Thermoplastic Cassava Flour

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1. Introduction

Stocks of oil in the world are limited and most synthetic plastics cannot be degraded by the environment, whereby people are investigating other sources of raw materials aimed at the production of materials less aggressive to the environment, to serve to decrease the amount of plastic waste.

The food industry plays an important role in the use of plastic for protection before, during and after food harvest to ensure the integrity of these (Weber, 2001; De Graff et al, 2003; Tharantahan, 2003, Halley, 2005); for example, the common consumer products such as plates, cups, spoons, knives, disposable, film or coating films and bags (Wang et al, 2003; De Graff et al, 2003; Averous & Boquillon, 2004; Bastioli, 2001, Garcia et al, 2000, Shogren et al, 2003; Thompson, 2003, Wang et al, 2003).

The plastics produced from fossil sources have contributed significantly to increasing environmental pollution caused by the accumulation of solid waste that cannot degrade in landfills, so that has prompted the search for new biodegradable materials not only in the food, but also in the medical, automotive, among others. Renewable natural raw materials become an important alternative, including flour, starch, natural fibers, proteins, and others prominent in developing options for bioplastics (Tharantahan, 2003). Currently there is growing interest to use raw materials and agricultural byproducts in obtaining biodegradable plastics, such as from corn and cassava and potato tubers. However, plastics developed from these sources have certain drawbacks of structural stability compared to conventional plastics, caused by its stiffness or weakness due to its high hygroscopicity and rapid aging (Villada, 2005). Therefore, the research efforts must be maintained and increased in this field, taking into account the use of local products in the region such as cassava, which are being studied in research projects, through which it is intended that the methodology production of biodegradable plastics is reproducible on an industrial scale, taking into account the specific functional requirements for various applications.

This document presents some excerpts related to thermoplastic cassava flour as a raw material useful for packaging applications.

2. Cassava

Cassava (Manihot esculenta Crantz), also known as mandioca, is a starchy root belonging to the Euphorbiaceae family and is one of the most important energy sources for tropical areas...
of the world. Although cassava thrives in fertile soil, its comparative advantage to other more profitable crops is their ability to grow in acidic soils of low fertility, with sporadic rainfall or long periods of drought. The crop is widely adapted as it is planted from sea level up to 1800 meters, at temperatures between 20 and 30°C with an optimum of 24°C, relative humidity between 50 and 90% with an optimum of 72% and an annual rainfall between 600 and 3000mm with an optimum of 1500mm (Casaca, 2005). It is widely cultivated in tropical Africa, Asia and Latin America, and it is the fourth most important global crop in developing countries, with an estimated production in 2006 of 226 million tonnes. It is characterized by great diversity of uses both roots and leaves can be eaten by humans and animals. Cassava products can be used in industry mainly from the starch (Ceballos, 2002).

The bulk of cassava produced in farms of small farmers and marginal areas, so that a significant proportion of production is not recorded in the statistics accurately, in addition, these farmers are generally isolated from the distribution channels and the product processing industries, mainly in areas that have little or no access to improved varieties, fertilizers and other production inputs. Governments have not yet made the necessary investments to boost its value added, that would make cassava starch products uncompetitive internationally (FAO, 2007).

This root is composed of three tissues: the periderm (husk), the cortical parenchyma (cortex) and inner parenchyma, where approximately 80% of fresh weight of the root, corresponds to the parenchyma or pulp, which is the tissue that plant stores starch. The dry matter content of cassava root fluctuates between 30% and 40%, dry matter is composed of parenchyma, mostly (90% to 95%), the nitrogen fraction, ie, carbohydrates (starch and sugars), the rest of this dry matter corresponds to fiber (1% to 2%), fats (0.5% to 1.0%), ash and minerals (1.5% to 2.5%) and protein (2.0%); starch also represents most of the carbohydrates (96%) and it is, therefore, the main component of root dry matter (FAO, 2007).

Moreover, cassava varieties can be classified as bitter, which contain a cyanogenic glycoside called linamarin, which are hidrolized in the presence of enzymes and acids linamaraza, resulting in the formation of hydrocyanic acid. This acid is under the skin of the roots, inside a layer of viscous-looking latex, white and with characteristic odor, usually this variety is used for industrial processes.

