## **THERMOPLASTIC STARCH: THE PREPATION METHOD**

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## Abstract

This work presents a systematic study about thermoplastic starches. Corn starch was mixed with 2 and 4 wt.% of carboxylic acid and 20 to 30 wt.% of water. The samples were prepared in an internal mixer coupled to a torque rheometer, and the torque values were monitored during mixing. The specimens for mechanical tests were calendered and cut with a knife. The mixtures were characterized by mechanical testing (tensile strength), scanning electron microscopy, and thermal analysis. The torque curves indicated that the samples with and without adipic acid addition suffer retrogradation. When the water content is increased, the glass transition temperature values decrease because water acts as a plasticizer for starch. The mechanical test results showed that samples with 2 wt.% acid content present the highest values of elastic modulus and tensile strength, and the lowest values of elongation at rupture.

## Introduction

In the last decades the consumption of polymeric materials has been increasing across the planet. In Brazil, the apparent consumption of processed plastic was approximately 4 million tons in 2000 rising up to 6.2 million in 2010 (56.3% higher)[1]. This brings us a problem because with the increase in consumption there is an increased demand for resources (petroleum in case of most polymers) and generation of waste.

Because polymers generally have low density, they occupy much volume when they are discarded of in landfills and dumps. In addition, they cause a large ecological impact because they originated (the majority) from petroleum, which is a non-renewable resource.

There are waste disposal methods applied to polymers which can solve the space problem. Some alternatives are incineration and recycling[2]. However both techniques have problems and restrictions.

Another alternative is to use biodegradable polymers and biopolymers or green polymer. These polymers are from natural origin, they can be produced by the bodies of living beings or been made from substances derived from such organisms. The advantage of using these types of polymers is the source of raw materials which, by being renewable, causes less impact environmental during its extraction [3][4]. A polymer that is most studied, that is both biodegradable as renewable source (biopolymer) is starch. Most studies are focused on improving its performance and processability. Since most biodegradable polymers, especially starch has poor mechanical, thermal and rheological properties. Moreover because of the strong intermolecular and intramolecular hydrogen bonds in starch, native starch is not a true thermoplastic. These properties can be improved by adding plasticizers to starch, generating the thermoplastic starch [3,5, 6,7,8]. In presence of plasticizers (e.g. water, glycerol, etc.) at high temperatures (90–180°C) and under shear, starch readily melts and flows, allowing for its use as an injection, extrusion or blow molding material, similar to most conventional synthetic thermoplastic polymers[6].

In most reported studies on thermoplastic starch (TPS) polyols, like glycerol, sorbitol and glycol were used as plasticizers. But this TPS tend to retrogradate after storage for a long period of time. To try to resolve this problem, the carboxylic acids like adipic, citric and malic can be used.

The objectives of this research is to find better formulation to prepare TPS with and without carboxylic acids, studying thermal properties, FTIR, mechanical properties and the torque generated during the mixing process.

#### Materials

Corn Starch containing about 14% moisture (Amidex 3001) was supplied by Corn Products Brazil Ltda. The glycerol and carboxylic acids: citric, tartaric, adipic and malic was supplied by Casa Americana Ltda. The chemical structure is showed in Figure 1.



Figure 1. Chemical structure carboxylic acids: (a) citric acid, (b) malic acid and (c) adipic acid

# **Preparation of TPS**

Corn Starch was dried at 110°C for 48h in vacuum (250mbar). Afterwards, corn starch was mixed with 30

wt% glycerol, distillated water and acid for 20 minutes at 1500rpm in mechanical stirrer IKA<sup>®</sup> Werke Eurostar. This mixture was stored in an oven at 25°C for at least 24h [6].

The starch: glycerol mixtures containing different water contents and acids types were placed in a Rheomix 600 mixer connected to a HAAKE torque rheometer. The process conditions used were: 125°C for 8 minutes and 100rpm. The compositions of the samples can be seen in Table 1.

Sample	Carboxlyc Acid	Moisture (%)	Acid (%)
NA	-	20	0
AA2	Adipic Acid	20	2
AA3		30	2
CA2	Citric Acid	20	2
CA3		30	2
CA4		30	4
MA2	Malic Acid	20	2
MA3		30	2

Table 1 – Composition of the sample

## Characterization

The IR spectra were measured with a Nicolet-210 spectrophotometer (Nicolet Co., USA). The samples were prepared by mixing the fine powder with KBr and pressing them. The spectra were obtained at a resolution of 4 cm<sup>-1</sup> in the range 4000–400 cm<sup>-1</sup>.

Samples of thermoplastic starch were observed by SEM Philips XL 30. Firstly the samples were cryogenically fractured, after gold was deposited and the samples were analyzed at 5 kV.

Sample powders were dried in the oven at 80°C. Samples for TGA were stored in sealed plastic bag at 25°C. Thermal properties were measured with Netzsch STA 449 F1 Jupiter. About 10 mg sample was positioned in alumina pans. Samples were heated from room temperature to 1000°C at a heating rate of 10°C/min in a nitrogen atmosphere.

