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**Environmental Technology**

# Synthesis and characterization of the poly-(sorbitol *co*-citrate adipate) a biopolymer aiming to obtain a biomaterial

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## ABSTRACT

This work describes the synthesis and physicochemical and microstructural characterization of poly(sorbitol adipate co-citrate) with the aim of obtaining a sustainable biopolymer derived from renewable and non-toxic sources intended for applications such as biomaterial. Polymerizations at three different ratios of sorbitol and adipic and citric acids (A, B and C) were studied. The materials were characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques. Such analyses showed that only in state C was an amorphous copolyester obtained, with different particle sizes and visibly hard and with a translucent yellowish color.

**Keywords**: Global environment; Polymerization; Copolyester; Sustainability

## 1 INTRODUCTION

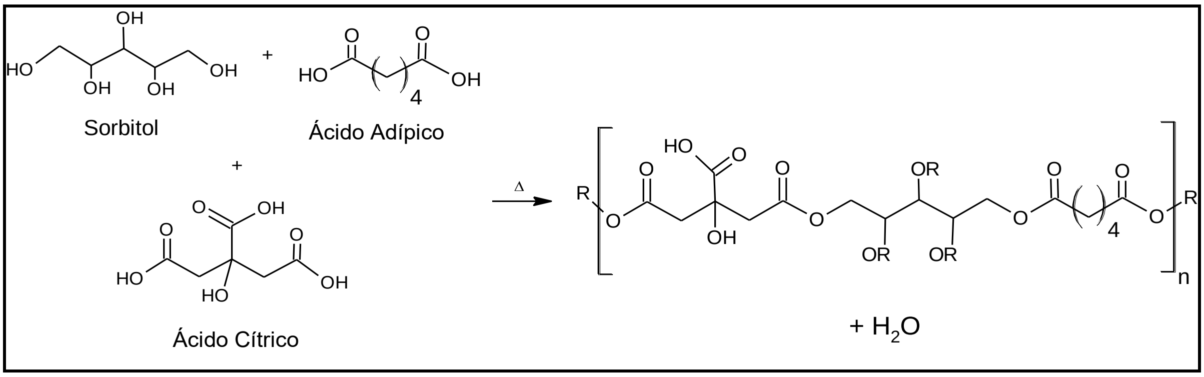
Polymeric materials are commonly present in the daily life of humanity. By the year 2019, it is estimated that almost 8.3 million tons of plastic have been produced on a global scale and that approximately 9% of these have been recycled, 12% have been incinerated and 79% have been disposed of in dumps, landfills and in environment since the fifties (EPOCA, 2020).

Plastics, rubbers, fibers and resins have several and varied applications, from the manufacture of toys, automotive parts, paints and varnishes, fibers for fabrics to prostheses and medicinal implants with high added value (UTERLASS, 2015).

Such jobs are mainly derived from its physical-chemical and mechanical properties that give it, among other features, expressive durability. And it is exactly this characteristic, which today, has aroused environmental concern. Allied to this fact, it is noteworthy that, for the most part, polymers are produced using petrochemical inputs, that is, non-renewable raw material, which makes their indiscriminate use worrying.

There is growing scientific and technological interest in the development of new polymers, derived from renewable sources that act as an ecologically sustainable alternative. Biopolymers are produced from renewable sources and, in general, are biodegradable, constituting a viable alternative to conventional polymers, although, commonly, they have a higher production cost. To produce them, for example, biomass derivatives (starch, sugar cane, cassava, sunflower oils, soybeans, castor, cellulose, etc.) are used as starting material.

Figure 1 – Polyesterification using sorbitol and adipic and citric acids




Source: (Adapted THAM *et al*.)

A special use for biopolymers is when applying them as biomaterials. For this, materials are developed in order to be used in biological systems, such as in devices for controlled release of drugs, dressings, artificial skins and support for cell growth (TROVATTI *et al.,* 2016). In this context, the present study sought to produce and characterize a biopolymer, poly- (sorbitol co-citrate adipate) using raw materials, sorbitol, citric acid and adipic acid (Figure 1), from renewable and low sources cost in substitution of petroleum-derived polymers, aiming at applications such as biomaterial (DE FARIAS *et al.*, 2016; 2015).