Sweet varieties have low or no presence of hydrocyanic acid, therefore its use is safe after cooking (Aristizabal & Sanchez, 2007). If cassava use is for human consumption, it will be called culinary quality, but it used for the manufacture of products such as flour, starch or dry pieces it be called industrial cassava, and finally it can be called dual purpose if it is intended to human consumption or industrial use (Aristizabal & Sanchez, 2007). In Colombia, CIAT, Corpoica and CLAYUCA have developed improved varieties of cassava for growth in certain areas of the country, taking into account biological and climatic factors. The Cauca region is located within zone which it can grow varieties such as HMC-1, MPER 183, MBRA 383, among others (Cadavid, 2005).

Cassava roots are rich in calories but deficient in protein, fats, minerals and vitamins. It also presents several secondary compounds in the root tissues as polyphenols, tannins, carbohydrates and cyanogenic compounds (Sanchez & Alonso, 2002).
2.1 Cassava flour

After harvest, fresh cassava roots can deteriorate very quickly, since they have a 65% water content (Ceballos, 2002). In order to preserve the fresh cassava, an alternative is by drying to obtain dried pieces, which can be obtained flour, whether for food, feed or industrial use. The cassava flour for human consumption can be classified as fermented (gari) or not fermented. Unfermented flours are made by grinding the roots peeled or cut into small pieces, then the resulting material is dried and milled (Ceballos, 2002). According to the Codex standard for edible cassava flour (Manihot esculenta Crantz), it is the product obtained from cassava chips or pasta with a grinding process, followed by screening to separate the fiber from flour. In the case of edible meal prepared with the bitter cassava (Manihot utilissima Pohl) it shall be made by soaking the tubers detoxification in water for several days prior to drying in the form of milled whole tuber (pasta) or small pieces.

Cassava flour is obtained by grinding dried cassava chips, as explained in detail below (Alvarado & Cornejo, 2009):

- Receiving. A visual inspection of the raw material is performed. The performance process is determined by the cassava weight.
- Washing. It removes dirt and other debris present in cassava roots with water.
- Peeling. When the process is done on a small scale, cassava peel is removed by abrasive equipment or knives. When the shell is not removed you get cassava meal.
- Cutting. Cassava is cut into small pieces.
- Crushed. The roots will dry quickly, so, it is necessary to increase the surface exposed to hot air grinding cassava chips until slurry.
- Drying. It can be accomplished by hot air dryers or in yards by sunlight.
- Milling. Once dried cassava chips, reducing the particle size using a hammer mill generally.
- Sieving. The ground flour is passed through a series of mesh to determine particle size. According to the CODEX STAND 176-1989, cassava flour is fine when at least 90% passes through a 0.6mm mesh sieve and it is thick when 90% passing through a 1.20mm mesh sieve.

Cassava flour consists mainly of starch (80 - 90%) and fiber (1.5-3%) depending on the variety of cassava from which one obtains (Charles, Sriroth, & Huang, 2005). It is considered a potential raw material in the field of developing new materials, including biocomposites, because of its high concentration of starch, (Martínez et al, 2007).

Cassava flour should have a moisture content no greater than 13% for easy storage and transport conditions (Codex Stand 176, 1989). Cassava flour can also be classified as integral or bakery. The integral flours are the result of grinding the dried cassava chips with bark, which is used as a substitute for carbohydrates in cereals (maize, wheat, sorghum) and it is usually used in food formulations for animals. The bakery is obtained by grinding the dried pieces of peeling cassava, passing the product through a fine sieve. If the product of grinding through a sieve less dense, it is obtained granulated or cassava semolina (Montaldo, 1985).
2.1.1 Applications

In Latin America and other continents, cassava flour is sold primarily as a potential substitute for cereal flours (wheat and sorghum) in the field of baking (Shittu et al, 2008, Benitez et al, 2008). However, cassava flour has cyanogenic content (specific processing technology) that limit their applications in this niche market, because the standards set in these components in relation to human consumption (Ceballos, 2002).

It is possible to develop higher value-added products based on cassava flour in order to expand production and processing and open new markets, promoting the establishment of rural industries and providing the opportunity to expand the income of small farmers (Garcia et al, 2005).