The formulations that presented optimized properties (like homogeneous microstrutucture after plasticizing) were processed in a calendar, at  $80^{\circ}$ C, in order to form a 3mm thick film. Each one was cut into tensile test sample. Tensile properties were evaluated according to ASTM D638-10 using an Instron Universal Testing Machine at a rate of 50 min<sup>-1</sup>. At least five bars were tested for each sample and the average calculated. The tensile tests were made in 2 directions: vertical calendering direction (y) and horizontal calendering direction (x), as shown in Figure 2.



Figure 2 - Directions used in tensile tests.

#### **Results and Discussion**

During the processing of the blends torque value as a function of mixing time was recorded. According to Bousmina [5] the torque curve has at least two peaks . The first peak represents the loading of the sample, when placed in the sample chamber corresponding to the increased resistance to the free rotation of the rollers due to the introduction of the material. When this resistance is overcome, the torque required to rotate the rollers can quickly decrease and reach a steady state. The second peak increases rapidly due to the disruption of the starch granules, which can lead to the fusion (or softness) of the material, and then reaches to a new steady state. At the end of the curve decrease in torque may occur, indicating the plasticization, or increase in torque, indicating crosslinking of the material. In practice, the time difference between the first and the second stage is small, rarely observed.

The curves for different samples have different behaviors. Figure 3 shows such behavior. In samples without acid and adipic acid, torque after 4 minutes tends to increase. As for the samples with citric acid and malic acid (Fig. 3c and 3d ), the tendency is in decrease torque values. When a plasticizer is added to the polymer, the plasticizer molecules begin to penetrate the polymer phase, and spread between the polymer macromolecules, increasing mobility between the chains (physical interaction ). This interaction may occur due to the greater freedom of motion of macromolecules caused by the plasticizer. The same would happen with increase in the percentage of moisture, because the presence of water facilitates molecular motion. Another factor that contributes to the reduction of the torque is splitting of polymeric chains, caused by the hydrolysis reaction with citric acid. This division reduces the molecular weight of the starch, and its viscosity. The adipic acid molecules are less reactive and do not interact sufficiently with the starch molecules, then the torque curves related to these samples show a peak gelatinization followed by an increase in torque values due to retrogradation.



Figure 3. Torque curves obtained during the mixing process in a torque rheometer: (a) without CA; (b) adipic acid; (c) citric acid and (d) malic acid.

The homogeneity of the mixtures was analyzed by scanning electron microscopy. The results are shown in Figure 4. It may be noted that the samples with 30 wt% water are more homogenous. All samples have circular structures that appear on the surfaces of fractured samples due to plasticity of the material.



Figure 4 - SEM images of samples without acid, AA2 and AA3

Thermogravimetric analysis showed that all samples with carboxylic acid, the degradation occurred in three stages. But in native starch and the sample without acid, the degradation occurs in two stages, as shown in Figure 5. For native starch and sample without carboxylic acid (Figure 5 (a)), the first mass loss stage, at around 190°C, corresponds to decomposition of the glycerol, and the second due to the starch (between about 250 and 350°C). In the samples with carboxylic acids (Figure 5 (b)), there is a third mass loss stage, which corresponds to decomposition of acids. The mass loss corresponding to the beginning of the decomposition of the acids starts at temperatures of about 200°C for citric acid and of about 250°C for adipic and malic acids. Note that the samples with adipic acid suffered retrogradation. For the samples with different moisture, there was no significant change, the same occur for the samples with different citric acid content.



Figure 5 – Curves of thermogravimetric analysis: (a) native starch and sample without acid, and (b) samples with carboxylic acids.

Figure 6 shows the mechanical properties of the samples in the x and y directions. It may be noted that there were significant differences in the elastic modulus and the tensile strength in both calendering directions,

even though, there was a slight difference in stretching, larger in the x direction, which is perpendicular to the calendering direction. By observing the samples CA3 and CA4, there is the effect of the amount of acid. The lower the percentage of acid, the higher the values of elastic modulus and yield strength. However, the total elongation decreases. Finally, we note that there is no significant difference between samples CA2 and CA3, which differ in moisture content.





Figure 6 - Mechanical properties of the samples with acids in the calendering direction (y) perpendicular to the direction of calendering (x).

## Conclusions

Carboxylic acids can be used to increase the plasticisation of thermoplastic starch. However, it is necessary that the acid has some reactivity with starch and glycerol.

Citric acid is more effective as a plasticizer for starch than adipic acid is, because it is more reactive for having three hydroxyls at the end of the molecule, whereas the adipic acid has only two. On the other hand, malic acid demonstrated to be as effective as citric acid. TPS samples prepared with malic acid addition exhibit stiffness and tensile strength much higher than the ones obtained for TPS with citric acid. The humidity did not cause significant changes in the properties studied.

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