## 2 EXPERIMENTAL

### 2.1 Chemicals

All chemical reagents used were for analytical grade. Sorbitol (Dinâmica); adipic acid (Dinâmica); citric acid (Synth).

### 2.2 Copolyesther polimerization

The reaction was conducted for 2 h at 135.0 ± 5.0 °C, in a 100 mL reflux system under ambient atmosphere, in three different proportions according to Table 1. The obtained polymers were heat treated at 80.0 ± 10.0 °C, in ambient atmosphere for 8 days (PASUPULETI *et al*.,2011)

Table 1 – Different molar ratios of reagents used in polymerizations

| Experiments | Sorbitol (mol) | Adipic Acid (mol) | Citric Acid (mol) |
|---|---|---|---|
| A | 1.0 | 1.0 | 0.5 |
| B | 1.0 | 1.0 | 1.0 |
| C | 1.0 | 1.0 | 2.0 |

Source: Author (2019)

### 2.3 Fourier-Transform Infrared Spectroscopy (FTIR)

Chemical structure of the synthesized copolyesther was determined by FTIR measurements which were performed using KBr pelleted samples in a SHIMADZU - Affinity 1 FTIR spectrophotometer with a resolution of 4 $cm^{-1}$ in the range of 400 – 4000 $cm^{-1}$.

### 2.4 X-Ray Difraction (XRD)

X-ray diffractograms were obtained in assays performed at a 2 θ angular scanning range of 10 to 80 degrees. Measurements were performed at room temperature in continuous scan mode with 0.25 degree angular pitch and 0.3 second counting time. The voltage and current used in the tests were 40 KV and 15 mA, respectively.

### 2.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was performed on the ZEISS equipment (model DSM 940 A - coupled EDS and PGT model Prism Digital Spectrometer). A voltage of 15 kV was used and the images were analyzed at a 45° angle.

## 3 RESULTS AND DISCUSSION

The use of a polymer and / or biopolymer as a biomaterial requires, among other characteristics, that it be non-toxic. As a result, sorbitol and adipic and citric carboxylic acids were chosen as raw materials for the synthesis of the copolymer. Sorbitol is a natural polyalcohol, present in several vegetable species, mainly in fruits such as pear, apple, peach and plum ref. It is widely used in the food industry as a sweetener, as a biosurfactant in cleaning products and as an emollient in cosmetics, among other important applications (BUDAVARI,1986; BIRKHED *et al*.,1984). Adipic acid or hexanedioic acid is a biodegradable dicarboxylic acid, obtained through the oxidation reaction of cyclohexanol or cyclohexanone in the presence of nitric acid and copper and vanadium as catalysts. It has an acidifying and flavoring effect, which is why it is widely used in the production of fruit sodas, cheeses, marmalades, food powders and as an inducer of the formation of gels that resemble gelatin and jellies. It is also used in the manufacture of esters used in lubricants and plasticizers, adhesives, paints, medicines, resins, perfume fixers, etc. Another justification for the choice of adipic acid was due to reports found in the literature that showed that, as the straight section of the chain increased, that is, with the increase in the number of carbons in the monomer structure, there was an increase in the flexibility of the mesh polymeric, and consequent decrease in the glass temperature (ASKADSKI, 1996) resulting from the increase in the linear portion of the copolymer chain, results in an increase in the number of simple bonds that have a greater degree of freedom for rotation.