The probability that cassava flour can increase its demand in industrial applications such as adhesives plant, plywood, corrugated cardboard, thread cones, packaging materials, among others, is very high, due to environmental concerns that have emerged in recent decades, not only in Colombia, but also globally, so it requires implementation in the various products of renewable materials, cassava flour being one of the alternatives with great prospects in this area (Ceballos, 2002). However, the materials sector based on cassava flour is unexplored and little known in the market for this power plant.

2.1.2 Thermoplastic cassava flour

Cassava flour can be a thermoplastic material through the disruption of the molecular chains under specific conditions of temperature and presence of plasticizer (Rahman and Brazel, 2004, Martinez et al., 2007), so the TCF (Thermoplastic Cassava Flour) could become one of the important raw materials in the development of biodegradable plastics.

Several studies report the use of glycerol as a plasticizer in TCF (Ma, Yu & Wang, 2008; Ma et al, 2009; Chang et al, 2010), however the use of such TCF in the development of biodegradable materials has been limited due to problems associated with poor viability in the market, poor processability, low strength, low stability to humidity and retrogradation. For that, there have been implementing strategies to minimize these characteristics. Among them is the chemical modification of the flour (crosslinking and esterification) and TCF mixture with other polymers and biodegradable polyesters. However the industry has found a less expensive and more environmentally friendly through the use of natural fibers (Curvelo, Carvalho & Agnelli, 2001; Oksman, Skrifvars & Selin, 2003; Guan & Hanna, 2004; Avella et al, 2005; Ma, Yu & Kennedy, 2005; Teixeira et al, 2009). They have desirable characteristics such as low density, low cost, biodegradability, non-abrasive, good ductility and thermal properties (Wambua, Ivens & Verpoest, 2003; Martins et al, 2009), besides acting as a reinforcing material due to the strong bond that develops between the fiber-matrix interface due to the chemical similarity of starch in the flour and cellulose fibers (Luna, Villa & Velasco, 2009).

Within this area several studies indicate that when natural fibers are mixed with the TCF, improve mechanical properties (Lee & Wang, 2006; Martinez et al, 2007; Nair, Wang & Hurley, 2010). Other studies such as Carvalho and others (2005) investigated the influence of
plasticizer (glycerol) and fiber (cellulose) in TCF, finding that the use of plasticizer, significantly reduced the degradation of starch, while that the increase in fiber content, increased it.

There are few investigations made in TCF biodegradable packaging. At the international level have been evaluated physical and chemical properties of varieties of cassava flour for different applications, however, in the field of biocomposites studies are scarce. Researchers in Ghana, concluded that 31 varieties of cassava studied should not be wasted by their low quality cooking or high cyanogenic, however recommend its use in industrial applications such as extraction of starch and/or flour, sugar production, adhesives, among others (Aryee et al, 2006). In Nigeria, a study on the effect of type of material (pellets and cassava flour) and drying method (solar-oven) of material on the yield and physicochemical properties of starch in these materials and found that drying oven yielded the most appropriate results (Olomo & Ajibola, 2003). Venezuelan authors studied the effects of heat treatments on cassava meal, finding that pre-gelatinized flour decreased the tendency to retrogradation, consistency and rate of absorption and suggested the use of these conventional products and new product development (Pérez et al, 2007).

3. Related research

As part of the implementation of the program "Use By-Products of Cassava", cofinanced by the Agriculture and Rural Development Ministry, the Cauca University and the Cauca Productivity and Innovation Regional Center (Popayán, Cauca, Colombia), we have carried out some important technical developments for the use of cassava flour thermoplastic in the biodegradable materials manufacture. Next, we present some results of these studies of both raw materials and product obtained.

3.1 Characterization of cassava flour

In this regard, we have used the following techniques of analysis:

3.1.1 High Resolution Optical Microscopy- HROM

Samples were spread on glass sheets to be observed with optical microscope (Nikon Eclipse 80i, Japan) coupled to digital camera (Nikon DS-2MV 2Mp, Japan), through the bright field technique.

Photomicrographs of cassava flour in Figure 1 were captured with 10x (down) and 40x (up) objectives; in them may be observed longitudinal and amorphous fibers, and round/truncated starch granules.

