-Potato 1:7.5 | 6.50              | 0.92              | 85.85           |
| 4-Potato 1:8.5 | 7.49              | 0.99              | 86.78           |
| 5-Potato 1:10 | 8.35              | 0.83              | 90.06           |
| 1-Cassava 1:5 | 4.21              | 0.63              | 85.04           |
| 2-Cassava 1:6.5 | 5.25             | 0.87              | 83.43           |
| 3-Cassava 1:7.5 | 6.24              | 0.83              | 86.70           |
| 4-Cassava 1:8.5 | 7.09              | 0.81              | 88.58           |
| 5-Cassava 1:10 | 8.17              | 0.77              | 90.58           |

Figure 2. Dispersion of starch: water ratio data vs hardness.

Figure 3. Scatter plot of hardness vs potato - cassava.

Figure 4. Main effects for hardness.
The average hardness is found to be 78.9 Shore A, this value is comparable to the bioplastic generated based on coconut and papaya husk fibers in which a bioplastic with an intermediate hardness was shown [16]; different from other bioplastics based on starch and additives such as glycerin and urea, which can be characterized as a soft material [17].

3.4. Density
All relevant samples were taken according to the described method, volume and mass data were obtained and by means of Equation (2) the density calculation was performed, the data are shown in Table 3, to compare the resulting density in the biopolymer sheets the density of some petroleum derivative plastic materials shown in Table 4 are considered.

It is observed that the densities between the manufactured biopolymer and the petroleum-derived plastic materials are similar, since they are close to 1 g/cm$^3$, except for Polytetrafluoroethylene, which has a density higher than 2 g/cm$^3$; biopolymers generated with coconut husk and papaya fibers and others processed with starch and additives glycerin and urea present the same density behavior as the biopolymer based only on processed starch and water [17,18].

Table 3. Weight, volume, and density of the sheets.

| Proportion | Weight (g) | Volume (cm$^3$) | Density (g/cm$^3$) |
|------------|------------|-----------------|--------------------|
| 1-Potato 1:5 | 0.7        | 0.7             | 1.00               |
| 2-Potato 1:6.5 | 0.6        | 0.6             | 1.00               |
| 3-Potato 1:7.5 | 1.0        | 0.9             | 1.11               |
| 4-Potato 1:8.5 | 0.8        | 0.7             | 1.14               |
| 5-Potato 1:10 | 0.5        | 0.5             | 1.00               |
| 1-Cassava 1:5 | 0.8        | 0.7             | 1.14               |
| 2-Cassava 1:6.5 | 1.3        | 1.4             | 0.93               |
| 3-Cassava 1:7.5 | 1.6        | 1.3             | 1.23               |
| 4-Cassava 1:8.5 | 1.3        | 1.3             | 1.00               |
| 5-Cassava 1:10 | 0.9        | 0.9             | 1.00               |

Table 4. Density of some petroleum derivative polymers [18].

| Acronym | Material | Density (g/cm$^3$) |
|---------|----------|-------------------|
| HDPE    | High-density polyethylene | 0.97             |
| LDPE    | Low-density polyethylene  | 0.93             |
| PP      | Polypropylene              | 0.94             |
| PMMA    | Polymethyl methacrylate   | 1.20             |
| PS      | Polystyrene                | 1.10             |
| PA 6.6  | Nylon 66                   | 1.30             |
| PTFE    | Polytetrafluoroethylene   | 2.30             |
| PET     | Polylethylene terephthalate | 1.40          |
| PVC     | Polyvinyl chloride         | 1.29             |
| NBR     | Nitrile rubber             | 1.20             |

4. Conclusions
The analysis of the results shows that the low proportion of water in the polymeric matrix affects the homogeneity of the material and hinders molding; on the contrary, increasing the proportion of water causes the material to decrease its viscosity, facilitating molding, but increasing linear shrinkage; this linear shrinkage is above 80 % in all cases. Similarly, the hardness data show that the best ratio is in the range between 1:5 and 1:7.5; as a result, we found that the best starch - water ratio for all analyses is 1:6.5. Similarly, we can say that the characteristics of the biopolymers generated show that it is possible to use these materials to replace Petro-derived plastics, even though biopolymers tend to be brittle; to improve the physical-mechanical characteristics of these biopolymers, additives could be added to increase the plasticity of the material, adding plasticizers such as urea and glycerin to the polymer matrix.
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