Citric acid, or 2-hydroxy-1,2,3-propanotricarboxylic acid, is a weak, biodegradable organic acid found in derivatives of lemon or other citrus fruits. It is a natural preservative that has been widely used in industry, as a flavoring agent, capable of preventing or inhibiting damage caused by fungi, bacteria and other microorganisms (THAM *et al.,* 2013; SCOPEL *et al*., 2017). It is verified, therefore, that such raw materials are widely used for pharmaceutical and food purposes, consequently non-toxic, and except for adipic acid, they are of natural origin and, therefore, renewable. As a result, it is possible to define the studied polymer as a biopolymer, and that it is potentially applicable for purposes such as biomaterial due to the absence of toxicity of the reagents used in its synthesis. Previous studies of sorbitol / adipic acid polymerization have demonstrated the need to use a crosslinking agent, as the resulting polymer has shown to be brittle. Thus, in an attempt to improve the degree of polymerization, a crosslinking agent was introduced to this combination. This is a multifunctional molecule that allows the formation of bonds between polymeric chains (SHEFER and GOTTLIEB,1992), as is the case with citric acid, which has in its structure the organic functions such as carboxylic acid (-COOH) and hydroxyl (-OH). And based on (PASUPULETI *et al*.,2011) who report obtaining the polymers poly (sorbitol sebacate co-citric) and poly (sorbitol sebacate co- tartare), carried out in different molar proportions, we opted for the use of a lower molar ratio of citric acid that studied by them (1: 1: 1), because too much crosslinking, resulting from the process of polymeric crosslinking or crosslinking or even cross links, resulting from the interconnection, by covalent bonds, of the polymer chains would make the polymer structure not flexible and, therefore, Consequently, it would raise the glass transition temperature due to the fact that this property depends on the ability of the chains to move more or less in the reticule (SHEFER and GOTTLIEB,1992; SABA *et al.,*2017).

In order to evaluate the biopolymer production, via polycondensation, by the method of mass polymerization, sorbitol and adipic and citric carboxylic acids (Figure 1), different experiments were carried out, varying the molar proportion of the reagents, as shown in Table

Experiments A, B and C proceeded without considerable changes in the apparent characteristics of the material, which gradually became visually more viscous and yellowish during the synthesis. However, it was noticed the formation of bubbles in the reaction medium, which indicated the occurrence of polycondensation, via polyesterification, since the water molecules formed during the reaction, were being expelled from the liquid medium, in the form of steam, at the temperature studied (135.0 °C), in line with that presented in the literature for polycondensations (Figure 2) (SHOGREN *et al.,*2009).

Figure 2 – Image for the C polymer

Source: (The author, 2019)

After defining the most promising experimental conditions for obtaining a sustainable polymer, the characterization of the obtained materials was continued.

The physical-chemical and microstructural characterization of the materials obtained was performed by X-ray diffraction (XRD) (Figure 3), molecular absorption spectroscopy in the infrared region by Fourier Transform (Figure 4) and scanning microscopy analyzes (Figure 5), respectively.

The XRD analyzes (Figure 3), indicated that only in the case of condition C was the polymer obtained at approximately 19.78 2θ degrees, which showed characteristics of an amorphous material according to studies cited in the literature (SPERLING, 2006).

Figure 3 – X-ray spectrum for the A, B e C samples

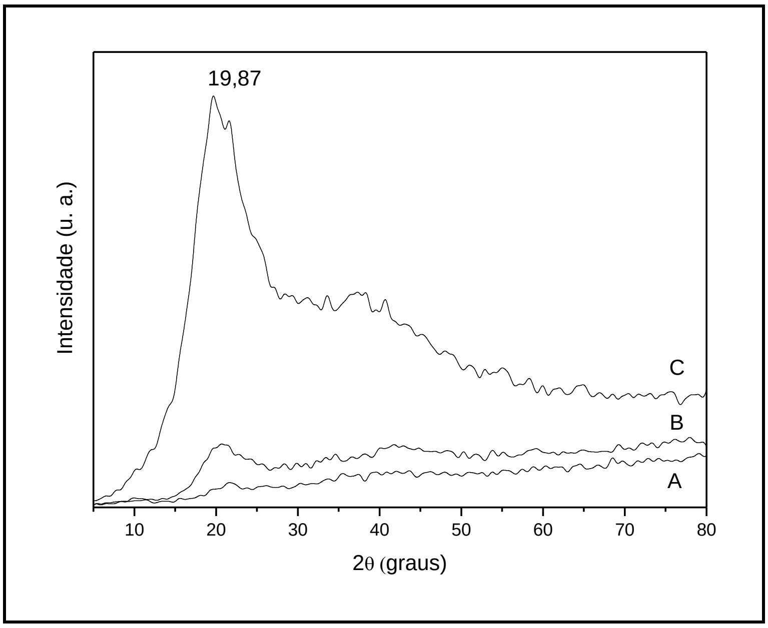
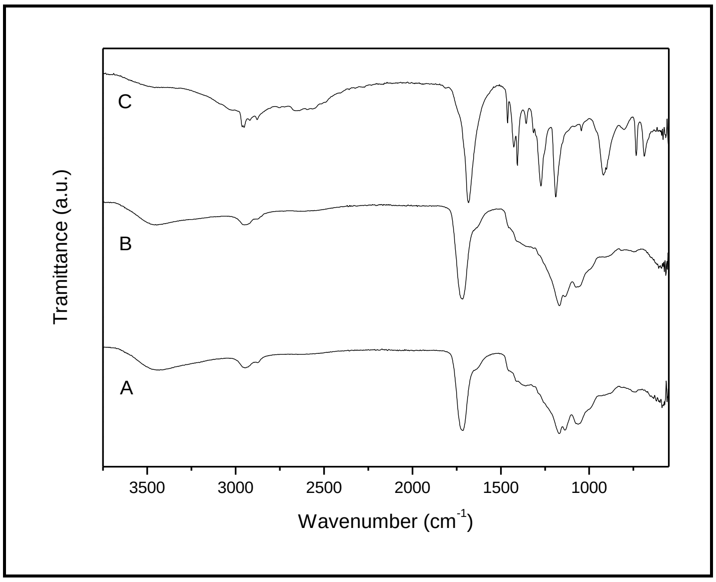