Fibers, stained blue-violet because dye used (toluidine blue), it were longitudinally elongated and not elongated amorphous. As shown in Figure 1, there is a greater number of starch granules by number of fiber (s) found in each catch, this is because the fiber content in the flours studied is very low, between 1.7 and 2.7% in wet basis, compared with the starch content, between 75 and 85% wet basis, according to proximate analysis results (not shown).
Moorthy, 2002, reported that the fiber content of cassava flour is usually between 2-3% and starch content accounts for 84% (Rodriguez et al., 2008). A recent study on cassava roots (Teerawanichpan et al., 2008) discusses the anatomy by light microscopy using toluidine blue and shows four types of tissues, sclerenchyma, parenchyma, secondary and primary xylem. Starch granules have spherical and semi-spherical forms, as reported by other studies of cassava starch morphology (Alvis et al., 2008) - some of them truncated features shown as flat surfaces on one or more sides of the granule.

![Fig. 1. HROM microphotographs cassava flour](image)

### 3.1.2 Scanning Electron Microscopy- SEM

The samples were spread out on cylindrical specimens with carbon tape and subjected to gold bath (JEOL JSM-6490) for 200 seconds with a gap of 40-60 mTorr.

Figure 2 shows starch granules of variable diameter that does not exceed 25μm, and truncated spherical shapes typical of cassava starch. Fractures were also observed in its structure, possibly by the effects of grinding, especially when you consider that the particles are broken because the process to reduce particle size at the beginning of the characterization process of raw material.

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3.1.3 X-Ray diffraction

Samples were analyzed between $\theta = 2^\circ$ and $\theta = 35^\circ$, in an X-ray diffractometer (Rigaku 2002, Japan), (wavelength = 0.15405 nm) at 40 kV and 30 mA. The scanning speed was 5°C/min.
The samples showed a peak at $2\theta$: 20°, which according to Zobel (1988, quoted in Singh, 2006), is attributed to the presence of amylose-lipid complexes in starches, whose intensity could be related to the proportion of them. There were strong peaks at $2\theta$: 15°, $2\theta$: 17°, $2\theta$: 18° and $2\theta$: 23°, characteristic of type A pattern (Van Soest et al., 1996; Cheetham & Tao, 1998; Rodriguez et al., 2007; Leblanc et al. 2008; Perdomo et al, 2009), which indicates that the crystalline arrangement is monocyclic.

3.2 Characterization of TPCF material

The material was obtained by manual molding technique. To determine the operating conditions, we developed an experimental factorial design as shown in Table 1. The results of this design, indicated that there were significant differences among the factors evaluated ($p < 0.05$), so an response surface analysis was developed using the software matlab (R2008a) to determine the process conditions: the content of plasticizer, drying time and particle size of cassava flour. Figures 4 and 5 show the results of the analysis.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Level</th>
<th>Response</th>
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<tbody>
<tr>
<td>Plasticizer content (%)</td>
<td>High:25</td>
<td>Tensile strength (MPa)</td>
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<tr>
<td></td>
<td>Low: 10</td>
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<td></td>
<td>Center: 17.5</td>
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<tr>
<td>Drying time at 45°C (hours)</td>
<td>High: 26</td>
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<td></td>
<td>Low: 8</td>
<td></td>
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<tr>
<td></td>
<td>Center: 17</td>
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<tr>
<td>Particle size of cassava flour (µm)</td>
<td>High: 600</td>
<td></td>
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<tr>
<td></td>
<td>Low: 250</td>
<td></td>
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<tr>
<td></td>
<td>Center: 425</td>
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Table 1. Experimental design moulded material process

Response surface analysis established that the particle size of 600 microns was the one who reported the highest value on the strength of tensile strength of the material, the same way, drying times above 20 hours at 45°C, interacting with a content of 15% plasticizer favor mechanical properties in tension, bearing in mind that this property is important because it will identify the functional applications of the material.