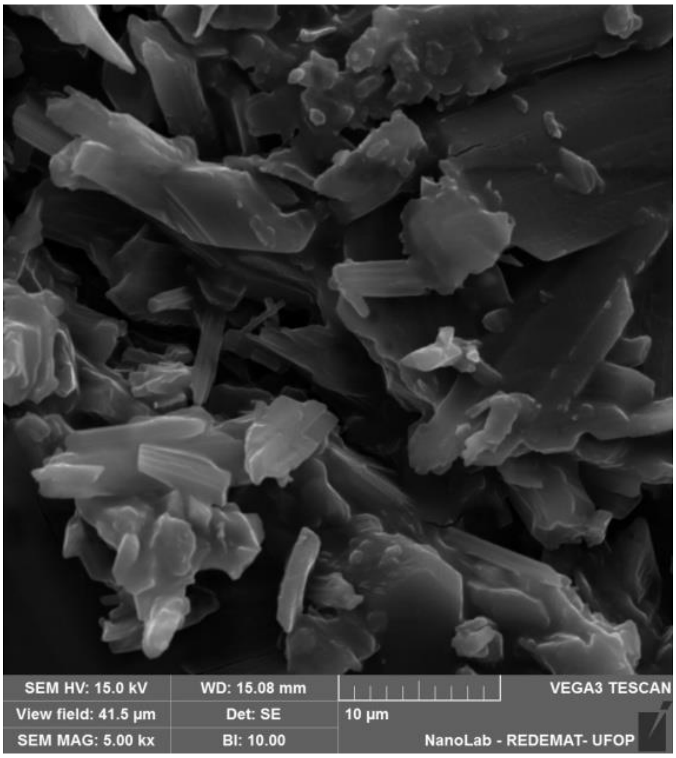

Figure 4 – FTIR spectrum for the A, B e C samples




FTIR analyzes (Figure 4) show that in the 1820-1600 $cm^{-1}$ range there is a strong, intense peak of medium width characteristic of axial deformations of esters and carboxylic acids. However, only in the C sample are the esters C-O bands - axial deformation with, 2 bands or more, one more intense than others in the 1300-1000 $cm^{-1}$ range.

The microscopies obtained (Figure 5) for samples A, B and C show that only sample C is characteristic of a polymer. In C microscopies, confirming the results of XRD analyzes, an amorphous, heterogeneous material with particles of different sizes is observed. (ZANKEL *et al.,*2017)

Figure 5 – SEM for the C sample




## 4 CONCLUSIONS

The results obtained demonstrate that the raw materials sorbitol and adipic and citric acids were effective in obtaining the biopolymer C in the 1: 1: 2 molar ratio studied. The material was visibly yellowish, translucent, homogeneous and rigid at room temperature. The analyzes carried out showed that it is a copolyester, amorphous and heterogeneous. Thus, we can say that using the proposed conditions it was possible to obtain a sustainable biopolymer, derived exclusively from renewable and non-toxic sources and promising for future studies that evaluate its use as biomaterial.

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