Figures 4 and 5 show the optimization of the variables evaluated (drying time, particle size and concentration of plasticizer). This optimization is valuable because it indicates the values of variables in which the response evaluated had the highest value. Small particle sizes cassava flour could be contributing to a greater absorption of water by the increased free volume between particles, which probably caused a lower response to stress. Water acts as a plasticizer, resulting in intermolecular mobility, therefore, a drier material (longer drying time), the higher rigidity and resistance to a tensile stress.

Some of the techniques to characterize the material valued based TPCF were:
Fig. 4. Response surface of TPCF material with particle size 250 µm

Fig. 5. Response surface of TPCF material with particle size 600 µm
3.2.1 Differential scanning calorimetry

Samples were evaluated according to ASTM D3418-08 applied to the analysis of polymeric materials, with some modifications. Equipment used was a DSC (TA Instruments, Q20, USA). The samples were stored in hermetically sealed aluminum pans and subjected to heating from -50°C to 225°C at a heating rate of 20°C/min, then cooling to -50°C and a final heating similar to the first.

Figure 6 shows the three cycles that were submitted material samples in DSC. In the first heating scan showed a first endothermic peak before 0°C, then a glass transition and a second endothermic peak of melting of the material close to 150°C. Sample was then cooled with the drop from the flow of heat and finally heated in the third cycle, evidencing only an endothermic peak below 0°C, as presented in the first cycle.

The first scan was performed to remove the thermal history of material, that is, to prevent abnormal results because thermal processes to which the material was subject, which can alter the phase transitions characteristic of the sample, so it is expected that with the initial heating the material molecules were casted, and then, with the cooling the material molecules get to organize freely (second cycle) to obtain the real phase transitions of the material in the third cycle. No clutch, the first cycle performed (Figure 6) shows the typical transitions of the material, which was not presented in the third or second heating cycle, as usually (Mohamed et al, 2010). Some authors report that the Tg (glass transition temperature) was obtained only in the first heating, and melting temperature in the first and
second heating in polylactide films samples mixed with thermoplastic cassava starch extruded (Lee, Chen & Hanna, 2008). Possibly, the material molecules can not organize freely during cooling, maybe because they require a much slower process for ordering, which resulted in no evidence of the glass transition and fusion of material on third cycle, further, cooling after first heating is probably causing irreversible structural changes and transformations at the molecular level, which prevents phase transitions evident in the first heating cycle, but it was evident by the second one.

In Figure 6, can be seen that the glass transition temperature is above 110°C, this is an indication of the high stability of the material, since in future applications, it may be subjected to temperatures near 100°C maintaining its stability because it is in their glassy solid state.

3.2.2 Thermogravimetric Analysis - TGA

TGA equipment was used (Q50, TA Instruments). Samples between 10 and 20 mg were assessed of molded material, according the ASTM E1131-08. The sample was placed in a platinum tray open and subjected to heating from 25°C to 500°C at a rate of 10°C/min. The tests were carried out in a controlled environment using nitrogen level UAP.

![TGA curve](image)

Fig. 7. Termogram TGA material of TPCF

The TGA curve has four main areas, namely: the area of highly volatile material (200°C or less) represented by moisture, plasticizers, residual solvents and other components of low boiling point, the material area average volatility (between 200 and 750°C) represented by compounds of polymer degradation, oil; area where combustible material degrades oxidized material such as coal nonvolatile (temperature depends on the material), and the area of ash corresponds to non-volatile residue in an oxidizing atmosphere including metal components, inert fillers or reinforcements (ASTM E1131). Figure 7 shows the first two zones in the TGA curve, represented by 7.820% in highly volatile material, and the area
average volatility material that starts at 134.89°C and ends at 470.6°C and a residue of 18.69%. The degradation temperature (Td) for the material presented was 299.28°C, meaning adequate thermal stability, comparable with thermoplastic cassava starch nanoreforced. Td which occurred between 309 and 327°C (Schlemmer, Angelica & Sales, 2010), and compounds near extruded and injection molded thermoplastic starch reinforced with lignocellulosic fibers whose degradation temperatures were between 335 and 339°C (Averous & Boquillon, 2004).

4. Conclusion

Cassava flour is a viable material for use as part of a processable thermoplastic matrix by molding technique, which allows to obtain materials with acceptable mechanical and thermal properties for agro-industrial applications.

5. Acknowledgment

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6. References


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Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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